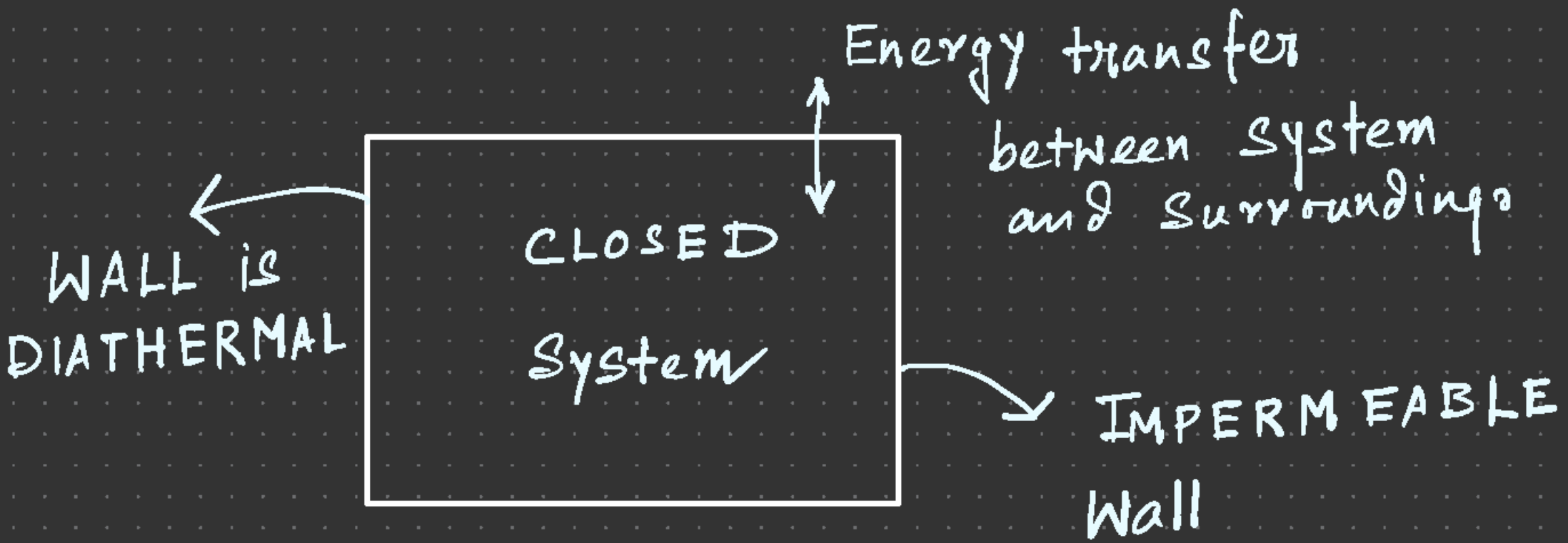
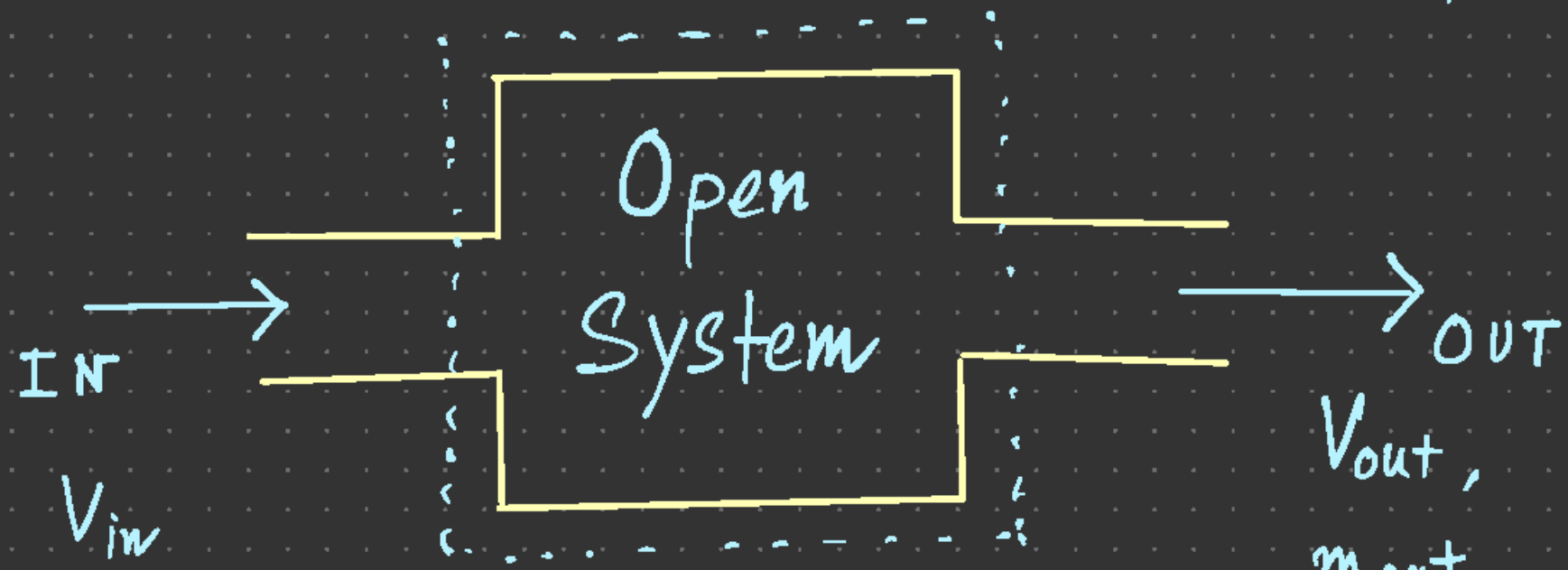


First Law:

$$dU = \delta q + \delta W$$ Differential form

$$\Delta U = q + W$$ Integral form

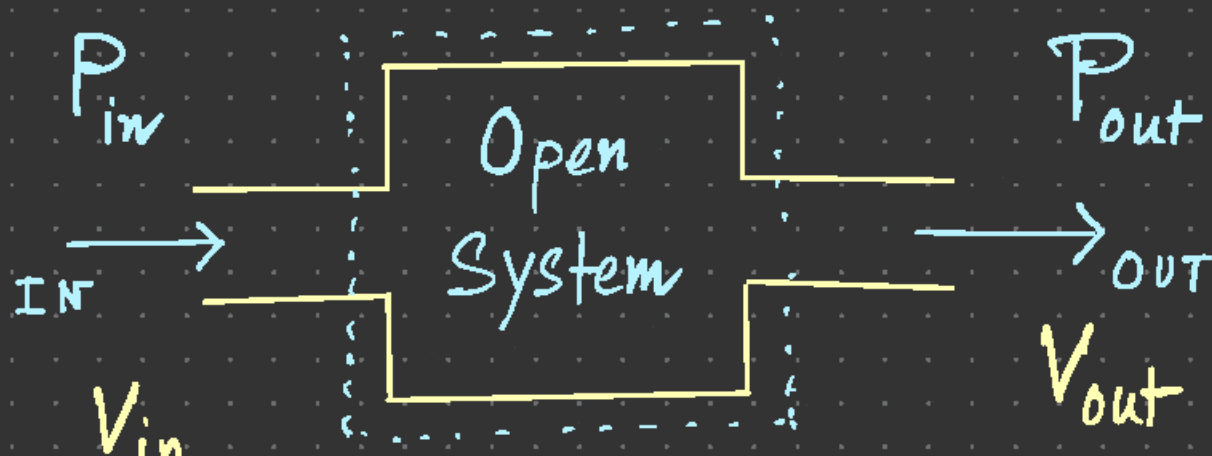
Transfer of MATTER and ENERGY across the Wall



Flow work

V_{in}, m_{in} — Volume and mass of matter entering the system

V_{out}, m_{out} — Volume and mass of matter leaving the system



$$\overrightarrow{V_{in}} = \frac{V_{in}}{\dot{m}_{in}}$$

$$\overrightarrow{V_{out}} = \frac{V_{out}}{\dot{m}_{out}}$$

$$\left(\text{Flow Work}\right)_{in} \downarrow \left(\dot{W}_F\right)_{in}$$

$$\left(\text{Flow Work}\right)_{out} \downarrow \left(\dot{W}_F\right)_{out}$$

$$\int p\,dV = \int p\,\bar{V}\,dm = \delta W_F$$

$p\bar{V}\delta m$ is +ve when matter enters

$p\bar{V}\delta m$ is −ve when matter leaves

$$(W_F)_{in} = \int_0^{m_{in}} p\,\bar{V}_{in}\,dm_{in}$$

p is constant at inlet $= P_{in}$

$$\therefore (W_F)_{in} = +P_{in}\,\bar{V}_{in}\,m_{in}$$

$$(W_F)_{out} = -P_{out}\,\bar{V}_{out}\,m_{out}$$

$$\delta q_{in} = +\overline{U}_{in}\, dm_{in} \qquad \delta W_{F_{in}} = +p_{in}\overline{V}_{in}\, dm_{in}$$

$$\delta q_{out} = -\overline{U}_{out}\, dm_{out} \qquad \delta W_{F_{out}} = -p_{out}\overline{V}_{out}\, dm_{out}$$

$\overline{U}_{in} = \dfrac{U_{in}}{m_{in}}$ specific internal energy per unit mass entering the system

Open system

$$dU = \delta q_{in} - \delta q_{out} + \delta W_{F_{in}} - \delta W_{F_{out}} + \delta q + \delta W$$

$$\left(\bar{U}_{in} + P_{in}\bar{V}_{in}\right) dm_{in}$$

$$- \left(\bar{U}_{out} + P_{out}\bar{V}_{out}\right) dm_{out}$$

$$+ \delta q + \delta w = dU$$

$$\left(U + PV\right)_{in} \qquad \left(U + PV\right)_{out}$$

$$\downarrow \qquad\qquad \downarrow$$

$$H_{in} \qquad\qquad H_{out}$$

Enthalpy

$$dU = \delta q + \delta W = \delta q - p\,dV$$

$$\Delta U = q - p\Delta V$$

(CONSTANT PRESSURE)

$$q = \Delta U + p\Delta V$$

q: heat input

ΔU: change in internal energy

Define a new state function

$$H = U + pV$$

H is an extensive variable

$\overline{H}$ – Specific enthalpy (enthalpy per unit mass)

or

H_m enthalpy per mole

Constant Pressure

$$H = U + pV$$

$$dH = dU + p\,dV + V\,dp$$

$$= dU + p\,dV \quad (\text{when } dP = 0)$$

$$dU = \delta q + \delta w \quad \Big\} \quad \delta q_p = dU + p\,dV$$

$$= \delta q - p\,dV \quad \Big\}$$

$$\therefore \; dH = \delta q_p \quad (\text{constant pressure})$$

$$dU = \delta q_v \quad (\text{constant volume})$$

MEASURABLE CHANGE

dZ (differential change)

$\Delta Z = Z_f - Z_i$

$$\Delta H = q_p$$

CONSTANT VOLUME $\quad dU = \delta q_v$

CONSTANT PRESSURE $\quad dH = \delta q_p$

Differential form

$$dH = dU + P\,dV \quad \text{(at constant } P\text{)}$$

Integrate between states i and f

$$\int_i^f dH = \int_i^f dU + P\int_i^f dV$$

$$H_f - H_i = U_f - U_i + P(V_f - V_i)$$

$$\Delta H = H_f - H_i$$
$$\Delta U = U_f - U_i$$
$$\Delta V = V_f - V_i$$

$$\Delta H = \Delta U + P\Delta V$$

Enthalpy of fusion (melting) of ice at 0°C and 1 atm. pressure is 6 kJ/mole.

Molar volume of ice at 0°C - 0·0196 L

Molar volume of water$_{(\ell)}$ at 0°C - 0·018 L

Find ΔH and ΔV of fusion at 0°C and 1 atm. pressure

Ice $\xrightarrow{\text{melting/fusion}}$ Water

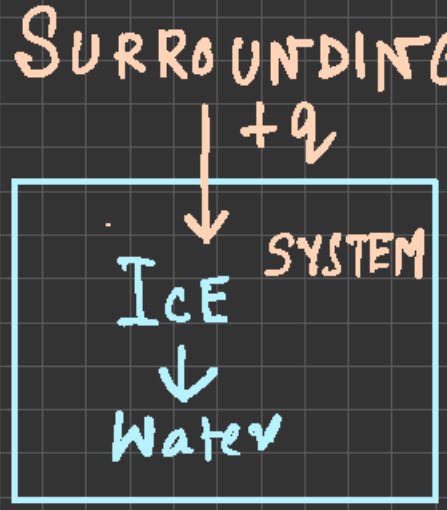
Endothermic Process - Heat absorbed by system from surroundings

↓

Heat input to system is +ve

Exothermic Process - Heat released by the system to the surroundings

Heat input to system is -ve



ICE (System) absorbs heat from Surroundings during it melting

— Endothermic

Ice → Water (Endothermic)

$\Rightarrow$ Heat Input to the system

$\Rightarrow +q$

At 1 atm., 1 mole of ice requires

6 kJ of heat input

$= 6000\ J$

$1\ L = 1\ dm^3$

$= 0.001\ m^3$

1 atm.

