1. TEMPERATURE & 0th LAW OF THERMODYNAMICS

§ Macroscopic POV

the study of any branch of natural science starts with the following definitions

Def. (System)

Region of space or finite portion of matter by means of a closed surface called **boundary**

the region WITHIN is the **system**.

Everything outside that has a **DIRECT bearing** on the system is known as the **SURROUNDINGS** which can be another system.

If **NO** matter crosses the boundary the system is **CLOSED** or open if viceversa

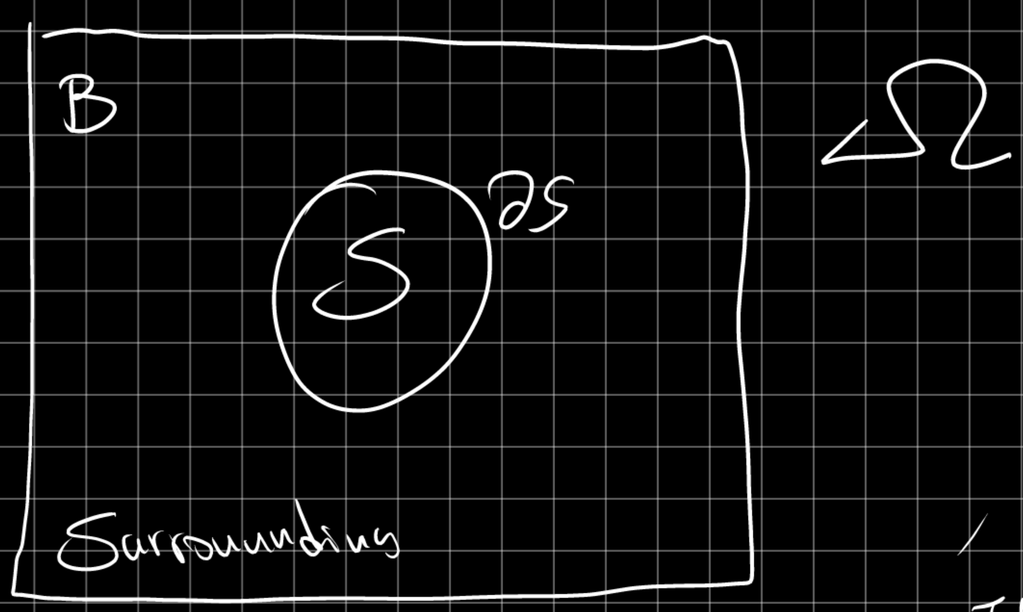


Fig 1: a system.

$\Omega \rightarrow$ universe

$S \rightarrow$ system ; $B \rightarrow$ surrounding $\left\{ \begin{array}{l} \text{system} \\ \text{something interacting} \end{array} \right.$

$\partial S \rightarrow$ boundary

If matter passes through $\partial S \rightarrow S$ is OPEN

If NO matter passes through $\partial S \rightarrow S$ is CLOSED

After choosing a system we need to describe it using quantities related to the behavior or interaction of the system w/ the surroundings.

There are two general POVs that can be chosen:

1- Microscopic $\rightarrow$ characteristics @ molecular or smaller level ($\leq 100 \text{ Å}$)

2- Macroscopic $\rightarrow$ human scale or larger ($\geq 1 \text{ cm} / 1 \text{ mm}$)

Take as an example the contents in a cylinder chamber of an automobile: a chemical analysis would find the following behavior

$$\text{hydrocarbons} + \text{air} \longrightarrow \text{combustion products}$$

A statement on the amount of these chemicals describes both $\left\{ \begin{array}{l} \text{mass} \\ \text{composition} \end{array} \right.$

A further description can be given by indicating the volume of the chamber (also via measuring). Another quantity is pressure of gases in the chamber. After ignition the pressure becomes large, smell after expulsion. In lab a gauge can be used to measure & record changes. Another quantity is Temperature

These are **Macroscopic coordinates**

Def (Macroscopic coordinates)

Coordinates which

- Involve no assumption within structure, fields / radiation
- Few in number
- fundamental
- can be (in general) be directly measure

Def (Thermodynamics)

Branch of physics which deals w/ macroscopic properties & ALWAYS includes Temperature

§ Microscopic POV

A microscopic system is a number N of particles w/ energy states ϵ_i, particles interacts via collision & / fields.

Systems can be considered isolated / embedded in similar systems aka ensemble systems

Equilibrium $\rightarrow$ state w/ highest probability. The problem to solve is finding # particles in each energy state (population of states) @ equilibrium

Def (Microscopic coordinates)

- Consider structure of matter, fields & / radiation
- Many quantities needed
- Described by mathematical models
- Must be calculated

§ 0th LAW OF THERMODYNAMICS

Law (Boyle)

Pressure & volume are independent but related

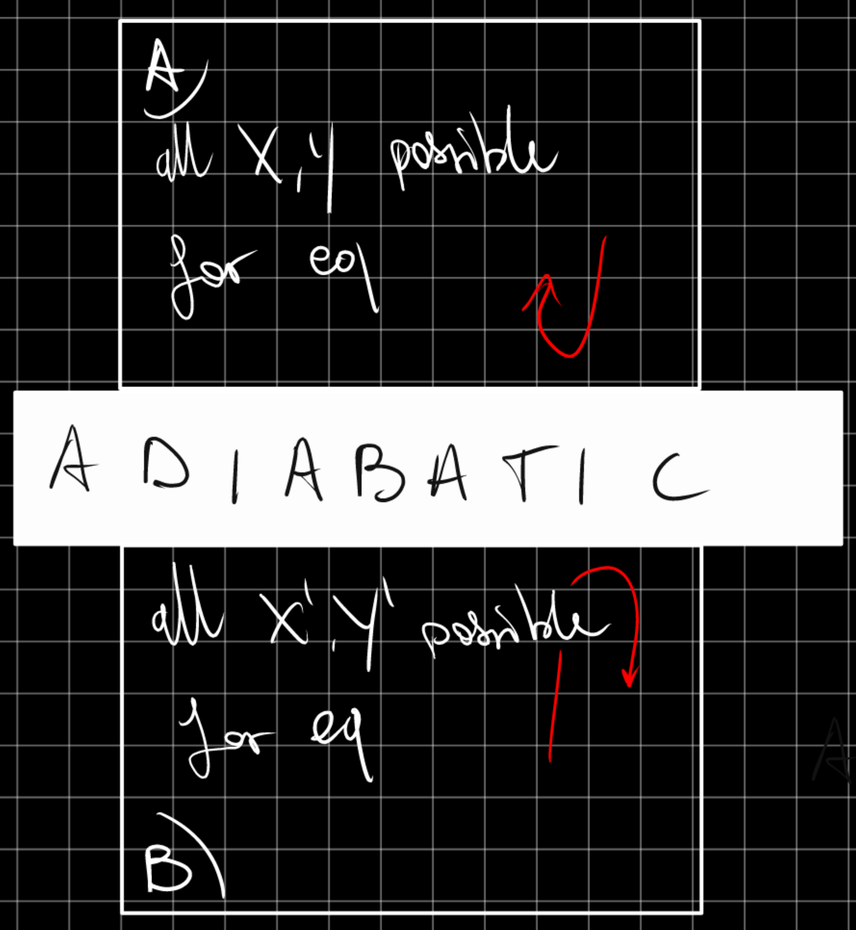
$$P \propto V^{-1}$$

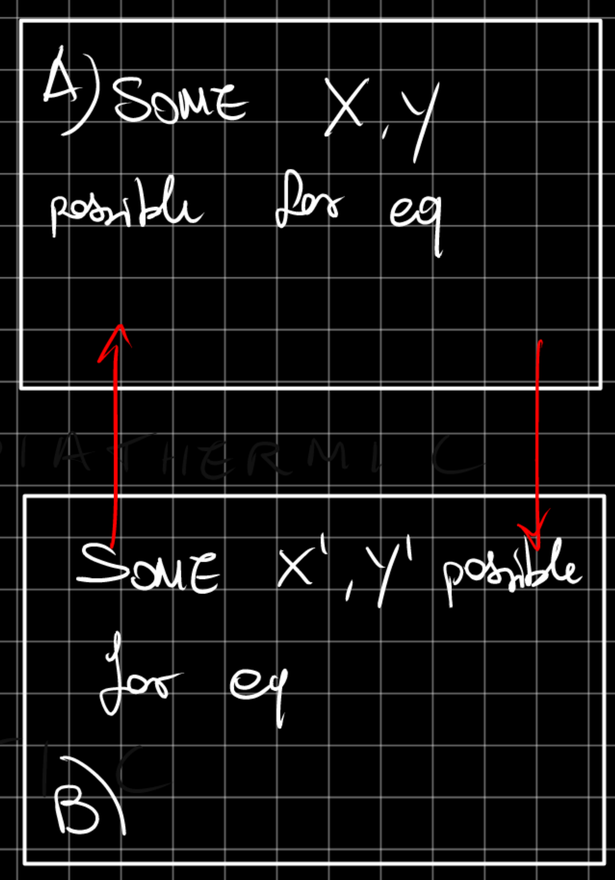
Said A a system w/ independent coordinates (X, Y), where $\begin{cases} X \rightarrow \text{gen force (pressure)} \\ Y \rightarrow \text{gen displacement (Volume)} \end{cases}$

A state for which (X, Y) are constant as long as the external conditions do not change is known as equilibrium state

Existence of equilibrium depends on proximity of system & nature of boundary. In general a boundary (wall) can be: {ideal} {A, B; system}

- adiabatic $\rightarrow$ Equilibrium of A & B independent $\forall (X, Y) \in A$; $(X', Y') \in B$
- diathermic $\rightarrow$ Equilibrium of A depends on B & vice versa; i.e. $|EQ\rangle = (X, Y, X', Y')$





a) A, B separated by ad wall

b) A, B separated by dt wall

In case b, the systems, when @ equilibrium, are said to be in thermal equilibrium

Def (Thermal equilibrium)

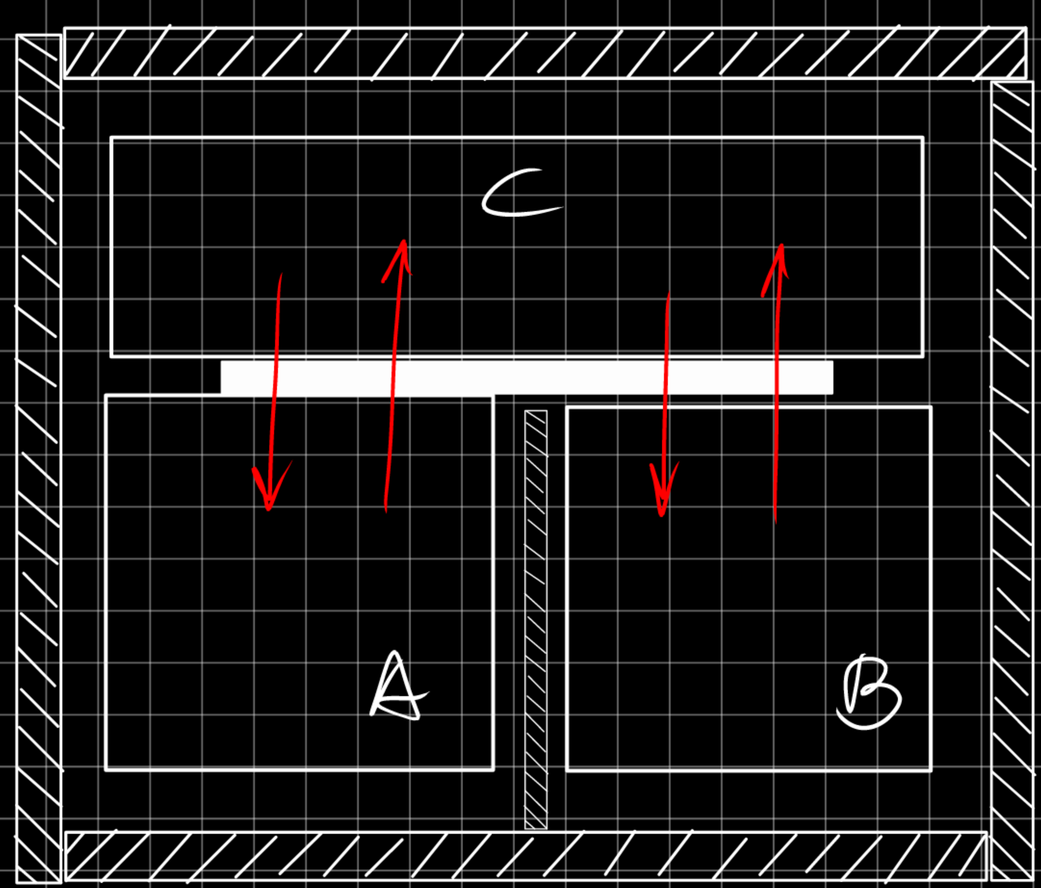
Thermal equilibrium is the state achieved by two or more systems characterized by restricted values of sys coordinates after they've been in contact through a dt wall.

N.B. an ad wall prevents the 2 system from communicating.

LAW (0th thermal law)

Suppose that two systems A, B are separated by an ad wall & in contact SIMULTANEOUSLY w/ C through a dt wall. Then:

$$\begin{cases} A \longleftrightarrow C \\ B \longleftrightarrow C \end{cases} \Longrightarrow A \longleftrightarrow B$$



$A \longleftrightarrow C$

$B \longleftrightarrow C$

$\therefore A \longleftrightarrow B$

Two systems in thermal equilibrium with a third one in thermal equilibrium w/ eachother

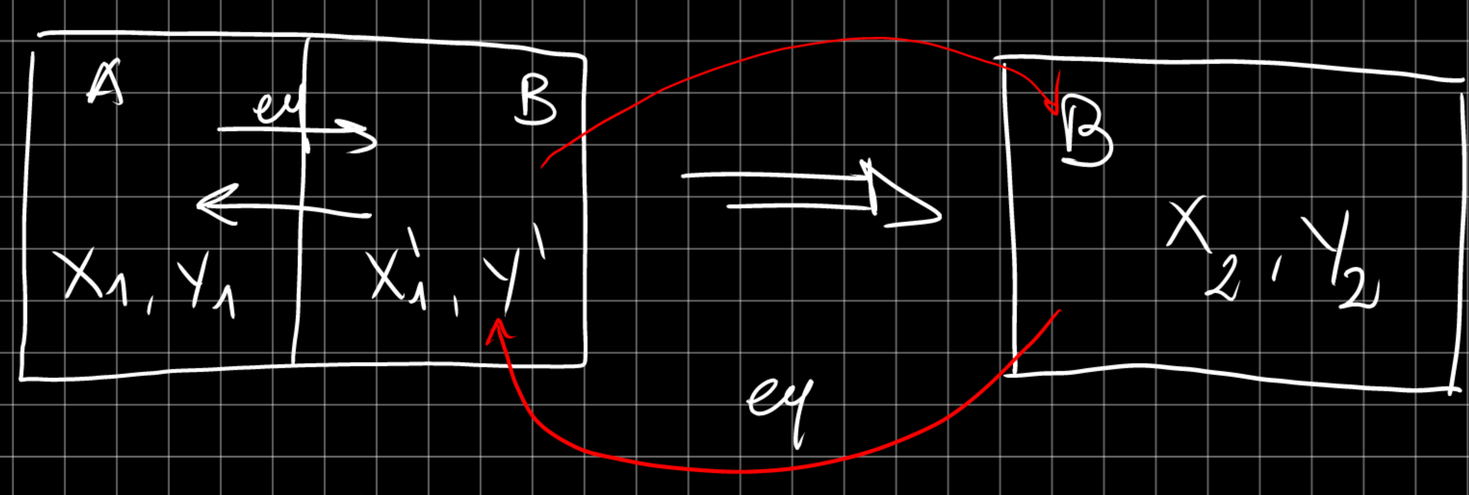
§ TEMPERATURE

Temperature, in common use, is the measure of "hotness" of something as felt. Microscopically it's tied to agitation, vibration or motion of atoms or molecules (KE). Note that something is always "hot" or "cold" wrt something else, therefore, due to this relativistic nature of this definition, define temperature as the

