Lecture #3

F is called the Helmholtz Potential, or Free Energy.

$$F(T,V,N) = U - TS$$

Temperature is the intensive dependent variable

Enthalpy: $V \to P$: $P = -\left.\frac{\partial U}{\partial V}\right|_{S,N}$

$$H = U + PV = H(P, S, N)$$

$$dH = dU + PdV + dPV = TdS - \cancel{PdV} + \mu dN + \cancel{PdV} + VdP$$

$$dH = TdS + VdP + \mu dN$$

$$\Rightarrow T = \left.\frac{\partial H}{\partial S}\right|_{P,N}, \quad V = \left.\frac{\partial H}{\partial P}\right|_{S,N}, \quad \mu = \left.\frac{\partial H}{\partial N}\right|_{S,P}$$

Gibbs Potential (Gibbs Free Energy)

Replace $(S, V) \to (T, P)$

$$G = U - TS + PV$$

$$\Rightarrow dG = -SdT + VdP + \mu dN$$

(Notice $U = TS - PV + \mu N \Rightarrow G = \mu N \Rightarrow g = \frac{G}{N} = \mu$

$$\left.\frac{\partial G}{\partial T}\right|_{P,N} = -S, \quad \left.\frac{\partial G}{\partial P}\right|_{T,N} = V, \quad \left.\frac{\partial G}{\partial N}\right|_{T,P} = \mu$$ 10

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Grand potential: replace $(S, N) \to (T, \mu)$

$$\Omega = U - TS - \mu N = \Omega(T, V, \mu)$$

$$d\Omega = \cancel{TdS} - PdV + \cancel{\mu dN} - \cancel{TdS} - SdT - \cancel{\mu dN} - Nd\mu$$

$$d\Omega = -PdV - SdT - Nd\mu$$

$$\left.\frac{\partial \Omega}{\partial V}\right|_{T,\mu} = -P, \quad \left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu} = -S, \quad \left.\frac{\partial \Omega}{\partial \mu}\right|_{V,T} = -N$$

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Other potentials also follow from entropy fundamental Equation

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In certain problems, it is convenient to reduce thermodynamic potentials to a set of easily measured quantities:

Coefficient of Thermal Expansion $\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P$

Isothermal Compressibility : $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$

Heat Capacity at constant Pressure, $C_P = \left.\frac{dQ}{dT}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_P$

(B)

Specific heat at Constant Pressure

$$c_p = \frac{1}{N} C_p = T \frac{\partial s}{\partial T}\Big|_p$$

Two other quantities that are useful, but hard to measure:

Adiabatic Compressibility : $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_S$

Heat Capacity at Constant Volume, $C_V = T\frac{\partial S}{\partial T}\Big|_V$

Specific heat " " " $c_v = T\frac{\partial s}{\partial T}\Big|_V$

Maxwell Relations

Example: $dU = TdS - PdV + \mu dN$

$$\frac{\partial T}{\partial V}\Big|_{S,N} = \frac{\partial}{\partial V}\left[\frac{\partial U}{\partial S}\Big|_{V,N}\right]_{S,N}$$

$$= \frac{\partial}{\partial S}\left[\frac{\partial U}{\partial V}\Big|_{S,N}\right]_{V,N} = -\frac{\partial P}{\partial S}\Big|_{V,N}$$

The fact that 2^{nd} order derivatives of U can be performed in either order $\Rightarrow$ relationships between 1^{st} order derivatives of U

Similarly, $\left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{V,N}$

and $-\left.\frac{\partial P}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial V}\right|_{S,N}$

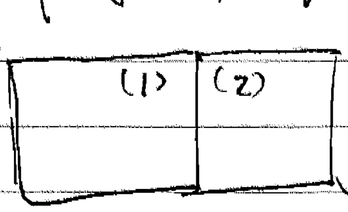
This ~~can~~ be repeated for all potentials

(see Callen for a complete list)

Note property of Thermodynamic potentials:

$S^{(1)}+S^{(2)}+S^{(r)} = \text{const.}$

$\delta S^{(r)} = -\delta S^{(1)} - \delta S^{(2)}$



Thermal Reservoir

$T^{(r)} = \text{constant}$

Minimize energy of system + reservoir, at const. entropy,

$\delta(U + U^{(r)}) = 0$ const $= S + S^{(r)}$

$= \delta\left(T^{(1)}\delta S^{(1)} + T^{(2)}\delta S^{(2)} + T^{(r)}\delta S^{(r)}\right.$