$= 101325\ Pa$

$q = q_p = \Delta H = +6000\ J$

$\Delta H = \Delta U + P\Delta V$

$\Delta V = V_{Water} - V_{ice}$

for 1 mole of ice

$$\Delta V = V_{water} - V_{ice}$$

$$= (0.018 - 0.0196)\ L$$

$$= -0.0016\ L$$

$$= -1.6 \times 10^{-3}\ L$$

$P = 1$ atm.

$$\therefore P\Delta V = 1 \times (-1.6 \times 10^{-3})\ \text{atm-L}$$

$$= -1.6 \times 10^{-3} \times 101.325\ J$$

$$= -0.16212\ J$$

1 atm-L

$= 101325 \times 0.001$ Pa-m^3

$= 101.325$ N-m

$= 101.325$ J

1 Pa = $\frac{1\ N}{m^2}$

$\Delta H = 6000\ \text{J}$

In CONDENSED Phases, PV work is negligible

$\Delta U = \Delta H - P\Delta V$

$= 6000 - \left(-0.16212\right)\ \text{J}$

$= 6000.16212\ \text{J}$

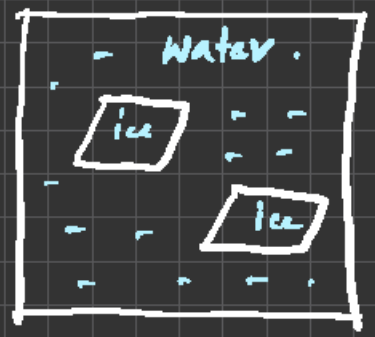
$\approx 6000\ \text{J}$

Phase change: ice → water

Both are condensed systems

$P\Delta V$ is negligible

A phase is a portion of matter which is chemically homogeneous, physically distinct and mechanically separable



Combustion Reaction

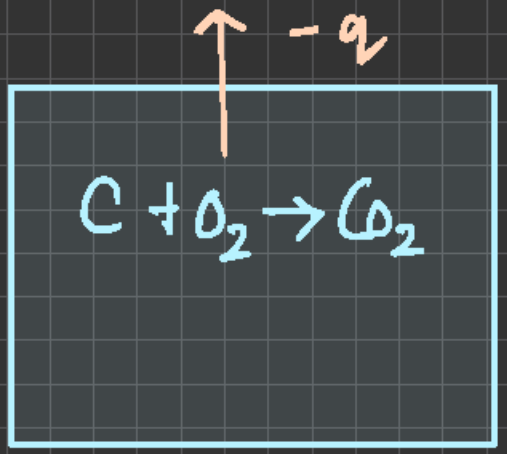
Burning fuel – involves gases such as oxygen

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

GRAPHITE OXYGEN CARBON DI OXIDE

Combustion produces heat

- > Heat released to surroundings
- > Exothermic
- > $-q$



298 K temperature and 1 atm. pressure

Molar volume of graphite = 0.0053 L

Molar volume of gases ?

$R = 8.314 \frac{J}{mol \cdot K}$

$PV = nRT$

$V = \frac{8.314 \times 298}{101325}$

$= 0.02445173 \ m^3$

$\approx 24.45 \ L$

STP

0°C = 273.15 K

1 atm = 101325 Pa

Volume = 22.4 L

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta H^{Reaction}$ or $\Delta H^{R} = -394 \ kJ/mol$

$$\Delta H^{\circ} = -394\ \text{kJ/mol}$$

Assumptions:

O_2 and CO_2 are ideal gases following the equation of state

$$pV = nRT$$

$$H = U + PV$$

$$= U + nRT$$

$$\therefore \quad dH = dU + d(nRT)$$

$$= dU + RT\,dn + nR\,dT$$

$$dH = dU + RT\,dn + nR\,dT$$

At constant T, $dT = 0$

$$dH = dU + RT\,dn$$

or, $$\Delta H = \Delta U + RT\,\Delta n$$

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

n (before reaction) $= 1$

n (after reaction) $= 1$

$$\Delta n = n_{product} - n_{reactant}$$

$$= 1 - 1 = 0$$

$$\Delta n = 1 - 1 = 0$$

$$\Delta H = \Delta U + RT\Delta n \quad (T \text{ is constant} = 298K)$$

$$\Delta H = -394 \text{ kJ/mol}$$

$$\therefore \quad \Delta U = \Delta H - RT\Delta n$$

$$= \Delta H$$

$$= -394 \text{ kJ/mol}$$

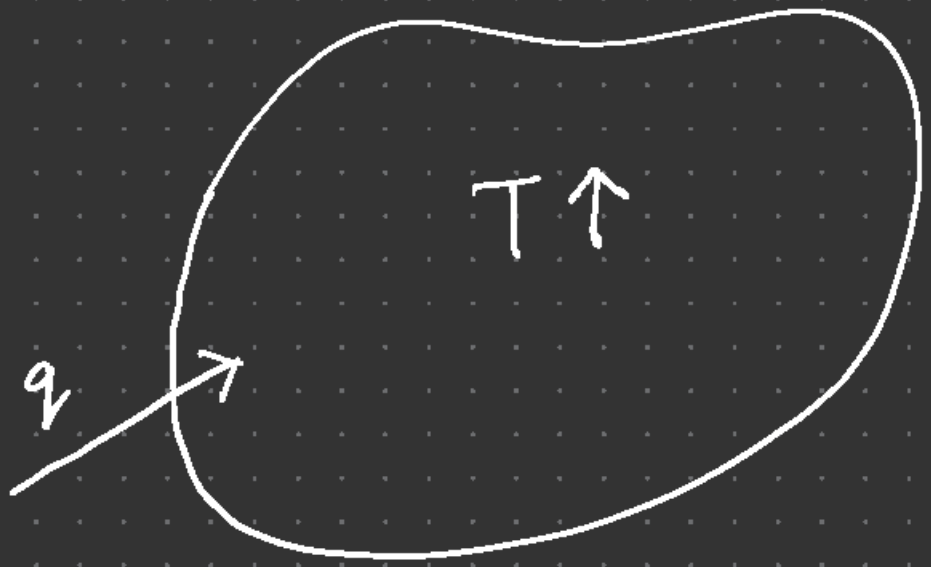
Moles of C(s) are not considered

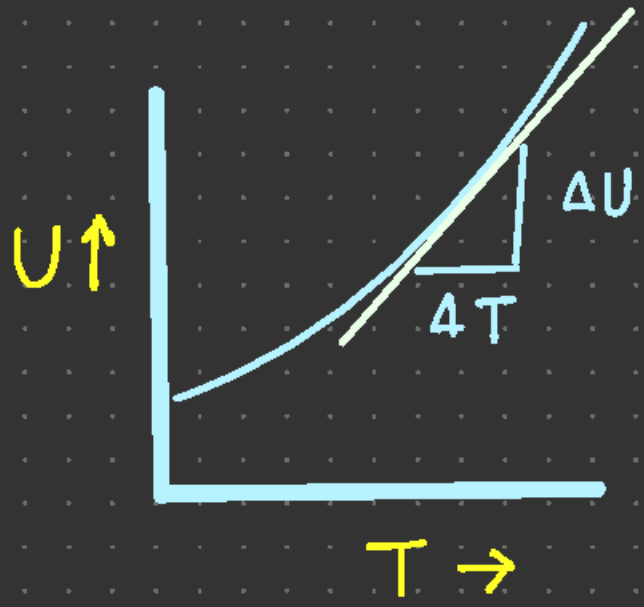
$$\underset{(g)}{N_2} + 3\underset{(g)}{H_2} = 2\underset{(g)}{NH_3}$$

Heat capacity

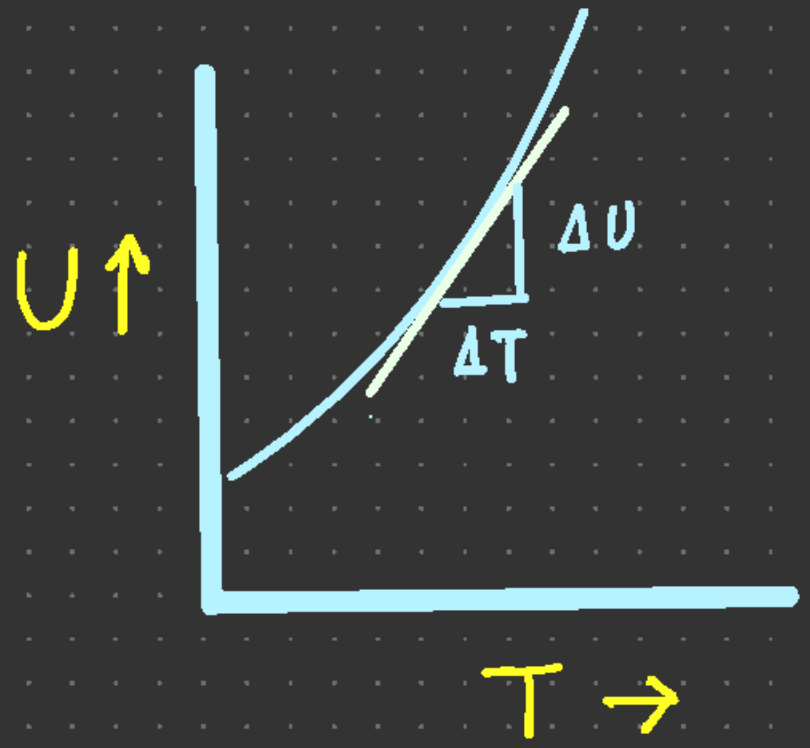
Amount of heat or thermal energy required to raise the temperature of a material (by 1°C or by 1 K)

$$\delta q = C\, dT$$



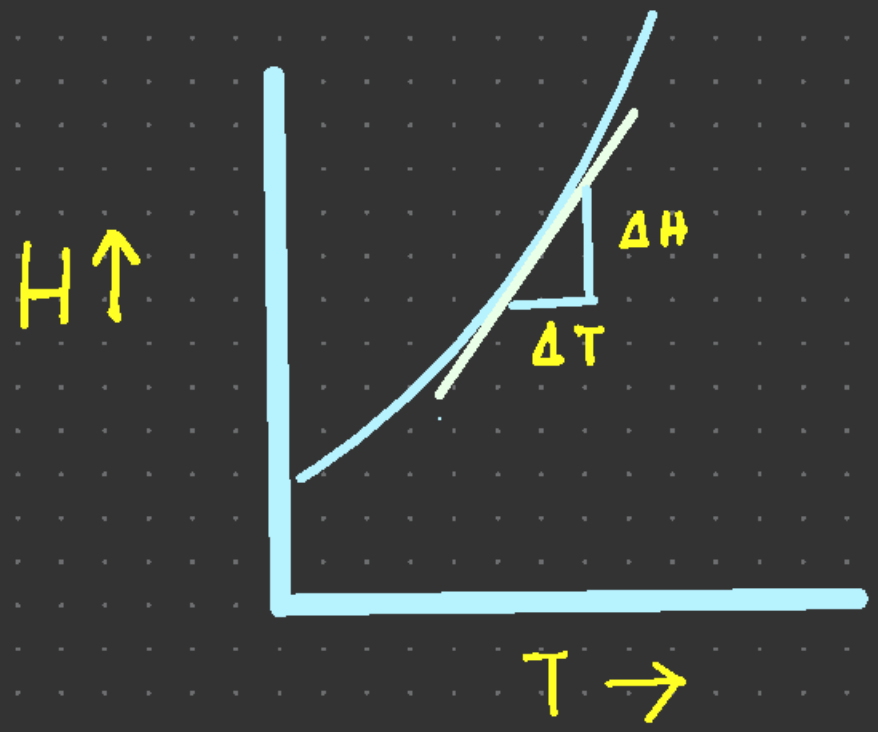


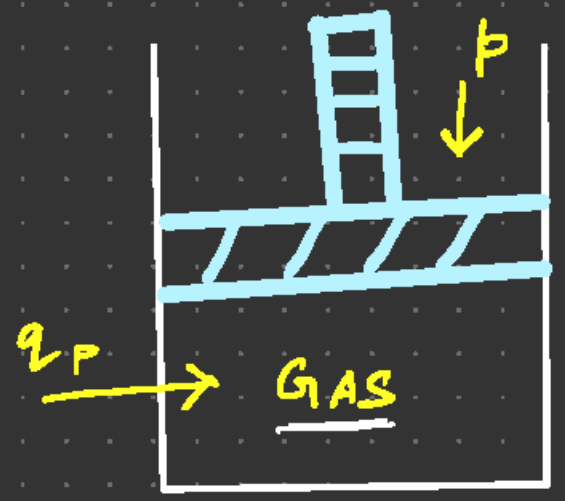
$$\lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T} = \frac{dU}{dT}$$



CONSTANT VOLUME

$$C_V = \frac{\delta q_V}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V$$





CONSTANT PRESSURE

$$C_P = \frac{\delta q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

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

Exact Differential

$$Z = Z(x, y)$$

$$dZ = M\,dx + N\,dy$$

$$M = \left(\frac{\partial Z}{\partial x}\right)_y \qquad N = \left(\frac{\partial Z}{\partial y}\right)_x$$

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

– Maxwell Relations

All state functions — exact differential

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

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

$$= C_V dT + \pi_T dV$$

$$dU = \delta q - p dV$$

$$= C dT - p dV$$

At constant temperature

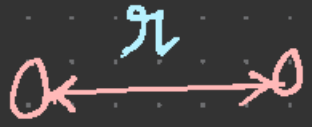
$$dU = -p dV$$

$$dU = C_V dT + \pi_T dV$$

$$\pi_T = -p$$

π_T – Internal pressure

Ideal gas – no interaction between molecules



$$F_{int} = 0$$

$$\pi_T dV = F_{int}\, dr$$

$$= 0$$

$$\pi_T = 0$$

$$H = U + PV$$

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$dU = C_V dT + \pi_T dV$$

$\pi_T = 0$ for perfect or ideal gas (no interactions)

Ideal gas: Equation of state $PV = nRT$

$dU = \delta q_v = C_v dT$

$\delta q_p = C_p dT$

What is $C_p - C_v$ for an ideal gas?

