Lecture Notes

Week 3

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Combine First Law & Second Law

$$\delta q_{rev} = T dS$$

First law: $dU = \delta q_{rev} + \delta w$

$$\delta w = -p dV$$

Second law: $\delta q_{rev} = T dS$

$$dU = T dS - p dV$$

$$dS \geq \frac{\delta q}{T}$$

(Clausius inequality)

Combined:

$$dU = T dS - p dV$$

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

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$dU = T\,dS - p\,dV$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad -p = \left(\frac{\partial U}{\partial V}\right)_S$$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

At constant pressure $dp = 0$

$$dH = C_p dT = dU + p dV$$

$$dU = C_v dT$$

$$C_p - C_v = f(T, V, \text{gas})$$

Use the combined first law and

Second law expression $dU = TdS - pdV$

to prove $$C_p - C_V = TV\frac{\alpha^2}{\beta}$$

$$V = V(T, P)$$

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

$$= V\alpha\, dT - V\beta\, dP$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha \qquad \left(\frac{\partial V}{\partial P}\right)_T = -V\beta$$

Isothermal Compressibility

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Volumetric coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$H = U + pV \rightarrow dH = dU + p\,dV + V\,dP$$

$$\frac{dH}{dT} = \frac{dU}{dT} + p\frac{dV}{dT} + V\frac{dP}{dT}$$

Isobaric $\Rightarrow dp = 0$

$$\underbrace{\left(\frac{\partial H}{\partial T}\right)_p}_{C_p} = \left(\frac{\partial U}{\partial T}\right)_p + p\underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{pV\alpha} \qquad -(1)$$

$$U = U(V, T)$$

$U = U(V,T) \longrightarrow$ $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad - (2)$$

Isobaric (constant P)

Divide (2) by dT and take P constant

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \quad - (3)$$

Substitute (3) in (1)

① $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

③ $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \longrightarrow C_V$

$\therefore \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha} + \left(\frac{\partial U}{\partial T}\right)_V + P\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha}$

$C_P = C_V + V\alpha\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$ — ④

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right]$$

$$dU = T\,dS - p\,dV$$ — Combined First & Second Law

$$dS = \frac{1}{T}(dU) + \frac{p}{T}\,dV$$

$$= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T dV + \frac{p}{T}\,dV$$

$$= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$ — (5)

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad - (6)$$

Compare (5) and (6)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]$$

$Z = Z(x,y) \rightarrow dZ = M\,dx + N\,dy$

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \Rightarrow \frac{\partial^2 Z}{\partial y\,\partial x} = \frac{\partial^2 Z}{\partial x\,\partial y}$$

$$\therefore \quad \frac{\partial^2 S}{\partial T\,\partial V} = \frac{\partial^2 S}{\partial V\,\partial T}$$

$$M = \left(\frac{\partial Z}{\partial x}\right)_y$$

$$N = \left(\frac{\partial Z}{\partial y}\right)_x$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T$$

$$\frac{\partial}{\partial V}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right\} = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T}\right\}$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial V\,\partial T} = \frac{1}{T}\left[\frac{\partial^2 U}{\partial V\,\partial T} + \left(\frac{\partial P}{\partial T}\right)_V\right] - \frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

$$\text{or,} \quad \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

$$\text{or,} \quad T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P$$

$$\text{or,} \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad -(7)$$

$$V = V(T, P)$$

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

If V is fixed, $dV = 0$

or, $$0 = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$= \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\partial V/\partial T\right)_P}{\left(\partial V/\partial P\right)_T} = -\frac{V\alpha}{-V\beta} = \frac{\alpha}{\beta}$$

$$C_P = C_V + V\alpha\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Use (7)

$$= C_V + V\alpha\left[P + T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$$

отн,

$$C_p = C_v + V\alpha\left[T\left(\frac{\partial P}{\partial T}\right)_V\right]$$

