

Physics

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Thermodynamics

E. Fermi, Halliday Resnick
+
Roberts.

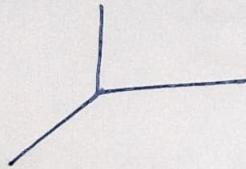
Laws experimental

universal nature

classical physics (not quantum)

Non-relativistic Theory

Thermodynamic Distances



Average (macroscopic)

pressure, temp^o, volume

p T v

Equilibrium state

Transformation, reversible form^o

$$f(p, v, T) = 0 \quad \text{eqn of state}$$

Ideal gas

$$pV = \frac{m}{M} RT$$



R → gas constant

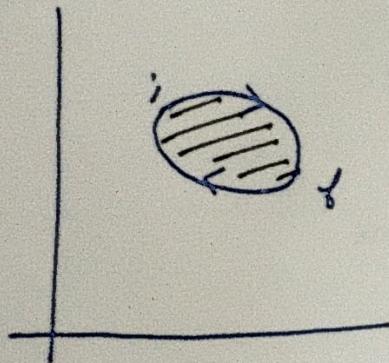
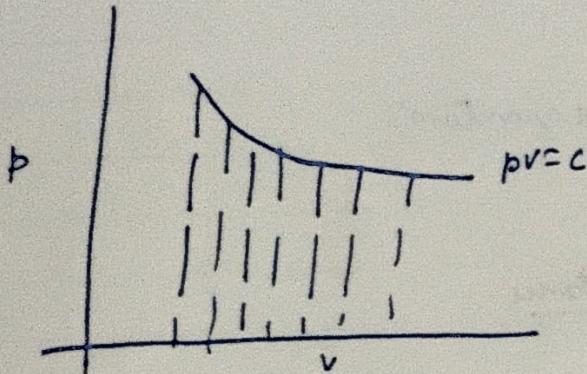
$$[R] = 8 \text{ Joules / A}$$

- Ideal Gas
- A collection of non interacting 2 point particles.
 - A Real gas behaves like an ideal gas for low density & high temp⁹¹.

ISOTHERMAL.

$$W = \int_{V_i}^{V_f} p dV = R \int_{V_i}^{V_f} \frac{dV}{V}$$

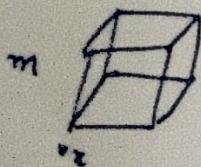
$$= RT \ln \frac{V_f}{V_i}$$



Microscopic picture

Kinetic Theory

Newton's Law



$$= (2mv_x v_{x,t}) \Delta A \Delta n$$

= Rate of change of momentum = F

$$v_{x,t} = 2mv_x^2 \Delta A \Delta n$$

$$\text{Pressure} = 2mv_x^2 n = \frac{-2N v_x^2}{V}$$

$$= n m v_x^2$$

$$p = \frac{8N}{V} m v_x^2$$

$$pV = mn v_x^2$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$= nm v_x^2$$

$$= nm \frac{v^2}{3}$$

$$pV = \frac{2}{3} N \left(\frac{mv^2}{2} \right) \rightarrow \text{Avg K.E per particle}$$

$$\frac{1}{2} \frac{3}{2} RT$$

$$pV = n \cancel{k} T$$

$$pV = RT$$

Boltzmann
constant

$$R = \cancel{N k} \xrightarrow{\text{Avogadro's Number}}$$

1st Law of Thermodynamics

$$U_f - U_i = \underbrace{\Theta}_{\substack{\text{heat} \\ \text{received}}} - \underbrace{L}_{\substack{\text{work} \\ \text{done}}}$$

$$\rightarrow dU = dq - dL$$

$$\rightarrow dU + dL = dq$$

$$\rightarrow dU + p dV = dq$$

L-2

1st law of Thermodynamics

AKA Energy conservation principle

$$dU + pdV = d\theta$$

Perfect / ideal gas

Based by

(I) $U(T)$, Joule's experiment

$$(II) \left\{ dU = \frac{\partial U}{\partial T} dT \right\}$$

$$\textcircled{1} \rightarrow \frac{\partial U}{\partial T} dT + pdV = d\theta$$

process where $V \rightarrow \text{constant}$, $dV = 0$

$$\rightarrow \left| \frac{\partial U}{\partial T} \right|_V + 0 = \left| \frac{d\theta}{dT} \right|_V = C_V$$

$$\left\{ C_V = \left. \frac{d\theta}{dT} \right|_V \right\}$$

$$\textcircled{2} \rightarrow pV = RT \rightarrow pdV + Vdp = RdT$$

$$\textcircled{II} \quad C_V dT + (RdT - Vdp) = d\theta$$

$$\{dU\}$$

$$\{pdV\}$$

$$\{d\theta\}$$

$$\rightarrow p \rightarrow \text{constant} \quad dp = 0$$

$$C_V + R = \left. \frac{d\theta}{dT} \right|_p = C_p$$

$$C_p = C_v + R$$

$$\{ C_p = C_v = c \text{ for solids} \}$$

(III)