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

$$pV = nRT$$

Equation of state

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

$$\delta W = -p\,dV$$

$$dU = \delta q + \delta W$$

$$\delta q = dU + p\,dV$$

$$\delta q_p = dH$$

$$= C_p\,dT$$

$$= C_v\,dT + p\,dV$$

$$C_p\,dT = C_v\,dT + nR\,dT$$

or,

$$C_p - C_v = nR$$

$$d(PV) = p\,dV + V\,dP$$

$$= d(nRT)$$

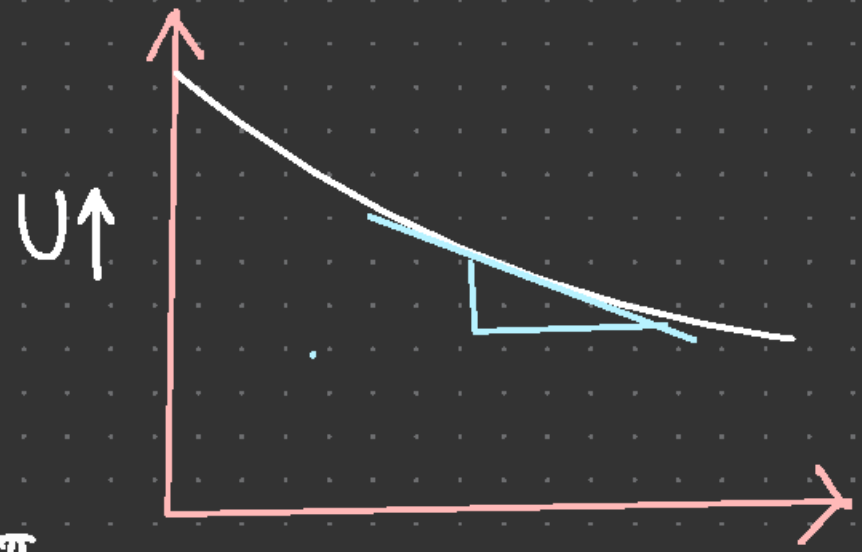
$$= RT\,dn + nR\,dT$$

{ Fix pressure and n }

$$p\,dV = nR\,dT$$

System with Interactions – Real gases

Interaction force between constituent atoms/molecules



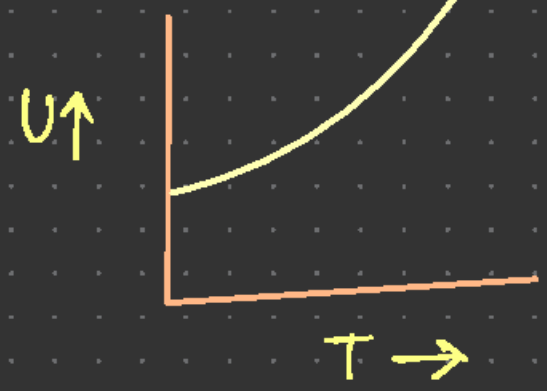
$$\text{Slope} = \left(\frac{\partial U}{\partial V}\right)_T$$

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

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

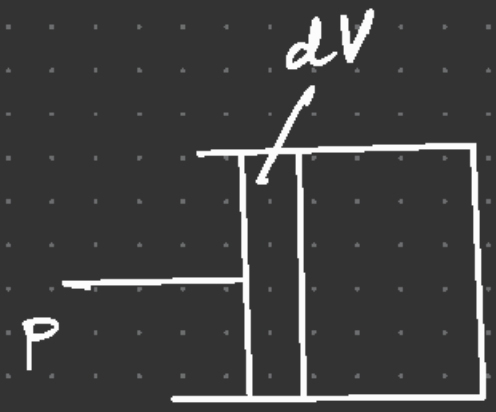
$$= C_V dT + \pi_T dV$$

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



$$dU = C_v\, dT + \pi_T\, dV$$

$$dU = \delta q - p\, dV$$



$\pi_T = -p$

↓

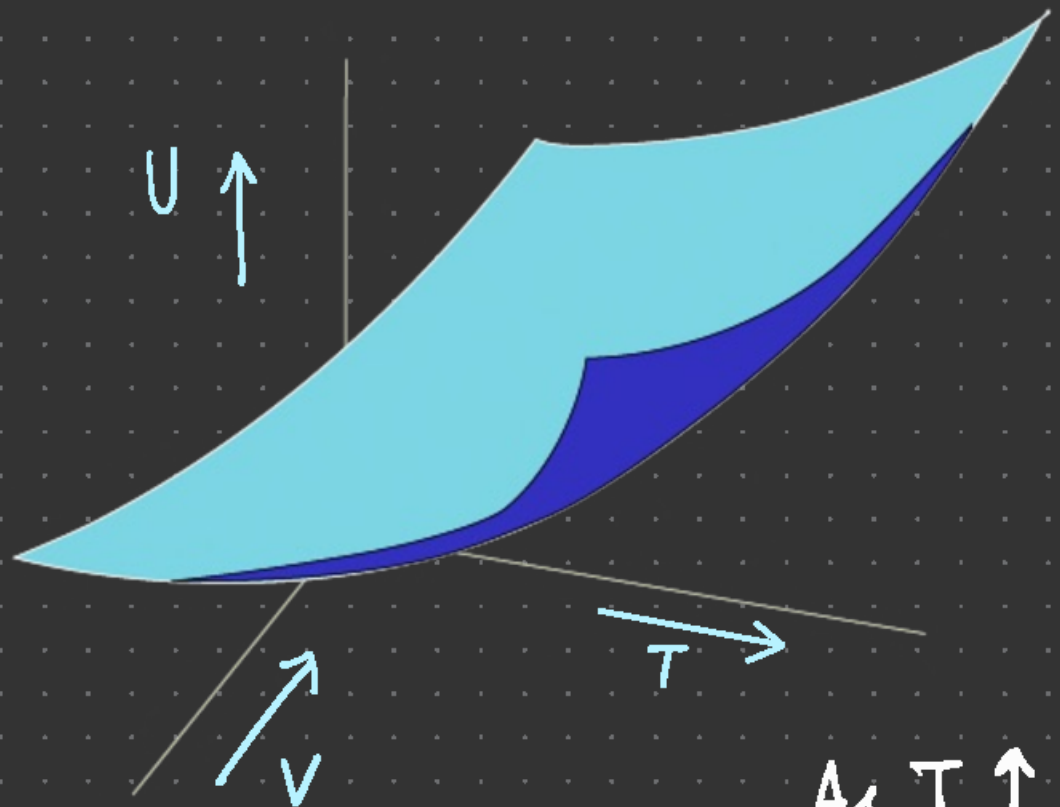
internal pressure

Ideal gas

- no Interaction

$\longrightarrow \pi_T = 0$

n – no. of moles of ideal gas



If the energy of an ideal gas is $\frac{3}{2}nRT$,

What is its molar heat capacity $C_{v,m}$?

$$c_v = C_{v,m} = \frac{C_v}{n}$$

n is the total no. of moles of a substance

As $T \uparrow$ $U \uparrow$
$V \uparrow$ $U \downarrow$ } Real gases

We denote $C_{v,m}$ as molar heat capacity at constant volume

$C_{p,m}$ as molar heat capacity at constant pressure

$$C_p - C_v = n R$$

$$C_{p,m} - C_{v,m} = R \qquad J/mol-K$$

Specifit heat - Heat capacity per unit mass

Specific heat c_p of water at room temperature and 1 atm. pressure is

$\sim 4\ J\ K^{-1}\ g^{-1}$.

Molar heat capacity: $C_{p,m} = ?$

Water - H_2O

H atomic mass = 1 amu

O atomic mass = 16 amu

Atomic mass = 18 gm.

$4\ \frac{J}{K\ gm} = 72\ \frac{J}{K \cdot mol}$

1 mole of H_2O - 18 gm of water

What is the relation between C_p and C_v?

$C_{p,m} - C_{v,m} = R$

Volumetric coefficient of thermal expansion α

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad K^{-1}$$

Compressibility (β or K_T)

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

Isothermal compressibility

$$C_p - C_v = \frac{\alpha^2 T V}{K_T}$$

For the general proof, we need to use Maxwell relations

Consider an ideal gas

$$PV = nRT$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{PV}$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = +\frac{nRT}{P^2 V} = \frac{1}{P}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

$$\therefore \quad \frac{\alpha^2 T V}{K_T} = \frac{V/T}{1/P} = \frac{PV}{T} = nR$$

$$C_{p,m} - C_{V,m} = \frac{nR}{n} = R$$

For solids and liquids,

$C_p - C_V$ is small

$1\ GPa^{-1} = (10^9\ Pa)^{-1}$

$= \quad =$

$K_T(Al) = 1.385 \times 10^{-11}\ Pa^{-1}$

$\alpha(Al) = 69.3 \times 10^{-6}\ K^{-1}$

$T = 298\ K$ Room temperature

$V = 10\ cm^3/mol$

$= 10^{-5}\ m^3/mol$

$$1 \text{ atm.} = 101325 \text{ Pa}$$

$$\frac{\alpha^2 TV}{K_T} = \frac{(69.3 \times 10^{-6})^2 \times 298 \times 10^{-5}}{1.385 \times 10^{-11}} \text{ J/mol-K}$$

$$\frac{\frac{1}{K^2} \; K \; \frac{m^3}{mol}}{\frac{\frac{m^2}{N}}{\frac{N \cdot m}{mol \cdot K}}} = \frac{J}{mol \cdot K}$$

$$\approx 1 \text{ J/mol-K}$$

$C_p - C_v$ is small for solids and liquids

$$H = U + PV$$

$$H \sim U$$

for condensed systems - liquids & solids

$$C_p \cong C_v$$

C as the heat capacity

Heat capacity of solids

Near Room temperature, heat capacity of most solids is $3k_B$ per atom

– Law of Dulong and Petit

Translational degrees of freedom – $\frac{3}{2} k_B T$ per atom

Vibrational degrees of freedom – $\frac{3}{2} k_B T$

Energy per atom of solid $= \frac{3}{2} k_B T + \frac{3}{2} k_B T$

From equipartition of energy $= 3 k_B T$

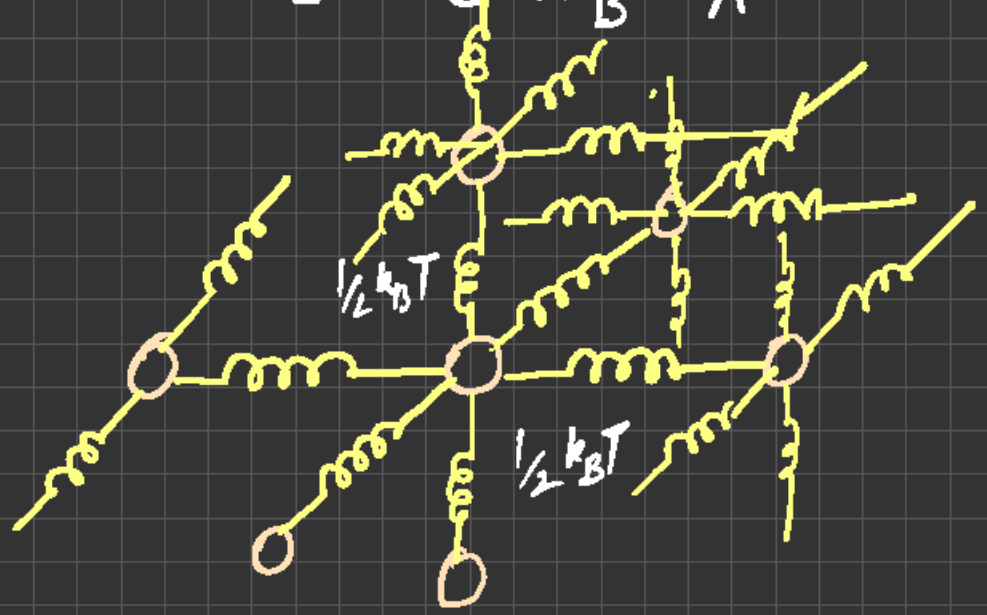
Internal energy per mole of solid

$$U = 3 k_B T N_A$$

N_A - Avogadro no.

$$C_{V,m} = \frac{\partial}{\partial T}\left(3 k_B T N_A\right)$$

$$= 3 k_B N_A = 3R \text{ / mole}$$



EACH ATOM IS AN OSCILLATOR WITH SIX DEGREES OF FREEDOM

However, C_V decreases as temperature decreases and vanishes at $T = 0$ K

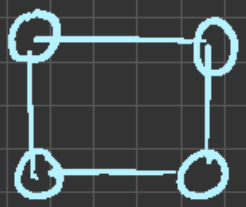
Einstein Model

Assumptions

i) Solid - a lattice structure with N atoms

Each atom moves independently within the lattice in 3D

- 3 degrees of freedom



ii) No interactions with each other

iii) All atoms vibrate at same frequency

Assumption ii is not correct

- Sound propagation through solid.
- Heat propagates through solid

$e^0 = 1$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3 N k_B \left(\frac{\theta_E}{T}\right)^2 \frac{\exp\left(\theta_E/T\right)}{\left(\exp\left(\theta_E/T\right) - 1\right)^2}$$

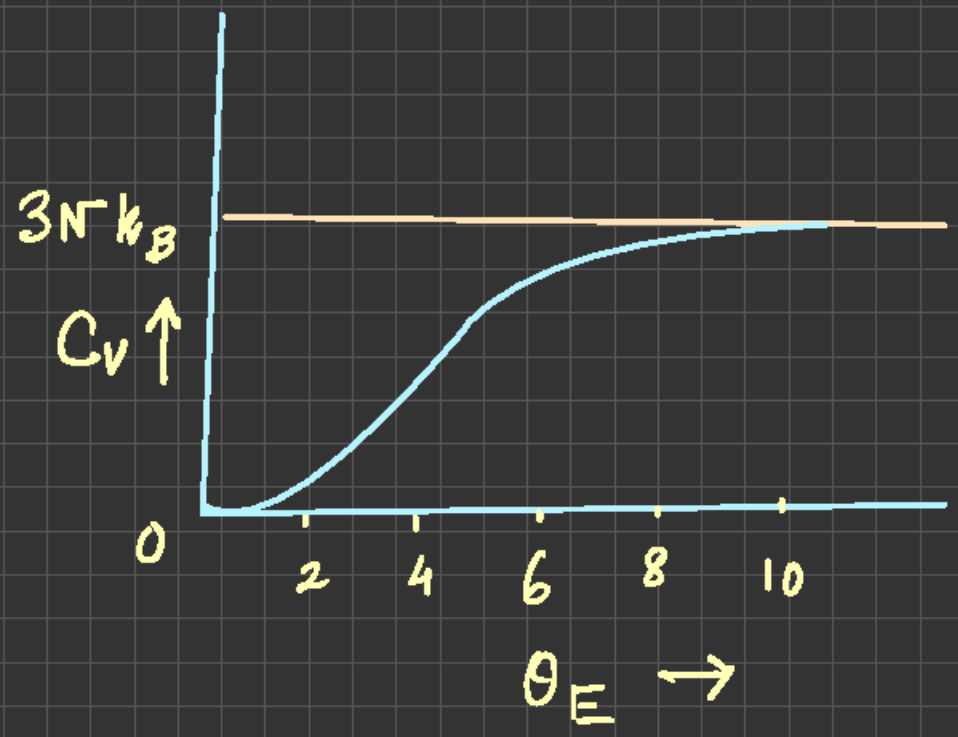
$$\left(1 + \frac{\theta_E}{T} + \cdots - 1\right)^2$$

$$\theta_E = \frac{h\nu}{k_B}$$

h - Planck's constant

$= 6.626070 15 \times 10^{-34}\ J \cdot Hz^{-1}$

Remember $E = h\nu$ for a photon



Dulong and Petit's

$$\frac{h\nu}{k_B T} \gg 1$$

T is very low

When $\left(\frac{\theta_E}{T}\right) \gg 1$ (Very low temperature)

$$C_v = 3Nk\left(\frac{\theta_E}{T}\right)^2 \exp\left(-\frac{\theta_E}{T}\right)$$