"degree of hotness above absolute zero"

A SCIENTIFIC understanding comes from the concept of thermal equilibrium. Let A be some system defined by ind. vars. (X_1, Y_1) & B by (X_1', Y_1') s.t. $A \leftrightarrow B$. Removed A, we have that

$$(X_1', Y_1') \leftrightarrow (X_2, Y_2)$$



It's shown that ∃ a set of states (X_i, Y_i) in equilibrium w/ (X_1', Y_1') of B, which must all be in thermal equilibrium (0th law)
Plotted the states in an (X, Y) plane lie in a curve known as Isotherm

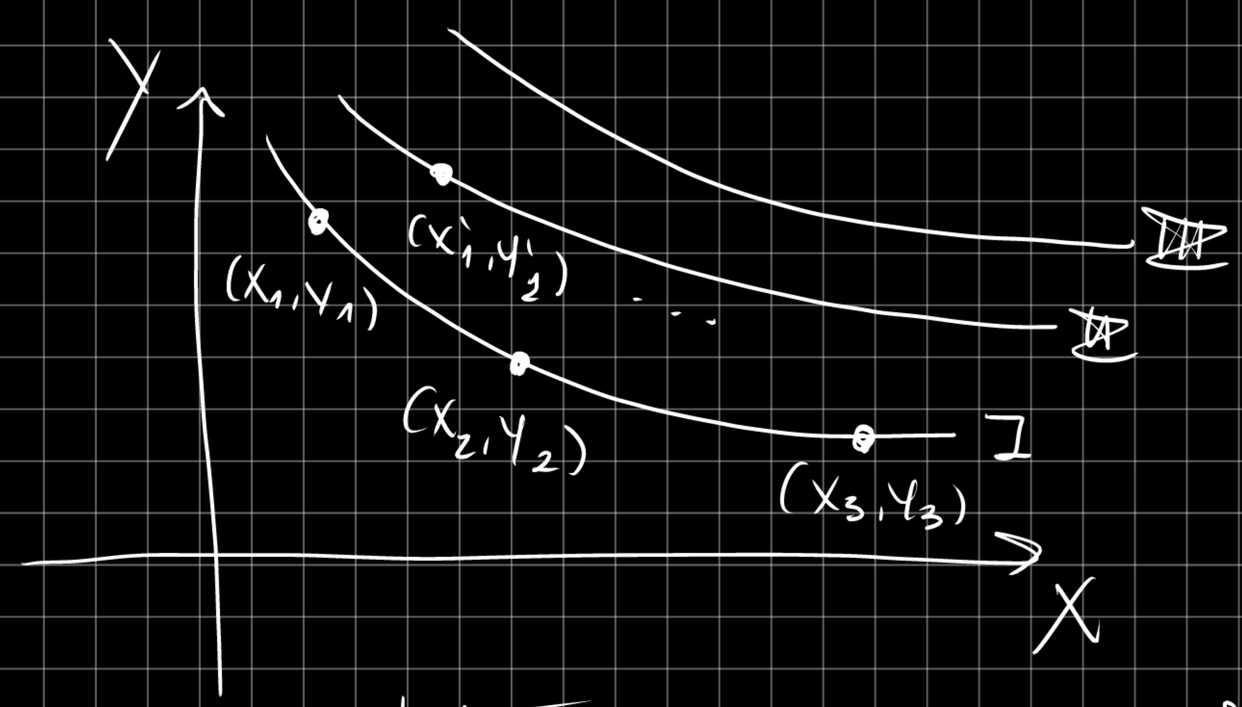


Fig 2.) Representation of isotherm curves {I, II, III} in plane (X, Y)

N.B.: it's assumed that AT LEAST a portion of the isotherm is continuous.
Doing the same analysis on A by removing B we find isotherms I', II', III' in an (X', Y') plane.
By definition, then, $I \leftrightarrow I'$, $II \leftrightarrow II'$, $III \leftrightarrow III'$, aka corresponding isotherms

We define the TEMPERATURE as the property in common b/w states in thermal

equilibrium.

Temperature MUST be scalar → defined by a number. For each value T corresponds a set of isotherms I_T.

Therefore the N & S condition for thermal equilibrium b/w two systems is that $T_A = T_B$, where T_A, T_B are the temperatures of the two systems

§§ Thermometers & temperature measurement

In order to define an empirical scale for temperature, we study a system with coordinates (X, Y), a thermometer, & adopt a set of rules for assigning a Θ for each isotherm. The test procedure

→ Take a convenient path in (X, Y) (i.e. $Y = Y_1$) ∴ $\Theta \equiv \Theta(X)$

•) $\Theta(X)$, thermometric function; X thermometric property.

- Arbitrarily we choose $\Theta(X) \propto X$

$$\rightarrow \Theta_A(X) = aX, \quad a \in \mathbb{R}$$

Θ_A → ABSOLUTE SCALE ($\Theta_A = 0 \Rightarrow X = 0$) e.g. { Kelvin, Rankine

STANDARD GAS FOR THERMOMETRIC EVAL → H_2

By definition the fixed point Y_1 for defining a thermometric scale is the TRIPLE POINT of H_2O ($T = 273.16\,K = 0.01\,°C$); thus

$$\Theta_A(X_{TP}) = a X_{TP}$$

$$\rightarrow a = \frac{273.16\,K}{X_{TP}}$$

gen:

$$\Theta_A(X) = 273.16 \frac{X}{X_{TP}}$$

THUS!:

$$\Theta(P) = 273.16\,K \frac{P}{P_{TP}} \quad (\text{const. } V)$$

$$\Theta(V) = 273.16\,K \frac{V}{V_{TP}} \quad (\text{const. } P)$$

{ same goes for R_{el}, emf

NOTATION:

TP: Triple Point (Gas + Liquid + Solid)

NSP: Normal Sublimation Point (Solid → Gas)

NMP: Normal Melting Point (Solid → Liquid)

§ TEMPERATURE SCALES FOR IDEAL GASES

LAW (Ideal Gases)

$$pV = nRT$$

$\begin{cases} p \to \text{pressure} \\ V \to \text{volume} \\ T \to \text{Temperature} \end{cases}$ $\begin{cases} n \to \text{mol} \\ R \to \text{molar gas const.} \end{cases}$

Note, @ const V θ (absolute temp)

$$\theta(P) = 273.15 \frac{P}{P_{TP}} \text{ K}$$

by def, for ideal gases THERE IS NO TRIPLE POINT. Thus

$$T = 273.15 \lim_{P_{TP} \to 0} \left(\frac{P}{P_{TP}} \right) \text{K} \quad \text{(stupid def.)}$$

§ Celsius, Rankine, Fahrenheit scales

- Celsius [Anders Celsius (SWE)]

$$T(°C) = T(K) - 273.15 \quad (\text{defined at NMP } H_2O \ \{273.15 \text{ K}\})$$

- Rankine [Willium Rankine (UK)]

$$T(R) = \frac{9}{5} T(K)$$

- Fahrenheit [Daniel G. Fahrenheit (PL/DEU)]

$$T(°F) = T(R) - 459.67$$

Thus: $\begin{cases} T(°F) = \frac{9}{5} T(K) - 459.67 \\ T(°F) = \frac{9}{5}\left(T(°C) + 273.15\right) - 459.67 \end{cases}$ $\left[T(R) = \frac{9}{5}\left(T(°C) + 273.15\right) \right.$

Also: $T(°F) = \frac{9}{5} T(°C) + 32$

Or: $T(°F) = 1.8\, T(°C) + 32$

[Simple Systems]

§ Thermodynamic equilibrium

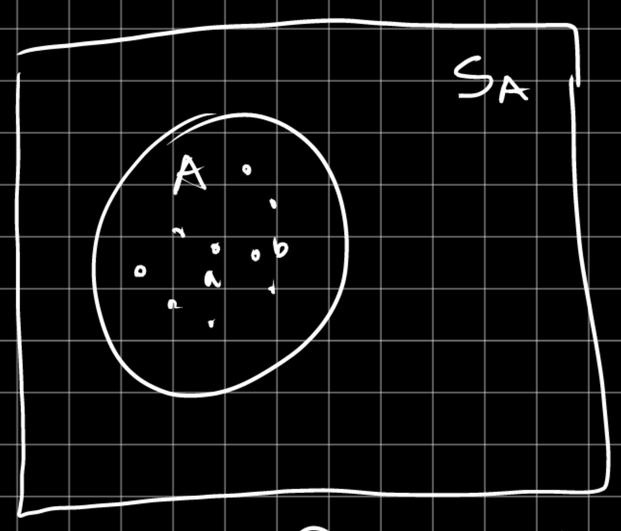
Def (Change of state)

Take a system A for which macroscopic coordinates have been chosen. When the coordinates change in any way the system undergoes a <<change of state>>.

When the system is not influenced, it's said to be <<isolated>> (not important in thermodynamics)

Examples of equilibrium:

- Mechanical equilibrium → balanced forces
- Chemical equilibrium → no spontaneous chemical reactions + Mechanical equilibrium
- Thermal equilibrium → Chemical + Mechanical eq + no change of coords when separated from surroundings w/ $\underline{dt}$ wall
- Thermodynamical equilibrium → Mech + Chem + Thermal equilibrium



$\underline{F}_{N_A} = \sum_{i=1}^{N} \underline{f}_{i_A} = 0 \Rightarrow$ Mechanical equilibrium (1)

$a \rightleftarrows b$ or $a \rightleftarrows a \Rightarrow$ chemical eq (2)

iff ∂A $\underline{dt} \Rightarrow$ iff (1) + (2) & no change $\Rightarrow$ Thermal (3)

(1) + (2) + (3) $\Rightarrow$ Thermodynamical equilibrium (4)

In (4) no change of state for A or S_A. Describable by macro coords s.t. $\frac{dq^i}{dt} = 0$

If (1) ✗ $\Rightarrow$ NONEQUILIBRIUM STATE $\Rightarrow$ NOT DESCRIBABLE W/ THERMODYNAMICS

{ Accelerations $\Rightarrow P_A(x_1) \neq P_A(x_2)$ & $T_A(x_1) \neq T_A(x_2) \Rightarrow \nexists\, T_A, P_A$

Def (Equation of state)

Consider some mass m of gas in a vessel s.t. $\frac{dm}{dt} = 0$, if we fix V and θ, then p can't be chosen, if V, θ are fixed $\Rightarrow$ p is natural; p, θ chosen $\Rightarrow$ V natural.

Therefore, given (p, V, θ) ONLY 2 ARE INDEPENDENT

$\therefore \exists f(p, V, \theta) = 0$ at equilibrium that defines one of the 3 as a parameter

$f(p, V, \theta) = 0$ is known as equation of state (empirical, not necessarily unique)

EOS valid only in thermal equilibrium.

Def (hydrostatic system) system w/ uniform pressure, const. mass m, in absence of surf, grav, $\underline{E}$, $\underline{H}$ effects

Categorization:

- pure substance : single chemical constituent
- homogeneous mixture: two or more chem. constituents (uniform)
- heterogeneous mixture: two or more chem constituent (active)

Hydrostatic systems at equilibrium can be described by (p, V, θ)

$[p] = N/m^2 = kg/ms^2 = Pa = lb/in^2 = atm = mmHg = inHg$

$[V] = m^3$

$[T] = [\theta] = K$

§ PURE SUBSTANCES, pV DIAGRAM

Consider H_2O @ $T = 94°C$ in a vessel w/ $V \simeq 2\,m^3$ with no air water will evaporate completely $\Rightarrow$ system in unsaturated vapor. If it's compressed slowly $\Rightarrow$ p rises $\Rightarrow$ saturated vapor (steel graph pg 29 fig 2-1)

In fig 2-1 there's a pV-diagram for this process.

A starting point, A $\rightarrow$ B compression, saturated vapor at B. Continue compressing: $H_2O_{(g)}$ is compressible $\rightarrow P_B = P_C$ & @ C $H_2O_{(g)} \rightarrow H_2O_{(l)}$ (saturated liquid)

A $\rightarrow$ unsaturated mix, B $\rightarrow$ 100% saturated gas, C $\rightarrow$ 100% saturated liquid.

N.B. $T_A = T_B = T_C = T_D$! When D is reached after continuous compression ($H_2O_{(l)}$ incompressible) therefore

$P_A < \underbrace{P_B = P_C}_{\text{vapor pressure}} << P_D$. Note that

BW/ A & B vapor phase

BW/ B & C vapor & liquid in equilibrium

BW/ C & D liquid phase

The line ABCD is a typical isotherm for a pure substance in a pV diagram

It's notable that the liquid-vapor isotherms get smaller w/ increasing pressure p until they reach a CRITICAL POINT @ T_C (triple point)

for $T > T_C$ we have gas phase (no distinction b/w liquid & vapour)

for $T = T_C$ (critical isotherm). At the critical point we have the critical state

$$(P_C, V_C, T_C)$$

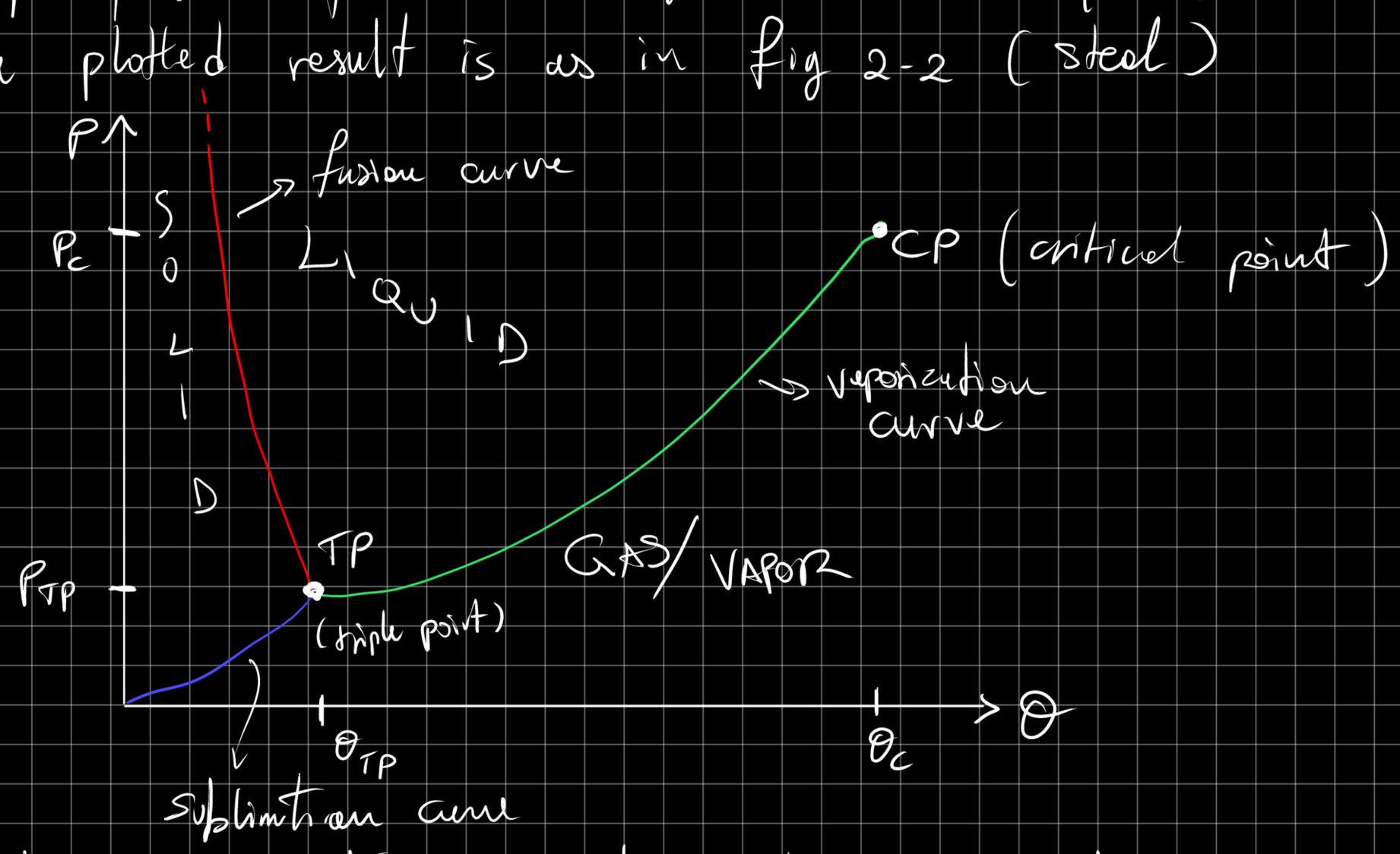
Saturated liquid & gas phases lay on their respective lines. These intersect @ the critical point