Adiabatic Transformation (No heat exchange)
 $\{ d\theta = 0 \}$

$$dU + p dV = d\theta$$

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

$$C_v dT + \frac{RT}{V} dV = 0$$

$$\frac{dT}{T} + \frac{R}{C_v} \frac{dV}{V} = 0$$

$$\int \frac{dT}{T} + \int \frac{R}{C_v} \frac{dV}{V} = 0$$

$$\ln T + \ln V^{\frac{R}{C_v}} = 0$$

$$T V^{\frac{R}{C_v}} = \text{constant}$$

$$\frac{PV}{R} V^{\frac{R}{C_v}} = PV^{\left(\frac{R}{C_v} + 1\right)} = \text{constant}$$

$$\left\{ \frac{R + C_v}{C_v} = \frac{C_p}{C_v} = \gamma \right\}$$

Adiabatic $PV^\gamma = \text{constant}$, $\gamma > 1$

Isothermal $PV = \text{constant}$

How do we get this?

$$\textcircled{1} \quad \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP + P \left(\left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \right) = dQ$$

$$\textcircled{2} \quad \left(\frac{\partial U}{\partial V} \right)_P dV + \left(\frac{\partial U}{\partial P} \right)_V dP + P dV = dQ$$

similarly for

\textcircled{3} \quad T, V

a) Decrease in temp^o as we go above earth surface.

assumption: Expansion occurs adiabatically

$$P = \rho g z \quad \rho = \text{density of air}$$

$$dP = -\rho g dz$$

we can calculate $\frac{dT}{dz}$ with this.

$$P = \frac{m}{M} v \frac{RT}{v}$$

$$\cancel{\rho} = \frac{P M}{R T}$$

2nd Law of Thermodynamics

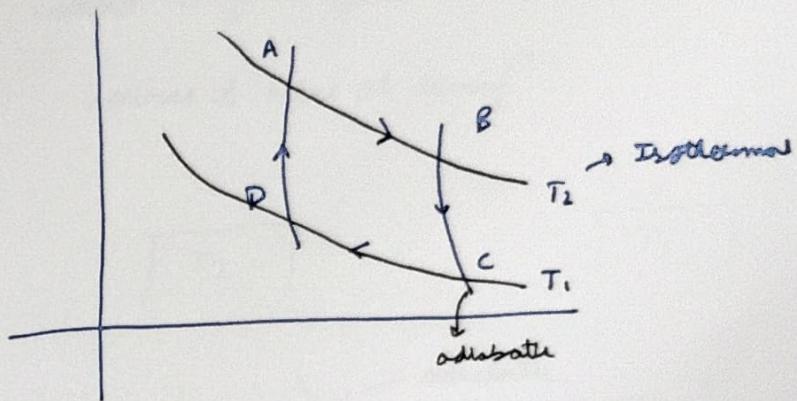
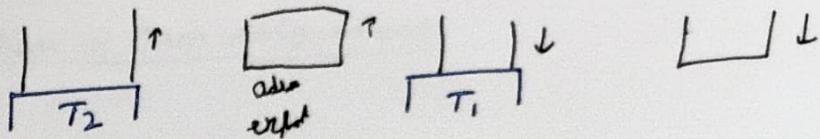
$$W \rightarrow \theta \checkmark$$

$$\theta \rightarrow W$$

Sadi Carnot

Carnot cycle/engine

source of heat at temp T.



$$T_2 > T_1$$

$$\eta \text{ (efficiency)} = \frac{W}{\vartheta_2} = \frac{\vartheta_2 - \vartheta_1}{\vartheta_2} = 1 - \frac{\vartheta_1}{\vartheta_2}$$

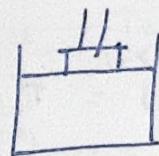
PTO

2nd law of Thermodynamics

$$W \rightarrow Q \checkmark$$

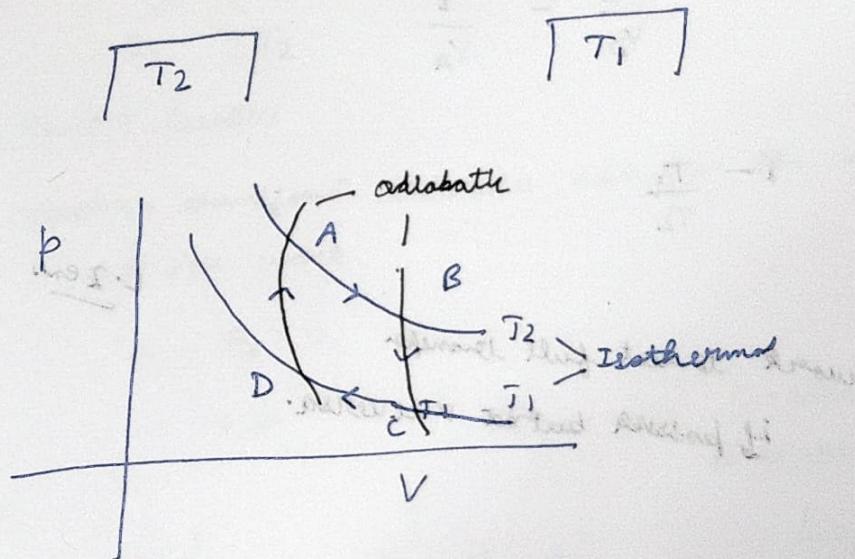
$$Q \neq W$$

Sadi Carnot



Carnot engine/cycle

source of heat at temp T^o



$$T_2 > T_1$$

$$\eta \text{ (efficiency)} = \frac{W}{Q_2} = \frac{\Theta_2 - \Theta_1}{\Theta_2}$$