$\exp\left(-\frac{\theta_E}{T}\right) \rightarrow 0$

$\frac{\theta_E}{T} \rightarrow \infty$ as $T \rightarrow 0$

$e^{-\infty} \rightarrow 0$

$\therefore C_v \rightarrow 0$ as $T \rightarrow 0$

High temperature limit (T is Large) $\frac{\theta_E}{T} \ll 1$

$$C_v \approx 3Nk$$

Put $N = N_A$

Then, $C_v = 3R$

Model by Peter Debye

- Concept of phonons or lattice vibrations
- Not oscillations of single atom but collective motion of lattice propagating through the material

$$\epsilon = \hbar\omega$$

Energy of phonon

$$\hbar = \frac{h}{2\pi}$$

ω – angular frequency

$$\omega = v_s |\vec{q}|$$

$\vec{q}$ – wave vector

$$n_E = \frac{1}{\exp(E/k_B T) - 1} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

no. of phonons in a state with energy E

Phonon do not have infinite modes of frequency

N – primitive unit cells – N modes of phonon frequency

Maximum allowed phonon frequency

or Debye frequency,

$$\omega_D = \omega_{max} = v_s \left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

N/V is number density of atoms

Energy U = Phonon energy X Avg no of phonons X number of modes

$$\theta_D = \frac{\hbar \omega_{max}}{k_B}$$

(Debye temperature)

$$U = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}\,dx$$

$$\theta_D = \frac{\hbar\omega_{max}}{k_B}$$

At high T, x is small

$$9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2\,dx$$

$$= 9Nk_BT\left(\frac{T}{\theta_D}\right)^3 \left(\frac{\theta_D}{T}\right)^3 \cdot \frac{1}{3}$$

$$\simeq 3Nk_BT \quad \text{or,} \quad C_V = 3Nk_B$$

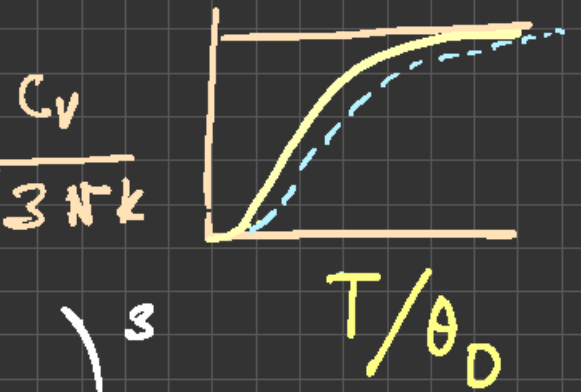
At low T,

$$\frac{\theta_D}{T} \longrightarrow \infty$$

$$\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$U = \frac{3\pi^4 N k_B T^4}{5\theta_D^3}$$

$$C = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$



Atomic mass (amu)

Pb 207

Cu 63.6

$3R$ J/mol-K

Specific heat in J/gm-K are different

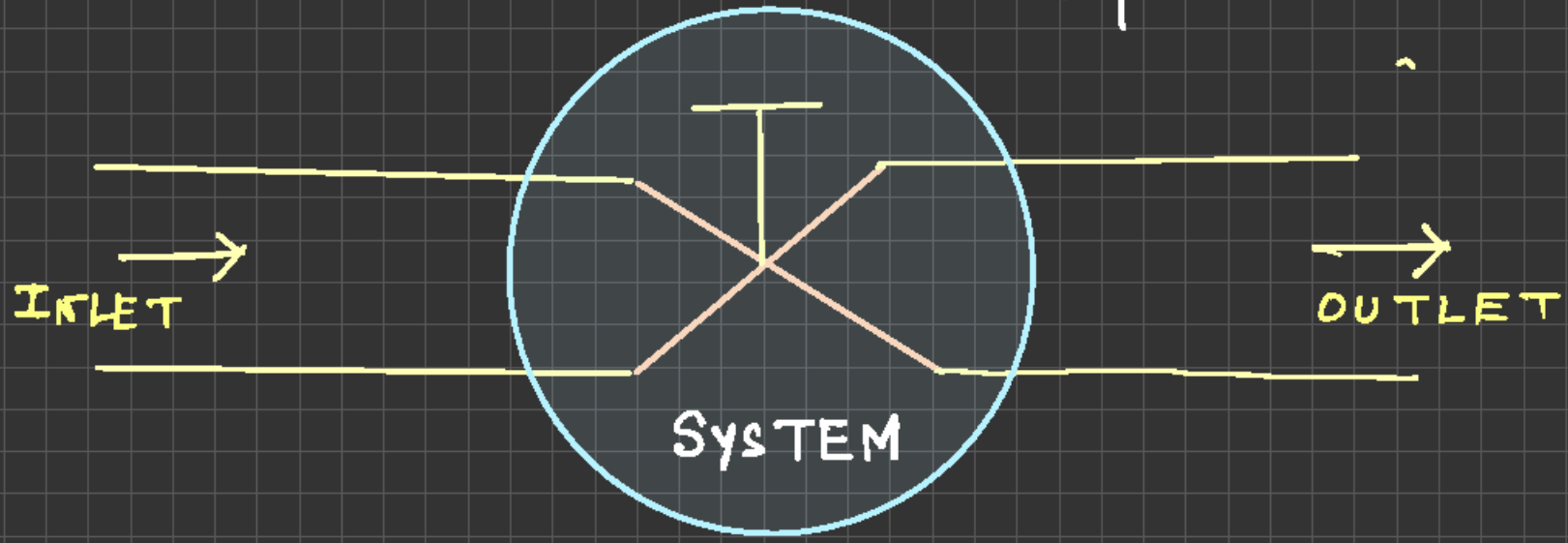
Pb has lower Specific heat than Cu — Verify

$\frac{3R}{207}$ Pb $\frac{J}{gm\text{-}K}$

$\frac{3R}{63.6}$ Cu $\frac{J}{gm\text{-}K}$

Adiabatic flow through a valve

– Joule Thomson Expansion



ADIABATIC – Heat cannot be added to the system, cannot be removed from system

ISOENTHALPIC PROCESS

Real gases cool upon expansion

The process is adiabatic

Enthalpy or heat content does not change

J-T coefficient $\eta_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

$$H = H(P, T)$$

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

$$z = z(x, y)$$

Reciprocal Identity

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

Euler chain rule

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$$

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{-1}{\left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P}$$

$$= -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P$$

Thus, $$dH = -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

For isoenthalpic process,

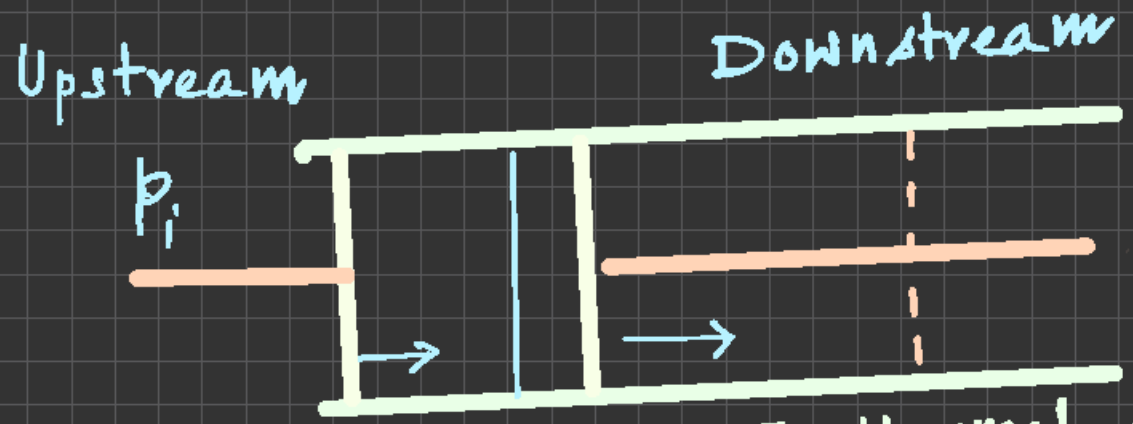
$$dH = -\eta_{JT} C_p \, dP + C_p \, dT$$

$dH = 0$ (Isoenthalpy)

$$\therefore \quad \eta_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$q = 0$ (ADIABATIC)

$\Delta U = W$



$p_f < p_i$

$$W_1 = -\int_{V_i}^{0} p\,dV$$

$$W_1 = -p_i(0 - V_i) = p_i V_i$$

$$W_2 = -p_f(V_f - 0) = -p_f V_f$$

$$U_f - U_i = w = P_i V_i - P_f V_f$$

$$U_f + P_f V_f = U_i + P_i V_i$$

or $$H_f = H_i$$

Isoenthalpic

For real gases,

$$dT = \eta_{JT}\, dP$$

$$T_f - T_i = \eta_{JT}\,(P_f - P_i)$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\partial H/\partial P\right)_T}{\left(\partial H/\partial T\right)_P}$$

Unit of η_{JT} is K/Pa

Below inversion temperature,

$\eta_{JT} > 0$

$\because dP < 0$

$dT < 0$.

Cooling

Above inversion temperature

$\eta_{JT} < 0$

$\because \frac{dP < 0}{dT > 0}$

warming ✓

All real gases have an inversion point where μ_{JT} will change sign

Inversion temperature of $O_2 = 491°C$

For ideal gases,

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$H = U + PV$$

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

$$= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - P\,\frac{nRT}{P^2} + V$$

$$= 0 - V + V = 0$$

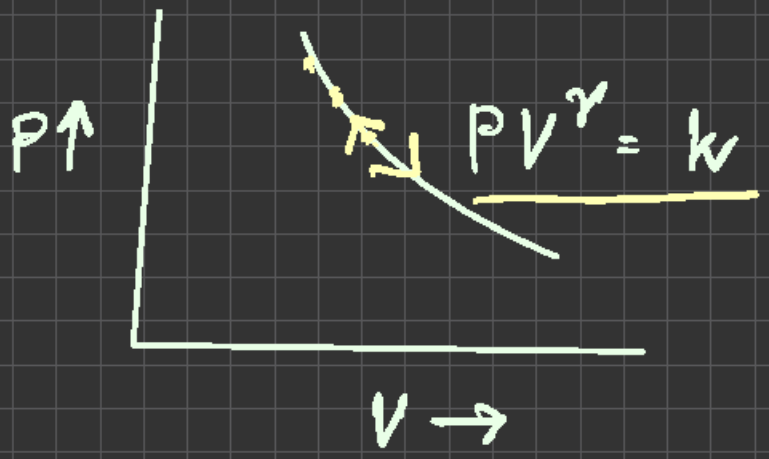
$$\eta_{JT} = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = 0$$

Reversible Adiabatic Expansion of An Ideal Gas

$$\delta W = -p\,dV$$ where p is the pressure applied

$$\delta q = 0$$

$$dU = C_V\,dT$$



Equation of state

$$pV = nRT$$

$$\delta q = 0 \quad \delta W = -p\,dV$$

$$dU = C_V\,dT$$

First Law

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$C_v\,dT = 0 - p\,dV$$

$$pV = nRT$$

$$\therefore p = \frac{nRT}{V}$$

$$C_v\,dT = -nRT\,\frac{dV}{V}$$

$$C_v \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_v \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} = nR \ln \frac{V_i}{V_f}$$

$$\ln \frac{T_f}{T_i} = \frac{nR}{C_v} \ln \frac{V_i}{V_f}$$

$$\frac{C_v}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

$$\left(\frac{T_f}{T_i}\right)^{C_v/nR} = \left(\frac{V_i}{V_f}\right)$$

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{nR/C_v}$$

$$\therefore \quad C_v \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} = nR \ln \left(\frac{V_i}{V_f} \right)$$

Let $\chi = \dfrac{C_v}{nR}$

$$\chi \ln \left(\frac{T_f}{T_i} \right) = \ln \left(\frac{V_i}{V_f} \right)$$

or,
$$\left(\frac{T_f}{T_i} \right)^{\chi} = \frac{V_i}{V_f} \Rightarrow \frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{1/\chi}$$

$$\frac{P_i V_i}{P_f V_f} = \frac{T_i}{T_f} \Rightarrow \frac{T_i}{T_f} = \left(\frac{V_f}{V_i} \right)^{1/\chi}$$

$$\gamma = \frac{C_P}{C_V} \qquad C_P - C_V = nR$$

Ideal gas

$nR \rightarrow C_p - C_v$

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i}\right)^{\frac{nR}{C_v}} = \left(\frac{V_f}{V_i}\right)^{\frac{C_p - C_v}{C_v}} = \left(\frac{V_f}{V_i}\right)^{\left(\frac{C_p}{C_v} - 1\right)}$$

$$\chi = \frac{C_v}{C_p - C_v} = \left(\frac{C_p - C_v}{C_v}\right)^{-1} = \left(\frac{V_f}{V_i}\right)^{\gamma - 1}$$

$$= \left(\gamma - 1\right)^{-1} = \frac{1}{\gamma - 1}$$

$$\therefore \frac{P_i}{P_f} = \frac{V_f}{V_i} \cdot \frac{T_i}{T_f} = \frac{V_f}{V_i}\left(\frac{V_f}{V_i}\right)^{\gamma - 1}$$

$$= \left(\frac{V_f}{V_i}\right)^{\gamma}$$

or, $\underline{P_i V_i^{\gamma}} = \underline{P_f V_f^{\gamma}} = \underline{k}$

$PV = nRT$

$P_i V_i = nRT_i$

$P_f V_f = nRT_f$

Isothermal T is same

$$P_i V_i = P_f V_f = k_{Isotherm} = PV$$

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} = PV^{\gamma} = k_{Adiabatic}$$

Second law of thermodynamics

There are two types of processes

- Natural or Spontaneous processes that does not require work to be done on the system