§ pT (pθ) diagram

$\theta \rightarrow$ ideal gas temp

$T \rightarrow$ Kelvin temp

Measuring the vapor pressure of a solid until the TC & the same for a liquid, the plotted result is as in fig 2-2 (steel)



The fusion, sublimation & vaporization curves define all states for which (resp):

1) solid - liquid equilibrium (steam line - H_2O)
2) solid - vapor equilibrium (frost line - H_2O)
3) liquid - vapor equilibrium (ice line - H_2O)

The slopes of the sublimation & vaporization lines are always >0. ⊛

Note that the triple point (TP) is represented by a point <u>only</u> in pθ diagrams.

§ PVθ - SURFACE

Representation of the informations obtained on (p, V, θ) measurements. (steel fig 2-3, 4, 5)
fig 2-5 shows the pVθ surface for water, including 7 triple points (19 known)

⊛ for the fusion line slope $\gtrless 0$. Depends if V increases ($s/>0$) or decreases ($s/<0$) upon melting, see H_2O.

§ EQUATIONS OF STATE

IT'S IMPOSSIBLE TO DESCRIBE THE BEHAVIOR OF A SUBSTANCE OVER THE $pV\Theta$ SURFACE!

There are various equations of state:

1) Low p, gas

$$p\nu = R\Theta \quad \text{(IDEAL GAS)}$$

a) $\nu = \frac{V}{n}$ (molar volume), $n \rightarrow$ moles of gas

b) $R \rightarrow$ gas constant

2) $(p, V, \Theta) \dot{>} (p, V, \Theta)_{T_r}$, adjustable

$$\begin{cases} p\nu = \frac{1}{\nu} R\Theta (1-\epsilon)(\nu + B) - \frac{A}{\nu} \quad \text{(BEATTIE-BRIDGEMAN)} \\ A = A_0\left(1 - \frac{a}{\nu}\right) \\ B = B_0\left(1 - \frac{b}{\nu}\right) \\ \epsilon = \frac{c}{\nu \Theta^3} \end{cases}$$

3) Empirical

4) From kinetic theory & / stat mech

$$\left(p + \frac{a}{\nu}\right)(\nu - b) = R\Theta \quad \text{(VAN DER WAALS)}$$

N.B.

$R \rightarrow$ "universal gas constant"

§ DIFFERENTIAL CHANGES OF STATE

IN THERMODYNAMICS

Said dV, dp the differential forms of Volume & pressure their differentials are defined as such:

1) given a Volume V, $dV << V$, but dV is big enough to be macroscopic

2) given a pressure p, molecular perturbations δp, then

$$\delta p \ll dp \ll p$$

I.e. $\begin{cases} \left|\frac{dp}{p}\right| \ll 1 \\ \left|\frac{dp}{\delta p}\right| \ll 1 \end{cases}$

In this regime p, V can be considered mathematically continuous, & for what we said

$$\begin{cases} V \equiv V(p, \theta) \\ p \equiv p(V, \theta) \end{cases} \qquad \theta \equiv \theta(p, V)$$

therefore

$$\begin{cases} dV = \frac{\partial V}{\partial p} dp + \frac{\partial V}{\partial \theta} d\theta \\ dp = \frac{\partial p}{\partial V} dV + \frac{\partial p}{\partial \theta} d\theta \end{cases} \qquad d\theta = \frac{\partial \theta}{\partial p} dp + \frac{\partial \theta}{\partial V} dV$$

DEFINED

1) $\beta \rightarrow$ volume expansivity (average)

$$\beta = \frac{1}{V}\frac{\partial V}{\partial \theta} = \frac{\partial}{\partial \theta} \log V \quad [K^{-1}]$$

2) $\kappa \rightarrow$ isothermal compressibility

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = -\frac{\partial}{\partial p} \log V = \frac{\partial}{\partial p} \log\left(\frac{1}{V}\right) \quad [Pa^{-1}]$$

Then:

$$dV = -V\kappa\, dp + V\beta\, d\theta$$

$$d \log V = -\kappa\, dp + \beta\, d\theta \quad (\text{ex. } 2.6b)$$

(*) $1\ bar = 10^5\ Pa$

§ DINI THEOREM (IMPLICIT FUNCTION)

Suppose $f(x,y,z)$ is a function such that, for a given point (x,y,z)

1) $f(x,y,z)=0$

2) $\nabla f \neq 0$

Then: $f(x,y,z) = f\big(x(y,z), y(x,z), z(x,y)\big) \quad \forall (x,y,z) \in B_\epsilon((x,y,z))$

&

$$dx = \frac{\partial x}{\partial y}dy + \frac{\partial x}{\partial z}dz \;\text{ (a)}, \quad dy = \frac{\partial y}{\partial x}dx + \frac{\partial y}{\partial z}dz \;\text{ (b)}, \quad dz = \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy$$

Taken (a), (b), then

$$\begin{cases} dx = \partial_y x\, dy + \partial_z x\, dz \\ dy = \partial_x y\, dx + \partial_z y\, dz \end{cases} \Rightarrow dx = \frac{\partial x}{\partial y}\left(\frac{\partial y}{\partial x}dx + \frac{\partial y}{\partial z}dz\right) + \frac{\partial x}{\partial z}dz$$

$$\therefore \left(\frac{\partial x}{\partial y}\frac{\partial y}{\partial x} - 1\right)dx + \left(\frac{\partial x}{\partial z} + \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\right)dz = 0$$

(1) $dz=0 \Rightarrow \frac{\partial x}{\partial y}\frac{\partial y}{\partial x} = 1$

$$\therefore \frac{\partial x}{\partial y} = \left(\frac{\partial y}{\partial x}\right)^{-1}$$

(2) $dx=0 \Rightarrow \frac{\partial x}{\partial y}\frac{\partial y}{\partial z} = -\frac{\partial x}{\partial z}$

$$\therefore \frac{\partial x}{\partial y}\frac{\partial y}{\partial z}\frac{\partial x}{\partial z} = -1$$

For a hydrostatic system $\big(f = f(p,V,\theta)\big)$

$$\begin{cases} \frac{\partial p}{\partial V}\frac{\partial V}{\partial \theta} = -\frac{\partial p}{\partial \theta}; \\ \begin{cases} \beta = \frac{1}{V}\frac{\partial V}{\partial \theta} \\ \kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = -\frac{1}{V}\left(\frac{\partial p}{\partial V}\right)^{-1} \end{cases} \end{cases} \Rightarrow \begin{cases} \frac{\partial V}{\partial \theta} = V\beta \\ \frac{\partial p}{\partial V} = -\frac{1}{\kappa V} \end{cases} \Rightarrow \left(-\frac{1}{\kappa V}\right)(V\beta) = -\frac{\partial p}{\partial \theta}$$

$$\therefore \Rightarrow \frac{\partial p}{\partial \theta} = \frac{\beta}{\kappa}$$

Therefore

$$dp = \frac{\partial p}{\partial V}dV + \frac{\partial p}{\partial \theta}d\theta = -\frac{1}{\kappa V}dV + \frac{\beta}{\kappa}d\theta$$

[Work & Quasi static processes]

Def (Internal / External work)

External work $\longrightarrow$ work exerted from the system to the surroundings

Internal work $\longrightarrow$ Work exerted from ONE PART OF THE SYSTEM TO ANOTHER

ONLY EXTERNAL WORK IS SIGNIFICANT (IN THERMODYNAMICS)

Def (Quasi-static process)

INFINITESIMAL perturbation of thermodynamic equilibrium. The system is always approximately to be in an equilibrium state

An equation of state is therefore valid for each state of the process.

§ Work & hydrostatic system

Consider a hydrostatic system contained by adiabatic walls inside a piston cylinder.

By definition, if S is the surface of the piston, then the pressure exerted by the system is

$$p = \frac{F}{S}$$

By definition, $đW = \underline{F} \cdot \underline{dl}$, if the movement happens only in the x-direction, then

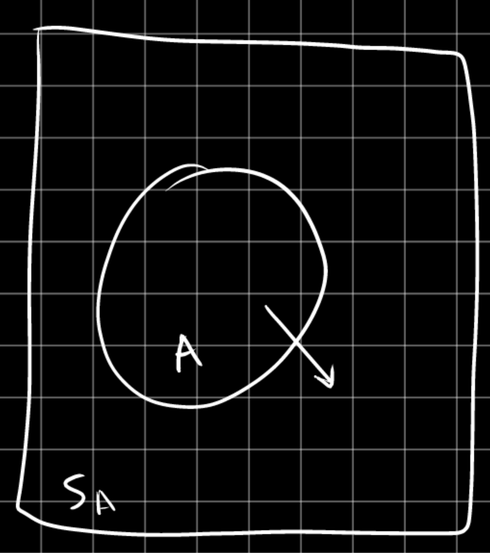
$$\begin{cases} đW = -F dx \\ F = pS \end{cases}$$

Thus

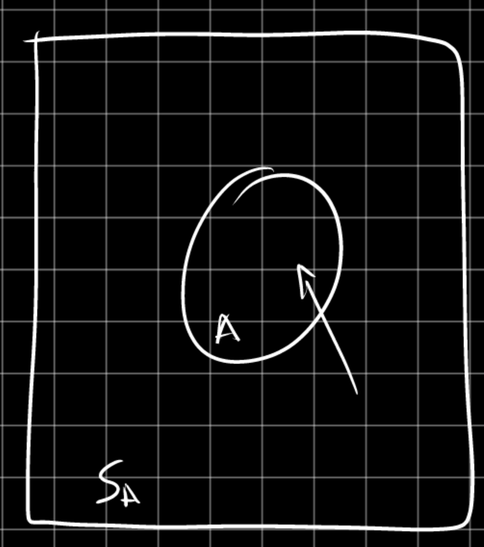
$$đW = -pS dx = -p dV$$

where $dV = S dx$ is the volume change in a dislocation of the piston by dx. The minus sign is just a convention indicating that

- Expansion $\longrightarrow$ $đW < 0$ (work from the system to surroundings)
- Compression $\longrightarrow$ $đW > 0$ (work from surroundings to system)



$đW < 0$



$đW > 0$

For a quasi static process going through a transformation $V_i \to V_f$, the work can be expressed as:

$$\Delta W = -\int_{V_i}^{V_f} p\, dV$$

Since the process is quasi static p is a thermodynamic coordinate, & $p \equiv p(V, \theta)$ via means of a state equation.

Note that in general:

$$W = \int_{\gamma} \underline{F} \cdot \underline{\hat{t}}\, dl$$

I.e. W is PATH DEPENDENT. The path can is determined only if we know explicitly the relation $\theta \equiv \theta(V)$. Thus, if we indicate

$$W_{if} = -\int_{V_i}^{V_f} p\, dV \quad , \quad W_{fi} = -\int_{V_f}^{V_i} p\, dV$$

If the path is quasistatic $\to W_{if} - W_{fi} = 0$

Note that

$$[W] = [p][V] = Pa \cdot m^3 = \frac{N}{m^2} m^3 = Nm = J$$

In thermodynamics is useful to change to non standard units

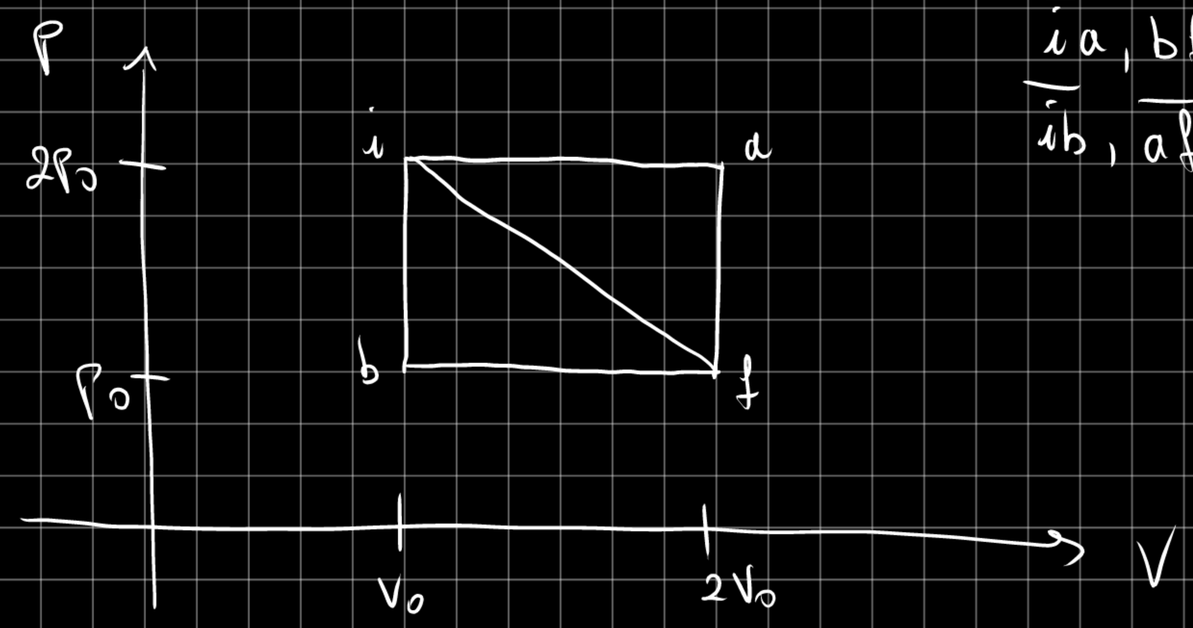
$$[p] = atm = 101.325\, kPa$$

$$[V] = l = 1\, dm^3 = 10^{-3}\, m^3$$

Thus

$$[W] = l \cdot atm = (101.325 \cdot 10^3\, Pa)(10^{-3}\, m^3) = 101.325\, Pa\, m^3 = 101.325\, J$$

Consider now 3 different processes on a pV plane:



$\overline{ia}, \overline{bf} \to$ isobaric process ($p = const$)

$\overline{ib}, \overline{af} \to$ isochoric process ($V = const$)

The paths $\overline{if}$, $\overline{iaf}$, $\overline{ibf}$ are all valid paths for going from state i to state f. Clearly the work is different! Note that:

$$\begin{cases} W_{iaf} = -\int_{iaf} p\,dV = -2p_0 \int_{ia} dV = -2p_0(2V_0 - V_0) = -2p_0 V_0 \\ W_{ibf} = -\int_{ibf} p\,dV = -p_0 \int_{bf} dV = -p_0(2V_0 - V_0) = -p_0 V_0 \neq W_{iaf} \quad (!!) \\ W_{if} = -\int_{if} p\,dV = -\frac{3}{2}(p_0 V_0) \neq W_{iaf} \neq W_{ibf} \quad (!!) \end{cases}$$

Work depends strictly on intermediate states (path)!