$$= C_v + TV\frac{\alpha^2}{\beta}$$

$\frac{\alpha}{\beta}$ }

$$C_p - C_v = R$$

$$C_p(T) = a + bT + c/T^2 + dT^2$$

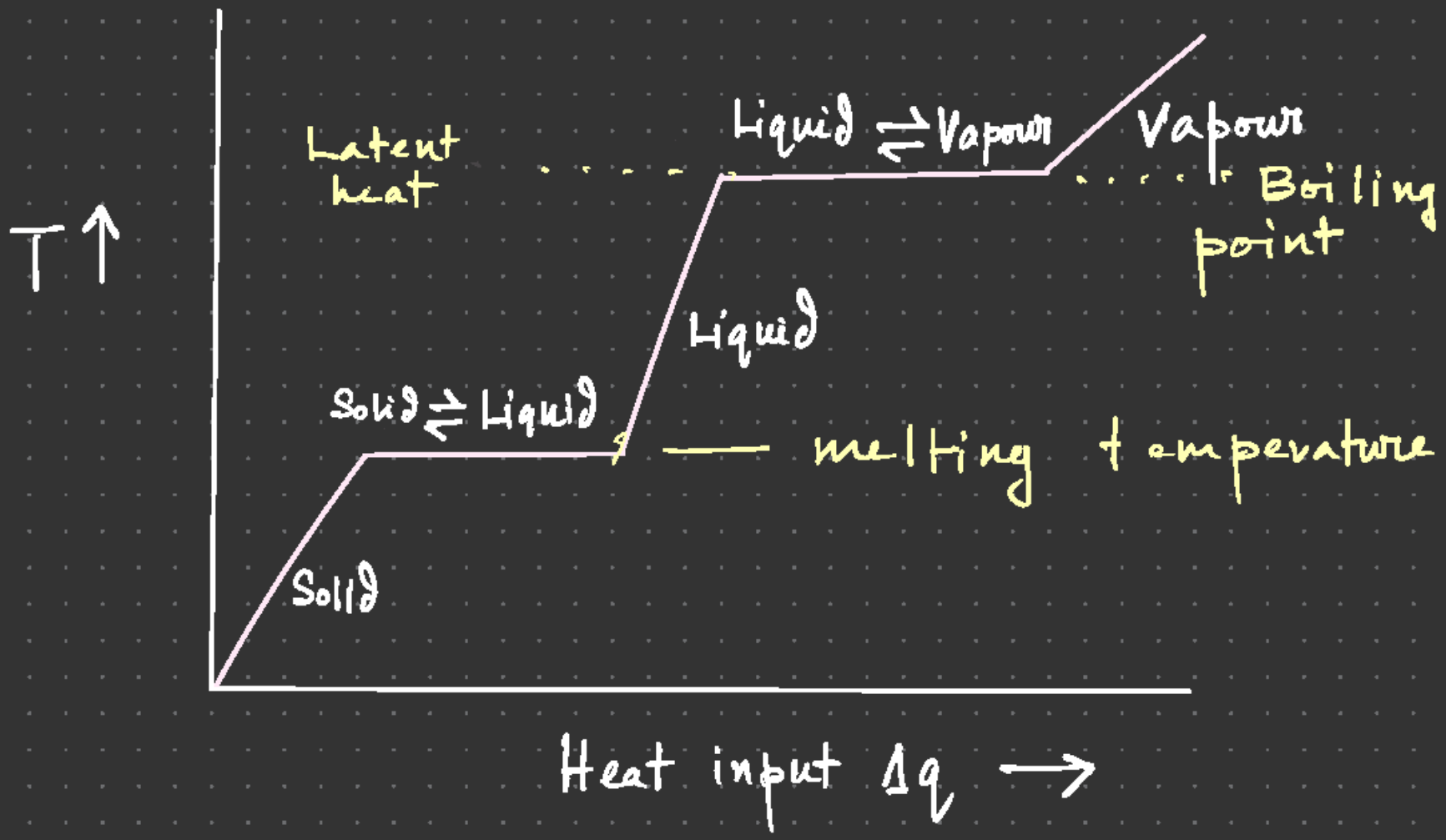
— For a given phase

$$\delta q_{p,rev} = TdS = dH = C_p dT$$

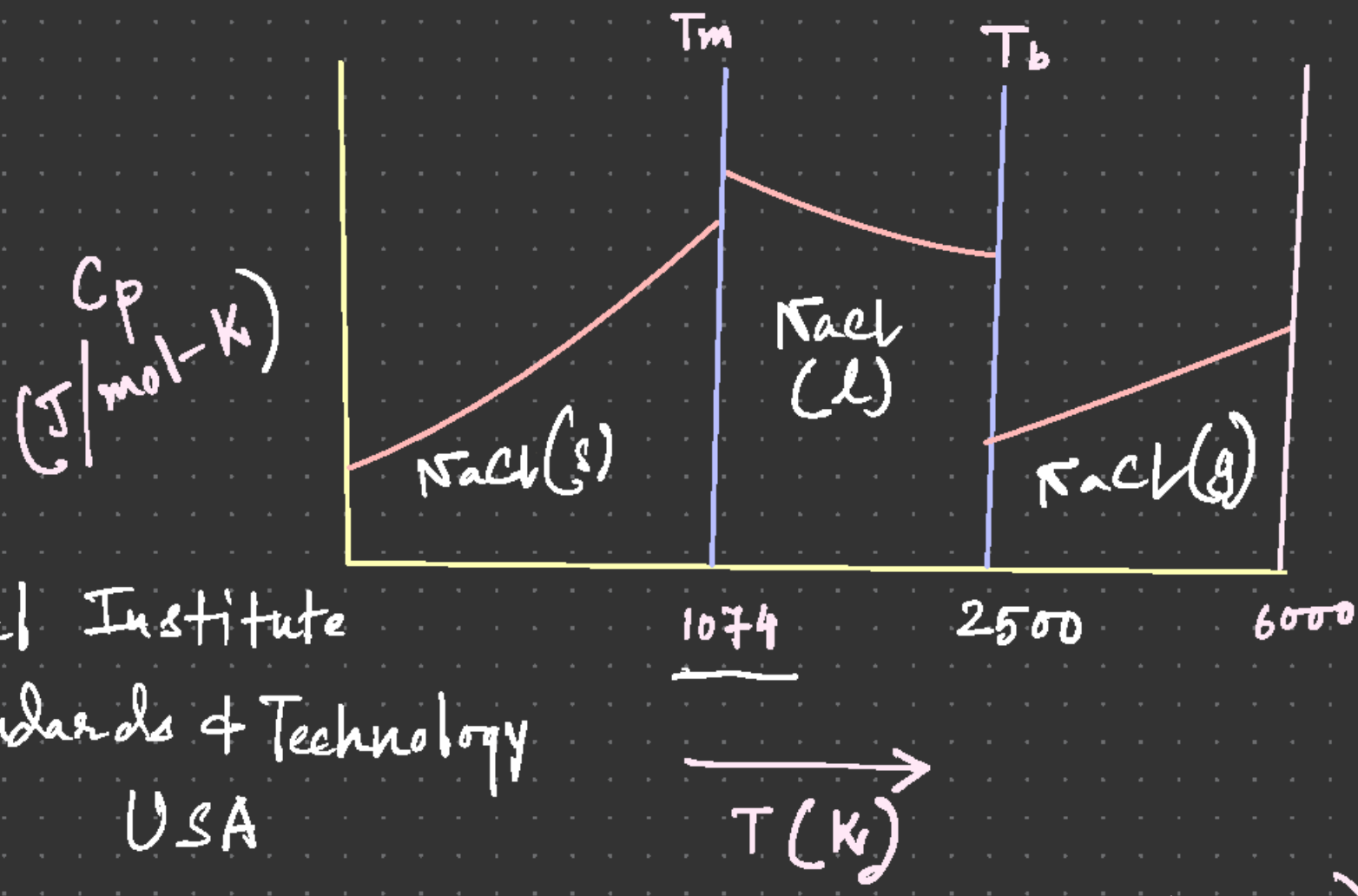
$$\therefore \quad dS = \frac{C_p}{T} dT \qquad \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

$dH = dU + pdV = \delta q_p = C_p dT = TdS$

	a	b ($1/K$)	c (K^2)	d ($1/K^2$)	Range
Ag(s)	21.30	8.54×10^{-3}	1.51×10^5	—	298 – 1234 K
Ni (l)	38.49	—	—	—	1728 – 1900 K



phase change process



National Institute of Standards & Technology USA

Data: NIST Webbook

Sodium chloride (NaCl)