$$= 1 - \frac{\Theta_1}{\Theta_2}$$

$$\left. \begin{cases} \Theta_2 = R T_2 \ln \frac{V_B}{V_A} \\ \Theta_1 = R T_1 \ln \frac{V_C}{V_D} \end{cases} \right\}$$

$$\eta = 1 - \frac{R T_1 \ln(V_C/V_D)}{R T_2 \ln(V_B/V_A)}$$

$$\rightarrow \textcircled{BC} \quad T_2(v_B)^{y-1} = T_1(v_C)^{y-1} \quad Pv^y = C$$

$$\rightarrow \textcircled{DA} \quad T_2(v_A)^{y-1} = T_1(v_D)^{y-1} \quad \frac{RT}{V} v^y = C$$

$$\frac{T_2}{T_1} = \left(\frac{v_C}{v_B} \right)^{y-1} = \left(\frac{v_D}{v_A} \right)^{y-1}$$

$$\frac{v_C}{v_D} = \frac{v_B}{v_A}$$

$$\Rightarrow \eta = 1 - \frac{T_1}{T_2}$$

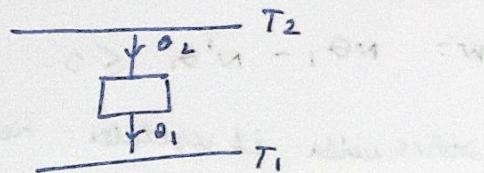
L-Z end

work to heat full transfer
if possible but not nice area.

L 3

Kelvin: A transformation where only final outcome is to get work from a single heat source is not possible.

(J)



Clauses: A transform² where only final outcome is the transfer of some amount of heat from cold source to hot source.



Kelvin \Rightarrow clauses

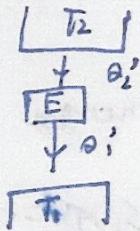
consider a transformⁿ that takes heat from the cold source
 $\rightarrow +ve$ work.

$$w = \theta_2 - \theta_1$$

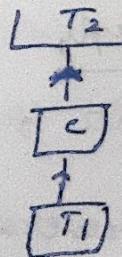
$$L \rightarrow \theta$$

C \rightarrow cannot / inaccessible
E \rightarrow arbitrary engine

$$T_2 > T_1$$



$$n' = \frac{\theta_2' - \theta_1'}{\theta_2'}$$



$$\frac{\theta_2'}{\theta_2} = \frac{N}{N'}$$

$$\theta_2' N' = \theta_2 N$$

E \rightarrow performs N' cycles

C \rightarrow same ~~cycles~~ in N cycles

$$W = (N'\theta_2' - N\theta_2) - (N'\theta_1' - N\theta_1)$$

↓

$$\left\{ \begin{array}{l} N'\theta_2' = \theta_2 N^2 \\ \end{array} \right.$$

$$W = N\theta_1 - N'\theta_1' \leq 0$$

otherwise it violates Kelvin.

$$N\theta_1 - N'\theta_1' \leq 0$$

$$\frac{N}{N'} \leq \frac{\theta_1'}{\theta_1}$$

$\left\{ \begin{array}{l} \frac{N}{N'} = \frac{\theta_2'}{\theta_2} \\ \end{array} \right.$

$$\frac{\theta_2'}{\theta_2} \leq \frac{\theta_1'}{\theta_1}$$

$$\underbrace{1 - \frac{\theta_1'}{\theta_2}}_{n_c} \geq \underbrace{1 - \frac{\theta_1'}{\theta_1'}}_{n_E}$$