$= T^{(1)}\delta S^{(1)} + T^{(2)}\delta S^{(2)} - T^{(r)}\left[\delta S^{(1)} + \delta S^{(2)}\right] = 0$

must vanish for all $\delta S^{(1)}$ and $\delta S^{(2)}$

$\Rightarrow T^{(1)} = T^{(2)} = T^{(r)}$

Generally $\delta(U + U^{(r)}) = \delta U + T^{(r)}\delta S^{(r)} = \delta(U - T^{(r)}S) \equiv \delta F$

since $T^{(r)}$ is const.

Sim. w/ other potentials.

$\Rightarrow \delta(U + U^{(r)}) = 0 \longleftrightarrow$

Helmholtz Free Energy has Extremum for a fixed T, $\delta F = 0$, $T = T^{(r)}$

Therefore, the requirement that $\delta(U+U^{(r)})=0$ is equivalent to the statement that the Helmholtz Free Energy, F, have an extremum for a fixed temperature.

$$\delta F = 0 \quad \text{for } T = T^{(r)}$$

Check the extremum is a minimum.

$$\delta^2(U+U^{(r)}) = \delta^2 U + \delta^2 U^{(r)}$$

$$\delta^2 U^{(r)} = \sum_{ij}\left[\frac{\partial^2 U^{(r)}}{\partial X_i^{(r)}\partial X_j^{(r)}}\right]\delta X_j^{(r)}\,\delta X_i^{(r)}$$

[ ] scales as 1/size of reservoir $\to \infty$

$$\therefore\ \delta^2 U^{(r)} = 0$$

$$\therefore\ \delta^2(U+U^{(r)}) = \delta^2 U > 0$$

, note δ is w.r.t. (S,V,N). $\therefore\ \delta^2 S = 0$ because S is linear

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Same story with Enthalpy and a pressure resorivor.

Equilibrium values of any unconstrained internal parameter in a system in contact with a pressure reservoir minimized the enthalpy of the manifold of states of constant pressure.

$$\delta H = \delta(U + P^{(r)}V) = 0, \quad (P = P^{(r)})$$

$\delta^2 H > 0$; Similar principles for other Legendre transformed.

The response functions may be related to each other:

Thermal expansion $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_P = \frac{1}{V}\frac{\partial^2 G}{\partial T\,\partial P}\Big|_N$, since $\frac{\partial G}{\partial P}\Big|_{T,N} = V(T,P,N)$

isothermal compressibility $\chi_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T = -\frac{1}{V}\frac{\partial^2 G}{\partial P^2}\Big|_{T,N}$, since $\frac{\partial G}{\partial P}$ ↓

Heat capacity @ const. pressure $C_P = T\frac{\partial S}{\partial T}\Big|_P = -T\frac{\partial^2 G}{\partial T^2}\Big|_{P,N}$, since $\frac{\partial G}{\partial T}\Big|_{P,N} = -S(T,P,N)$

Adiabatic compressibility $\kappa_S = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_S = -\frac{1}{V}\frac{\partial^2 H}{\partial P^2}\Big|_{S,N}$, since $\frac{\partial H}{\partial P}\Big|_{S,N} = V(S,P,N)$

Heat capacity @ const volume $C_V = T\frac{\partial S}{\partial T}\Big|_V = -T\frac{\partial^2 F}{\partial T^2}\Big|_{V,N}$, since $\frac{\partial F}{\partial T}\Big|_{V,N} = -S(T,V,N)$

Notice $\frac{\partial^2 G}{\partial T^2}\Big|_{P,N} = -\frac{C_P}{T}$; $\frac{\partial^2 G}{\partial P^2}\Big|_{T,N} = -V\chi_T$

$\frac{\partial^2 G}{\partial T\,\partial P}\Big|_N = V\alpha \Rightarrow C_P,\ \chi_T,\ \alpha$ are related

$$\boxed{\begin{aligned} dG(T,P,N) &= \frac{\partial G}{\partial T}\Big|_{P,N}dT + \frac{\partial G}{\partial P}\Big|_{T,N}dP + \frac{\partial G}{\partial N}\Big|_{T,P}dN \\ \Rightarrow \frac{\partial G}{\partial T}\Big|_{V,N} &= \frac{\partial G}{\partial T}\Big|_{P,N} + \frac{\partial G}{\partial P}\Big|_{T,N}\frac{\partial P}{\partial T}\Big|_{V,N} + 0 \end{aligned}}$$

