Thermodynamic Potentials — useful for describing equilibrium conditions as specific extensive and intensive quantities are held fixed.

Enthalpy — describes approach to equilibrium w/ no heat exchange ($đQ = 0$), while constant forces J_i are applied.

Quasistatic change of system $\qquad đW = \sum_i J_i \, dx_i$

Non-quasistatic → can be dissipation $\qquad đW \leq \sum_i J_i \, \delta x_i$

$đQ = 0 \;\Rightarrow\; \delta E = đQ + đW \leq \sum_i J_i \, \delta x_i$

not necessarily in equilibrium during change.

$$\delta \left(E - \sum_i J_i x_i \right) \leq 0$$

Equilibrium: $\quad \boxed{H \equiv E - \sum_i J_i x_i} = \text{minimum}$

Enthalpy

In equilibrium, $\quad dH = dE - d\left(\sum_i J_i x_i\right) = dE - \sum_i J_i \, dx_i - \sum_i x_i \, dJ_i$

$$= T \, dS + \sum_i J_i \, dx_i - \sum_i J_i \, dx_i - \sum_i x_i \, dJ_i$$

$$\boxed{dH = T \, dS - \sum_i x_i \, dJ_i}$$

Natural variables for describing enthalpy: $H = H(S, J_i)$

$$x_i = -\left.\frac{\partial H}{\partial J_i}\right|_{S, J_{j \neq i}}$$

Instead consider H as fn. of T, J_i

$$C_P = \left.\frac{đQ}{dT}\right|_P = \left.\frac{d(E + PV)}{dT}\right|_P = \left.\frac{dH}{dT}\right|_P$$

Helmholtz Free Energy — Isothermal transformations w/ no work
$$(dW = 0)$$

Clausius's thm $\longrightarrow$ At const. T, $dQ \leq T\delta S$

$$\delta E = dQ + dW \leq T\delta S$$

$$\delta(E - TS) \leq 0$$

Equilibrium: $\boxed{F \equiv E - TS}$ = minimum

$\uparrow$ Helmholtz Free Energy

In equilibrium, $dF = dE - d(TS)$

$$= T dS + \sum_i J_i \, dx_i - T dS - S dT$$

$$\boxed{dF = -S dT + \sum_i J_i \, dx_i}$$

Natural variables $F = F(T, x_i)$

$$\boxed{J_i = \left.\frac{\partial F}{\partial x_i}\right|_{T, x_{j \neq i}}} \quad , \quad \boxed{S = -\left.\frac{\partial F}{\partial T}\right|_{x_i}}$$

Internal energy $E = F + TS = F + T\left(-\left.\frac{\partial F}{\partial T}\right|_{x_i}\right)$

$$= -T^2 \frac{\partial}{\partial T}\left(\frac{E}{T}\right)\Big|_{x_i}$$

Gibbs Free Energy — isothermal transformations w/
mechanical work at constant external force.

$$\not{d}W \leq \sum_i J_i \delta x_i \qquad (\text{allows dissipation})$$

$$\not{d}Q \leq T \delta S \qquad (\text{allows irreversibility})$$

$$\delta E \leq T \delta S + \sum_i J_i \delta x_i$$

$$\delta \left(E - TS - \sum_i J_i x_i \right) \leq 0$$

Equilibrium:

$$\boxed{G = E - TS - \sum_i J_i x_i} = \text{minimum}$$

↑ Gibbs Free energy

In equilibrium, $\quad dG = dE - d(TS) - d\left(\sum_i J_i x_i\right)$

$$\Rightarrow \boxed{dG = -S dT - \sum_i x_i dJ_i}$$

Natural variables for $G = G(T, J_i)$
Note that T, J_i are intensive in many cases

When chemical reactions are relevant, change in
number of particles of different species →
change in internal energy
$\qquad \rightarrow$ chemical work $\quad \not{d}W = \sum_\alpha \mu_\alpha dN_\alpha$

↑ chemical potential of species α.

In that case, $G = E - TS - \sum_i J_i dx_i$

$$\boxed{dG = -S dT - \sum_i x_i dJ_i + \sum_\alpha \mu_\alpha dN_\alpha}$$

$$G = G(T, J_i, N_\alpha)$$

Grand Potential — chemical equilibrium w/ no mechanical work.

Equilibrium: $\boxed{\mathcal{G} = E - TS - \sum_{\alpha} \mu_{\alpha} N_{\alpha}}$ = minimum

$\underset{\color{red}{\text{Grand Potential}}}{\color{red}{\uparrow}}$

In general, $d\mathcal{G} = -S\,dT + \sum_i J_i\,dx_i - \sum_{\alpha} N_{\alpha}\,d\mu_{\alpha}$

Example: Consider N particles of supersaturated steam in a container of volume V at temperature T. The system evolves to an equilibrium mixture w/ N_w liquid particles and N_s gas particles.

$$\begin{array}{|c|}\hline V, N \\ \cdots \\ N_s = N - N_w \\ \hline \end{array} \; T$$

$\quad N_w$
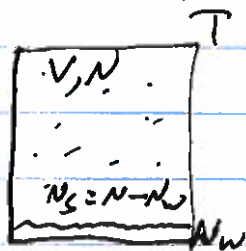
Fixed: $V, T, N \Rightarrow$ use $F(V, T, N)$