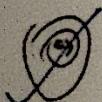
Entropy

→ state function / U → internal energy

A reversible ^{transfⁿ} ~~cycle~~ → $\Delta S = S(B) - S(A) = 0$

$\textcircled{A} \rightarrow \textcircled{B}$

Any irreversible transfⁿ → $\Delta S \geq 0$



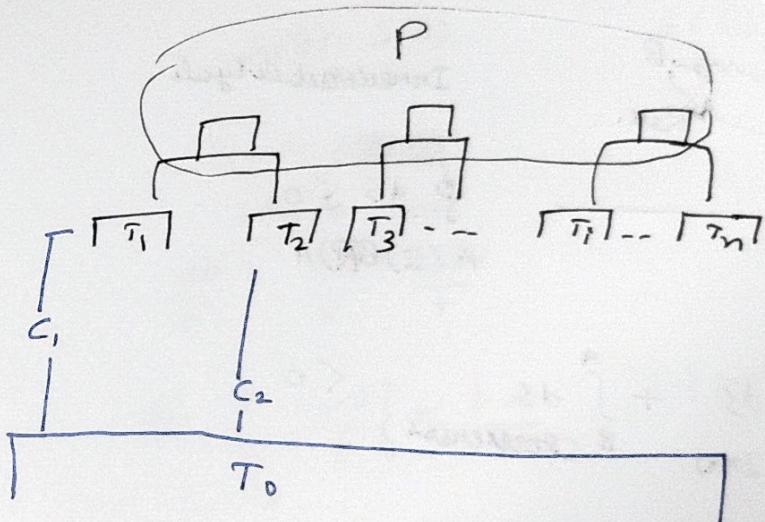
If entropy is a state fn (A → B) then may differ
for reversible & irreversible.

Entropy "f" in some sense defines Thermodynamic arrow of time.

$$\frac{d^2 x}{dt^2} = \frac{\text{force}}{m}$$

$$\rightarrow dS = \frac{d\theta}{T}$$

$$\rightarrow T_0 \text{ per unit } \sum \frac{\theta_{0i}}{T_i} \leq 0$$



\leftrightarrow wavy line

n heat sources

n Carnot / reversible & reversible cycle.

such a way that whatever heat is used by eng is supplied by Carnot.

θ_{0i} = heat taken by ith Carnot from source

$$\left\{ \frac{\theta_{0i}}{\theta_i} = \frac{T_0}{T_i} \right\}$$

$$\sum_{i=1}^n T_0 \frac{\theta_i}{T_i} \leq 0$$

Max. heat

\rightarrow Clapeyron Eqⁿ

$$T_0 \sum_{i=1}^n \frac{\theta_i}{T_i} \leq 0$$

for continuous source

\Leftrightarrow

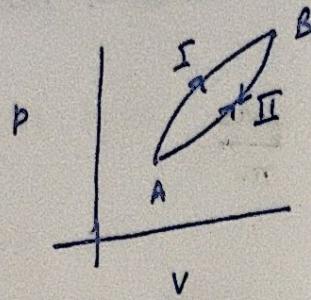
$$\oint \frac{d\alpha}{T} \leq 0$$

$$= \oint dS \leq 0$$

L-3 Only

L⁴

Reversible
Additive
Irrever./slow
State f"



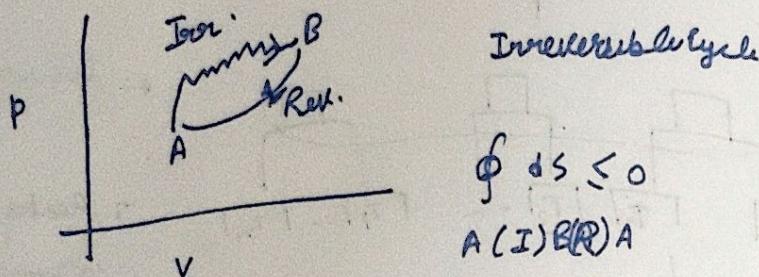
calculation

$S = \text{Sum of Microscopic properties of System}$

for reversible change

$$\Delta S = \int_A^B dS + \int_{B \text{ II}}^A dS = \int_A^B dS + \int_{A \text{ I}}^B dS = S(B) - S(A)$$

$$\oint dS = 0$$



$$\oint dS \leq 0$$

A (I) B (R) A

$$\int_A^B dS + \int_{B \text{ (reversible)}}^A dS \leq 0$$

$$\int_A^B dS \leq -S(A) + S(B)$$

A (rev)

If this system to be isolated

$$S(B) - S(A) > 0$$

$$S = S_1 + S_2$$

$$\frac{\partial S}{T} = \frac{\partial S_1}{T} + \frac{\partial S_2}{T} = \frac{\partial S}{T}$$

$$d\theta = dU + dW$$

$$dq_1 = dU_1 + dW_1$$

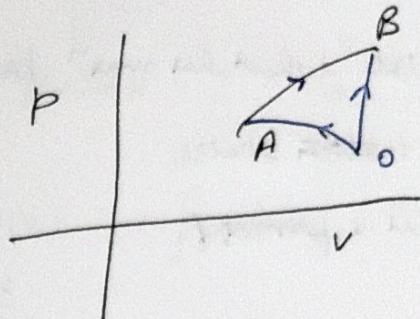
$$dq_2 = dU_2 + dW_2$$

gas

1.
liquid

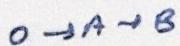
not add due entropy here

but generally its additive.



$$S(B) - S(A)$$

$$S(B) - \underbrace{S(0)}_{\text{def}}$$



$$\begin{aligned} & S(\overline{A}) - S(0) + S_B - S_A \\ & = \frac{S_B - S_0}{O \rightarrow B} \end{aligned}$$

