Postulates of Thermodynamics

- **Postulate 1:**
  - Macroscopic state $\longrightarrow$ U V N

intern energy
volume
# of particles

WALLS		Restriction
• Adiabatics	$\longrightarrow$	heat flux
• fixed	$\longrightarrow$	Volume
• Impervious	$\longrightarrow$	Particle flux.

} Composed system

- **Postulate 2:**

$\exists \quad S = S(U_1, V_1, N_1, U_2, V_2, N_2, \ldots)$ Entropy

$\forall$ all state in equilibrium

  - S grows when a constriction is removed.
  - S is a fundamental equation.

- **Postulate 3:**
  - $S(U_1, V_1, N_1, U_2, V_2, N_2) = S(U_1, V_1, N_1) + S(U_2, V_2, N_2)$
  - S is continuous, and differentiable.
  - monotonic increasing of U.

$\rightarrow \dfrac{\partial S}{\partial U} > 0 \longrightarrow$ Positive temperature

also, $\quad \exists \; U = U(S, V, N)$

more over

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$ homogeneous function.

let $\lambda = \dfrac{1}{N}$

then, $\dfrac{1}{N} S(U, V, N) = S\left(\dfrac{U}{N}, \dfrac{V}{N}, 1\right) = S(u, v)$

- Postulate 4:

$$S = 0 \text{ if } \left(\frac{\partial U}{\partial S}\right)_{V,N} = 0.$$

Intensive parameters

$$U = U(S, V, N) \qquad \text{Energy representation}$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,S} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

$$\Delta U = \Delta Q + \Delta W_{mechanic} + \Delta W_{chemical} \qquad \text{Energy conservation}$$

$$= T\Delta S - p\Delta V + \mu \Delta N$$

$$T := \left(\frac{\partial U}{\partial S}\right)_{V,N} = T(S,V,N) \qquad \text{Temperature}$$

$$p := -\left(\frac{\partial U}{\partial V}\right)_{S,N} = p(S,V,N) \qquad \text{Pressure}$$

$$\mu := \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu(S,V,N) \qquad \text{Chemical potential}$$

- State equations

  $\longrightarrow$ Fundamental equation.

- Homogeneous of grade zero.

$$T(\lambda S, \lambda V, \lambda N) = T(S,V,N) \qquad \text{Intensive variables}$$

Entropy representation

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$F_1 = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \; ; \; F_2 = \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T} \; ; \; F_3 = \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

$$U(S,V,N) = N u(s,v)$$

$$\left(\frac{\partial u}{\partial s}\right)_{v} ds + \left(\frac{\partial u}{\partial v}\right)_{s} dv = T ds + p dv$$

Since $\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial u}{\partial s}\right)_v = T$

and $\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\partial u}{\partial v}\right)_s = -p$

Example: Monoatomic classical ideal gas.

$$\begin{cases} pV = NK_BT \qquad U = \frac{3}{2}NK_BT \\ \frac{P}{T} = \frac{NK_B}{V} \longrightarrow \left(\frac{\partial s}{\partial v}\right)_u = \frac{K_B}{v} \\ \frac{1}{T} = \frac{3NK_B}{2U} \longrightarrow \left(\frac{\partial s}{\partial u}\right)_v = \frac{3K_B}{2u} \end{cases}$$

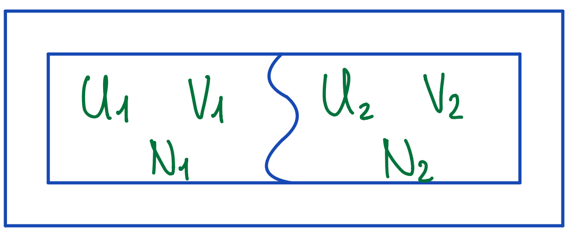
$$\begin{cases} s(u,v) = K_B \ln(v) + f(u) \\ s(u,v) = \frac{3}{2}K_B \ln(u) + g(v) \end{cases}$$

$$\rightarrow s(u,v) = \frac{3}{2}K_B\ln(u) + K_B\ln(v) + K_Bc$$

$$\rightarrow S(U,V,N) = Ns\left(\frac{U}{N}, \frac{V}{N}\right)$$

$$= \frac{3}{2}NK_B\ln\left(\frac{U}{N}\right) + NK_B\ln\left(\frac{V}{N}\right) + NK_Bc$$