Therefore $đW$ is an inexact differential ($đ$) since $\nexists!\, W(p,V,\theta) = \int đW$!

{ Work in quasi static processes for ideal gases

Consider now an ideal gas system, where therefore holds

$$pV = nR\theta$$

Then $p(V,\theta) = \frac{nR\theta}{V}$, and for ISOTHERMAL ($\theta = \text{const}$) compressions / expansions

$$W = -\int_{V_i}^{V_f} p\,dV = -nR\theta \int_{V_i}^{V_f} d\log(V) = -nR\theta \log\left(\frac{V_f}{V_i}\right)$$

{Note that if $\theta = \theta(V,p)$ this is not true any more}

e.g. 1

2 kmol of some gas are kept at constant temperature of $0°C$. If the gas is compressed from a volume of $4\,m^3$ to $1\,m^3$, then

$$W = nR\theta \log\left(\frac{V_f}{V_i}\right) = (2\cdot 10^3\,mol)\,R\,(273.15\,K)\log\left(\frac{1}{4}\right) \qquad \begin{cases} n = 2000\,mol \\ \theta = 0°C = 273.15\,K \\ V_f/V_i = \frac{1}{4} \end{cases}$$

Noting that $R = 8.314\,\frac{J}{K\,mol}$ (Joule / Kelvin·mole) is the ideal gas constant, we have

$$W = (2\cdot 10^3\,mol)\left(8.314\,\frac{J}{K\cdot mol}\right)(273.15\,K)\log\left(\frac{1}{4}\right)$$

$$W = 2\,(831.4)\,(273.15)\log\left(\frac{1}{4}\right) J \simeq 6'300'000\,J = 6300\,kJ = 6.3\,MJ$$

Note that $W > 0 \Rightarrow$ work was <u>DONE</u> to the gas.

e.g. 2 : (Quasi static isothermal pressure increase on a solid)

Suppose that 100 kg of $Cu_{(s)}$ has pressure increased at 0°C from 1 atm to 1000 atm.

We have

$$\begin{cases} W = -\int p\,dV \\ dV = \frac{\partial V}{\partial p}dp + \frac{\partial V}{\partial \theta}d\theta \end{cases}$$

Since $\theta = \text{const} \Rightarrow d\theta = 0$, thus

$$dV = \frac{\partial V}{\partial p}dp = -V\kappa\,dp \quad \left\{ \kappa = -\frac{1}{V}\frac{\partial V}{\partial p} \right\}$$

Thus:

$$W = -\int_{V_i}^{V_f} p\,dV = \int_{p_i}^{p_f} \kappa p V\,dp = \frac{\kappa V}{2}\left(p_f^2 - p_i^2\right) = \frac{\kappa V}{2}\left(1000^2 - 1\right) atm^2$$

By definition $V = \frac{m}{\rho}$ w/ ρ being the density. For $Cu_{(s)}$ at 0°C we have

$\rho = 8930 \frac{kg}{m^3}$, $\kappa = 7.16 \cdot 10^{-12}\, Pa^{-1}$, $m = 100\, kg$, $p_i = 0\, atm$, $p_f = 1000\, atm = 101.325 \cdot 10^6\, Pa =$

$= 1.013 \cdot 10^8\, Pa$, we have

$$W = \frac{m\kappa}{2\rho}\left(p_f^2 - p_i^2\right) = \frac{100\, kg \cdot 7.16 \cdot 10^{-12}\, Pa^{-1}}{2 \cdot 8930\, kg/m^3}\left((1.013)^2 \cdot 10^{16}\, Pa^2\right) \simeq 0.411\, N \cdot m = 0.411\, kJ$$

pg. 63 (3-13)

+ ch. 4 pg. 68

§ Composite systems

Consider 2 hydrostatic systems divided by a dt wall. The complessive system has coordinates (p, V, p', V', θ) & two EOS $f_1(p, V, \theta)$, $f_2(p', V', \theta)$. If both systems are in contact w/ a piston (each), then the complete work is

$$đW = -p\,dV - p'\,dV'$$

In general, for a composite system w/ 4 thermodynamic coordinates + temperature we have

$$đW = Y\,dX + Y'\,dX'$$

where then $(X, Y, X', Y', \theta) \equiv (X, Y(X), X', Y'(X'), \theta)$

Dini theorem w/ EOS
$f_1(X, Y, \theta)$
$f_2(X', Y', \theta)$

[Ist LAW OF THERMODYNAMICS]

§ Heat

There are various ways to induce a change of state w/ out performing work on a system
Consider 3 cases

1) piston & system in adiabatic expansion ($W \neq 0$)

2) System over flame ($W = 0$, $?? \neq 0$)

3) ① + ② ($W \neq 0$, $?? \neq 0$)

in all 3 cases there's a change of state, thus "something" (??) gets exchanged in case ② & ③ which is not just mechanical or expansion work.
This "something" is known as <<heat>>. In a calorimetric definition we have

<u>Def</u> (Heat, calorimetric)

Heat is that which is transferred b/w a system & its surroundings by virtue of temperature only. With this definition

<u>ad</u> wall → heat insulator
<u>dt</u> wall → heat conductor

§ Adiabatic work

Consider a system enclosed in an adiabatic cylinder chamber w/ a piston. In order to add work to the system ADIABATICALLY:

-) Quasi-static motion of the piston → $W = -\int p\,dV$

-) Non quasi-static motion of the piston → <<free expansion>>

{ -) Joule effect w/ R
-) EM effects }

For a generic thermodynamic graph we can say that there are multiple ways of going from a state to another using only adiabatic transformations. Note that, in this special adiabatic case

Work is path independent → $W = -\int_{\gamma} p\,dV = -\int_{\gamma'} p\,dV \iff \gamma \sim \gamma' \in [a,b] \to \mathbb{R}^3_{(p,V,\theta)}$

Therefore $\exists!\, U(p,V,\theta) = \int dW$ aka INTERNAL ENERGY FUNCTION

Thus: $W_{12}(p,V,\theta) = \mathcal{U}(p_2,V_2,\theta_2) - \mathcal{U}(p_1,V_1,\theta_1)$ $\begin{cases} > 0 & \text{if work is DONE ON SYSTEM} \\ = 0 & \text{if NO WORK is done} \\ < 0 & \text{if work is DONE FROM SYSTEM} \end{cases}$

§ INTERNAL ENERGY FUNCTION

The function $\mathcal{U}(p,V,\theta)$, & therefore $\Delta\mathcal{U}$, define the CONSERVATION of energy of the system when <u>ad</u> work is done.

It's not needed to know the exact functional shape of $\mathcal{U}$, but just the fact that it exists.

Since w/ EOS we have always one coordinate fixed, we have:

$$\begin{cases} \mathcal{U}_1(p,V) \\ \mathcal{U}_2(V,\theta) \\ \mathcal{U}_3(\theta,p) \end{cases} \Rightarrow \begin{cases} d\mathcal{U}_1 = \frac{\partial \mathcal{U}_1}{\partial p}dp + \frac{\partial \mathcal{U}_1}{\partial V}dV \\ d\mathcal{U}_2 = \frac{\partial \mathcal{U}_2}{\partial V}dV + \frac{\partial \mathcal{U}_2}{\partial \theta}d\theta \\ d\mathcal{U}_3 = \frac{\partial \mathcal{U}_3}{\partial \theta}d\theta + \frac{\partial \mathcal{U}_3}{\partial p}dp \end{cases}$$

Note that $\frac{\partial \mathcal{U}_1}{\partial V} \neq \frac{\partial \mathcal{U}_2}{\partial V}$!

$\mathcal{U}_1 \equiv \mathcal{U}_1(p,V)$, $\mathcal{U}_2 \equiv \mathcal{U}_2(V,\theta)$

New notation:

$$\mathcal{U}(X,Y) \;\&\; \mathcal{U}(X,\theta) \Rightarrow \begin{cases} d\mathcal{U} = \frac{\partial \mathcal{U}}{\partial X}dX + \frac{\partial \mathcal{U}}{\partial Y}dY \\ d\mathcal{U} = \frac{\partial \mathcal{U}}{\partial X}dX + \frac{\partial \mathcal{U}}{\partial \theta}d\theta \end{cases}$$

For avoiding confusion:

$$\begin{cases} d\mathcal{U} = \left(\frac{\partial \mathcal{U}}{\partial X}\right)_Y dX + \left(\frac{\partial \mathcal{U}}{\partial Y}\right)_X dY \\ d\mathcal{U} = \left(\frac{\partial \mathcal{U}}{\partial X}\right)_\theta dX + \left(\frac{\partial \mathcal{U}}{\partial \theta}\right)_X d\theta \end{cases}$$

There is no confusion b/w $\left(\frac{\partial \mathcal{U}}{\partial X}\right)_Y$ & $\left(\frac{\partial \mathcal{U}}{\partial X}\right)_\theta$

read as "pdv of $\mathcal{U}$ wrt X at const θ or Y"

§ 1st LAW OF THERMODYNAMICS

Consider a system, on which we perform two experiments

1) change of state $i \to f$ adiabatically
2) change of state $i \to f$ <u>NON</u> ad

For ①, we know that

$$W_{ad} = \Delta\mathcal{U}_{if}$$

While for ②

$$W_{nad} \neq \Delta\mathcal{U}_{if}$$

but, since Energy is conserved $\to$ energy has been transferred via other means which are not work $\to$ <u>heat</u> (depends only on $\Delta\theta$)

Def (Heat, thermodynamic)

Consider a system A & its surroundings S_A, for which $\theta_A \neq \theta_{S_A}$, the difference b/w $\Delta\mathcal{U}$ & W is heat, indicated by Q. Thus

$$Q = \Delta\mathcal{U} - W \Rightarrow \Delta\mathcal{U} = Q + W$$

Convention: $Q>0$ when heat enters A, $Q<0$ when heat leaves A. 1st Law

$$\Delta U = Q + W \quad (\text{1st law})$$

The first law implies:

1) $\exists\, U(p, V, \theta)$
2) $\Delta E_{TOT} = 0$
3) Q is ENERGY IN TRANSIT by means of $\Delta\theta \neq 0$ (Joule, 1840-1849)

§ CONCEPT OF HEAT

By definition, heat is NOT known during the process, but HEAT FLOW is known. Thus

$$Q = \int_{\tau_1}^{\tau_2} \frac{dQ}{dt}\, dt$$

Remember that internal energy is not separable in mechanical (W) and thermal (Q). The idea of heat in a body doesn't make any sense.

Q, as work, depends on the path → it's not a function of (p, V, θ). Thus, the heat differential is INEXACT.

Consider now 2 systems A, B in thermal contact, surrounded by ad walls. Going from state i to state f we have

$$\begin{cases} \Delta U_A = Q + W \\ \Delta U_B = Q' + W' \end{cases}$$

Defined $\Delta U = \Delta U_A + \Delta U_B$ as the total change of energy, we have then that

$$\begin{cases} W_T = W + W' & \text{composite system} \\ Q_T = Q + Q' & \text{work \& heat} \end{cases}$$

Since the composite system $A \oplus B$ is surrounded by ad walls (no heat exchange)

$$Q_T = Q + Q' = 0$$
$$\therefore Q = -Q' \quad \Rightarrow \text{ad condition!}$$

Thus, under ad conditions

$$Q_T = 0$$

which implies that the heat gained (lost) from A is the heat lost (gained) from B

§ DIFFERENTIAL FORM OF 1ST LAW OF THERMODYNAMICS

Consider a differential change in thermodynamic coordinates, then:

$$dU = đQ + đW \quad (1st, \text{ diff})$$

If the process is quasi-static, then $dU \equiv dU(p,V,\theta)$, $đW \equiv đW(p,V,\theta)$. If the system is also hydrostatic, then

$$đW = -p\,dV$$

$$\therefore dU(p,V,\theta) = đQ - p(V,\theta)\,dV$$

§§ Heat capacity & measurements

During a change of state, there might or <u>might not</u> be a change in temperature of the system.

The average heat capacity is known, then, as:

$$\langle c \rangle = \frac{Q}{\Delta\theta}$$

The heat capacity is then defined as:

$$C = \frac{đQ}{d\theta}$$

Since heat capacity & internal energy & such are <u>extensive</u> it's useful to use <u>SPECIFIC</u> versions of these quantities (per unit mass). If specific heat is c, then

$$[c] = \frac{J}{kg\,K}$$

An useful unit is the "mole", defined as the amount of substance containing as much entities as $0.012\ kg = 12\,g$ of ^{12}C; i.e. N_A (Avogadro's number)

$$N_A = 6.023 \cdot 10^{23}\ mol^{-1}$$

If we have an atom A with mass m, then 1 mol weighs

$$m(1\ mol) = m N_A = \mathcal{M}$$

where $\mathcal{M}$ is the molar mass. By def., the number of moles in m_A mass of substance A is

$$n_A = \frac{m_A}{\mathcal{M}}$$

The specific heat (molar) is then

$$c = \frac{C}{n} = \frac{1}{n}\frac{đQ}{d\theta}\ ; \quad [c] = \frac{J}{mol\,K}$$

Note that $C \lesseqgtr 0$ or also $C = \infty$ depending on the process.
For a hydrostatic system it has <u>two</u> specific values

$$\begin{cases} C_p(p,\theta) = \left(\frac{đQ}{d\theta}\right)_p \approx c_p & \text{(heat capacity at } p = \text{const)} \\ C_V(V,\theta) = \left(\frac{đQ}{d\theta}\right)_V \approx c_V & \text{(heat capacity at } V = \text{const)} \end{cases}$$

§ DEFINITION OF CALORIES

<u>Def</u> (calorie)

A «calorie», or cal, is the amount of heat necessary to raise the temperature of 1 g of H_2O by $1°C$, thus for measuring heat change one needs to know only the temp. change & the mass of water. In general

1) for $\Delta\theta = 1°C$, $\theta_i = 14.5°C$, $\theta_f = 15.5°C$ per <u>unit mass</u> of water

$$1 \text{ cal} = 4.1860 \text{ J}$$

§ Equations of a hydrostatic system

As we determined before, for a hydrostatic system

$$du = đQ - p\,dV$$
$$đQ = du + p\,dV$$

Thus, choosing coordinates (θ, V)

$$\begin{cases} du = \left(\frac{\partial u}{\partial \theta}\right)_V d\theta + \left(\frac{\partial u}{\partial V}\right)_\theta dV \\ đQ = \left(\frac{\partial u}{\partial \theta}\right)_V d\theta + \left(\frac{\partial u}{\partial V}\right)_\theta dV + p\,dV \end{cases}$$

Thus:

$$đQ = \left(\frac{\partial u}{\partial \theta}\right)_V d\theta + \left[\left(\frac{\partial u}{\partial V}\right) + p\right] dV$$

$$\boxed{\frac{đQ}{d\theta} = \left(\frac{\partial u}{\partial \theta}\right)_V + \left[\frac{\partial u}{\partial V} + p\right]_\theta \frac{dV}{d\theta}}$$ <u>I st LAW</u>

a) $V = \text{const} \Rightarrow \frac{dV}{d\theta} = 0$

$$\left(\frac{đQ}{d\theta}\right)_V = \left(\frac{\partial u}{\partial \theta}\right)_V = c_V (!)$$

b) $p = \text{const}$

$$\left(\frac{đQ}{d\theta}\right)_p = \left(\frac{\partial u}{\partial \theta}\right)_V + \left[\left(\frac{\partial u}{\partial V}\right)_\theta + p\right]\left(\frac{\partial V}{\partial \theta}\right)_p$$

By definition, $\left(\frac{\partial V}{\partial \theta}\right)_p = V\beta$, therefore

$$\left(\frac{đQ}{d\theta}\right)_p = C_V + \beta V\left[\left(\frac{\partial U}{\partial V}\right)_\theta + p\right] = C_p$$

Since $\left(\frac{\partial U}{\partial V}\right)_\theta$ is the only unknown, we have

$$\left(\frac{\partial U}{\partial V}\right)_\theta = \frac{C_p - C_V}{\beta V} - p$$

§ QUASI-STATIC HEAT FLOW, RESERVOIRS (last before ch. 5, p. 85, ch. 5 p 101)

In quasi static processes, the temperature differences b/w a system & its surroundings are infinitesimal, therefore uniform & slow changing throughout the process. Therefore the flow of heat is slow and easily evaluable using thermodynamic coordinates (p, V, θ).