$S(0)$

IDEAL Gas

v, T are indep⁷ variable

$$\frac{d\theta}{T} = \frac{du}{T} + \frac{pdv}{T}$$

$$\frac{d\theta}{T} = \frac{C_V dT}{T} + \frac{pdv}{T} \quad \left\{ \begin{matrix} pdv = RT \\ \end{matrix} \right\}$$

$$dS = \frac{d\theta}{T} = C_V \frac{dT}{T} + \frac{RT}{T} \frac{dv}{v}$$

$$dS = C_V \frac{dT}{T} + R \frac{dv}{v}$$

$$S = C_V \ln T + R \ln v + \alpha_{\text{int const.}}$$

$$S = C_V \ln T + R \ln \frac{RT}{P} + \alpha$$

$$S = C_V \ln T + R \ln T - R \ln P + R \ln R + \alpha$$

$$S = C_p \ln T - R \ln P + (R \ln R + \alpha)$$

$S \rightarrow$ Related to number of available microstates of the system.

Thermodynamic state $\rightarrow U, P, V$

"Microscopic present" \rightarrow

System will reach to a state which has max^m probability.

$\Omega \rightarrow$ no. of microscopic states

$$S = f(\Omega) \quad | \text{ derive a form of } f.$$

$$S = S_1 + S_2 = f(\Omega_1) + f(\Omega_2)$$

$$\begin{matrix} S_1 & S_2 \\ \Omega_1 & \Omega_2 \end{matrix}$$

$$f(\Omega) = f(\Omega_1, \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

$$\text{choose } \Omega_2 = (1 + \varepsilon) \cancel{\Omega_2}$$

$\varepsilon \rightarrow$ small quantity

$$f(\Omega_1, (1 + \varepsilon)) = f(\Omega_1) + f(1 + \varepsilon)$$

$$f(\Omega_1 + \varepsilon, \Omega_2) = f(\Omega_1) + f(\Omega_2 + \varepsilon)$$

Taylor's exp"

as at $\varepsilon = 0$, we get $f(1) =$

$$f(\Omega_1) + \varepsilon \Omega_1 \frac{df}{d\Omega_1} = f(\Omega_1) + f(1) + \varepsilon \frac{df}{d\Omega_1} \Big|_{\Omega_2=1}$$

$$\Omega \frac{df}{d\Omega} = k$$

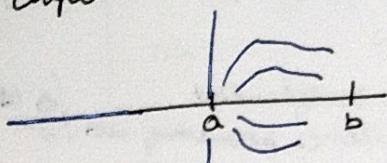
$$df = k \frac{d\Omega}{\Omega}$$

$$f = k \ln \Omega + c$$

$$S = k \ln \Omega$$

State f

Clapeyron's Eqⁿ / phase transition



$$\int_a^b g(x) dx = g(x) \Big|_a^b = g(b) - g(a)$$

$$f(x, y) \rightarrow \int_A^B df = \int \left| \frac{\partial f}{\partial x} \right|_y dx + \int \left| \frac{\partial f}{\partial y} \right|_x dy$$

perfect
differentiation

$$df \Big|_A^B = f(B) - f(A)$$

$$dz = M_x(x, y) dx + N_y(x, y) dy$$

$$\left\{ \begin{array}{l} N_y = \frac{\partial f}{\partial y}, \quad M_x = \frac{\partial f}{\partial x} \end{array} \right\}$$

$$\left\{ \begin{array}{l} \frac{\partial N_y}{\partial x} = \frac{\partial M_x}{\partial y} \end{array} \right\} \quad \text{perfect differential}$$

$$\left\{ \begin{array}{l} \frac{\partial}{\partial x} \frac{\partial}{\partial y} f = \frac{\partial}{\partial y} \frac{\partial}{\partial x} f \end{array} \right\}$$

~~df~~

$$d\theta = dU + pdV \quad | \text{ Ideal gas}$$

$$d\theta = C_V dT + \frac{RT}{V} dV$$

(T, V) are independent
 $pV = RT$

{ Not perfect differentials
Hence not state-fn } $\left(\frac{\partial U}{\partial V} \right)_T = \frac{p}{T}$

$$dS = \frac{d\theta}{T} = \frac{C_V dT}{T} + \frac{R}{V} dV$$

{ This becomes independent
of path hence possessing our entropy is state-fn } $\left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T}$

$$d\theta = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad | \text{ Not ideal gas}$$

$$+ pdV$$

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

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

~~Demand~~ Demand
the dS is
a perfect differential. $\left\{ \frac{\partial f}{\partial V \partial T} = \frac{\partial f}{\partial T \partial V} \right\}$

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

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

~~$\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T$~~ $- \frac{1}{T^2} p + \frac{1}{T} \left(\frac{\partial p}{\partial T} \right)_V$

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

V, T fixed \Rightarrow p_{var}

converted to Clapeyron's eqn

We can apply it to an ideal gas as it is general eqn for all types of gas.