T_m — melting temperature

T_b — boiling temperature

→ Gases generally have lower heat capacity than solids or liquids

→ Liquids often possess higher heat capacity than solids

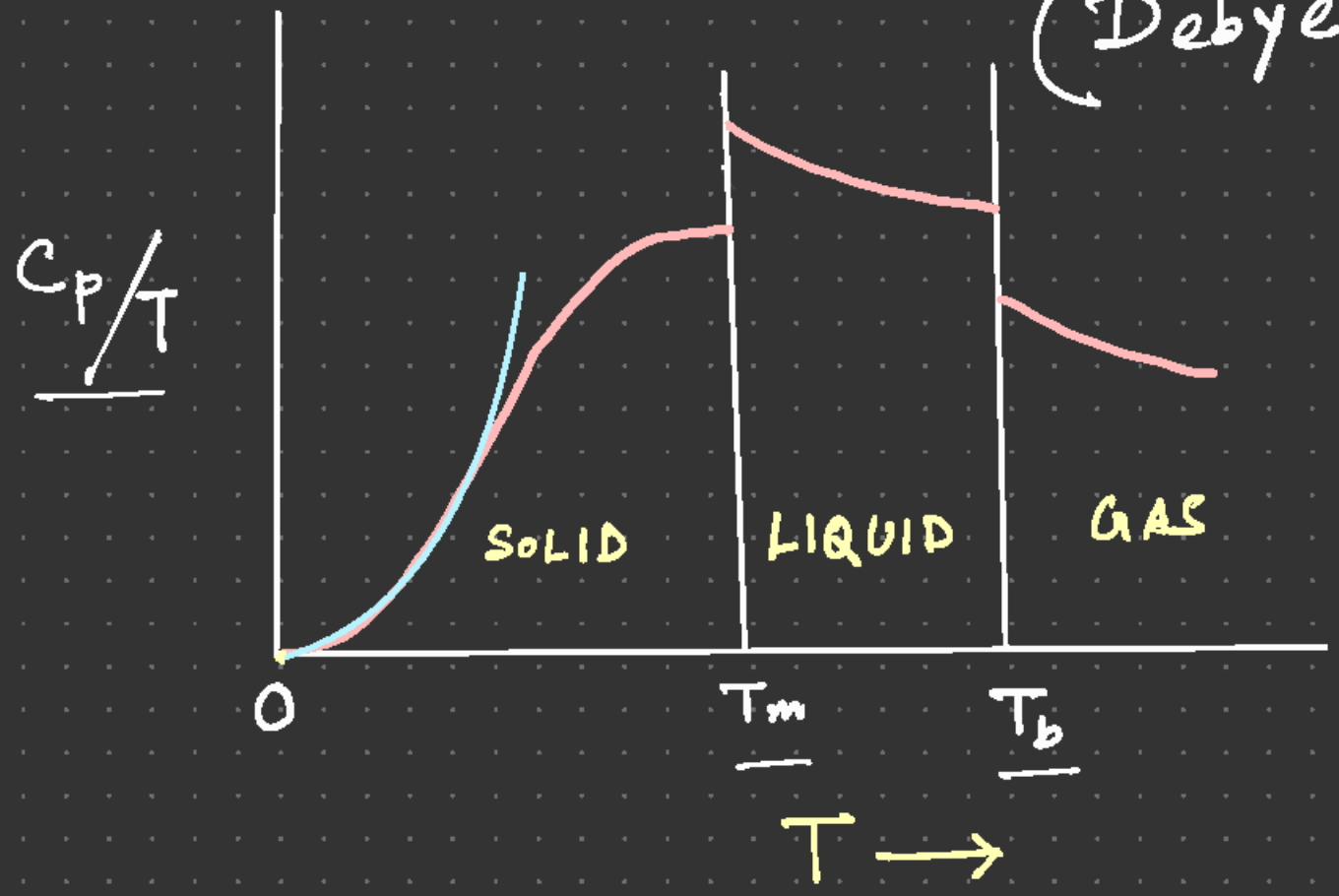
	C_p
Na (vapour, 1200K)	– 12.47 J/mol-K
Na (liquid)	– 31.51 J/mol-K
Na (solid)	– 28.20 J/mol-K

$C_p(Na,l) > C_p(Na,s) > C_p(Na,v)$

$C_p \to 0$ as $T \to 0$

Assume $C_p = aT^3$ to be valid at low T till 0 K

(Debye Extrapolation)



$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T}\, dT = S(T_f) - S(T_i)$$

Constant-pressure molar heat capacity $C_{p,m}$ or C_p of a certain solid at 10 K is 0.51 J/mol-K.