Consider a system in thermal contact w/ a body w/ mass $M \gg m$, with m being the system's mass.

$\therefore$ A finite amount of heat transfer <u>WILL NOT</u> bring an appreciable change on the bigger body.

This body is known as a << heat reservoir >>

<u>Def</u> (Heat reservoir)

Body with a mass so large that it might absorb or reject an unlimited quantity of heat without suffering an appreciable change of state.

There <u>IS</u> a change of state $(p_1, V_1, \theta_1)_R \to (p_2, V_2, \theta_2)_R$, but it's <u>NEGLIGIBLE</u>

$$(p_1, V_1, \theta_1)_R \simeq (p_2, V_2, \theta_2)_R$$

Any quasi static process of a system in contact with a reservoir <u>IS</u> <u>ISOTHERMAL</u>

Consider a series of reservoirs w/ temps θ_k, $k = i, \dots, f$ in contact w/ the system & ∂ $p = \text{const}$. Then the flow of heat is quasi-static, and by def:

$$\left(\frac{đQ}{d\theta}\right)_p = C_p \Rightarrow Q_p = \int_{\theta_i}^{\theta_f} C_p \, d\theta$$

If $C_p(\theta) \approx C_p$, then

$$Q_p = C_p \Delta\theta \quad \text{(isobaric process)}$$

If instead $V = \text{const}$

$$\left(\frac{đQ}{d\theta}\right)_V = C_V \Rightarrow Q_V = \int_{\theta_i}^{\theta_f} C_V \, d\theta$$

$C_V(\theta) \approx C_V$, then

$$Q_V = C_V \Delta\theta \quad \text{(isochoric process)}$$

§ Heat conduction

The heat transfer b/w 2 systems with different temperatures is known as HEAT CONDUCTION.

Consider a slab thick Δx w/ surface area A. One face is at temp θ & the other is at $\theta + \Delta\theta$.

We want to measure the heat that goes $\perp$ to the slab for a time τ. We have

$$\frac{Q}{\tau} \propto A \frac{\Delta\theta}{\Delta x}$$

Combining $\Delta x \to 0$, $\tau \to 0$, we have

$$\frac{dQ}{dt} = -kA\frac{d\theta}{dx}$$

k → Thermal conductivity

$-$ → $Q>0 \Rightarrow x>0$

k, the thermal conductivity, indicates the capacity of a material to conduct heat. Thus:

$$k \begin{cases} \gg 0 & \text{thermal conductor} \\ = 0 & \text{perfect insulator} \\ \ll 1 & \text{thermal insulator} \end{cases}$$

In general $k \equiv k(x,y,z)$, but we can consider $k(x,y,z) \approx k$

we have

$$\begin{cases} k = -\frac{1}{A}\frac{dQ}{dt}\left(\frac{d\theta}{dx}\right)^{-1} \\ \therefore [k] = \frac{1}{m^2}\left(\frac{J}{s}\right)\left(\frac{m}{K}\right) = \frac{J}{s}\left(\frac{1}{m\cdot K}\right) = \frac{W}{mK} \end{cases}$$

Suppose that we want to measure the thermal conductivity k of some metal, then:

1) create a bar w/ insulated surface
2) heat one side electrically
3) cool the other side with water

For most metal the heat lost through the insulation is then evaluated by subtracting the heat supplied by the electrode & that which enters in the water

For a temperature measured by 2 thermocouples distant (ℓ) from eachother, we have

$$k = -\frac{\ell}{A\Delta\theta}\frac{dQ}{dt}$$

If $\Delta\theta \ll 1$ then $k = \langle k \rangle_\theta$

The same general method is used with non metals made in thin disks or blocks enclosed b/w 2 $Cu_{(s)}$ blocks

Note that

-) impurities in metal change RADICALLY k. Eg. take Cu w/ As impurities

$$k_{Cu} \approx 3 k_{Cu,As}$$

-) Continuous heating or changes in pressure change k

-) $k_{(e)} < k_{(s)}$

-) $\theta_1 < \theta_2 \Rightarrow k_{(e)}(\theta_1) < k_{(e)}(\theta_2)$

-) Non metallic solids behave like liquids

-) For metals $k(\theta_1) > k(\theta_2) \leq k_{max}$

-) $\frac{\partial k}{\partial p} \approx 0$ for gases, & limiting pressure $P_{e,gas} << P_{atm}$, $\frac{\partial k}{\partial \theta} > 0$

IDEAL GASES

§ EOS OF A GAS

Gases are the best behaved thermometric substances since

$$\lim_{p\to 0}\left(\frac{p}{p_{TP}}\right) \longrightarrow \text{is independent from the gas nature}$$

With this definition, we have

$$\theta = 273.15 \lim_{p\to 0}\left(\frac{p}{p_{TP}}\right) K \quad \text{(IDEAL GAS TEMPERATURE)}$$

This behavior can be investigated by measuring the way that pV depends on density ρ. Suppose now that we have n moles of gas, w/ molar volume ν. Thus, we can write

$$p\nu = \sum_{k=0}^{\infty} \frac{a_k}{\nu^k} \; ; \quad a_k = (A, B, C, \dots)$$

The coefficients a_k are known as << Virial coefficients >>, and $a_i \equiv a_i(\theta; \dots)$

For $0\,atm < p < 40\,atm$ we have that

$$p\nu \propto \nu^{-1}$$

It is found that

$$\lim_{p\to 0}(p\nu) = A(\theta)$$

Thus, since

$$\theta = 273.16 \lim_{p\to 0}\left(\frac{p}{p_{TP}}\right)_{V,n} K$$

$$\theta = 273.16 \lim_{p\to 0}\left(\frac{p\nu}{p_{TP}\nu}\right) K = 273.16 \frac{\lim(p\nu)}{\lim(p\nu)_{TP}} K$$

I.e.:

$$\lim_{p\to 0}(p\nu) = \frac{\lim(p\nu)_{TP}}{273.16\,K}\,\theta$$

We then define the << UNIVERSAL GAS CONSTANT >>

$$R = \frac{\lim(p\nu)_{TP}}{273.16\,K} \simeq 8.31441 \frac{J}{K\cdot mol}$$

Thus, finally

$$\lim_{p\to 0}(pV) = nR\theta = A(\theta)$$

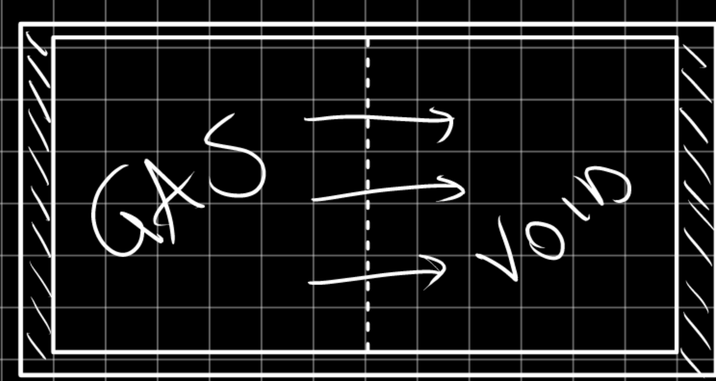
And the virial expansion becomes

$$\frac{p\nu}{R\theta} = 1 + \sum_{k=1}^{\infty} \frac{a_k}{\nu^k}$$

§ INTERNAL ENERGY OF AN IDEAL GAS

Consider a thermally insulated vessel w/ some ideal gas in a compartment and another compartment empty. If the separation is removed b/w the compartments we will have a

free-expansion



where

$$\begin{cases} W = 0 \\ Q = 0 \end{cases} \quad (!!)$$

From the first law then

$$dU = đQ + đW = 0$$

$$\therefore U = U_0$$

In general then

$$dU = \left(\frac{\partial U}{\partial \theta}\right)_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV = 0$$

If $d\theta = 0$ in the free expansion, we have

$$\left(\frac{\partial U}{\partial V}\right)_\theta dV = 0 \Rightarrow \left(\frac{\partial U}{\partial V}\right)_\theta = 0 \; !$$

$$U \equiv U(\theta)$$

We redefine in terms of coordinates (p, θ). Thus

$$dU = \left(\frac{\partial U}{\partial \theta}\right)_p d\theta + \left(\frac{\partial U}{\partial p}\right)_\theta dp = 0$$

$$\therefore d\theta = 0 \Rightarrow \left(\frac{\partial U}{\partial p}\right)_\theta dp = 0$$

$$\therefore U \equiv U(\theta)$$

Since $U(p, V, \theta) \equiv U(\theta)$, for a FREE EXPANSION ONLY

$$U \equiv U(\theta)$$

$$\therefore dU = \frac{\partial U}{\partial \theta} d\theta$$

§ IDEAL GAS

ONLY IN THE LIMIT $p \to 0$ we have

$$\begin{cases} pV = nR\theta \\ \left(\frac{\partial U}{\partial p}\right)_\theta = 0 \end{cases}$$

Note that

$$\left(\frac{\partial U}{\partial V}\right)_\theta = \left(\frac{\partial U}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial V}\right)_\theta$$

But

$$p(V,\theta) = \frac{nR\theta}{V} \Rightarrow \left(\frac{\partial p}{\partial V}\right)_\theta = -\frac{nR\theta}{V^2} = -\frac{p}{V} \neq 0$$

Therefore, by definition

$$\left(\frac{\partial U}{\partial V}\right)_\theta = -\frac{p}{V}\left(\frac{\partial U}{\partial p}\right)_\theta = 0$$

Thus

$$U(p,V,\theta) \equiv U(\theta)$$

FOR AN IDEAL GAS U depends only on θ. Now, for the Ist LAW

$$\begin{cases} đQ = dU - đW \\ đW = -p\,dV \\ dU = \frac{\partial U}{\partial \theta} d\theta = C_V\, d\theta \end{cases} \Rightarrow đQ = \frac{\partial U}{\partial \theta} d\theta + p\,dV$$

$$\boxed{đQ = C_V\, d\theta + p\,dV} \quad \text{Ist LAW (IDEAL)}$$

For all equilibrium states we have

$$pV = nR\theta$$

Thus, in a quasi-static process

$$d(pV) = p\,dV + V\,dp = nR\,d\theta$$

$$\therefore p\,dV = nR\,d\theta - V\,dp$$

$$đQ = (C_V + nR)\,d\theta - V\,dp$$

Therefore

$$\boxed{\frac{đQ}{d\theta} = C_V + nR - V\frac{dp}{d\theta}}$$

Note: for $p = \text{const}$

$$\left(\frac{đQ}{d\theta}\right)_p = C_p = C_V + nR$$

Therefore

$$\begin{cases} C_V = \frac{\partial U}{\partial \theta} \\ C_p = C_V + nR \end{cases}$$

Also

$$\begin{cases} đQ = C_V\, d\theta + p\,dV \\ đQ = C_p\, d\theta - V\,dp \end{cases}$$

§§ Determination of C_p & C_v

1) All gases (common molar quantities)

a) $C_v \equiv C_v(\theta)$

b) $C_p \equiv C_p(\theta) > C_v(\theta)$

c) $C_p - C_v = R$

d) $\frac{C_p}{C_v} = \gamma \equiv \gamma(\theta) > 1$

2) MONOATOMIC GASES $\{He, Ne, \dots\}$

a) $C_v \simeq \frac{3}{2} R$

b) $C_p = C_v + R \simeq \frac{5}{2} R$

c) $\gamma = \frac{C_p}{C_v} \simeq \frac{5}{3}$

3) DIATOMIC GASES $\{H_2, O_2, N_2, \dots\}$

a) $C_v \simeq \frac{5}{2} R$

b) $C_p \simeq \frac{7}{2} R$

c) $\gamma \simeq \frac{7}{5}$

d) $\frac{\partial C_v}{\partial \theta} > 0$, $\frac{\partial C_p}{\partial \theta} > 0$, $\frac{\partial \gamma}{\partial \theta} < 0$

4) POLYATOMIC GASES

-) C_p, C_v, γ depend strongly on θ

IN GENERAL:

$$\begin{cases} \frac{1}{R} C_p(\theta) = \frac{7}{2} + f(\theta) \\ f(\theta) = \left(\frac{b}{\theta}\right)^2 \frac{\exp(\theta/2)}{(\exp(\theta/2) - 1)^2} \end{cases}$$

$\leftarrow$ stat mech

§ QUASI-STATIC ADIABATIC PROCESSES

From the first law, we have

$$\begin{cases} đQ = c_V d\theta + p dV \\ đQ = c_p d\theta - V dp \end{cases}$$

In an adiabatic process $đQ = 0$, thus

$$\begin{cases} p dV = -c_V d\theta \\ V dp = c_p d\theta \end{cases}$$

Solving the system we have

$$\frac{V}{p}\frac{dp}{dV} = -\frac{c_p}{c_V} = -\gamma$$

Multiplying by V^{-1} we have

$$\frac{1}{p}\frac{dp}{dV} = -\frac{1}{V}\gamma$$

And separating the variables

$$\left[\frac{dp}{p} = -\gamma\frac{dV}{V}\right]$$

Considering that $\gamma \approx$ const, we have finally

$$\log(p) = -\gamma \log(V) + \text{const.}$$

$$\log(pV^\gamma) = \text{const}$$

$$\left[\therefore pV^\gamma = \text{const.}\right]$$

$pV^\gamma = \text{const}$ HOLDS ONLY IFF THE PROCESS IS QUASI-STATIC.