$$\boxed{\frac{\partial U}{\partial V} = 0}$$

$$pV = RT$$

We will use Clapeyron eqn for phase transition of a lot of Van der Waals gas & the thermodynamic potential will be in next class. (minimum)

L-5

$$\boxed{T_1 S_1 \quad \leftarrow \frac{\Delta q}{T_1} \quad S_2 T_2}$$

$$T_2 > T_1$$

$$\Delta S = \frac{\Delta q}{T_1} + \left(-\frac{\Delta q}{T_2} \right) > 0$$

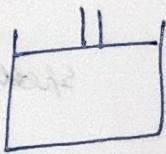
$$\boxed{\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P}$$

"causes - clapeyron eq"

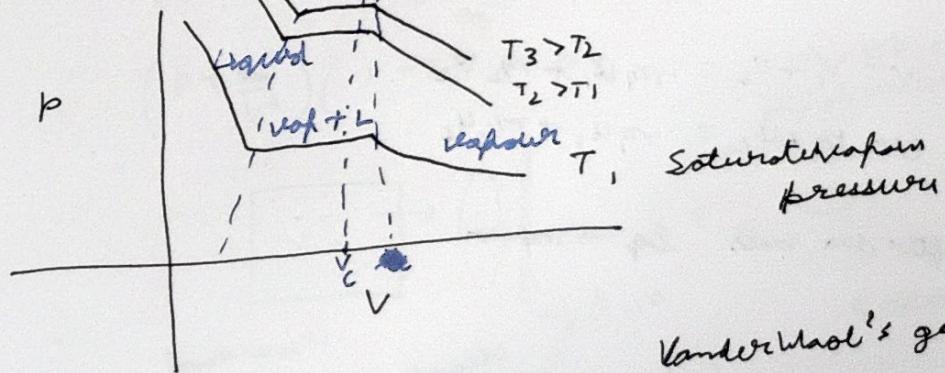
Creates

liquids \leftrightarrow vapours
phase transition

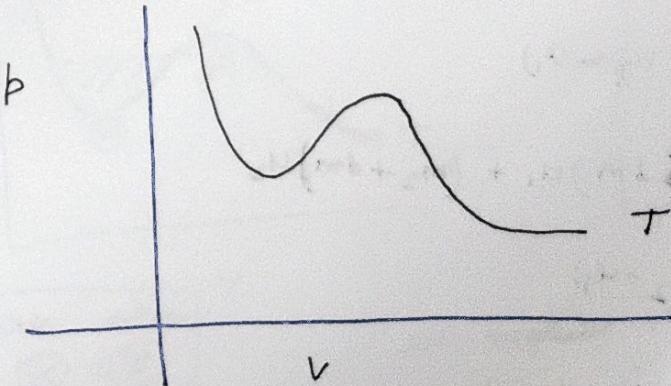
Experimental

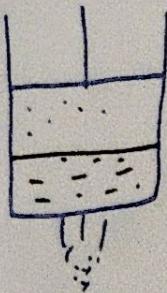


point of inflection
critical isotherm $| T_c$



Vanderwaal's graph





$$m_{\text{total mass}} = \frac{dm}{dq + v_{\text{ref}}} + m_2^{\text{ref.}}$$

$$v = v_1 + v_2$$

↓ ↓
liq vapour

Specific volume v_1 Volume / mass (liq.)

$\cdots \cdots \cdots$ v_2 Volume / mass (vap.)

Specific energy u_1 Energy / mass (liq.)

u_2 (ref)

dm mass of liq. \rightarrow vapour

$$v = v_1 + v_2 = m_1 v_1 + m_2 v_2$$

$$u = u_1 + u_2 = m_1 u_1 + m_2 u_2$$

after dm mass liq. \rightarrow vapour

$$v + dv = (m_1 - dm)v_1 + (m_2 + dm)v_2$$

$$\delta v = dm(v_2 - v_1)$$

$$u + du = (m_1 - dm)u_1 + (m_2 + dm)u_2$$

$$\delta u = dm(u_2 - u_1)$$

$$\delta \theta = \delta u + p \delta v$$

$$\delta \theta = (u_2 - u_1)dm + p(v_2 - v_1)dm$$

$$\frac{\delta \theta}{dm} = u_2 - u_1 + p(v_2 - v_1) = \lambda \text{ (latent heat)}$$

we can now use Clausius eqn

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

$$\frac{\partial U}{\partial V} \Big|_T = \frac{\partial U}{\partial V} \Big|_T = \frac{U_2 - U_1}{V_2 - V_1}$$

$$\boxed{\frac{\partial P}{\partial T} \Big|_V = \frac{\lambda}{T(V_2 - V_1)}}$$

at const V so $\lambda = U_2 - U_1$
only.

now we get eqn for ideal gas eqn from our expression.
we can do it using Van der Waal's state.