Find its molar entropy at 10 K $\quad C_p = aT^3$

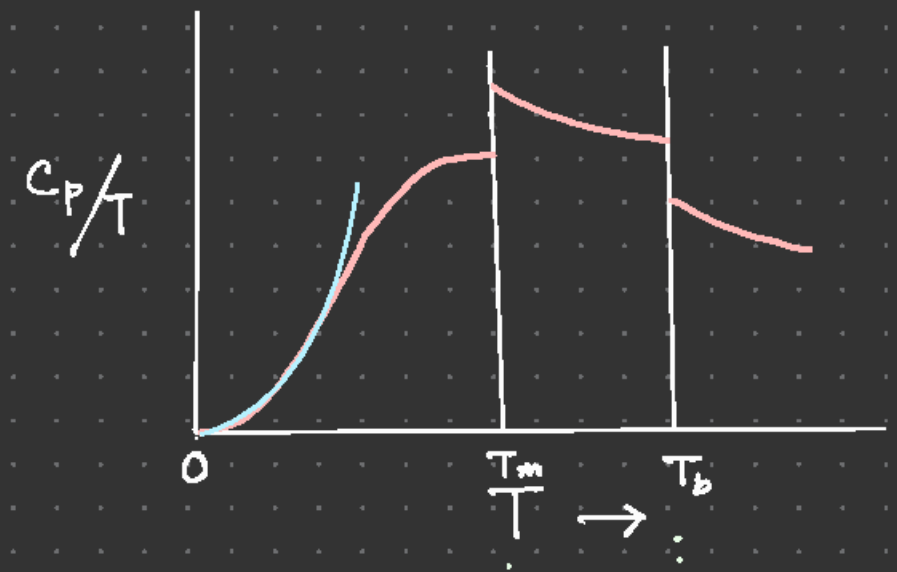
At low temperatures $C_p(T) = aT^3$

$T_f = 10$ K $\qquad T_i = 0$ K

$$S_m(T) - S_m(0) = \int_0^T \frac{aT^3}{T}\, dT = \frac{1}{3} aT^3$$

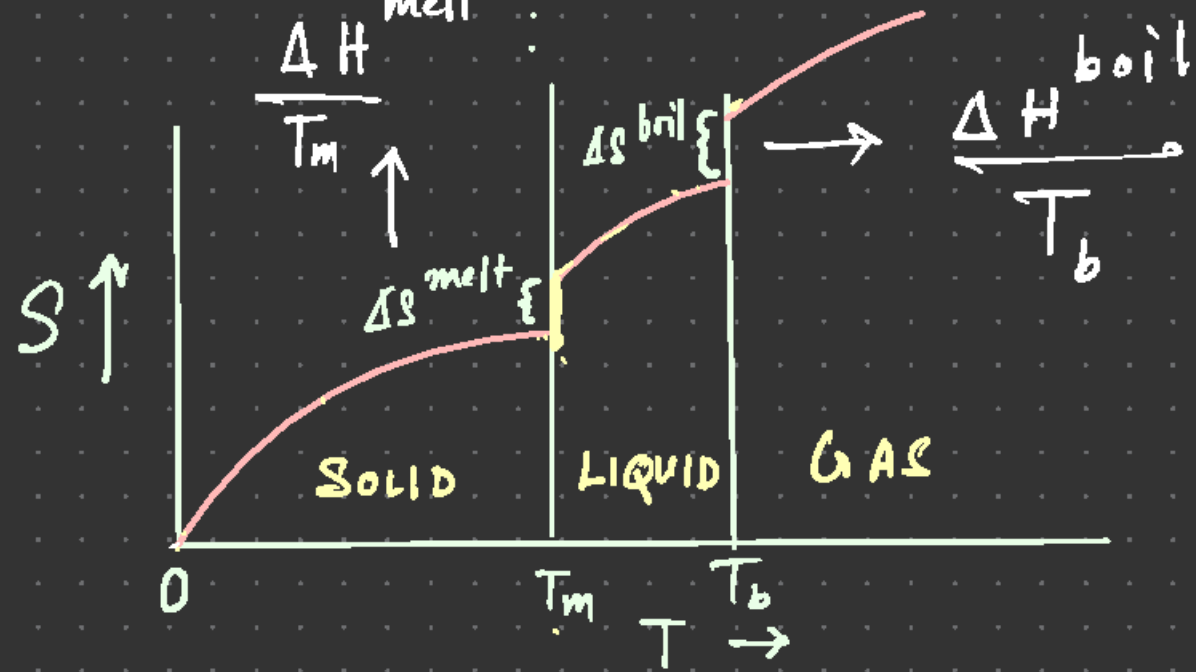
or, $S_m(T) - S_m(0) = \frac{1}{3} C_p(T)$

$$\therefore \quad S_m(10\text{ K}) = S_m(0) + \frac{1}{3}(0.51) = S_m(0) + 0.17 \text{ J/mol-K}$$



$$dS = \frac{C_p}{T}\,dT$$

$$S = \int \frac{C_p}{T}\,dT$$



$$S(T) = S(0) + \int_0^{T_m} \frac{C_p(s)}{T}\,dT + \frac{\Delta H^{s\to l}}{T_m} + \int_{T_m}^{T_b} \frac{C_p(l)}{T}\,dT + \frac{\Delta H^{l\to g}}{T_b} + \int_{T_b}^{T} \frac{C_p(g)}{T}\,dT$$

$$H = U + pV$$

$$\delta q_p = dH$$

$$dS = \frac{dH}{T}$$

$$Sn\,(\text{gray}, 286) \rightleftharpoons Sn\,(\text{white}, 286)$$

α, non-metallic + brittle, $< 13^\circ C$

β, metallic + ductile, $> 13^\circ C$

Legend {
Napoleon's Russia campaign 1812

Tin buttons on soldier's uniforms became powdery and crumbled

$$\Delta H^{tr}\ (\text{gray} \rightarrow \text{white}) = +2.1\ \text{kJ/mol}$$

Find ΔS^{tr}

$$\Delta S^{tr} = \frac{\Delta H^{tr}}{T^{tr}}$$

Thermodynamic Temperature

$$\epsilon = 1 - \frac{T_c}{T_H}$$ { Carnot efficiency }

$$\frac{T_c}{T_H} = 1 - \epsilon$$

$$T_c = (1 - \epsilon) T_H$$

Put $\epsilon = 1$, then $\underline{T_c} = 0\ K$

Third law

Entropy change associated with any physical or chemical transformation as the temperature approaches 0.

$\Delta S \to 0$ as $T \to 0$

— Nernst Heat Theorem

Statement of third law

At absolute zero ($T = 0\ K$) all perfect crystalline substances have the same entropy, and it is zero.

$$S(0\,k) = 0$$ for all substances in perfectly crystalline form

Third law lets us calculate absolute entropies.