  Example – Free expansion of a gas

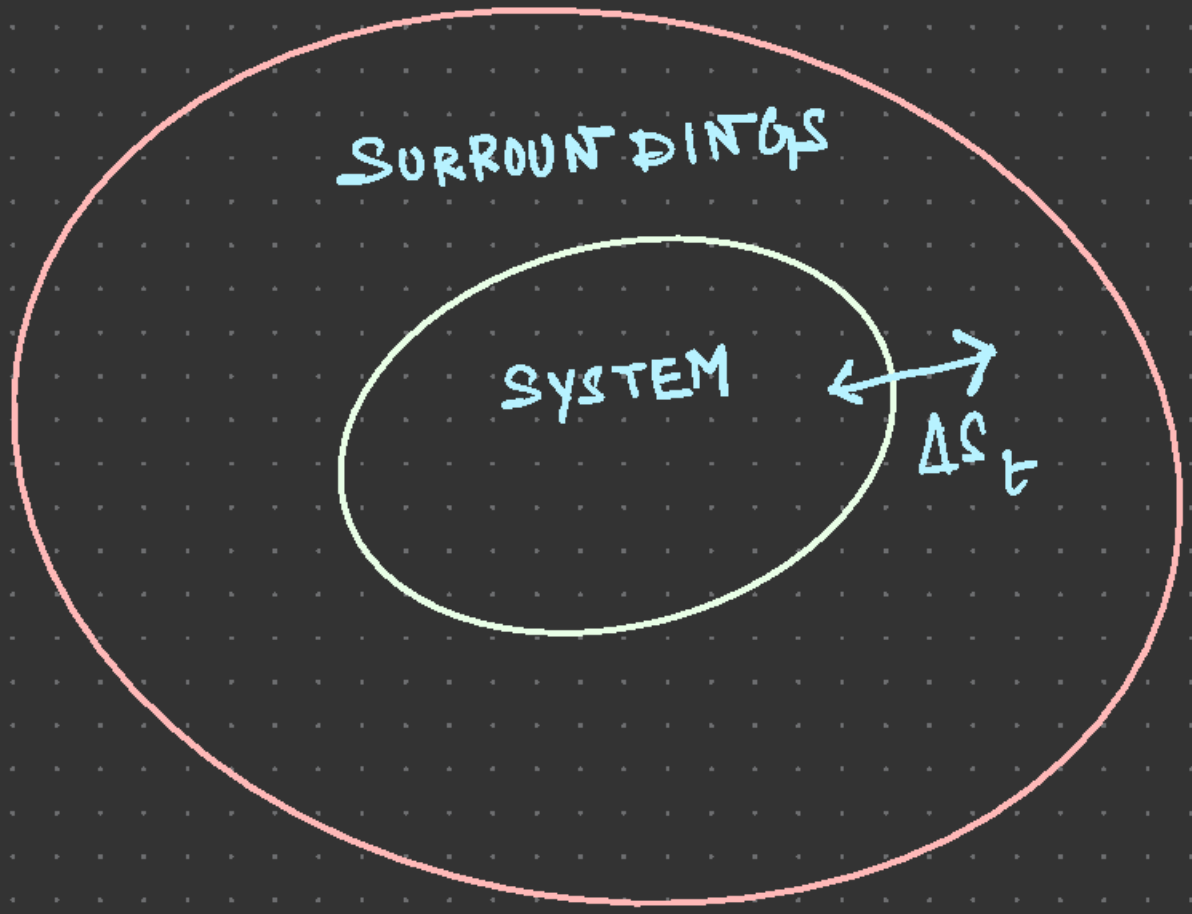
- Non-Spontaneous or artificial proces that requires work to be done on the system

Second law defines a state function called entropy (S)

$S_{universe}$ or S_{total} always increases in the direction of spontaneous change.

$\Delta S_{universe} > 0$ for a spontaneous change

Note: dS or ΔS measures the change in entropy



$\Delta S_{universe} > 0$ for a natural process

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

ΔS_t – Entropy transfer between the system and the surroundings

ΔS_p – Entropy production term

What is entropy production?

Spontaneous processes — natural, irreversible

Water kept at 150°C in a oven will vaporize — unless the surroundings are changed cannot be reversed

Balloon — fill with air — keep in a refrigerator

Balloon will expand when taken outside refrigerator. Bring it back to the refrigerator — it will collapse

For a given system and surrounding, there is a natural direction for any process

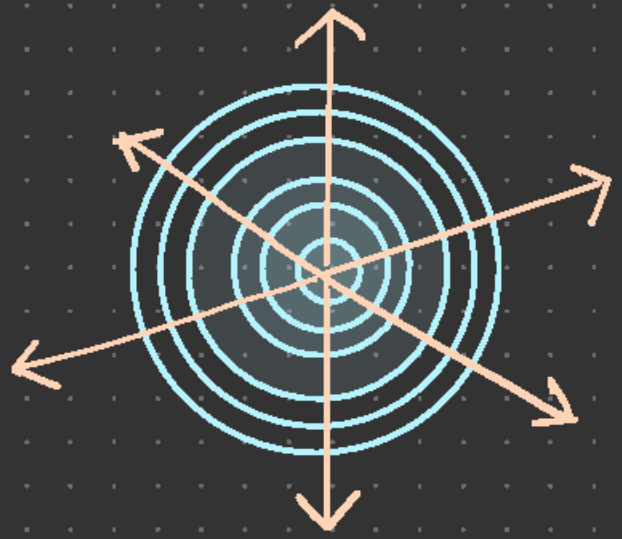
"Entropy is time's arrow"

Spontaneous process - Dissipation of energy

Throw a stone in a pond. K.E. of stone is dispersed in the form of water waves upon impact

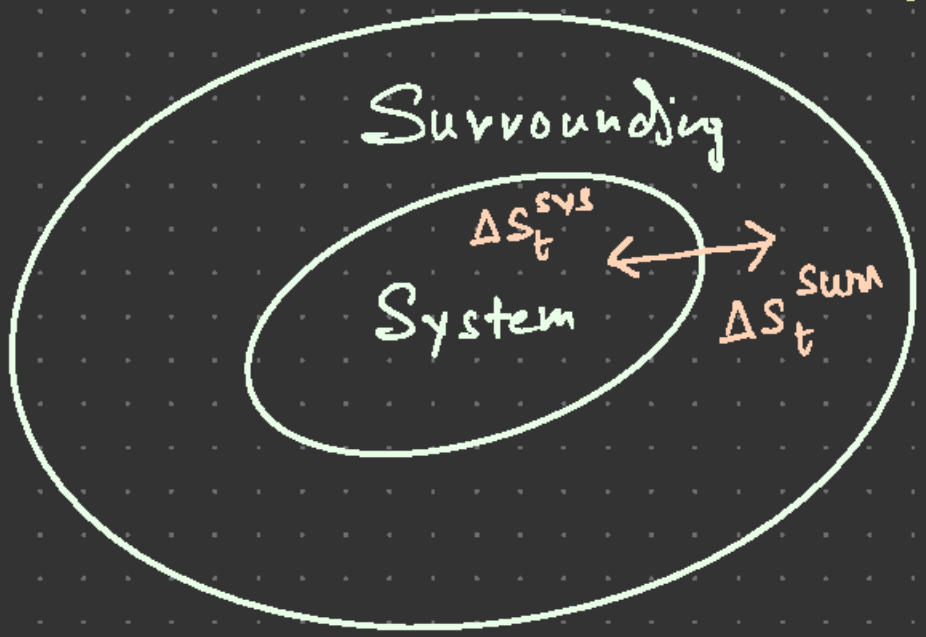


Reversal is impossible



Dissipation

→ Positive entropy production



Surroundings:

$$\Delta S_t^{surr} + \Delta S_p^{surr} = \Delta S^{surr}$$

System:

$$\Delta S_t^{sys} + \Delta S_p^{sys} = \Delta S^{sys}$$

$$\Delta S_t^{sys} = -\Delta S_t^{surr}$$

$$\Delta S_{universe} = \Delta S^{sys} + \Delta S^{surr}$$

$$\Delta S_p^{sys} = 0 \text{ (Reversible)} = \Delta S_p^{sys} + \Delta S_p^{surr} \geq 0$$

$$\Delta S_p^{surr} = 0 \text{ (Reversible)} \qquad \geq 0$$

For a reversible process

$$\Delta S_{p}^{sys/surr} = 0$$

$$\delta q_{rev} = \delta q_{reversible}$$

δq_{rev} is the heat absorbed during an infinitesimal step in the reversible process

Let the temperature of the system be T

δq_{rev} is a path function (Not an exact differential)

Entropy - Dispersion of energy in the form of heat

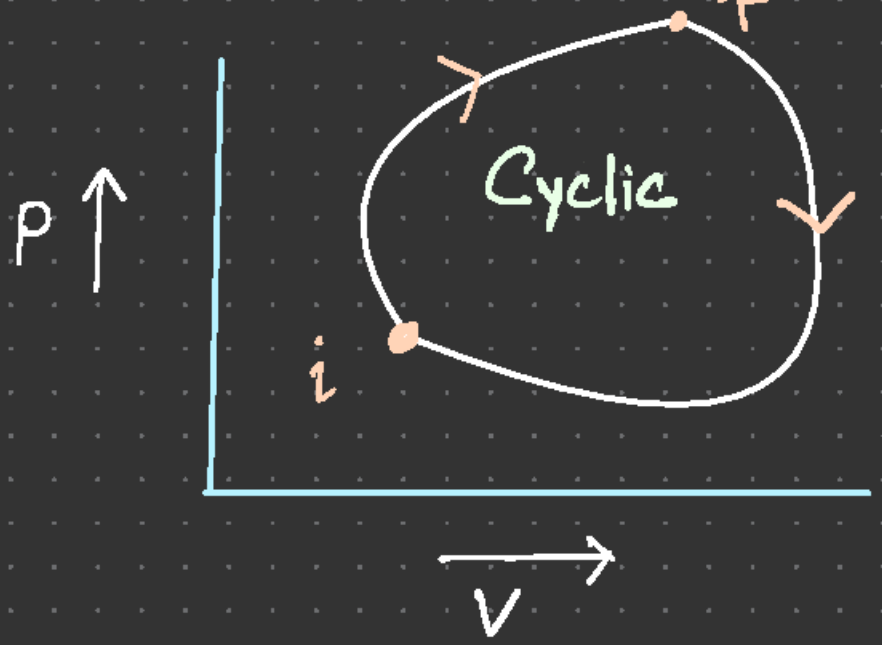
T is a state function

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

$$\Delta S = \int_i^f \frac{\delta q_{rev}}{T} = \int_i^f dS$$

$q_{in} \neq \int_i^f \delta q_{rev}$ Wrong

Prove that entropy is a state function



$$\oint \frac{\delta q_{rev}}{T} = \oint dS = 0$$

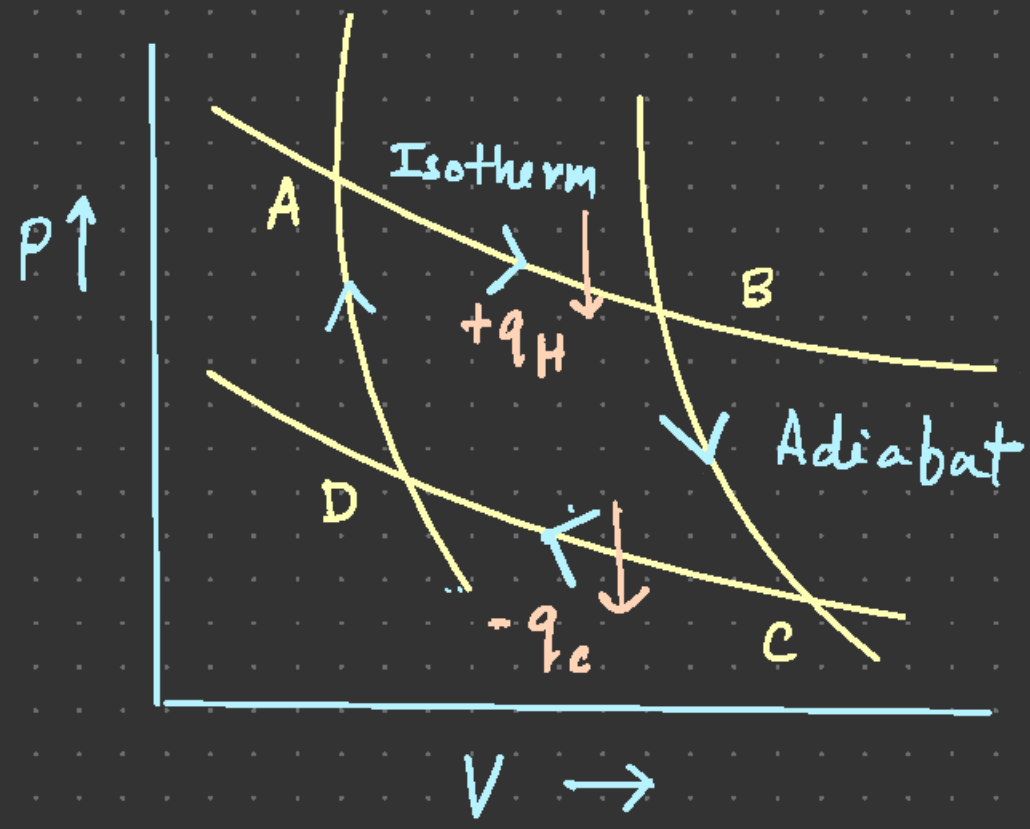
$$\delta q_{rev} = T\,dS$$

$i \to f$	
$S_f - S_i$	
$f \to i$	
$S_i - S_f$	

For an arbitrary cyclic process, no matter the path, the integral

$$\oint \frac{\delta q_{rev}}{T} = S_i - S_f + S_f - S_i$$

$$= 0$$



Carnot Cycle

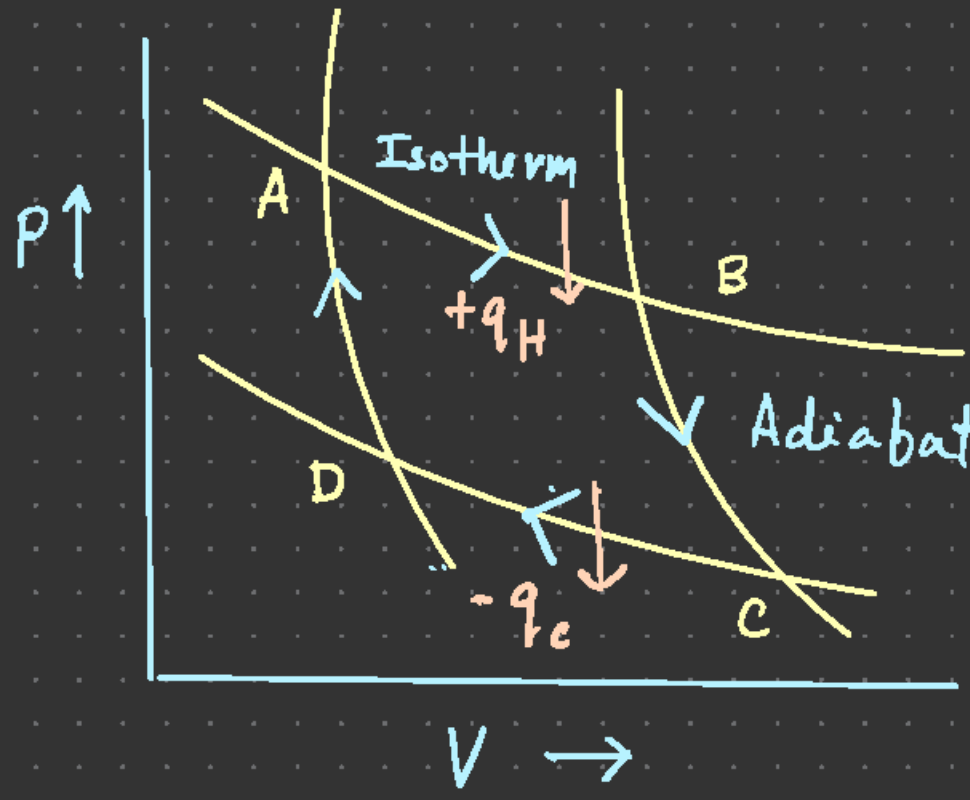
ABCD cycle

1. A → B
REVERSIBLE ISOTHERMAL EXPANSION – Temperature T_H
Heat Input – q_H

2. B → C
REVERSIBLE ADIABATIC EXPANSION – Temperature drops from T_H to T_c

3. C → D
REVERSIBLE ISOTHERMAL COMPRESSION at T_c –
Heat Released – q_c

4. D → A
REVERSIBLE ADIABATIC COMPRESSION – Temperature increase from T_c to T_H



1. $A \rightarrow B$
   Entropy change $= \frac{q_H}{T_H}$
2. $B \rightarrow C$
   Entropy change $= 0$
3. $C \rightarrow D$
   Entropy change $= \frac{q_c}{T_c}$
4. $D \rightarrow A$
   Entropy change $= 0$