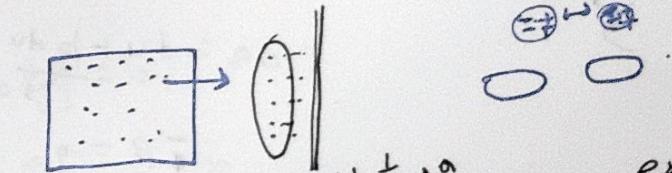
Van Der Waal's eqn of State

$$PV = RT \text{ empirical eqn}$$

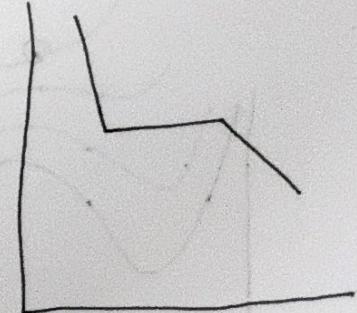
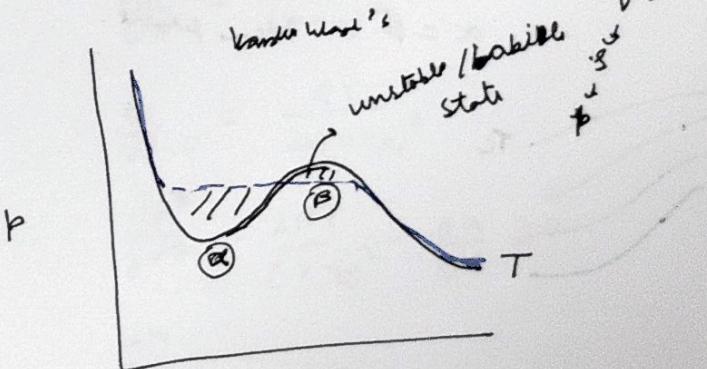
$b \rightarrow$ fixed volume of mol.

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

, $a, b > 0$
Dipolar interaction



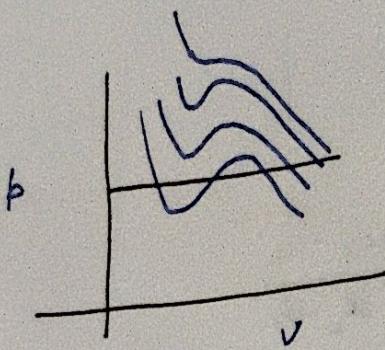
experimental



$$\boxed{\text{area } A = \text{area } B}$$

we neglected V^2 approx as it will be a higher order approx hence neglected.

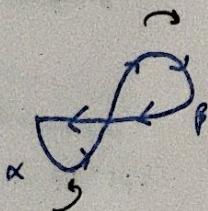
$$\frac{a}{(V-b)^2} = \frac{a}{V^2 + b^2 - 2Vb} = a \left(1 + \frac{2b}{V} + \frac{b^2}{V^2} \right)$$



a, b which real gas (they deviate on gas).

$$\oint \frac{dq}{T} \leq 0 \quad (\text{isov})$$

$$\oint \frac{dq}{T} = 0 \quad (\text{isothermal})$$



$$\frac{1}{T} \int dq = 0$$

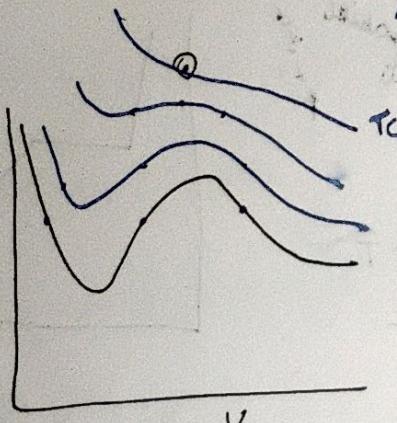
$T = \text{constant}$

$$\left\{ \begin{array}{l} dq = 0 \\ du = 0 \end{array} \right. \quad (T = \text{const})$$

$$dq = du + \underbrace{pdv}_{\neq 0}$$

$$\alpha \neq \beta = 0$$

$\alpha = \beta$ Hence proved.



$$(pv^2 + a)(v - b) = RTv^2$$

$$pv^3 + v^2(-pb + RT) + va - ab = 0$$

$$pv^3 - v^2(pb + RT) + va - ab = 0$$

$$\rightarrow T_c \quad v_c \quad p_c$$

$$p_c(v - v_c)^3 = 0$$

$$v_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8}{27} \frac{a}{Rb}$$

$$P = \frac{RT}{v^2 - b} - \frac{a}{v^2}$$

$$\frac{\partial P}{\partial v} = 0$$

$$-\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2}$$

$$\frac{a}{v^3} \cdot v = \frac{RT}{2v(v-b)^2}$$

$$\frac{\partial^2 P}{\partial v^2} = \frac{2RT}{(v-b)^2} - \frac{6a}{v^4} = 0$$

$$\frac{RT}{(v-b)^3} = \frac{3RT}{2v(v-b)^2}$$

$$v_c = 3b$$

using v_c we get

$$T_c = \frac{8a}{27b^3}$$

L-7

Vander Waal's eq"

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT$$

$$\text{Reduced Variables} \Rightarrow p_{\text{r}} = \frac{p}{p_c}$$

$$v_R = \frac{V}{V_c}$$

p_{r} → reduced
we are measuring
in terms of x_c .

$$\left(p_{\text{r}} + \frac{3}{V_{\text{r}}^2} \right) \left(V_{\text{r}} - \frac{1}{3} \right) = \frac{8}{3} T_{\text{r}}$$

Law of corresponding state

Gas 1

$$T_{\text{r}_1} = \frac{T_1}{T_{\text{C}_1}}$$

Gas 2

$$T_{\text{r}_2} = \frac{T_2}{T_{\text{C}_2}}$$

$$\text{if } T_{\text{r}_1} = T_{\text{r}_2}$$

⇒ They will behave in a similar way
they are called in corresponding states.