In a pV diagram, we have a curve with slope

$$\left(\frac{\partial p}{\partial V}\right)_S = -\gamma \,\text{const}\, V^{\gamma-1}$$

at constant S, adiabatic

$$\therefore \left(\frac{\partial p}{\partial V}\right)_S = -\gamma\frac{p}{V}$$

For each value of θ we have an EQUILATERAL HYPERBOLA

Note that an isothermal curve has slope

$$\left(\frac{\partial p}{\partial V}\right)_\theta = -\frac{p}{V} > \left(\frac{\partial p}{\partial V}\right)_S$$

THERMAL ENGINES & II LAW

§ Heat - Work conversion

Work (W) of any kind may be done to a system in contact to a reservoir, giving a flow of heat (Q)

From the Ist law one might think that $Q = W$ and therefore there's a process w/ 100% efficiency that can be continued indefinitely

Considering an isothermal expansion of an ideal gas ($dU = 0$) we have from the Ist law that

$$Q = -W \Rightarrow 100\% \text{ conversion}$$

This process continues till $p = p_{atm}$, therefore it's not indefinite

Def (Cycle)

Each series of processes in which a system is brought back to the initial state is known as a <<thermodynamic cycle>>. For a cycle, we have

-) $|Q_H|$ absorption (by system)

-) $|Q_c|$ discarded (by system)

-) $|W|$ work done (by the system)

If $|Q_H| > |Q_c|$ & $|W| \neq 0 \Rightarrow$ we have a <<thermodynamical system>>

The <<thermal efficiency>> η of an engine is defined then as:

$$\eta = \frac{|W|}{|Q_H|}$$

From the first law (integral) we have

$$\begin{cases} \Delta U = Q_T + W_T = 0 \\ Q_T = |Q_H| - |Q_c| \\ W_T = |W| \end{cases}$$

coming back

Thus

$$|W| = |Q_H| - |Q_c|$$

$$\frac{|W|}{|Q_H|} = 1 - \frac{|Q_c|}{|Q_H|} \Rightarrow \eta = 1 - \left|\frac{Q_c}{Q_H}\right|$$

$\eta = 100\%$ iff $|Q_c| = 0$ (no heat transfer from the system)

There are 2 types of thermodynamical engines that accomplish this process:

-) Internal combustion energy (gasoline, diesel)
-) External combustion engines (Stirling, steam)

external combustion → heat source outside the system
internal combustion → system does a cycle and gets brought to combustion

§ Stirling Engine

The Stirling engine is a hot air engine that converts heat from fuel to work
The cycle of hot air is:

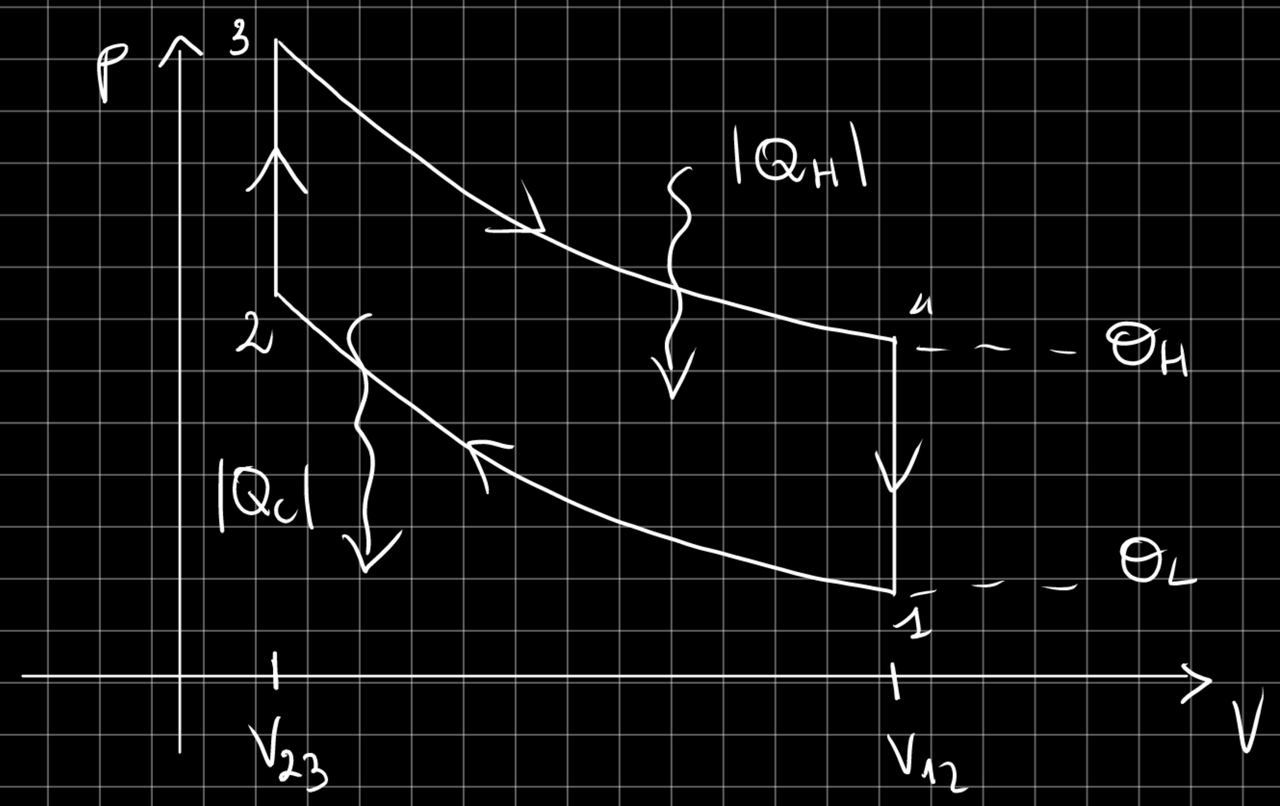


Fig. Stirling cycle

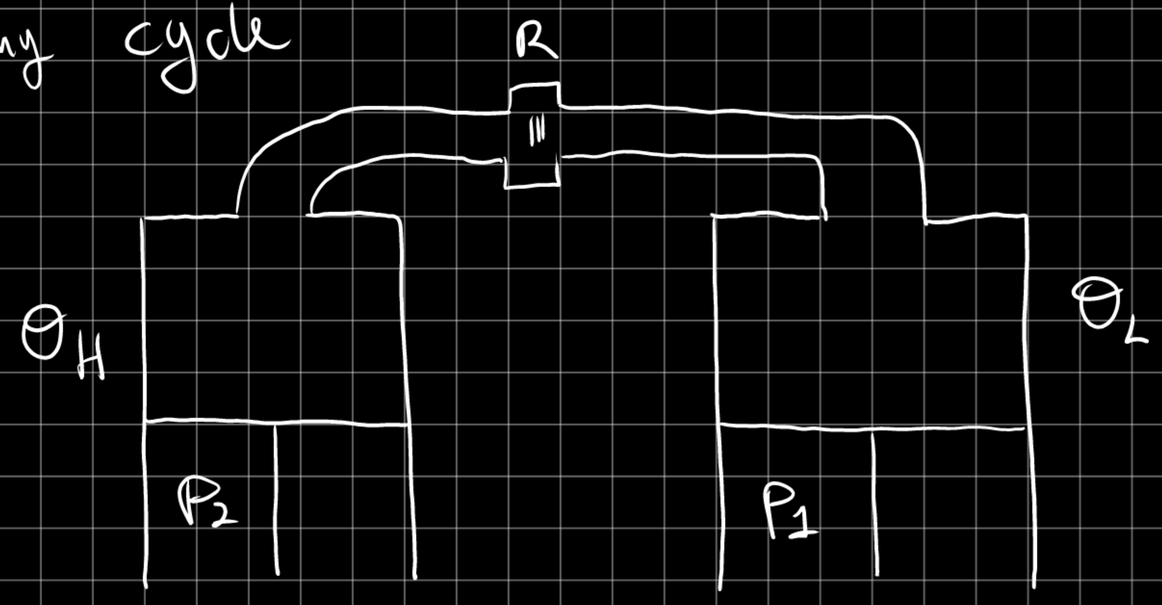


Fig. Stirling engine. R → regenerator

1 → 2 : isothermal compression of the gas in P_1 @ θ_L w/ $Q = -|Q_c|$

2 → 3 : isochoric heating of gas (P_1 up, P_2 down, $V = cost.$) release of $|Q_R|$ to R

3 → 4 : isothermal expansion (P_1 still, P_2 down) release of $|Q_H|$ @ θ_H

4 → 1 : isochoric refrigeration (P_2 up, P_1 down) release of $|Q_R|$ to R & movement to P_1 @ θ_L

At the end → $\underset{1\to2}{-|Q_c|} \rightarrow \underset{2\to3}{|Q_R|} \rightarrow \underset{3\to4}{|Q_H|} \longrightarrow -|Q_R|$

∴ $Q_T = |Q_H| - |Q_c| = |W|$ (ideal system)

§ ICE

- Six processes (strokes)

1) Intake (get a mix of fuel & air)

2) Compression

3) Ignition (spark, high θ & high p)

4) Power (expansion)

5) Valve exhaust (expansion to colder outside)

6) Exhaust stroke (piston pushes out)

IDEAL ICE : OTTO ENGINE (DIESEL)

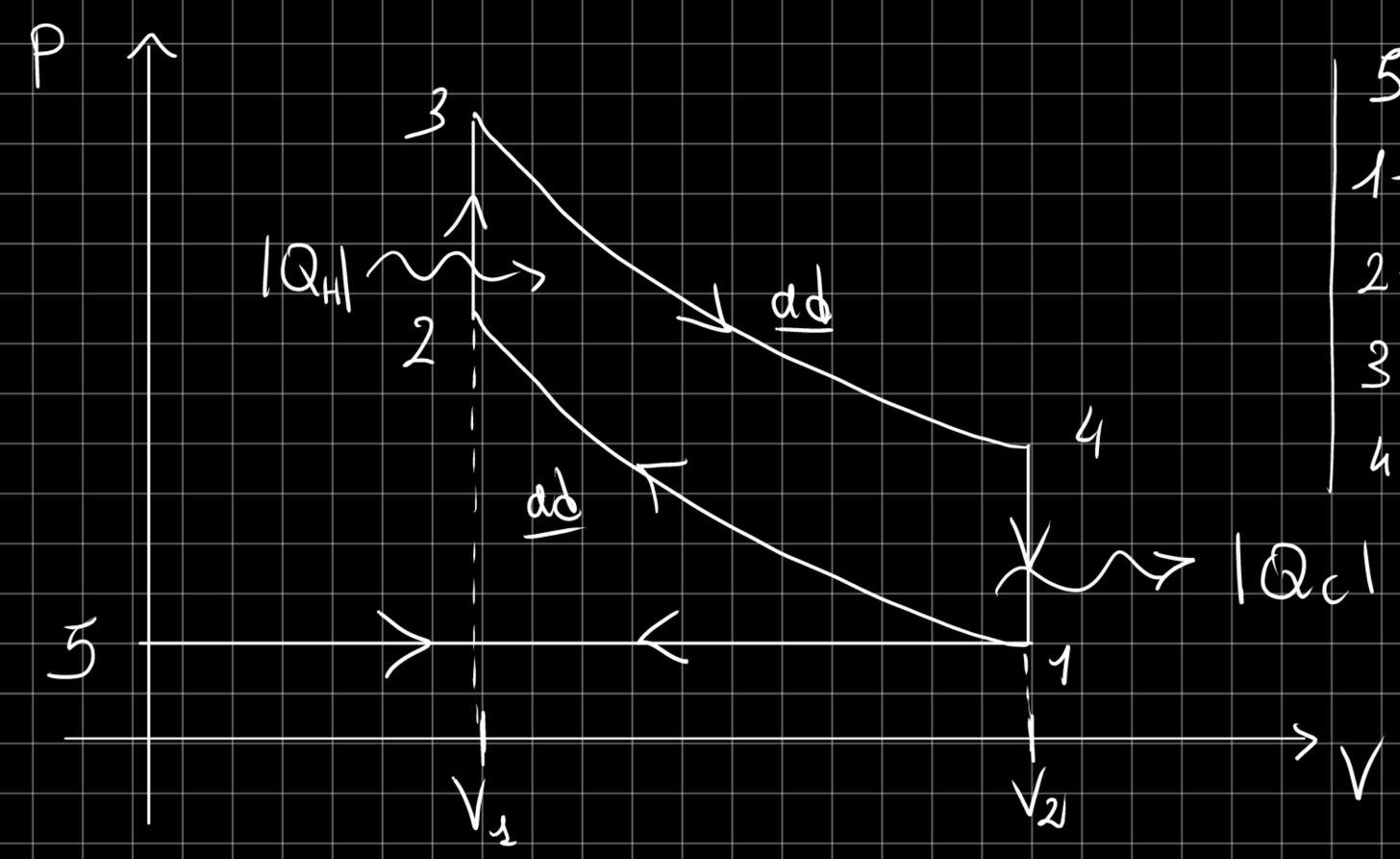
Approximations:

-) Working substance: air, ideal gas

-) Quasi-static processes

-) No friction

§ AIR-STANDARD OTTO CYCLE



$5 \to 1$ isobaric intake ($V_5 = 0$, V_1)

$1 \to 2$ adiabatic compression

$2 \to 3$ isochoric heating

$3 \to 4$ adiabatic expansion

$4 \to 1$ isochoric cooling

$1 \to 5$ isobaric exhaust

$5 \to 1$, increase of moles to n_1 @ P_1, θ_1

$$P_1 V = n R \theta_1$$

$1 \to 2$, adiabatic compression, heating from θ_1 to θ_2

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \; ; \; P_2 = \frac{nR\theta_2}{V_2} \Rightarrow \theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1}$$

$2 \to 3$ isochoric heating, absorption of $|Q_H|$ from reservoirs @ θ_2, θ_3

$3 \to 4$ adiabatic expansion w/ cooling from θ_3 to θ_4

$$\begin{cases} \theta_3 V_3^{\gamma-1} = \theta_4 V_4^{\gamma-1} \\ V_3 = V_2 \ , \ V_4 = V_1 \end{cases} \Rightarrow \theta_3 V_3^{\gamma-1} = \theta_4 V_4^{\gamma-1}$$

$4 \to 1$ isochoric cooling, emission of $|Q_c|$ to external reservoirs @ θ_4, θ_1

$1 \to 5$ isobaric exhaust, $V: V_1 \longrightarrow 0$, $n: n_1 \longrightarrow 0$, $\theta = \theta_1$ (const)

Note that in an ideal engine & system $1 \to 5$ cancels $5 \to 1$.