Equilibrium



$$S = S_1(U_1,V_1,N_1) + S_2(U_2,V_2,N_2)$$

let V_1, V_2, N_1 and N_2 be constants, and $U_1 + U_2 = \text{constant} = U_0$

$S \rightarrow$ Maximum.

$$\frac{\partial S}{\partial U_1} = \frac{\partial S_1}{\partial U_1} + \frac{\partial S_2}{\partial U_1} = \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} = \frac{1}{T_1} - \frac{1}{T_2} = 0$$

$$\rightarrow T_1 = T_2$$

$$\frac{\partial^2 S}{\partial U_1^2} = \frac{\partial^2 S_1}{\partial U_1^2} - \frac{\partial}{\partial U_1}\left(\frac{\partial S_2}{\partial U_2}\right) = \frac{\partial^2 S_1}{\partial U_1^2} + \frac{\partial^2 S_2}{\partial U_2^2}$$

$$= \frac{\partial}{\partial U_1}\left(\frac{1}{T_1}\right) + \frac{\partial}{\partial U_2}\left(\frac{1}{T_2}\right) = \frac{-1}{T_1^2}\frac{\partial T_1}{\partial U_1} - \frac{1}{T_2^2}\frac{\partial T_2}{\partial U_2}$$

$$= -\frac{1}{T_1^2}\frac{\partial T_1}{\partial U_1} - \frac{1}{T_2^2}\frac{\partial T_2}{\partial U_2} < 0$$

$$\longrightarrow \left(\frac{\partial T}{\partial U}\right)_{V,N} > 0$$

$C_V := \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}$ Specific heat at constant volume

$$= \frac{T}{N}\frac{\partial S}{\partial U}\frac{\partial U}{\partial T} = \frac{T}{N}\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_{V,N}$$

$$\rightarrow \left(\frac{\partial T}{\partial U}\right)_{V,N} = \frac{1}{\left(\frac{\partial U}{\partial T}\right)_{V,N}} = \frac{1}{NC_V} > 0$$

$$\rightarrow C_V > 0$$

Now, also we are able to put free walls.

$$S = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2)$$

for N_1 and N_2 constants.

$$U_1 + U_2 = U_0 = \text{constant}, \qquad V_1 + V_2 = V_0 = \text{constant}.$$

$$\frac{\partial S}{\partial U_1} = 0 \rightarrow T_1 = T_2$$

$$\frac{\partial S}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = \frac{P_1}{T_1} - \frac{P_2}{T_2} = 0 \longrightarrow P_1 = P_2.$$

Euler & Gibbs relations.

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N)$$

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} S + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} V + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} N$$

$$= U(S,V,N)$$

for $\lambda = 1 \rightarrow TS - pV + \mu N = U$ Euler equation

$$\rightarrow \cancel{TdS} + SdT - \cancel{pdV} - Vdp + \cancel{\mu dN} + Nd\mu = \cancel{dU}$$

$$SdT - Vdp + Nd\mu = 0$$

$d\mu = v\,dp - s\,d\mu$ Gibbs - Duhem relation

$\mu = \mu(p,T)$ is fondamental with v and s being state equations.