Total change of entropy

$$\oint dS = \frac{q_H}{T_H} + \frac{q_c}{T_c}$$

$A \to B$

$$\Delta U = q + W$$

Isothermal $\Rightarrow \Delta U = 0 \quad \therefore \; q_H = -W_H$

$$W_H = -\int_{V_A}^{V_B} p\,dV \qquad pV = nRT$$

$$= -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$\therefore \; q_H = nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$B \to C$ Adiabatic expansion

$$V_B T_H^{\chi} = V_C T_C^{\chi}$$

$D \to A$ Adiabatic compression

$$V_A T_H^{\chi} = V_D T_C^{\chi}$$

$$\left(\frac{T_f}{T_i}\right)^{\alpha} = \frac{V_i}{V_f} \quad \therefore$$

$$V_f T_f^{\alpha} = V_i T_i^{\alpha}$$

$$V_A V_C T_H^{\chi} T_C^{\chi} = V_B V_D T_H^{\chi} T_C^{\chi}$$

$$V_A V_C = V_B V_D$$

or, $$\frac{V_A}{V_B} = \frac{V_D}{V_C}$$

C → D Isothermal Compression

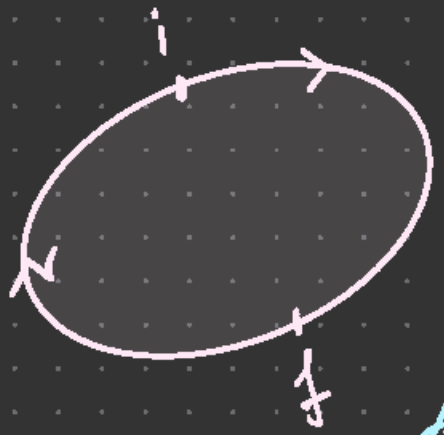
$$q_C = -W_C = nRT_C \ln\left(\frac{V_D}{V_C}\right) = nRT_C \ln\left(\frac{V_A}{V_B}\right)$$

$$= -nRT_C \ln\left(\frac{V_B}{V_A}\right)$$

$$\frac{q_H}{q_C} = -\frac{nR\underline{T_H}\ln\left(\frac{V_B}{V_A}\right)}{nR\underline{T_C}\ln\left(V_B/V_A\right)} = -\frac{T_H}{T_C}$$

Carnot Cycle

$$\oint dS = \frac{q_H}{T_H} + \frac{q_C}{T_C} = -\frac{q_C}{T_C} + \frac{q_C}{T_C} = 0$$



$$\frac{q_H}{q_C} = -\frac{T_H}{T_C} \Rightarrow \frac{q_H}{T_H} = -\frac{q_C}{T_C}$$

$$\oint \frac{\delta q_{rev}}{T} = \oint dS = 0$$

$\Delta S = S_i - S_i$

$= 0$

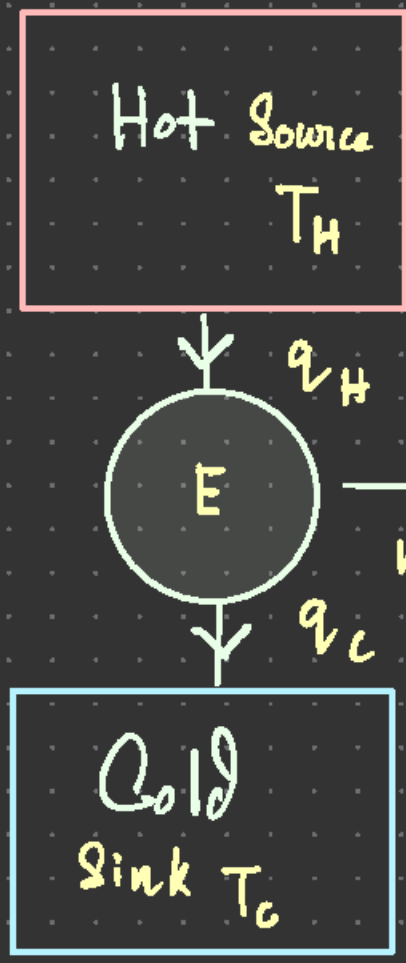
Define efficiency of a heat engine

$$\epsilon = \frac{\text{work performed}}{\text{heat absorbed}} = \frac{|w|}{q_H}$$

$$\epsilon = \frac{|W|}{q_H}$$

q_H - Heat absorbed

$|W|$ — Work done by the system



$$\frac{q_c}{q_H} = -\frac{T_c}{T_H}$$

$$\epsilon = \frac{q_H + q_c}{q_H} = 1 + \frac{q_c}{q_H} = 1 - T_c/T_H = \frac{T_H - T_c}{T_H}$$

All reversible engines have same efficiency regardless of material used

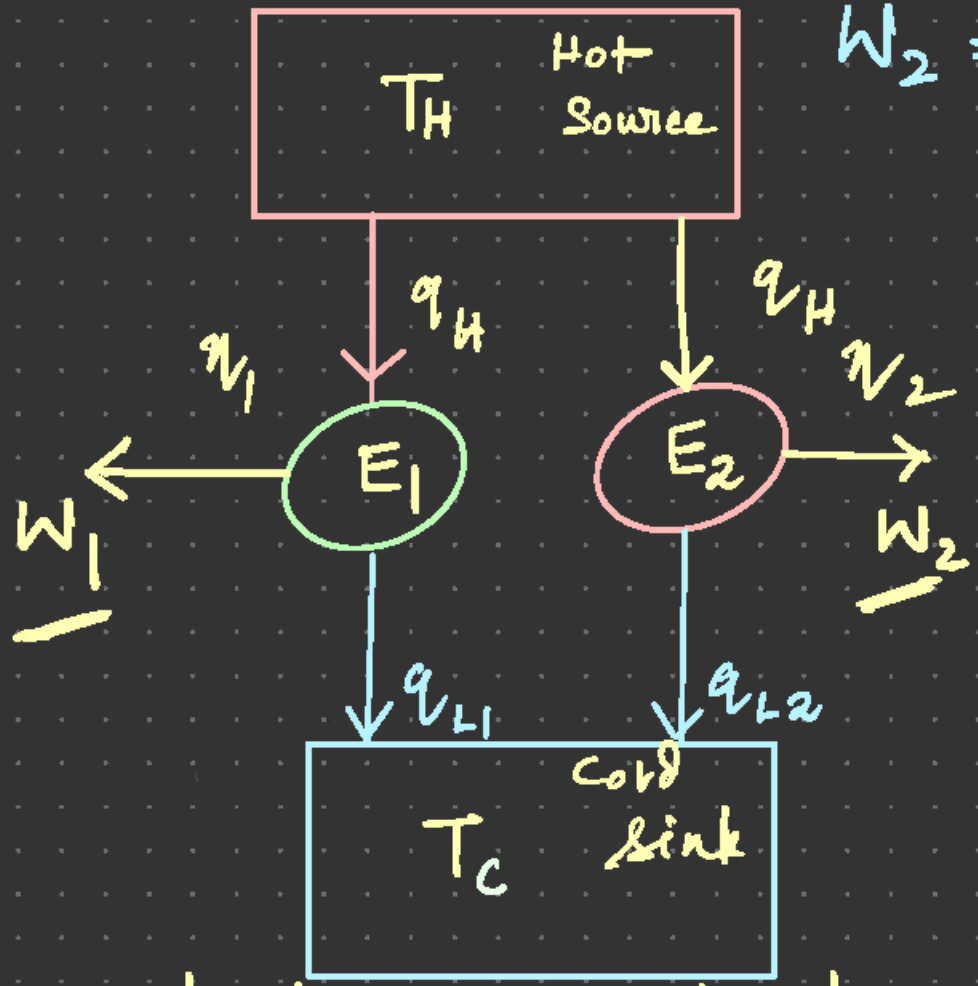
When $T_c = 0\,K$, then $\epsilon = 1$

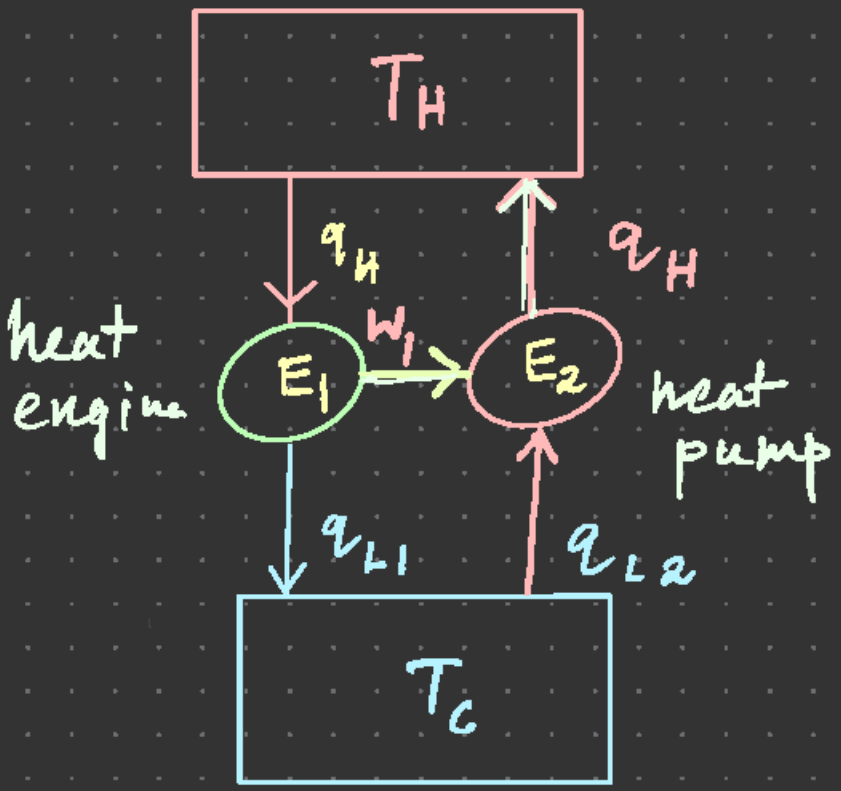
$$\epsilon = \frac{T_H - T_c}{T_H} < 1$$

$W_1 = q_H - q_{L1}$

$W_2 = q_H - q_{L2}$

$q_H - q_{L1} = W_1$





$\eta_1 = \dfrac{|W_1|}{q_H}$ $\eta_2 = \dfrac{|W_2|}{q_H}$

What is the net result?

$\eta_1 > \eta_2 \rightarrow |W_1| > |W_2|$

$\oint dV = 0$ $\quad q_{L2} + W_1 = q_H$

$\Rightarrow \quad q_H - W_2 + W_1 = q_H$

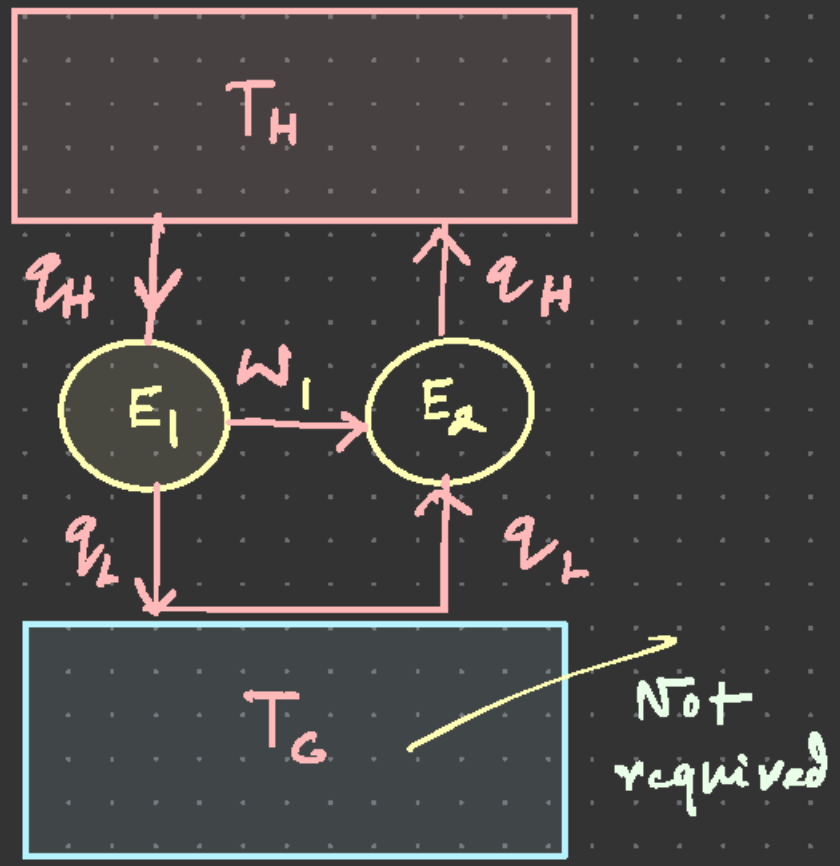
$\Rightarrow \quad W_1 - W_2 = 0$

$q_H - q_{L1} = W_1$

$q_{L2} + W_1 = q_H$

$+ W_1 = q_H$

$\oint p\,dV \neq 0$



$q_H - q_{L2} = W_2$

$q_{L2} = q_H - W_2$

$$\epsilon = \frac{\overset{(+)}{q_H} + \overset{(-)}{q_C}}{q_H}$$

q_C is -ve

$$= 1 + \frac{q_C}{q_H}$$

$$= 1 - \frac{T_C}{T_H}$$



$$\epsilon = \frac{T_H - T_C}{T_H}$$

If T_C is fixed, we want to make T_H as large as possible

So that ϵ comes close to unity

Using an ideal gas we proved

$$\oint \frac{\delta q_{rev}}{T} = \oint dS = 0$$

for a cyclic process

Thus $\frac{q_{rev}}{T}$ or S is a state function

First law

$$dU = \delta q - p\,dV \quad -(1)$$

$$\oint dU = 0$$

$\int \delta q$ – path dependent

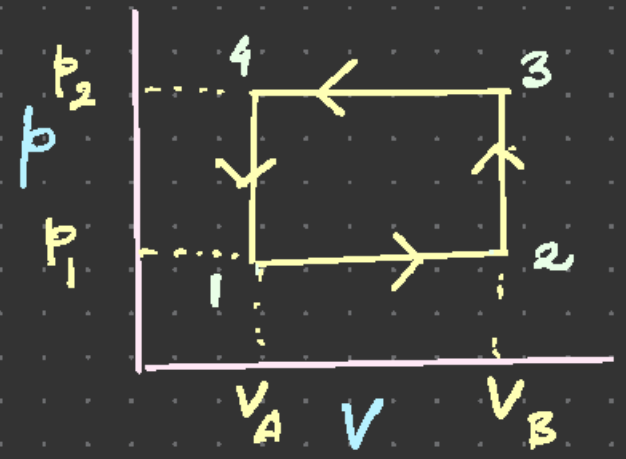
$\int \frac{\delta q}{T}$ → path independent