<u>Note</u>:

There heat absorption at $2 \to 3$, $|Q_H|$ & emission at $4 \to 1$ of $|Q_c|$

$2 \to 3$) By definition

$$|Q_H| = \int_{\theta_2}^{\theta_3} C_v \, d\theta = C_v(\theta_3 - \theta_2) > 0$$

$4 \to 1$)

$$|Q_c| = \int_{\theta_4}^{\theta_1} C_v \, d\theta = C_v(\theta_1 - \theta_4) < 0$$

Thus:

$$\eta = 1 - \left|\frac{Q_c}{Q_H}\right| = 1 - \left|\frac{\theta_4 - \theta_1}{\theta_3 - \theta_2}\right| = 1 - \frac{\theta_4 - \theta_1}{\theta_3 - \theta_2}$$

The temperatures are found from the <u>ad</u> processes $1 \to 2$ & $3 \to 4$ $(V_4 = V_1, V_3 = V_2)$

$$a) \begin{cases} \theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1} \\ \theta_3 V_2^{\gamma-1} = \theta_4 V_1^{\gamma-1} \end{cases} \Rightarrow (\theta_1 - \theta_4) V_1^{\gamma-1} = (\theta_3 - \theta_2) V_2^{\gamma-1}$$

$$a) \Rightarrow \frac{\theta_1 - \theta_4}{\theta_3 - \theta_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

Thus

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r^{\gamma-1}} \ ; \ r \to \text{compression ratio}; \ r = \frac{V_1}{V_2}$$

Considering $r \simeq 9$ ($r = 10$ implies preignition), $\gamma \approx 1.5$ (1.4)

$$\eta = 1 - \frac{1}{\sqrt{9}} = 1 - \frac{1}{3} = \frac{3-1}{3} = \frac{2}{3} \simeq 67\%$$

§ AIR STANDARD DIESEL ENGINE (pg 143)

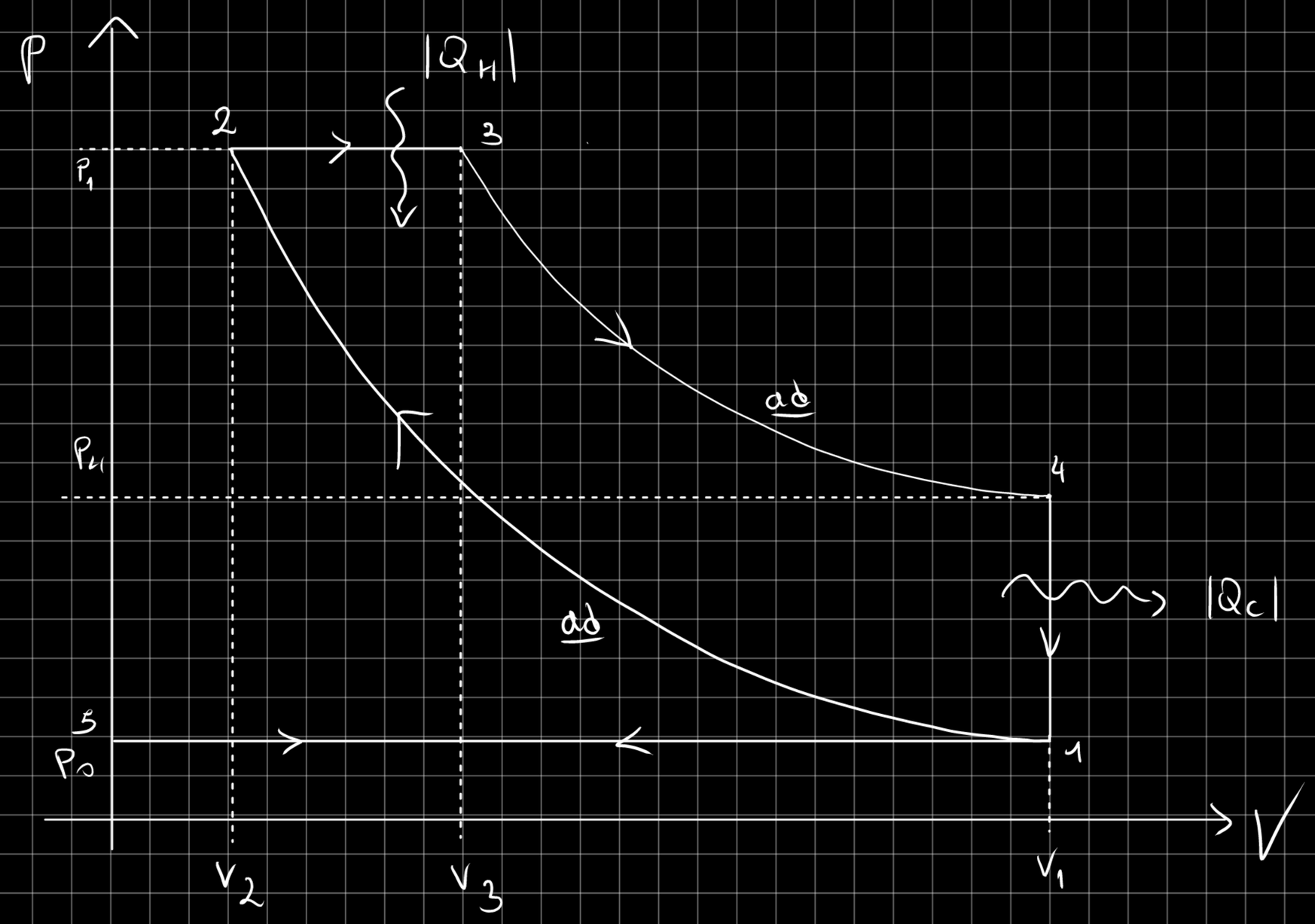


Fig. (Diesel) Air-standard diesel cycle

5→1) Air intake (isobaric expansion, $0 \to V_1$, $0 \to n$)

1→2) adiabatic compression until combustion ($P_0 \to P_1$, $V_1 \to V_2$)

2→3) isobaric increase of temperature ($V_2 \to V_3$) $|Q_H|$

3→4) adiabatic expansion ($P_1 \to P_4$, $V_3 \to V_1$)

4→1) isochoric decrease of temperature ($P_4 \to P_0$) $|Q_c|$

4→5) exhaust ($V_1 \to 0$, $n \to 0$)

ex.: find η

-) $\eta = 1 - \left|\frac{Q_c}{Q_H}\right|$

1) $đQ \neq 0$ in only 2→3, 4→1. $đQ \simeq C_v d\theta$

$$\therefore |Q_H| = C_v \left| \int_{\theta_2}^{\theta_3} d\theta \right| \quad ; \quad |Q_c| = C_v \left| \int_{\theta_1}^{\theta_4} d\theta \right|$$

2) 1→2) change of temperature $\theta_1 \to \theta_2$, 3→4) cost $\theta_3 \to \theta_4$

$$\begin{cases} P_0 V_1^{\gamma} = P_1 V_2^{\gamma} \\ P_1 V_3^{\gamma} = P_4 V_1^{\gamma} \end{cases} \qquad \left.\begin{cases} P_0 V_1 = nR\theta_1 \Rightarrow P_0 = \frac{nR}{V_1}\theta_1 \\ P_1 V_2 = nR\theta_2 \Rightarrow P_1 = \frac{nR}{V_2}\theta_2 \end{cases}\right\} \theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1}$$

$$\begin{cases} P_1 V_3 = nR\theta_3 \\ P_4 V_1 = nR\theta_4 \end{cases} \quad \left.\begin{cases} P_1 = nR\theta_3/V_3 \\ P_4 = nR\theta_4/V_1 \end{cases}\right\} \therefore \theta_3 V_3^{\gamma-1} = \theta_4 V_4^{\gamma-1}$$

3) $|Q_H| = C_V|\theta_3 - \theta_2|$, $|Q_C| = C_V|\theta_4 - \theta_1|$

$$\begin{cases} \theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1} \\ \theta_3 V_3^{\gamma-1} = \theta_4 V_1^{\gamma-1} \end{cases} ; \quad \eta = 1 - \left|\frac{Q_C}{Q_H}\right| = 1 - \frac{\theta_4 - \theta_1}{\theta_3 - \theta_2}$$

<u>Def</u> : $r_E = \frac{V_1}{V_3}$, $r_C = \frac{V_1}{V_2}$ (expansion / compression ratios)

$$\begin{cases} \theta_1 r_C^{\gamma-1} = \theta_2 \\ \theta_4 r_E^{\gamma-1} = \theta_3 \end{cases} \Rightarrow \theta_4 r_E^{\gamma-1} - \theta_1 r_C^{\gamma-1} = \theta_3 - \theta_2$$

maybe? "It is a simple matter"
Cit. M.W. Zemansky pg 145

F) $$\eta = 1 - \frac{1}{\gamma} \frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}}$$

In Diesel engines there's no fuel for preignition, therefore $r_C > 9$. Then for, for a diesel engine

$$r_C = 15 , \quad r_E = 5 , \quad \gamma = \frac{3}{2}$$

$$\therefore \eta = 1 - \frac{2}{3}\left(\frac{5^{-\frac{3}{2}} - 15^{-\frac{3}{2}}}{1/5 - 1/15}\right) \simeq 1 - 5(0.0895 - 0.0172) \simeq 64\%$$

Diesel engines are 4-stroke engines (4 piston strokes as in fig P)

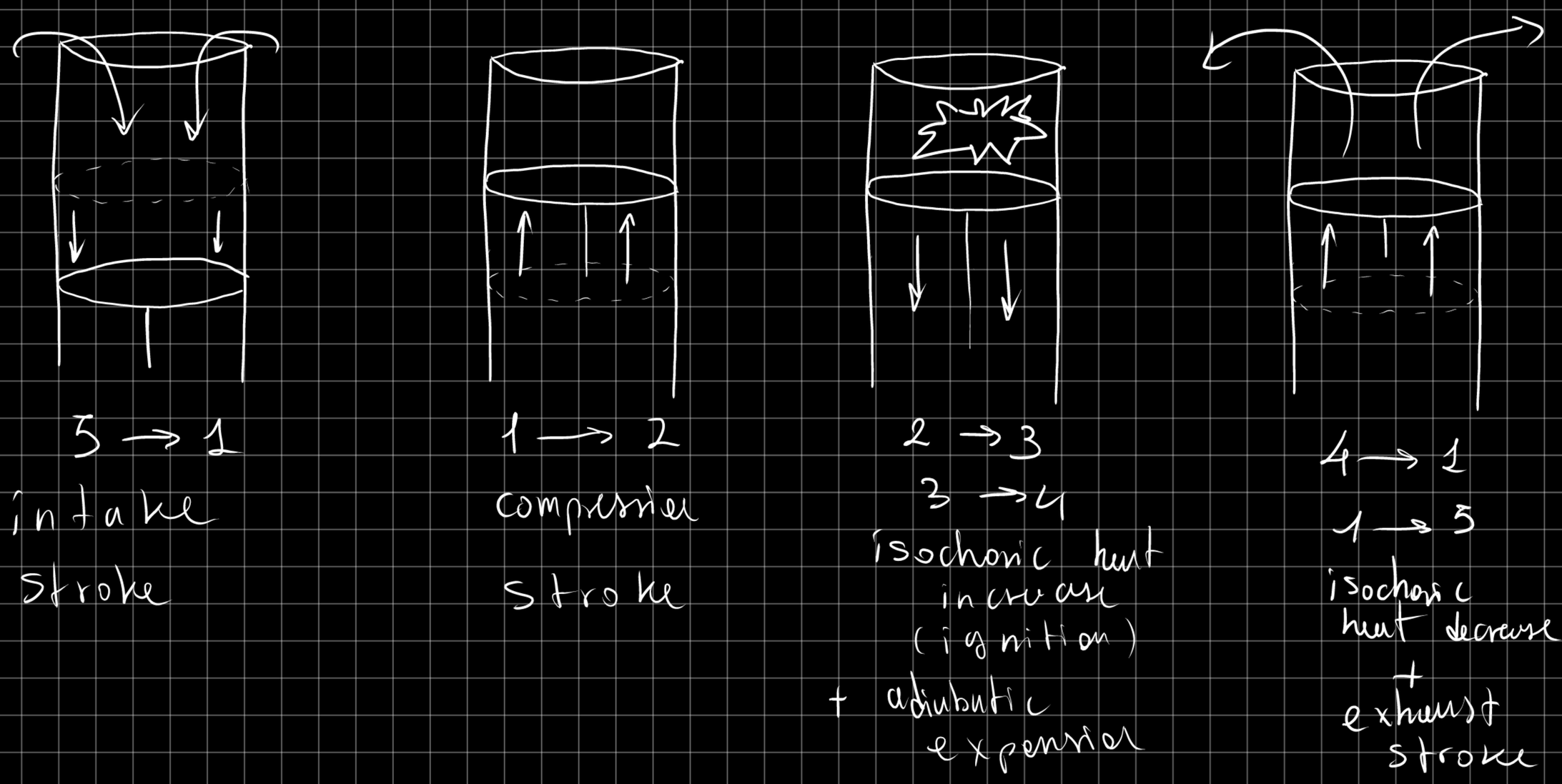


Fig. P) 4 piston movements of the diesel engine + cycle paths.

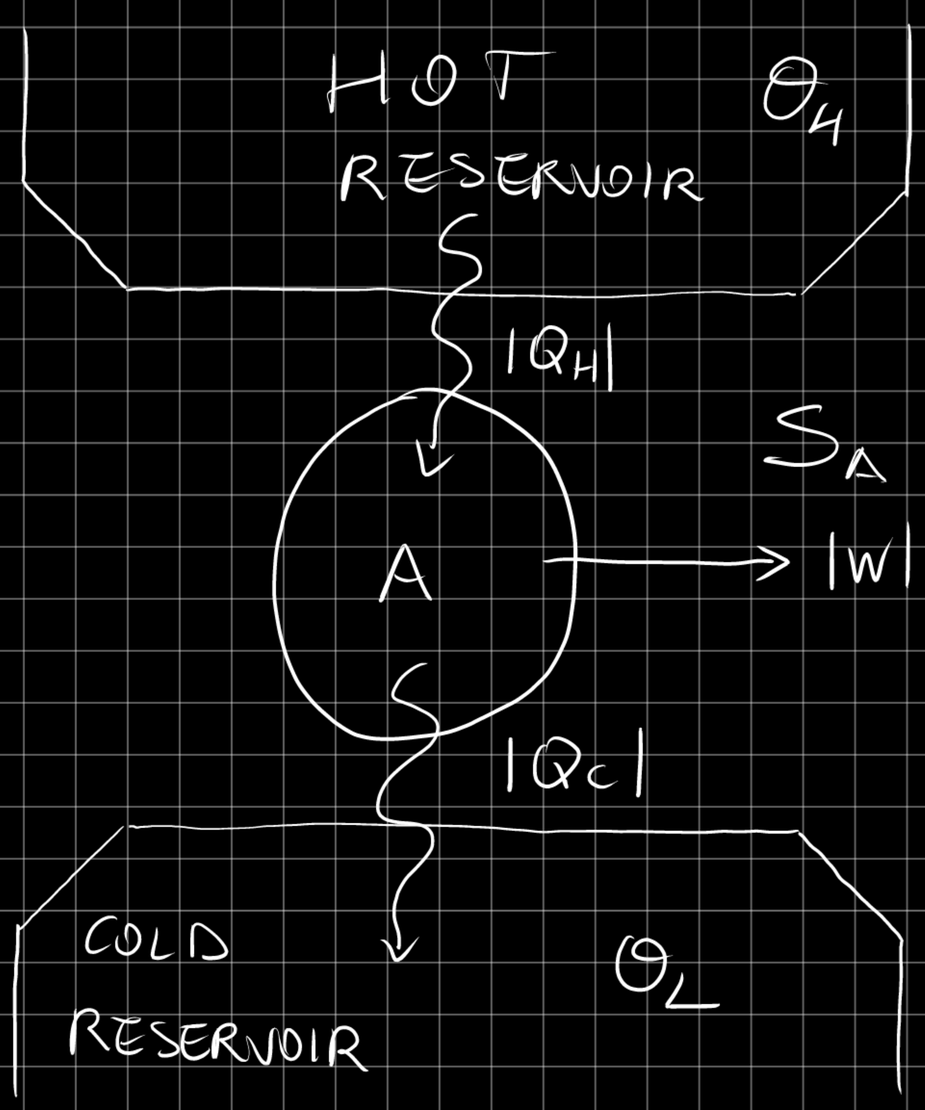
Note that only 1 is a power stroke. Since it uses only air it's possible to build a 2 stroke engine with 2 power strokes

§ II LAW OF THERMODYNAMICS

§§ Kelvin-Plank statement of the law

From heat engines we can deduce that:

1) There's an absorption of heat from a (hot) reservoir (θ_H)
2) There's a heat emission to a cold reservoir (θ_L)
3) Work is delivered to the surroundings