$$\Delta S_{0\to T} = \int_0^T \frac{C_p(T)\,dT}{T}$$

$$\delta q_{rev,P} = T\,dS = dH$$

$$\int_i^f dS = \int_{T_i}^{T_f} \frac{C_p\,dT}{T} \qquad C_p\,dT$$

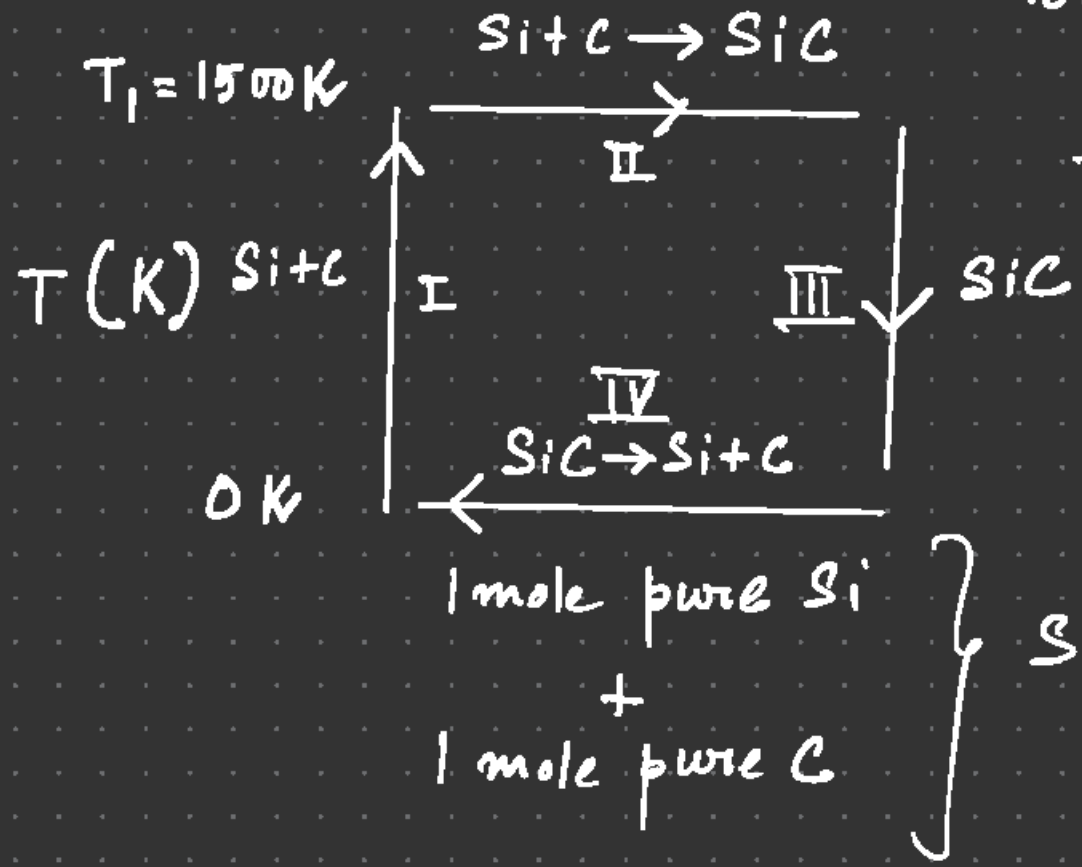
$S(0) = 0 \rightarrow S^{\phi}(T)$ or $S^{\circ}(T)$

Standard entropy at temperature T

S^{ϕ}_m (J/mol-K)

Graphite, C(s)	5.7
Diamond, C(s)	2.4
Water, $H_2O(l)$	69.9
Hydrogen, $H_2(g)$	130.7

S°_{298}



Total change in entropy

$$\underline{\Delta S^t} = \Delta S_{\underline{I}} + \Delta S_{\underline{II}} + \Delta S_{\underline{III}} + \Delta S_{\underline{IV}}$$

$\Delta S_{\underline{IV}}$ $(T = 0\ K)$

$= 0$

Note: heat capacity of SiC different from either Si or C

$\Delta S^t = 0$ (cyclic process)

$\Delta S_{IV} = 0$

$\therefore$ the entropy of pure SiC is the same as entropy of Si and C at $T = 0\ K$ $\left(S_{SiC}(0) = S_{Si}(0) = S_C(0) = 0 \right)$

ΔS_{III}
$= S_{SiC}(0)$
$- S_{SiC}(T_1)$
$= - S_{SiC}$

$\Delta S_I = S_{Si}(T_1)$
$+ S_C(T_1)$
$- S_{Si}(0)$
$- S_C(0)$
$\Delta S_I = S_{Si}(T_1) + S_C(T_1)$

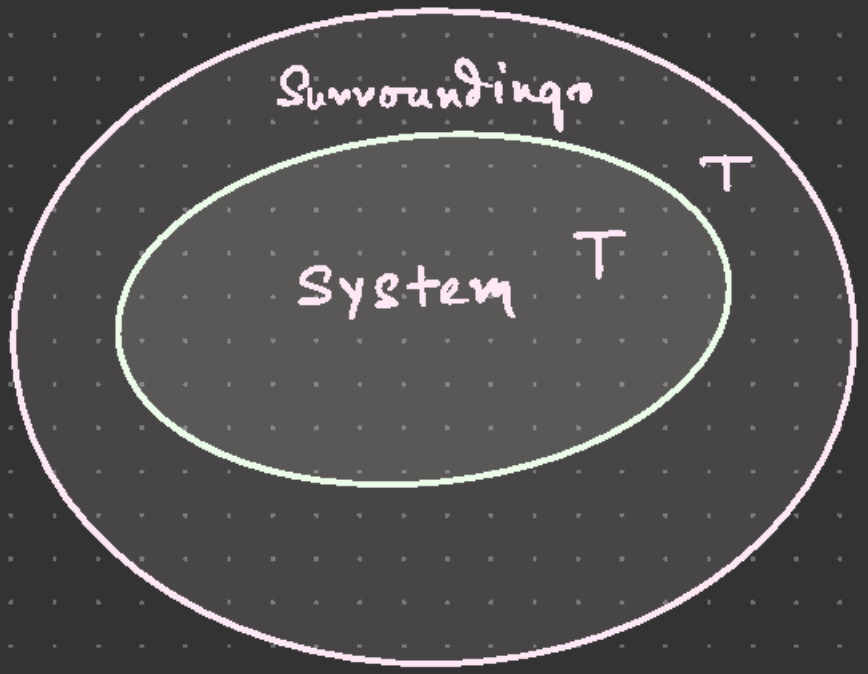
$\Delta S_I + \Delta S_{II} + \Delta S_{III} = 0$ — (A)

From (A)

$\Delta S_{II} = - \Delta S_I - \Delta S_{III}$

$\Delta S^{reaction}_{(Si+C \rightarrow SiC)}(T_1) = S_{SiC}(T_1) - S_{Si}(T_1) - S_C(T_1)$

$Si + C \xrightarrow{1500} SiC$



System in thermal equilibrium with the surroundings at temperature T

Clausius Inequality

$$dS \geqslant \frac{\delta q}{T}$$

Heating at constant volume (no non-expansion work)

$$\delta q_V = dU$$

$$dS \geqslant \frac{dU}{T} \quad (\text{constant } V)$$

$$TdS \geqslant dU$$

Constant internal energy $(dU = 0)$

$$dS_{U,V} \geqslant 0$$

$$dS \geqslant \frac{\delta q}{T}$$

$$\geqslant \frac{\delta q_V}{T}$$

$$\geqslant \frac{dU}{T}$$

Constant entropy

$$dU_{S,V} \leqslant 0$$

$dV = 0$

$dS = 0$

$$\Rightarrow dU_{S,V} \leqslant 0$$

Heat transfer at constant pressure

$$\delta q_p = dH \qquad \delta q_V = dU$$

$$T dS \geq dH$$

Constant enthalpy $dH = 0$

$$dS_{H,p} \geq 0$$

Constant entropy $dS = 0$

$$dH_{S,p} \leq 0$$

U
H
S
F

$dU - TdS \leq 0 \quad \therefore TdS \geq dU$

V, T

$F = U - TS$ – Helmholtz Free Energy

$dF = dU - TdS - SdT$

$dT = 0$ (constant T)