But $\oint p\,dV \neq 0$

(Check P-V diagram of the Carnot cycle, for example)

$$\therefore \quad \oint \delta q \neq 0$$

Divide (1) by T



$$\frac{dU}{T} = \frac{\delta q}{T} - \left(p/T\right) dV$$

$$pV = RT \quad \text{(Ideal gas)}$$

$$\frac{dU}{T} = \frac{\delta q}{T} - \frac{R}{V} dV$$

$$\oint \frac{dU}{T} = 0 \; ?$$

for an ideal gas

for an ideal gas

U is $U(T)$

$$dU = C_V \, dT$$

$$\oint \frac{dU}{T} = \oint \frac{C_V \, dT}{T}$$

$$\oint C_v \, d[\ln T] = \underline{0}$$

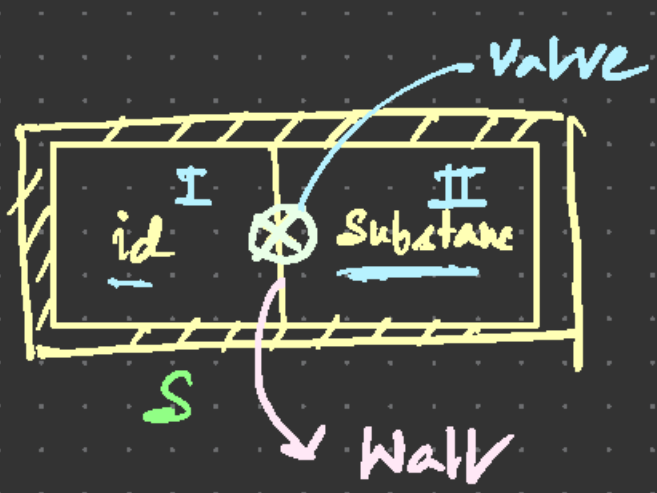
Also, $$\oint R \, d \ln V = 0$$

$$\therefore \quad \oint \frac{\delta q_{rev}}{T} = 0 = \oint dS$$

Question

Show that $\oint \underline{\delta q_{rev}}$ is not a path-independent function
P

What about other Substance 2



Denote ideal gas as id

Denote any substance as S

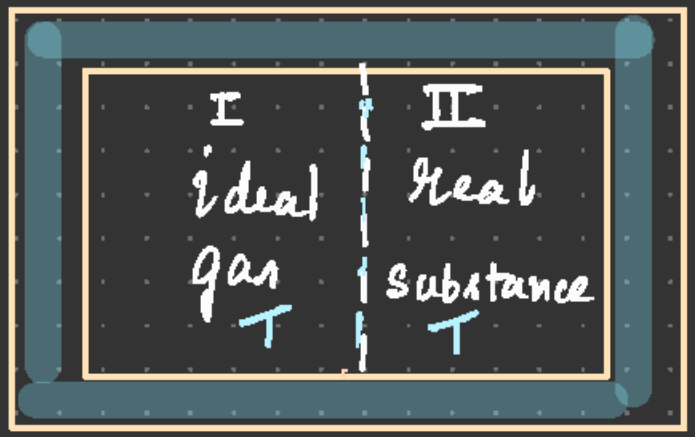
We know $\oint \frac{\delta q_{rev}}{T}(id) = 0$ ✓

$\Downarrow$? Is this true ?

$\oint \frac{\delta q_{rev}}{T}(sub) = 0$

See paper in J. Chem. Edu. 1988, 65, 5, 399
" " " 1986, 63, 10, 846

I and II are subsystems



TAKE AN ISOLATED SYSTEM

I and II can exchange heat reversibly

$$\delta q^{I} + \delta q^{II} = 0$$

I and II are in equilibrium

$$\therefore \oint \frac{\delta q^{I}_{rev}}{T}(id) + \oint \frac{\delta q^{II}_{rev}}{T}(sub) = 0$$

$$\text{Thus, } \oint \frac{\delta q_{rev}}{T}(id) = 0 \Rightarrow \oint \frac{\delta q_{rev}}{T}(sub)$$

Clausius Inequality

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

$$dU = \delta q + \delta W$$

$$= \delta q_{rev} + \delta W_{rev}$$

Note

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

$$dS > \frac{\delta q_{irr}}{T}$$

Work done by the system during a reversible process is

$-\delta W_{rev}$ $\quad |\delta W_{rev}| > |\delta W|$

Work done by the system during an irreversible process

$-\delta W$

$$\left.\begin{aligned} dS &= \frac{\delta q_{rev}}{T} \\ dS &> \frac{\delta q_{irr}}{T} \end{aligned}\right\}$$

$\delta q + \delta W = \delta q_{rev} + \delta W_{rev}$

$-\delta W_{rev} \geq -\delta W$

$\delta W - \delta W_{rev} = \delta q_{rev} - \delta q$

or, $\delta W - \delta W_{rev} \geq 0$

$$\delta q_{rev} - \delta q = \delta W - \delta W_{rev} \geq 0$$

$$\delta q_{rev} \geq \delta q$$

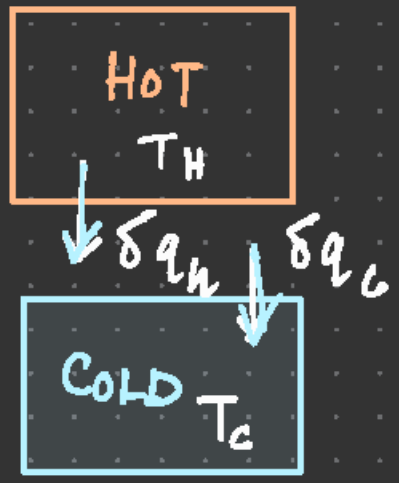
or, $\frac{\delta q_{rev}}{T} \geq \frac{\delta q}{T} \Rightarrow dS \geq \frac{\delta q}{T}$

$T_H > T_c$

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

$T_c < T_H$

< 0



$$dS \geq \frac{\delta q_h}{T_h} + \frac{\delta q_c}{T_c}$$

$\delta q_h \rightarrow$ leaving (so -ve)

$\delta q_c = -\delta q_h$

$\delta q_c \rightarrow$ entering (so +ve)

$$dS = \frac{\delta q_h}{T_h} - \frac{\delta q_h}{T_c} = \underbrace{\delta q_h}_{(-ve)} \underbrace{\left(\frac{1}{T_h} - \frac{1}{T_c}\right)}_{-ve}$$

$\therefore \frac{1}{T_h} - \frac{1}{T_c} < 0$ or $T_c \leq T_h$ for $dS \geq 0$

Isolated System

$\delta q = 0$ $\quad dS = 0$ (for reversible process)

$dS \geq 0$ $\quad dS > 0$ (for spontaneous proc.)

Entropy does not decrease in an isolated system when there is spontaneous change

At 100°C and 1 atm. pressure, $\delta q_p = dH$

$$\text{Water}(l) \overset{100^\circ C}{\rightleftharpoons} \text{Water}(\text{vapour}) \qquad q_{p,rev} = \Delta H$$

$q + W = \Delta U$

Transition temperature

Any transfer of heat is reversible at the transition temperature

$q_{p,rev} - p\Delta V = \Delta U$

$q_{p,rev} = \Delta U + p\Delta V$

$= \Delta H$

$= T^{tr}\Delta S$

$$q_{rev} = \underline{\Delta H^{tr}} = \underline{T\Delta S^{tr}}$$

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

Calculate the change in entropy when an ideal monoatomic gas at 30°C and 1atm. pressure is allowed to expand from 0.5 L to 1 L and is heated to 100°C at the same time.

1. Reversible isothermal expansion at 30°C

+

2. Reversible heating at constant volume

$$pV = nRT$$

$$dS = \frac{\delta q_{rev}}{T} \quad \therefore \Delta S = \int_i^f \frac{\delta q_{rev}}{T}$$

$$\int_i^f dS = \int_i^f \frac{\delta q_{rev}}{T} \qquad T \text{ is constant}$$

$$\downarrow$$

$$\Delta S$$

$$\Delta S = \frac{1}{T} \int_i^f \delta q_{rev} = \left[\frac{q_{rev}}{T} \right]_i^f$$

$$\Delta U = 0 = q_{rev} + W_{rev}$$

$$\therefore q_{rev} = -W_{rev}$$

rev → Reversible

$dU = 0$ ($T = 30^\circ C$ constant)

$$\therefore \underline{q_{rev}} = -\underline{W_{rev}} = \int_i^f p \, dV$$

$$p = \frac{nRT}{V}$$

$$= \underline{n}RT \int_i^f \frac{dV}{V}$$

$$= \underline{n} RT \ln \frac{V_f}{V_i}$$

$$\therefore \quad \Delta S = \frac{1}{T}\left\{ nRT \ln\left(\frac{V_f}{V_i}\right) \right\}$$

$$= nR \ln\left(\frac{V_f}{V_i}\right)$$

$$n = \frac{p_i V_i}{R T_i}$$

$$\therefore \quad \Delta S\,(\text{step 1}) = \left(\frac{p_i V_i}{T_i}\right) \ln\left(\frac{V_f}{V_i}\right) \quad \text{— (1)}$$

Step 2 - Volume $= V_f$ = constant

$$p\,dV = 0$$

$$q_{rev} = \int_{T_i}^{T_f} \delta q_{rev} = \int_{T_i}^{T_f} dU$$

$$\frac{q_{rev}}{T} = \int_{T_i}^{T_f} \frac{dU}{T}$$

$$dU = n C_{V,m}\, dT$$

Molar heat capacity $C_{V,m} = \frac{3}{2} R$ (from equipartition theorem)

$$\eta = \frac{p_i V_i}{R T_i}$$

$$\therefore \quad \Delta S(2) = \left(\frac{p_i V_i}{R T_i}\right) \frac{3}{2} R \int_i^f \frac{dT}{T}$$

$$= \frac{p_i V_i}{T_i} \ln\left(\frac{T_f}{T_i}\right)^{3/2} \quad -(2')$$

$$\Delta S^{\text{total}} = \Delta S(1) + \Delta S(2) = \frac{p_i V_i}{T_i} \ln\left\{\frac{V_f}{V_i}\left(\frac{T_f}{T_i}\right)^{3/2}\right\}$$

Check whether $\Delta S > 0$ ✓

Measuring entropy

Measurable quantities (Directly)

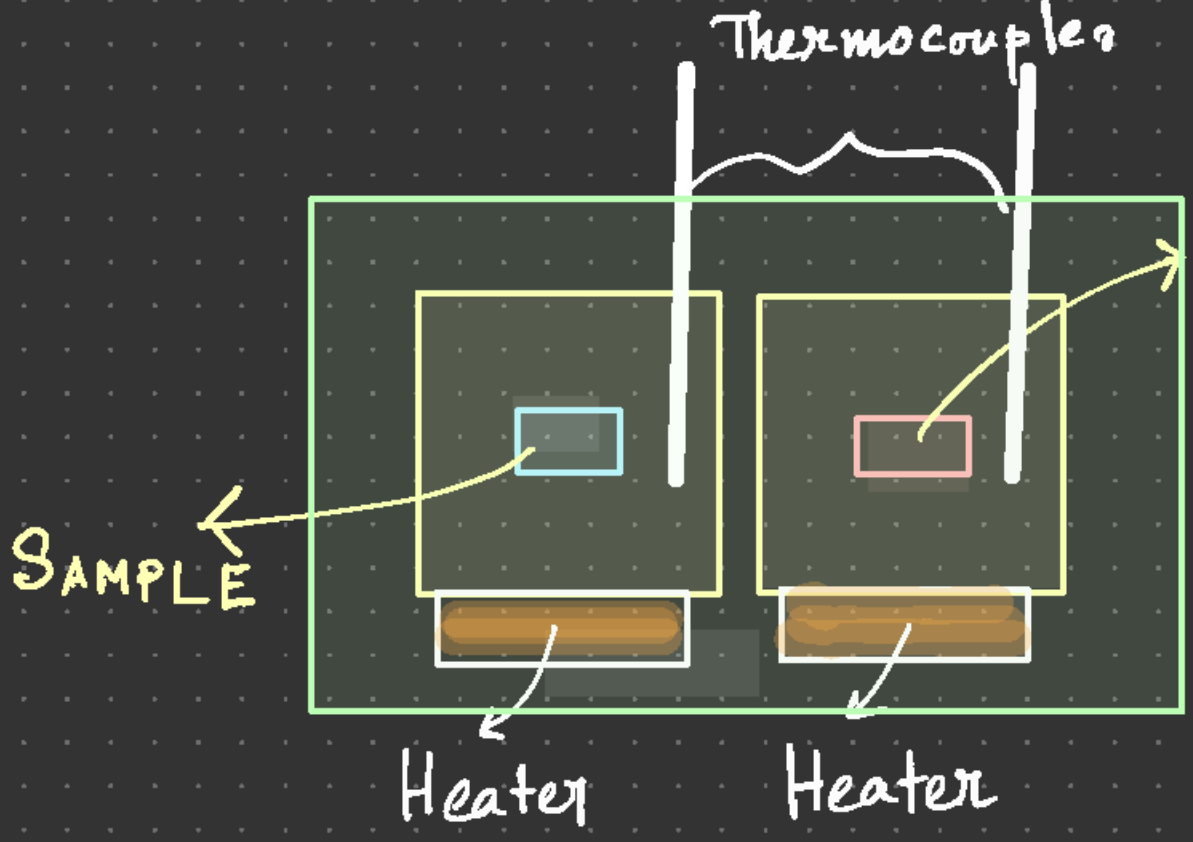
C_V, C_P

α, K_T (or, β)

T, P, V

Measurement of enthalpy

- Differential Scanning Calorimetry (DSC)



> Temperature of Sample & reference are increased at a constant rate (Scanning)

T_0 — Initial temperature

S_R → Scanning rate (Ks^{-1})

$$T(t) = T_0 + s_R t$$

$$C_p = C_p(T)$$

Maintain same temperature in both compartments — How?

