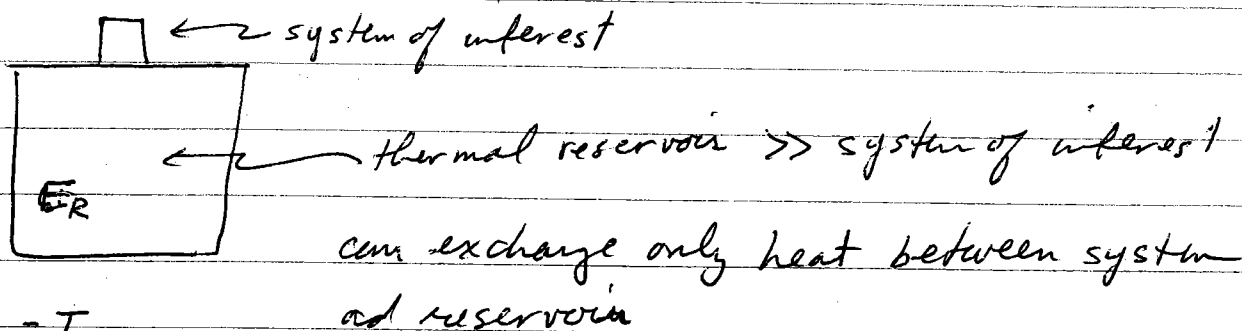


Extremum Principles for Free Energies

Concept of a thermal reservoir



$$\left(\frac{\partial E_R}{\partial S_R}\right)_{V,N} = T_R$$

Suppose we add heat $dQ = TdS$ to the reservoir.
The change in the reservoir's temperature T_R will be

$$\Delta T_R = \left(\frac{\partial T_R}{\partial S_R}\right) dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS$$

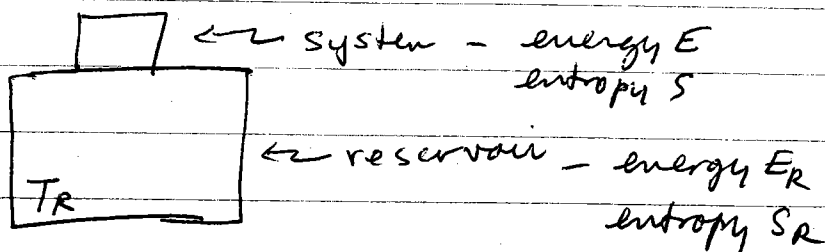
Since E_R and S_R are both extensive variables, they scale with the number of particles in the reservoir N_R .

So

$$\left(\frac{\partial^2 E_R}{\partial S_R^2}\right) \sim \frac{1}{N_R} \rightarrow 0 \quad \left. \vphantom{\left(\frac{\partial^2 E_R}{\partial S_R^2}\right)} \right\} \text{for infinitely large reservoir}$$
$$\Rightarrow \Delta T_R \rightarrow 0$$

Formally, a thermal reservoir is a system so large that its temperature does not change when it exchanges heat with the system of interest.

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 $E = E_R + E$
 total entropy is maximized

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

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

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

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

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

$$= S_R(E^{\text{tot}}) - (E - T_R S) / T_R$$

$T_R = T$
 \uparrow

$$= \underbrace{S_R(E^{\text{tot}})}_{\text{constant}} - \underbrace{A}_{\text{Helmholtz free energy}} / T_R$$

system temp

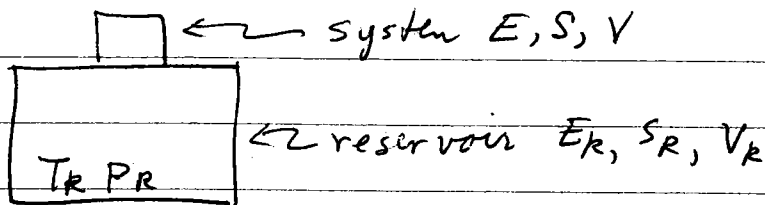
constant Helmholtz free energy

S^{tot} maximized \Rightarrow A minimized

\Rightarrow the equilibrium state of a system in contact with a thermal reservoir will be the one that 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 $E^{\text{tot}} = E_R + E = \text{constant}$

total volume conserved $V^{\text{tot}} = V_R + V = \text{const}$

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

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

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

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

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

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

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

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

and - the equilib 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_p 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

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

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

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

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

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

of 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

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

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} = -\kappa V / kT$$

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

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

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

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

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

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

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

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

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

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

So

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

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 $dz = 0$

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

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

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

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

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

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

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

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

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

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

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

See Callen for a systematic way to reduce all such derivatives to combinations of C_P , K_T , 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 , K_T , α]

Another useful relation

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

Since $dE = TdS - PdV$ (N fixed)

it follows that

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