$dH - TdS \leq 0 \quad \therefore TdS \geq dH$

$G = H - TS$ – Gibbs Free Energy

$dU - TdS \leq 0$

$\Rightarrow dF_{T,V} \leq 0$

$$dF_{T,V} \leq 0$$

At constant T and V

$$dF = dU - TdS \leq 0$$

$$\Rightarrow dF_{T,V} \leq 0$$

$$dG_{T,P} \leq 0$$

At constant T and P

$$dG = dH - TdS \leq 0$$

$$dG_{T,P} \leq 0$$

$$dH - TdS \leq 0$$

$$dG_{T,P} \leq 0$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$= dU + VdP + PdV - TdS - SdT$$

$$dP = 0$$

$$dT = 0$$

Postulatory approach

- Classic text

  Thermodynamics and Introduction to Thermostatistics (2nd edition)

  — Herbert B Callen

Defining potentials

- Recent text

  Thermodynamic Equilibrium And Stability of Materials

  Springer 2022

  — Long-Qing Chen

Simple system

- Thermal contribution to energy
- Mechanical contribution to energy
- Chemical contribution to energy

Entropy S — measure of thermal matter
Volume V — measure of mechanical matter
Mole number N_i — measure of chemical matter
(i^{th} species)

Electrical matter = q

Electrical energy = U_q

Electric potential $\phi = \frac{U_q}{q} = \frac{dU_q}{dq}$

$U \rightarrow U_T + U_M + U_C$

Thermal energy = U_T

Thermal matter = S

Thermal potential = $\frac{dU_T}{dS} = T$

Mechanical potential

Mechanical Energy = U_M

Mechanical Matter = V

Mechanical potential $-P = \frac{U_M}{V}$

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

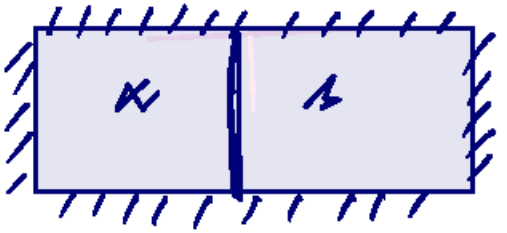
Chemical energy = U_C

Chemical matter = N

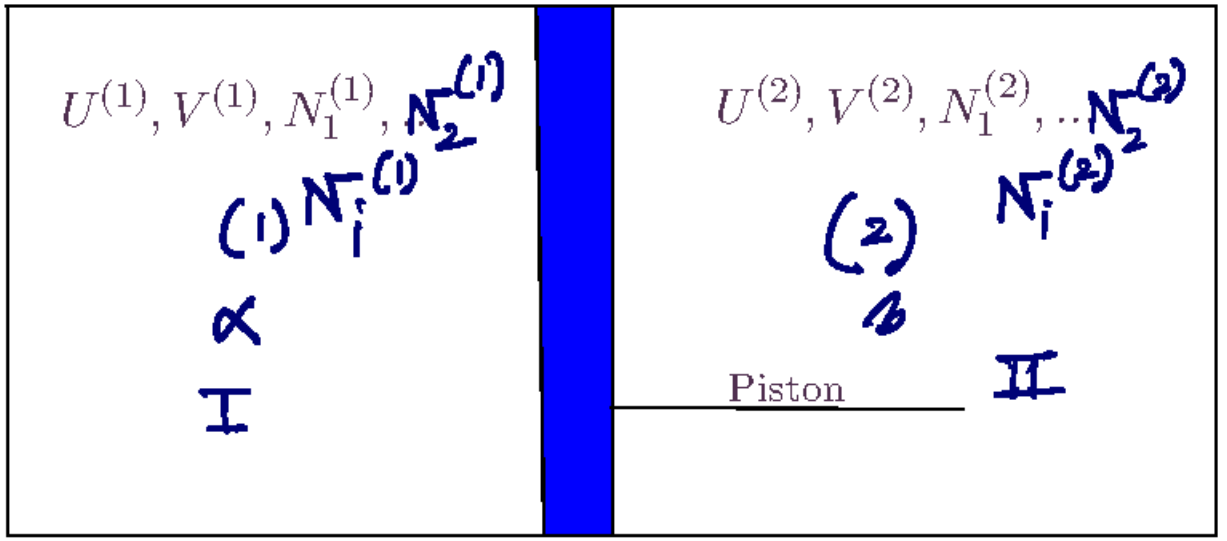
Chemical potential = $\frac{U_C}{N} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

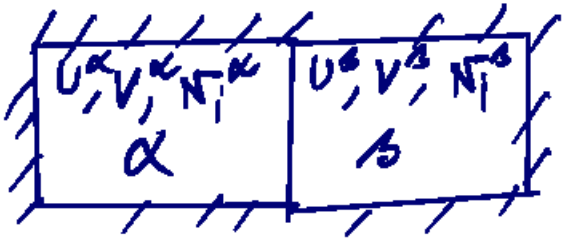
Thermodynamic problem

Determination of equilibrium states which results after the removal of internal constraints in an isolated, composite system



Wall
- Flexible (Rigid)
- Permeable (Impermeable)
- Diathermal (Adiabatic)





Phase
- chemically homogeneous,
physically distinct,
mechanically separable

Entropy function $S = S(U, V, N)$ defined for all equilibrium states: values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