Measurable quantities

Thermal expansion coefficient.

$$\alpha = \lim_{\Delta T \to 0} \frac{1}{V}\left(\frac{\Delta V}{\Delta T}\right)_{p,N} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$$

Isothermal compressibility

$$K_T = \lim_{\Delta p \to 0} -\frac{1}{V}\left(\frac{\Delta V}{\Delta p}\right)_{T,N} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

Isentropic (Adiabatic) compressibility

$$K_S = \lim_{\Delta p \to 0} -\frac{1}{V}\left(\frac{\Delta V}{\Delta p}\right)_{S,N} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N}$$

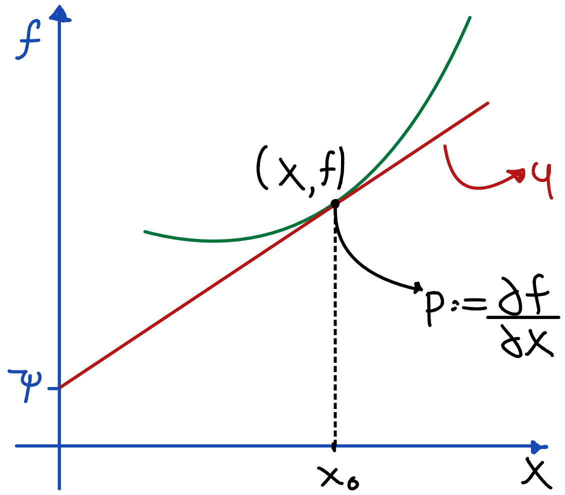
Specific heat at constant pressure

$$C_p = \lim_{\Delta T \to 0} \frac{1}{N}\left(\frac{\Delta Q}{\Delta T}\right)_{p,N} = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{p,N}$$

Specific heat at constant volume

$$C_V = \lim_{\Delta T \to 0} \frac{1}{N}\left(\frac{\Delta Q}{\Delta T}\right)_{V,N} = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

Legendre Transformation



$$y = f'(x_0)(x - x_0) + f(x_0)$$

If $x = 0$, then $y = \psi$

$$\rightarrow \psi = -f'(x_0)x_0 + f(x_0)$$

$$p := f'(x_0)$$

$$\rightarrow \psi = \psi(p) = f(x) - px$$

$$f(x) = ax^2 + bx + c$$

$$\psi(p) = ax^2 + bx + c - px \qquad p = \frac{df}{dx} = 2ax + b$$

$$\longrightarrow x = \frac{p-b}{2a} \rightarrow \psi(p) = \frac{-1}{4a}p^2 + \frac{b}{2a}p - \frac{b^2}{4a}$$

If f is convex, then ψ is concave

Example:

$$\mathcal{L} = \mathcal{L}(q, \dot{q}, t) \qquad \text{Lagrangian}$$

$$p = \frac{\partial \mathcal{L}}{\partial \dot{q}}$$

$$-\mathcal{H}(q, p, t) = \mathcal{L}(q, \dot{q}, t) - p\dot{q}$$

$$\mathcal{L} = \frac{1}{2}m\dot{x}^2 - \frac{1}{2}kx^2 \qquad \text{Harmonic oscillator}$$

$$-\mathcal{H} = \mathcal{L} - \dot{x}p_x \qquad p_x = \frac{\partial \mathcal{L}}{\partial \dot{x}} = m\dot{x}$$

$$\longrightarrow \mathcal{H} = \frac{1}{2m}p_x^2 + \frac{1}{2}kx^2$$

Thermodynamic potentials

$$U[T] = F(T, V, N)$$

$$= U(S, V, N) - \left(\frac{\partial U}{\partial S}\right)S \qquad \text{Helmholtz free energy}$$

$= U - TS$

$U[p] = H(S, p, N)$ Enthalpy

$= U + pV$

$U[\mu] = f_1(S, V, \mu) = U - \mu N$

$U[T, p] = G(T, p, N)$ Gibbs free energy

$= U - TS + pV$

$U[T, \mu] = \Phi(T, V, \mu)$ Great thermodynamic potential

$= U - TS - \mu N$

$U[p, \mu] = f_2(S, p, \mu)$

$= U + pV - \mu N$

$U[T, p, \mu] = U - TS + pV - \mu N = 0$

$\longrightarrow G(T, p, N) = N\mu - N\mu(T, p)$

and $\Phi(T, V, N) = -Vp = -Vp(T, \mu)$

If we take $S = S(U, V, N)$

Massieu potentials.