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2} \quad \text{--- (B)}$$

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

$$\left. \frac{\partial P}{\partial T} \right|_V = \frac{R}{v-b}$$

$$\left. \frac{\partial U}{\partial V} \right|_T = \frac{TR}{(v-b)} - \left(\frac{RT}{v-b} - \frac{a}{v^2} \right)$$

$$= - \frac{a}{v^2}$$

$$U = \int \frac{a dv}{v^2} = -\frac{a}{v} + f(T)$$

$$\left\{ \begin{array}{l} \left(\frac{\partial U}{\partial T} \right)_V = C_V = \frac{df}{dt} \\ \rightarrow f = C_V t + C \end{array} \right\}$$

$$\boxed{U = -\frac{a}{v} + C_V t + \text{const.}} \quad \text{--- (C)}$$

PE
due to interparticle ~~attraction~~ interaction

$$d\theta = dU + Pdv$$

$$ds = \left. \frac{d\theta}{T} \right|_V \rightarrow ds = \frac{dU}{T} + \frac{P dv}{T}$$

$$\text{using (C) \& (B). } dU = \frac{a}{v^2} dv + C_V dT$$

$$ds = C_V dT + R \ln(v-b)$$

$$\frac{C_p}{C_v}$$

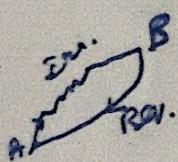
$pV = \text{constant}$

$$\delta Q = 0, \delta S = 0$$

$$T(V-B)\frac{R}{C_V} = \text{constant.}$$

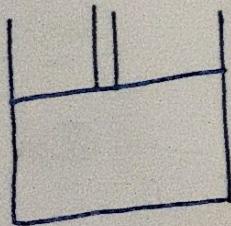
FREE ENERGY:

$$F = U - TS$$



$$\int_A^B \frac{\delta Q_r}{T} \leq S(B) - S(A)$$

System that is at fixed Temp T.



$$\int_A^B \delta Q_r \leq TS(B) - TS(A)$$

$$\delta Q_r = \delta U + \delta W$$

$$\delta W = \delta Q_r - \delta U$$

$$\leq TS(B) - TS(A) - (U(B) - U(A))$$

$$\delta W \leq (U(A) - TS(A)) - (U(B) - TS(B))$$

$$\delta W \leq F(A) - F(B)$$

$$\delta W \leq -\delta F$$

$$\delta w \leq -\delta F \Rightarrow \delta w \leq F(A) - F(B)$$

Mechanical system
 \downarrow
~~W~~

$$\delta q = \delta U + \delta w$$

$$0 = \Theta$$

$$\delta w = -\delta U$$

Free energy will always decrease.

$$F(B) \leq F(A)$$

$U \rightarrow$ mechanical system

$F \rightarrow$ Thermodynamic system

$$\begin{array}{ccc} \text{mech} & & \text{Thermodynamic} \\ \text{energy} \rightarrow U & & F \\ \text{ext. "} \rightarrow \text{int. " potential} & & \text{A system is at its min free energy.} \\ \text{energy.} & & \end{array}$$

$$\delta q = \delta U + PdV$$

$$\delta S = \frac{\delta U}{T} + \frac{PdV}{T}$$

$$\delta U = T \delta S - PdV$$

$$\delta w \leq \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V \right) = \frac{\partial T}{\partial V} \Big|_S \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_T = \left. \frac{\partial P}{\partial S} \right|_V$$

Maxwell Rel's

$$\delta w \leq \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V = \left(\frac{\partial T}{\partial V} \right)_S$$

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_T = - \left(\frac{\partial P}{\partial S} \right)_V \quad \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$H \text{ (enthalpy)} = U + PV$$

$$F = U - TS \text{ (Helmholtz free energy)}$$

Gibbs free energy

$$G(T, P, N) = U - TS + PV$$

$$G = H - TS$$

$$\text{Grand potential } \Omega = U - TS + \mu N$$

μ = chemical potential

0th law $A \leftrightarrow B ; B \leftrightarrow C \Rightarrow A \leftrightarrow C$

1st law

2nd law

3rd law (Nernst's law)

$$\boxed{S(T=0) = 0}$$

$$S(A) = \int_{0\text{K}}^A dS = \int_{T=0}^T \frac{dQ}{T}$$