Recall $\frac{\partial F(T,\cancel{V},N)}{\partial T} = -S(T,N,V)$

$$\therefore dS = \left.\frac{\partial S}{\partial T}\right|_{V,N} dT + \left.\frac{\partial S}{\partial V}\right|_{T,N} dV + \left.\frac{\partial S}{\partial N}\right|_{T,V} dN$$

$$\left[\Rightarrow \left.\frac{\partial S}{\partial T}\right|_{P,N} = \left.\frac{\partial S}{\partial T}\right|_{V} + \left.\frac{\partial S}{\partial V}\right|_{T} \left.\frac{\partial V}{\partial T}\right|_{P} + 0\right] \otimes T$$

$$C_P = C_V + T \left.\frac{\partial S}{\partial V}\right|_{T} \left.\frac{\partial V}{\partial T}\right|_{P}$$

$$\left.\frac{\partial S}{\partial V}\right|_{T} = -\frac{\partial^2 F}{\partial T \partial V} = -\left.\frac{\partial P}{\partial T}\right|_{V}$$ (Maxwell Relation)

(from last time) $\left.\frac{\partial P}{\partial T}\right|_{V} = -\left.\frac{\partial P}{\partial V}\right|_{T} \Big/ \left.\frac{\partial T}{\partial V}\right|_{P} = -\left.\frac{\partial V}{\partial T}\right|_{P} \Big/ \left.\frac{\partial V}{\partial P}\right|_{T}$

$$\therefore \left.\frac{\partial P}{\partial T}\right|_{V} = +\frac{\alpha}{\kappa_T} \Rightarrow$$

$$\left.\frac{\partial V}{\partial T}\right|_{P} = -V\alpha$$

$$\boxed{\therefore C_P = C_V + \frac{TV\alpha^2}{\kappa_T}}$$

General Results for partial derivatives (8)

Consider $\psi(x, y, z) = 0$

$$d\psi = \frac{\partial \psi}{\partial x}\Big|_{y,z} dx + \frac{\partial \psi}{\partial y}\Big|_{x,z} dy + \frac{\partial \psi}{\partial z}\Big|_{x,y} dz = 0$$

hold z constant $\Rightarrow$ $\cancel{\frac{\partial \psi}{\partial x}\Big|_z}$

$$\frac{\partial x}{\partial y}\Big|_z = -\partial\psi/\partial y\Big|_{x,z} \Big/ \frac{\partial \psi}{\partial x}\Big|_{y,z}$$ (old result)

hold y const. $(dy = 0) \Rightarrow$

$$\frac{\partial z}{\partial x}\Big|_y = -\frac{\partial \psi}{\partial x}\Big|_{y,z} \Big/ \frac{\partial \psi}{\partial z}\Big|_{x,y}$$

hold x const. $(dx = 0) \Rightarrow$

$$\frac{\partial y}{\partial z}\Big|_x = -\frac{\partial\psi/\partial z|_{x,y}}{\partial\psi/\partial y|_{x,z}}$$

Multiply

$$\therefore \boxed{\frac{\partial x}{\partial y}\Big|_z \frac{\partial y}{\partial z}\Big|_x \frac{\partial z}{\partial x}\Big|_y = -1}$$

$f(x,y,z) = 0 \Rightarrow$ think of $x(y,z)$ or $y(x,z)$

therefore $$dx = \frac{\partial x}{\partial y}\Big|_z dy + \frac{\partial x}{\partial z}\Big|_y dz \quad (1)$$

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

then, keep z constant,

from (1) $\frac{\partial x}{\partial y}\Big|_z = \frac{\partial x}{\partial y}\Big|_z$; from (2) $\frac{\partial x}{\partial y}\Big|_z = \frac{1}{\frac{\partial y}{\partial x}\Big|_z}$

$$\therefore \frac{\partial y}{\partial x}\Big|_z = \frac{1}{\frac{\partial x}{\partial y}\Big|_z}$$

H.W. ~~#3~~. show $K_S = K_T - TV\frac{\alpha^2}{C_p}$

H.W. #1 : Callen 5.3-2
#2 : Callen 5.3-8

See Callen for systematic method to reduce all such derivatives to combinations of C_p, K_T, α, etc.