Maxwell relations

$F = U - TS$

$dF = dU - TdS - SdT = -SdT - pdV + \mu dN$

$dU = TdS - pdV + \mu dN$

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

$S = S(T, V, N)$ $p = p(T, V, N)$ $\mu = \mu(T, V, N)$

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \longrightarrow \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}$$

$$\frac{\partial^2 F}{\partial N \partial T} = \frac{\partial^2 F}{\partial T \partial N} \longrightarrow -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N}$$

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

$$G = U - TS - pV$$

$$dG = -S\,dT + V\,dp + \mu\,dN$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad ; \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad ; \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$$

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

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

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

Example:

$$S = \frac{3}{2} N K_B \ln\left(\frac{U}{N}\right) + N K_B \ln\left(\frac{V}{N}\right) + N K_B C$$

$$U = N\left(\frac{N}{V}\right)^{2/3} \exp\left[\frac{2}{3}\left(\frac{S}{NK_B} - C\right)\right]$$

$$F = U - TS$$

$$= N\left(\frac{N}{V}\right)^{2/3} \exp\left[\frac{2}{3}\left(\frac{S}{NK_B} - C\right)\right] - TS$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{2}{3K_B}\left(\frac{N}{V}\right)^{2/3} \exp\left[\frac{2}{3}\left(\frac{S}{NK_B} - C\right)\right]$$

$$\frac{3K_B}{2}\left(\frac{V}{N}\right)^{2/3} T = \exp\left[\frac{2}{3}\left(\frac{S}{NK_B} - C\right)\right]$$

$$\ln\left[\frac{3K_B}{2}\left(\frac{V}{N}\right)^{2/3} T\right] = \frac{2}{3}\left(\frac{S}{NK_B} - C\right)$$

$$\frac{S}{K_B N} = \frac{3}{2} \ln\left[\frac{3K_B}{2}\left(\frac{V}{N}\right)^{2/3} T\right] + C$$

$$F = N\left(\frac{N}{V}\right)^{2/3} \frac{3K_B}{2}\left(\frac{V}{N}\right)^{2/3} T - TNK_B \left\{\frac{3}{2} \ln\left[\frac{3K_B}{2}\left(\frac{V}{N}\right)^{2/3} T\right] + C\right\}$$

$$= N\frac{3}{2} K_B T - TNK_B \left\{\frac{3}{2}\left[\ln\left(\frac{3}{2} K_B T\right) + \frac{2}{3}\ln\left(\frac{V}{N}\right)\right] + c\right\}$$

$$= \frac{3}{2} NK_B T - TNK_B \left\{\frac{3}{2}\ln\left(\frac{3}{2}K_B T\right) + \ln\left(\frac{V}{n}\right) + c\right\}$$

$$= \frac{3}{2} NK_B T - TNK_B \frac{3}{2}\ln\left(\frac{3}{2}K_B T\right) - TNK_B \ln\left(\frac{V}{n}\right) - TNK_B C$$

$$F = -K_B TN - \frac{3}{2} K_B TN \ln\left(\frac{3}{2}K_B T\right) + NK_B T\left(\frac{3}{2} - C\right)$$

state equations:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = K_B N \ln\left(\frac{V}{N}\right) + \frac{3}{2} K_B N \ln\left(\frac{3}{2} K_B T\right) + NK_B C$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{K_B TN}{V}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,N} = -K_B T \ln\left(\frac{V}{N}\right) - \frac{3}{2} K_B T \ln\left(\frac{3}{2} K_B T\right) + \frac{5}{2} K_B T - CK_B T$$

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$