$dS = 0$ Extremum condition

S is an extensive property - additive. Total S of a composite system: sum of entropies of constituent subsystems:

$$S = \sum_{\alpha} S^{(\alpha)}$$

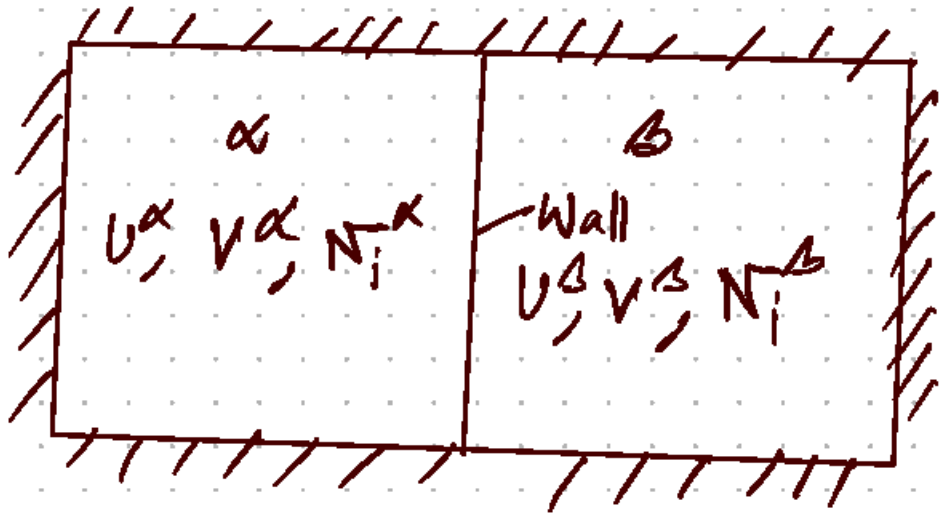
$d^2S < 0$ Maximum

Entropy of each subsystem: function of the extensive parameters of that subsystem

$$S^{(\alpha)} = S^{(\alpha)}\left(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, ..., N_r^{(\alpha)}\right)$$

The entropy is continuous and differentiable and is a monotonically increasing function of energy

In macroscopic thermodynamics — if one can describe the condition or state of a system using only thermodynamic variables, one describes a thermodynamic equilibrium state of the system



The partial derivative of entropy with respect to internal energy:

$$\left(\frac{\partial S}{\partial U}\right)_{V,N_1,N_2,...,N_r} > 0$$

$$S = S(U, V, N_1, N_2, ..., N_r)$$

$$\Rightarrow U = U(S, V, N_1, N_2, ..., N_r)$$

$$dU = TdS - PdV$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Entropy S is a homogeneous first order function of extensive parameters.

$$S(\lambda U, \lambda V, \lambda N_1, ..., \lambda N_r) = \lambda S(U, V, N_1, ..., N_r)$$

$$\underline{Z}(\lambda X, \lambda Y) = \lambda^n Z(X, Y)$$

$$\underline{n = 1}$$

Put $\lambda = 1/N = 1/\sum_k N_k$

$$S(U, V, N_1, ..., N_r) = N\, S(U/N, V/N, N_1/N, ..., N_r/N)$$

$$s(u, v) = S(u, v, 1)\ (\text{single} - \text{component system})$$

$N = N_1$

$N_1/N = 1$

$$\because S(U, V, N) = N\, S(U/N, V/N, 1)\ (\text{single} - \text{component})$$

U/N: energy per mole

V/N: volume per mole

Denote $s(u, v) = S(u, v, 1)$

$N = N_1 + N_2 \cdots + N_r$

N_1 — moles of component 1

N_2 — moles of component 2

N_r — moles of component r

Entropy of a system vanishes in the state for which $(\partial U/\partial S)_{V, N_1, ..., N_r} = 0$

$$X_1 = \frac{N_1}{N}$$

$$X_r = \frac{N_r}{N}$$

$s = S/N \rightarrow$ entropy per mole

$$s = s(u, v, X_1, X_2, \cdots X_r)$$

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

$$= TdS - pdV + \mu dN$$

If $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = 0$, then $S = 0$

Extensive and Intensive Parameters

$$U = U(S, V, N_1, N_2, ..., N_r)$$

Exact Differential

$$\mathrm{dU} = \left(\frac{\partial U}{\partial S}\right)_{V,N_1,...,N_r} \mathrm{dS} + \left(\frac{\partial U}{\partial V}\right)_{S,N_1,...,N_r} \mathrm{dV} + \sum_{j=1}^{r} \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_1,...,N_{k\neq j},...,N_r} \mathrm{dN}_j$$

Temperature: $\left(\frac{\partial U}{\partial S}\right)_{V,N_1,N_2,...,N_r} = T$

Pressure:

$$-\left(\frac{\partial U}{\partial V}\right)_{S,N_1,N_2,...,N_r} = P$$

Chemical potential: $\left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_1,...,N_{k\neq j}} = \mu_j \ (j^{\mathrm{th}} \,\mathrm{component})$

$$\mathrm{dU} = T\,\mathrm{dS} - P\,\mathrm{dV} + \mu_1 \mathrm{dN}_1 + \cdots + \mu_r \mathrm{dN}_r$$

Quasi-static mechanical work $\delta W_m = -P\,\mathrm{dV}$

Quasi-static heat flux $\delta Q = T\,\mathrm{dS}$ - quasi-static heat flux into the system increases the entropy of the system.

Quasi-static chemical work $\delta W_c = \sum_{j=1}^{r} \mu_j\,\mathrm{dN}_j$

$$\therefore \mathrm{dU} = \delta Q + \delta W_m + \delta W_c$$

Equations of state: homogeneous zero order

$T = T(S, V, N_1, ..., N_r)$

$P = P(S, V, N_1, ..., N_r)$

$\mu_j = \mu_j(S, V, N_1, ..., N_r)$

$T(\lambda S, \lambda V, \lambda N_1, ..., \lambda N_r) = T(S, V, N_1, ..., N_r)$

Intensive parameters (entropic)

$$S = S(U, V, N_1, ..., N_r)$$

$$\mathrm{dS} = \left(\frac{\partial S}{\partial U}\right)_{V, N_1, ..., N_r} \mathrm{dU} + \left(\frac{\partial S}{\partial V}\right)_{U, N_1, ..., N_r} \mathrm{dV} + \left(\frac{\partial S}{\partial N_j}\right)_{U, V, ..., N_r} \mathrm{dN}_j$$

Use chain rule:

$$\frac{\partial S}{\partial U} = \frac{1}{T}; \quad \frac{\partial S}{\partial V} = \frac{\partial S}{\partial U}\frac{\partial U}{\partial V} = -\frac{P}{T}; \quad \frac{\partial S}{\partial N_j} = \frac{\partial S}{\partial U}\frac{\partial U}{\partial N_j} = \frac{\mu_j}{T}$$

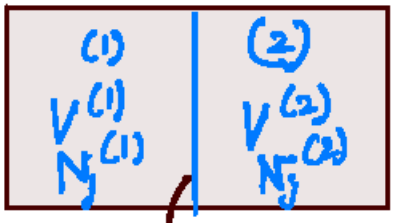
Thermal Equilibrium

Consider an isolated composite system containing two simple systems separated by a wall (rigid, impermeable to matter and diathermal i.e. allows the flow of heat)

Fixed: $V^{(1)}, V^{(2)}, N^{(1)}, N^{(2)}$ (volumes and mole numbers of each of the simple systems are fixed)

$U^{(1)}$ and $U^{(2)}$ are free to change.