Transfer excess energy to or from the sample undergoing a physical or chemical process

No physical/chemical change of the sample at temperature T

$$q_p = C_p \Delta T = C_p (T - T_0)$$

$\Delta T = T - T_0$
$= S_R t$

If physical / chemical change = TRUE,

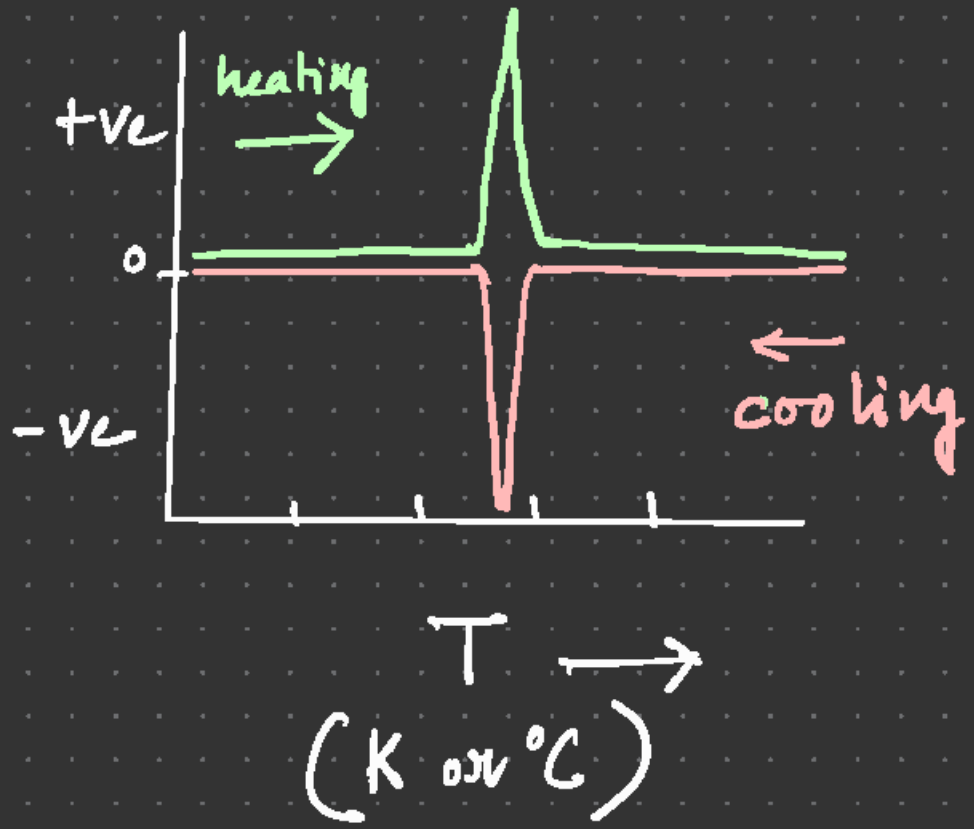
excess heat transfer to maintain same change in temperature in sample as in reference $\Rightarrow$

$$q_p + q_{p,xs} = (C_p + C_{p,xs}) \Delta T$$

$$C_{p,xs} = \frac{q_{p,ex}}{\Delta T} = \frac{q_{p,ex}}{s_R t} \quad \left(\frac{J}{K}\right)$$

Endo

Exo



$$\Delta H = \int_{T_1}^{T_2} C_{p,xs}\, dT$$

Measure entropy

Second law:

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

$$\delta q_{p,rev} = T dS = \underline{dH} = \underline{C_p dT}$$

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

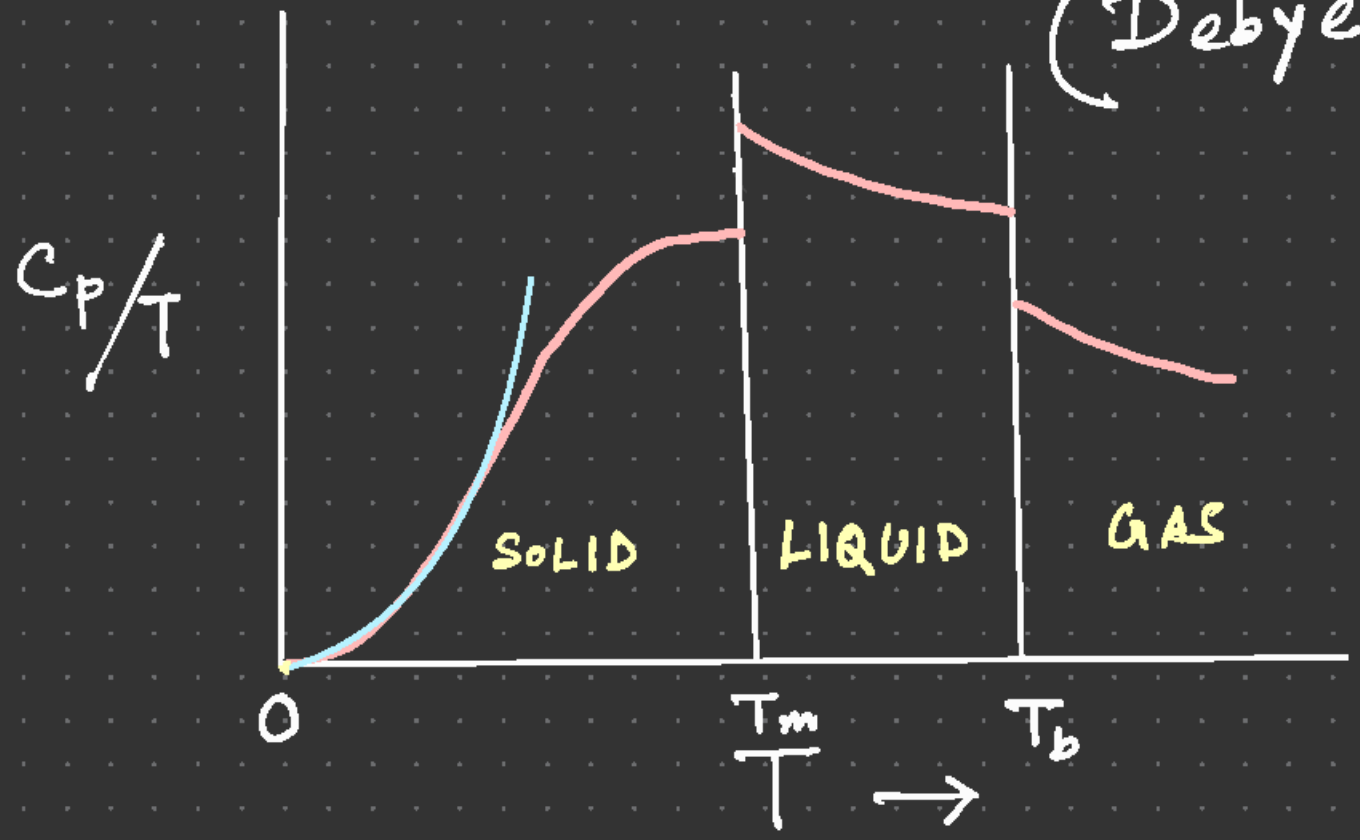
$$C_p(T) = a + bT + \frac{c}{T^2} + dT^2$$

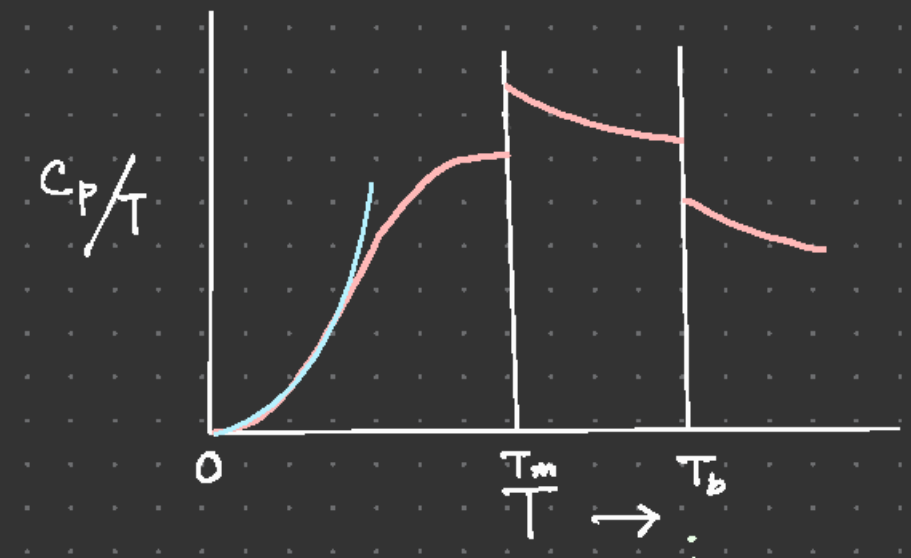
	a	$b\ (1/K)$	$c\ (K^2)$	$d\ (1/K^2)$	Range
$Ag(s)$	21.30	8.54×10^{-3}	1.51×10^{5}	–	298 – 1234 K
$Ni(l)$	38.49	–	–	–	1728 – 1900 K

$C_p \rightarrow 0$ as $T \rightarrow 0$

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

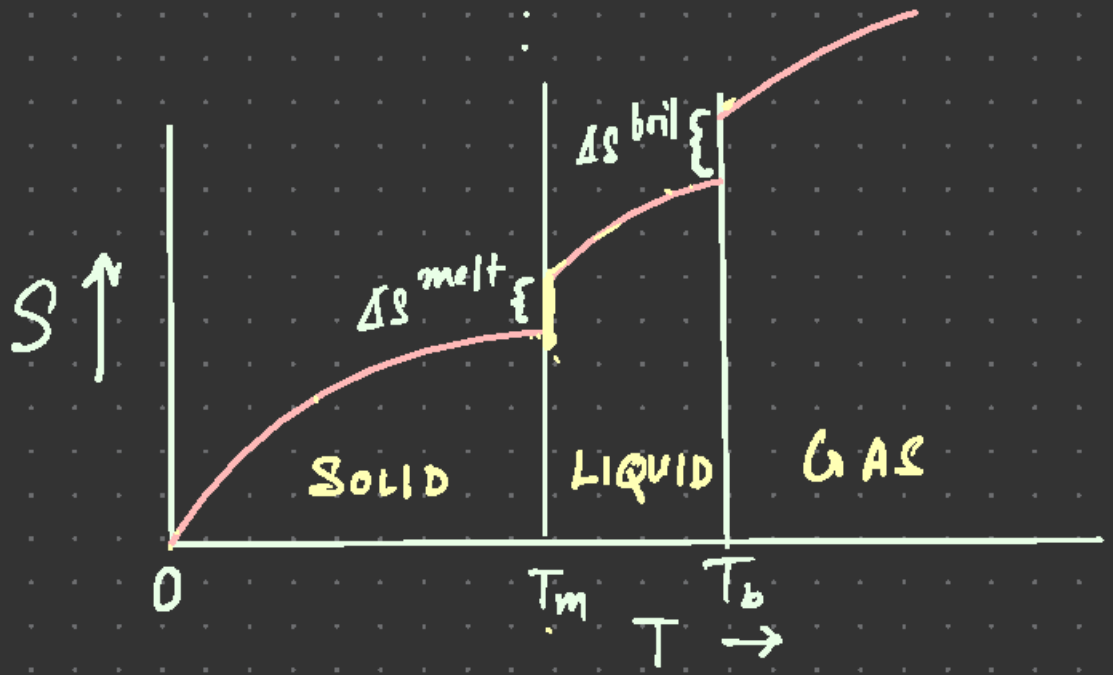
(Debye Extrapolation)





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

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



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

$$H = U + pV$$

$$\delta q_p = dH$$

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

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

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}

Thermodynamic Temperature

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

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

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

Put $\epsilon = 1$, then $T_C = 0$ 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

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

Combine first & second laws

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

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$= T dS - p dV$$

$$\delta q_p^{rev} = dH \qquad dH = dU + p dV + V dp$$

Isobaric $\rightarrow dP = 0$

$$\therefore \quad T dS = dU + p dV = dH$$

$$\text{or,} \quad dS = dH/T$$

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

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

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

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

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

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

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

$$H = U + pV$$

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

Isobaric $\Rightarrow dp = 0$

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

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

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

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)

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

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

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

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

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

$$dU = TdS - p\,dV$$

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

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

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

— (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)

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

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

$$dZ = M\,dx + N\,dy$$

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

$$\therefore \quad \frac{\partial^2 s}{\partial T\,\partial v} = \frac{\partial^2 s}{\partial v\,\partial T}$$

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\frac{\partial e}{\partial s}\right)_v = \frac{\partial}{\partial T}\left(\frac{1}{T}\frac{\partial e}{\partial s}\right)_T$$

$$\frac{\partial}{\partial v}\left\{\frac{1}{T}\left(\frac{\partial e}{\partial T}\right)_v\right\} = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left(\frac{\partial e}{\partial v}\right)_T + \frac{p}{T}\right\}$$

$$\frac{1}{T}\frac{\partial^2 e}{\partial v\,\partial T} = \frac{1}{T}\left[\frac{\partial^2 e}{\partial v\,\partial T} + \left(\frac{\partial p}{\partial T}\right)_v\right] - \frac{1}{T^2}\left[p + \left(\frac{\partial e}{\partial v}\right)_T\right]$$

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

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

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

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

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

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)

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

or,

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

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