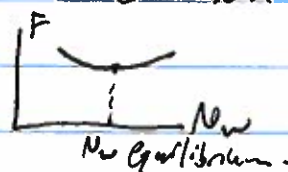$dF = d(E - TS) = -S\,dT - P\,dV + \sum_{\alpha} \mu_{\alpha}\,dN_{\alpha}$

Assume sufficiently slow approach to equilibrium
$\rightarrow$ can define $F(V, T, N | N_w) = F_w(T, N_w) + F_s(V, T, N - N_w)$

$\color{red}{\text{'ignores volume of liquid}}$

$\delta F = \left.\dfrac{\partial F_w}{\partial N_w}\right|_{T,V} \delta N_w - \left.\dfrac{\partial F_s}{\partial N_s}\right|_{T,V} \delta N_w = 0$ in equilibrium

$\left.\dfrac{\partial F_w}{\partial N_w}\right|_{T,V} = \mu_w$, $\left.\dfrac{\partial F_s}{\partial N_s}\right|_{T,V} = \mu_s$ from form of dF.

$\boxed{\mu_w(V, T) = \mu_s(V, T)}$ in chemical equilibrium

N_w Equilibrium.

Consequences of Extensivity

If the system is extensive, then
$$E(\lambda S, \lambda x_i, \lambda N_\alpha) = \lambda E(S, x_i, N_\alpha)$$

$$\frac{\partial}{\partial \lambda}\Big|_{\lambda=1} \Rightarrow \frac{\partial E}{\partial S}\Big|_{x_i, N_\alpha} S + \sum_i \frac{\partial E}{\partial x_i}\Big|_{S, N_\alpha, x_{j \neq i}} x_i + \sum_\alpha \frac{\partial E}{\partial N_\alpha}\Big|_{S, x_i} N_\alpha$$

$$= E(S, x_i, N_\alpha)$$

Use $dE = TdS + \sum_i J_i \, dx_i + \sum_\alpha \mu_\alpha \, dN_\alpha$

$$\Rightarrow \frac{\partial E}{\partial S}\Big|_{x_i, N_\alpha} = T, \quad \frac{\partial E}{\partial x_i}\Big|_{S, N_\alpha, x_{j \neq i}} = J_i ,$$

$$\frac{\partial E}{\partial N_\alpha}\Big|_{S, x_i} = \mu_\alpha$$

$$\Rightarrow \boxed{E = TS + \sum_i J_i x_i + \sum_\alpha \mu_\alpha N_\alpha}$$

$$dE = TdS + \sum_i J_i \, dx_i + \sum_\alpha \mu_\alpha \, dN_\alpha \rightarrow \boxed{SdT + \sum_i x_i \, dJ_i + \sum_\alpha N_\alpha \, d\mu_\alpha = 0}$$

Gibbs-Duhem Relation

Example: Fixed amount of gas along an isotherm $(dT = 0)$:

$$-VdP + N \, d\mu = 0 \Rightarrow d\mu = \frac{V}{N} dP$$

$$\text{Ideal gas: } PV = N k_B T$$

$$\Rightarrow d\mu = k_B T \frac{dP}{P} \Rightarrow \boxed{\mu = \mu_0 + k_B T \ln \frac{P}{P_0}}$$

<u>Maxwell relations</u> — follow from equality of mixed second partial derivatives

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$$

Consider $dE = TdS + \sum_i J_i dx_i + \sum_\alpha \mu_\alpha dN_\alpha$

$$\frac{\partial E}{\partial S}\bigg|_{x_i, N_\alpha} = T \, , \qquad \frac{\partial E}{\partial x_i}\bigg|_{S, x_{j \neq i}, N_\alpha} = J_i$$

$$\frac{\partial^2 E}{\partial S \partial x_i} = \frac{\partial^2 E}{\partial x_i \partial S} \implies \boxed{\frac{\partial T}{\partial x_i}\bigg|_{S, N_\alpha, x_{j \neq i}} = \frac{\partial J_i}{\partial S}\bigg|_{x_i, N_\alpha}}$$

From $dF = d(E - TS) = -SdT + \sum_i J_i dx_i$

$$\implies \boxed{-\frac{\partial S}{\partial x_i}\bigg|_{T, x_{j \neq i}} = \frac{\partial J_i}{\partial T}\bigg|_{x_i}}$$

Similarly for other thermodynamic potentials.

Example: $\frac{\partial \mu}{\partial P}\bigg|_{N,T}$ for ideal gas:

$$d(E - TS + PV) = -SdT + VdP + \mu dN$$

$$\frac{\partial \mu}{\partial P}\bigg|_{N,T} = \frac{\partial V}{\partial N}\bigg|_{T,P} = \frac{V}{N} = \frac{k_B T}{P}$$

Chain Rule:
$$\left.\frac{\partial S}{\partial V}\right|_{E,N} \left.\frac{\partial E}{\partial S}\right|_{V,N} \left.\frac{\partial V}{\partial E}\right|_{S,N} = -1$$

Consider $dE = TdS - PdV + \mu dN$.

At constant $E, N \rightarrow TdS - PdV = 0$

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

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

So $\left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{-\left.\frac{\partial E}{\partial V}\right|_{S,N}}{\left.\frac{\partial E}{\partial S}\right|_{V,N}}$