Conservation restriction: $U^{(1)} + U^{(2)} = U = \text{constant}$



The values of $U^{(1)}$ and $U^{(2)}$ are such as to maximize entropy

Extremum condition $\mathrm{dS} = 0$

$$S = S^{(1)}\left(U^{(1)}, V^{(1)}, ..., N_j^{(1)}, ...\right) + S^{(2)}\left(U^{(2)}, V^{(2)}, ..., N_j^{(2)}, ...\right)$$

$$S = S^{(1)}\left(U^{(1)}, V^{(1)}, ..., N_j^{(1)}, ...\right) + S^{(2)}\left(U^{(2)}, V^{(2)}, ..., N_j^{(2)}, ...\right)$$

Entropy change:

$$\mathrm{dS} = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)},...,N_j^{(1)},...} \mathrm{dU}^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V^{(2)},...,N_j^{(2)},...} \mathrm{dU}^{(2)}$$

$$\mathrm{dS} = \frac{1}{T^{(1)}}\mathrm{dU}^{(1)} + \frac{1}{T^{(2)}}\mathrm{dU}^{(2)}$$

$U^{(1)} + U^{(2)} = k$

$dU^{(1)} + dU^{(2)} = 0$

$dU^{(2)} = -dU^{(1)}$

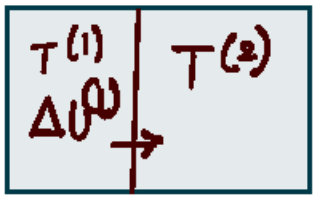
But $\mathrm{dU}^{(2)} = -\mathrm{dU}^{(1)}$

$$\mathrm{dS} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{dU}^{(1)}$$

$\mathrm{dS} = 0 \Rightarrow \frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}$ or, $T^{(1)} = T^{(2)}$ — Thermal equilibrium

Flow of heat: driving force

Assume $T^{(1)} > T^{(2)}$.



$$\Delta S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) \Delta U^{(1)}$$

$T^{(1)} > T^{(2)}$

$\Delta S > 0$ entropy of composite system increases during heat flow

$\because T^{(1)} > T^{(2)}$, $\Delta U^{(1)} < 0$ the internal energy of subsystem 1 decreases

Heat flows from subsystem 1 to subsystem 2 (spontaneous process).

$$\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} = \frac{T^{(2)} - T^{(1)}}{T^{(1)} T^{(2)}}$$

Mechanical Equilibrium

Movable, diathermal wall

Constraints: $U^{(1)} + U^{(2)} = \text{constant}\ V^{(1)} + V^{(2)} = \text{constant}$

$$\mathrm{dU}^{(2)} = -\mathrm{dU}^{(1)}, \mathrm{dV}^{(2)} = -\mathrm{dV}^{(1)}$$

Extremum principle: $\mathrm{dS} = 0$

$$\mathrm{dS} = \left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)\mathrm{dU}^{(1)} + \left(\frac{\partial S^{(1)}}{\partial V^{(1)}}\right)\mathrm{dV}^{(1)} + \left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)\mathrm{dU}^{(2)} + \left(\frac{\partial S^{(2)}}{\partial V^{(2)}}\right)\mathrm{dV}^{(2)}$$

$$\mathrm{dS} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{dU}^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right)\mathrm{dV}^{(1)} = 0$$

Mechanical Equilibrium

$$\mathrm{dS} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)\mathrm{dU}^{(1)} + \left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right)\mathrm{dV}^{(1)} = 0$$

Since $\mathrm{dU}^{(1)}$ and $\mathrm{dV}^{(1)}$ are arbitrary

$$\left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right) = 0$$

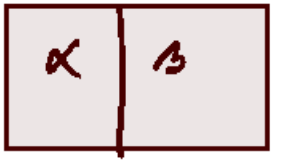
$$\left(\frac{P^{(1)}}{T^{(1)}} - \frac{P^{(2)}}{T^{(2)}}\right) = 0 \quad \rightarrow \quad \frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}}$$

$$\rightarrow \quad P^{(1)} = P^{(2)}$$

$T^{(1)} = T^{(2)};\ P^{(1)} = P^{(2)}$

Chemical equilibrium

Constraint: rigid, diathermal wall permeable to flow of component 1 and impermeable to all other components



$$dS = \frac{1}{T^\alpha} dU^\alpha + \frac{\mu_1^\alpha}{T^\alpha} dN_1^\alpha + \frac{1}{T^\beta} dU^\beta + \frac{\mu_1^\beta}{T^\beta} dN_1^\beta$$

$$dU^\beta = -dU^\alpha;\ dN_1^\beta = -dN_1^\alpha$$

$\therefore U^\alpha + U^\beta = \text{const}$

$N_1^\alpha + N_1^\beta = \text{const}$

$$dS = \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right) dU^\alpha + \left(\frac{\mu_1^\alpha}{T^\alpha} - \frac{\mu_1^\beta}{T^\beta}\right) dN_1^\alpha$$

$$\frac{1}{T^\alpha} = \frac{1}{T^\beta};\ \frac{\mu_1^\alpha}{T^\alpha} = \frac{\mu_1^\beta}{T^\beta} \quad \Rightarrow T^\alpha = T^\beta, \mu_1^\alpha = \mu_1^\beta$$

$$\left.\begin{aligned} T^\alpha = T^\beta = T^\gamma = T^\delta \\ P^\alpha = P^\beta = P^\gamma = P^\delta \\ \mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \mu_1^\delta \\ \mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \mu_2 \end{aligned}\right\}$$