N.B:

$$\underline{đQ = dU - đW}$$

Ist law (conservation of energy)

Fig IIa) Schematization of thermodynamic heat conversion into work

Everything that has been found in experiment can be resumed into the following statement

Statement (Kelvin-Planck)

No process is possible with a result of only absorbing heat and converting it into work (without emitting heat)

Perpetual motion machines:

first kind: creates its own energy

Second kind: uses energy from only one heat reservoir

§ REFRIGERATOR

Heat engine:

1) Heat is absorbed @ θ_H (Q_H), 2) $Q_C < Q_H$ is emitted @ θ_L, 3) W is done to surroundings

Opposite cycle → Absorption higher @ θ_C & emission @ θ_H + W {REFRIGERATOR}

A Stirling cycle can be reversed

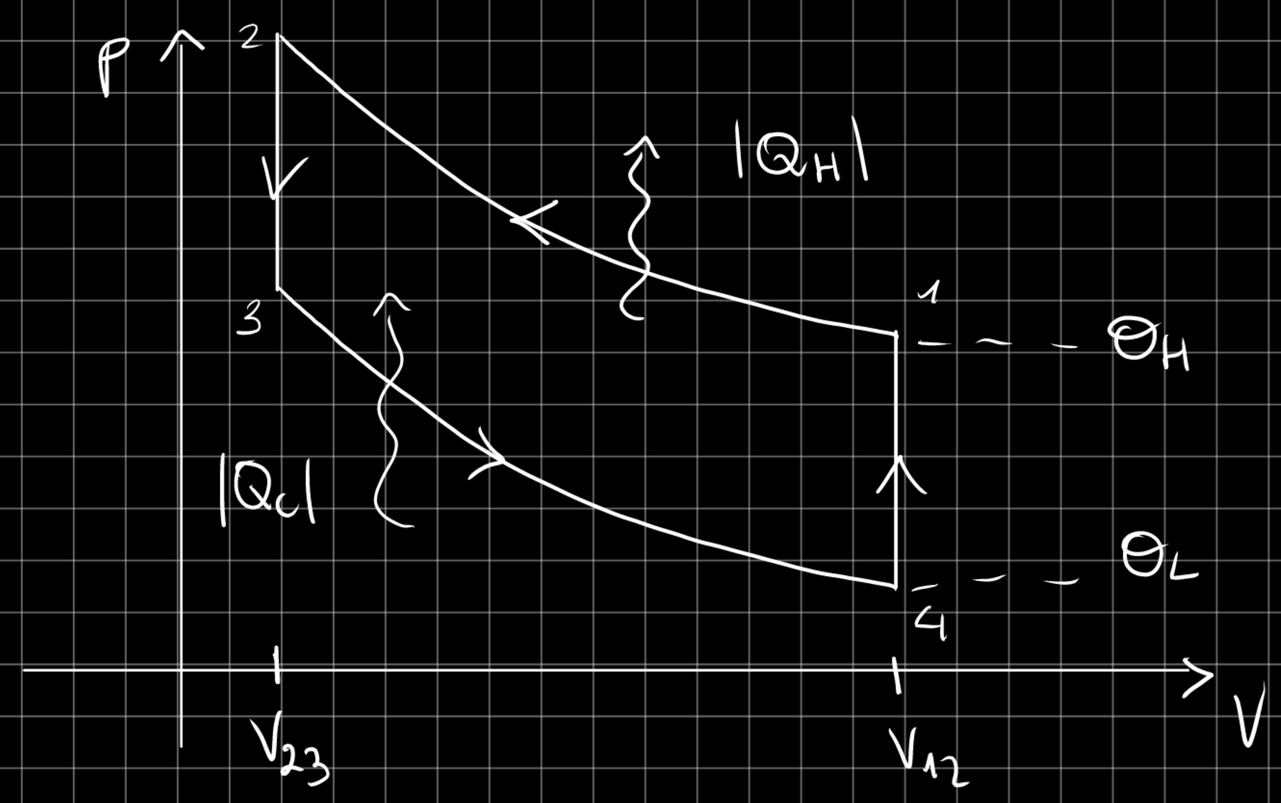


Fig SR) Stirling refrigerator cycle

1 → 2) Isothermal compression @ Θ_H, emission of $|Q_H|$ from hot reservoir
2 → 3) Isochoric cooling (real emits $|Q_R|$ to regenerator)
3 → 4) Isothermal expansion @ Θ_L, absorption of $|Q_c|$ from cold reservoir

Efficient ⟶ cooling from 90K to 12K (at the time of writing)

The efficiency of a refrigerator is measured w/ the coefficient of performance (ω)

$$\omega = \left|\frac{Q_c}{W}\right|$$

Note that $|W| = |Q_c - Q_H|$, therefore

$$\omega = \frac{|Q_c|}{|Q_c| - |Q_H|}$$

e.g. for $\omega = 5$, we have

$$\begin{cases} \omega = \left|\frac{Q_c}{W}\right| = 5 \\ |Q_c| = |Q_H| - |W| \end{cases} \Rightarrow \omega = \frac{|Q_H| - |W|}{|W|} = \left|\frac{Q_H}{W}\right| - 1 = 5$$

$$\therefore \left|\frac{Q_H}{W}\right| = 6$$

Therefore $|Q_H| = 6|W|$ & $|Q_c| = 5|W|$. Commercially, $2 \leq \omega \leq 7$

→ Work is always necessary to transfer heat from $|Q_c|$ to $|Q_H|$

The schematics of refrigerator are in fig. R5

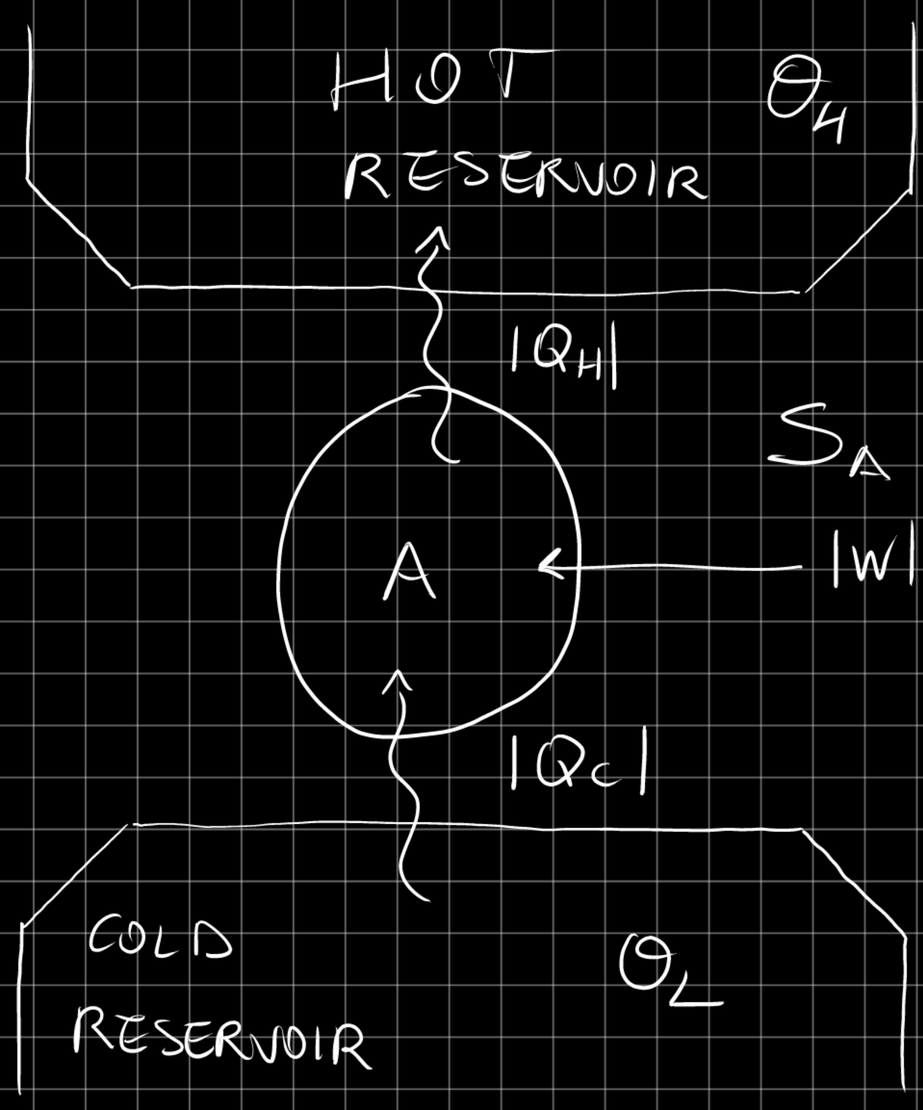


Fig R5) Refrigerator scheme. Note the inversion of work from "done to" to "done from"

The negative statement was given by Kelvin:

Statement (Clausius)

There exist NO process whose result is ONLY transferring heat from a hot to a cold reservoir.

The KP & C statements are identical

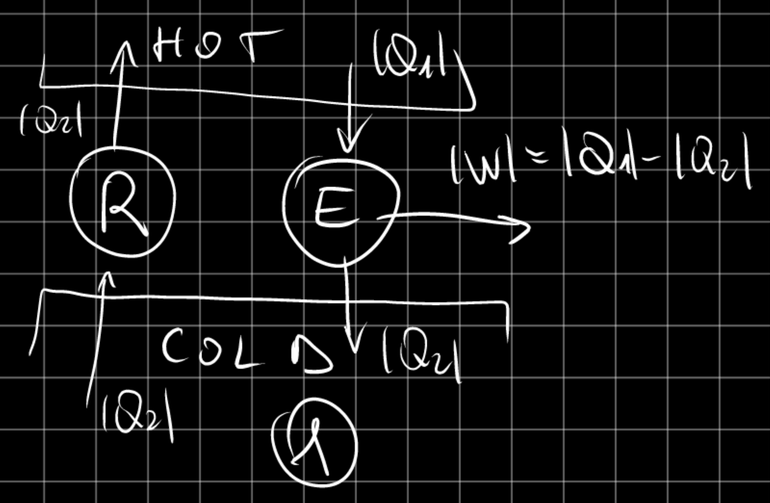
1) Consider a refrigerator for which $W = 0$ (violates Clausius) that transfers $|Q_2|$ from a cold to a hot reservoir.

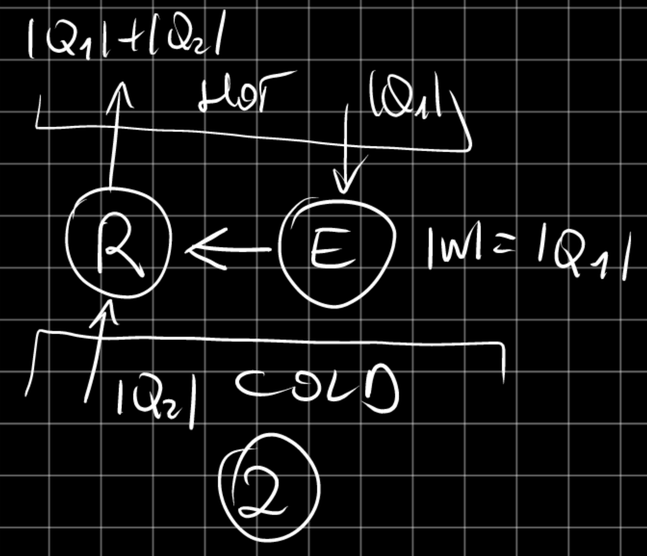
Suppose that a heat engine transfers $|Q_2|$ back to the cold reservoir (Kelvin-Planck)

Together E_1, E_2 in reality take $|Q| = |Q_1 - Q_2|$ & convert it all into work! ($\neg$KP, $\neg$C)

2) Suppose instead that we have a heat engine for which $|Q_C| = 0$ ($\neg$KP). Suppose that a refrigerator takes all the work b/w hot & cold (C). Together they make a perpetual machine that takes Q_2 from cold to hot w/ no work.

Scheme:





Therefore:

Clausius $\equiv$ Kelvin-Planck (Ex + Ch 7 p. 158)

REVERSIBILITY & ABSOLUTE TEMPERATURE

<u>Def</u> (Local & Auxiliary surroundings)

-) Local surroundings: part of surrounding that interact directly w/ system

-) Auxiliary surroundings: the opposite

<u>Def</u> (Reversibility)

Consider a process from a state A to a state B.
If in $A \to B$ Q heat is transferred & W is made, if in going $B \to A$ we have a transfer $-Q$ & $-W$ work, the process is <<reversible>>

i.e.: A process is reversible iff it can be performed two ways, returning to an initial state without producing changes @ Ω

§ MECHANICAL IRREVERSIBILITY

§§ EXTERNAL IRREVERSIBILITY

Consider isothermal work transformations as:

-) Irregular stirring of viscous fluid in contact w/ a reservoir
-) Coming to a rest of a rotating / vibrating liquid in contact w/ reservoir
-) Inelastic deformation of a solid in contact w/ reservoir
-) Magnetic hysteresis of a material in contact w/ reservoir.

For a <u>complete</u> restoration to the initial state, Q heat must be extracted from the reservoir & completely converted into work

$\to$ Violation of Kelvin-Planck

$\therefore$ Irreversible process

If the same processes are in a thermally insulated container, then there's a rise of θ, $\therefore dU \neq 0$. For returning to initial θ all heat $Q = \Delta U$ must be converted to work

$\to$ Violation of Kelvin-Planck

All here processes exhibit dissipative effects are irreversible.
If work is dissipated into internal energy

$\longrightarrow$ EXTERNAL MECHANICAL IRREVERSIBILITY

§ INTERNAL IRREVERSIBILITY

INTERNAL ENERGY → MECHANICAL ENERGY → INTERNAL ENERGY

e.g.

- Free expansion
- Gas seeping through porous plug (throttling)
- Snapping of a stretched wire
- Soap film collapse

Take free expansion:

No interaction → No load surroundings

Change of state of the gas $(V_i, \theta) \longrightarrow (V_f, \theta)$. For a restoration → isothermal compression to volume V_i:

1) No friction (quasi-static) → Work from external machine
2) Since $W > 0$, $Q < 0$ & $Q = -W$ ↯

→ VIOLATION OF KELVIN-PLANCK

§ THERMAL IRREVERSIBILITY

Consider a finite transfer of heat b/w system & reservoir @ temp. difference $\Delta\theta$

1) Conduction of heat from system to a reservoir w/ $\theta_r < \theta_s$
2) Conduction or radiation of heat through a system (unchanged) from R_1 to R_2 w/ $\theta_{R_1} < \theta_{R_2}$

For reversibility, heat must be transferred w/ a self-acting device from θ_c to θ_H

→ Violation of Clausius

∴ EXTERNAL THERMAL IRREVERSIBILITY

INTERNAL ⇔ if b/w system due to temperature non-uniformity.

§ CHEMICAL IRREVERSIBILITY

SPONTANEOUS CHANGES OF STRUCTURE

1) All chemical reactions $(A + B \rightarrow C)$
2) Mixing of substances: diffusion of 2 inert gases, water + alcohol mixing
3) Sudden phase change: Freezing supercooled liquid, condensation of supersaturated vapor
4) Transportation of matter b/w different phases: Osmosis, solution

→ ALL CHEMICALLY IRREVERSIBLE

→ ALL NATURAL SPONTANEOUS PROCESSES ARE IRREVERSIBLE

- violation of thermodynamical equilibrium
- Presence of dissipative phenomena

§ REVERSIBILITY

A process is reversible iff thermodynamical equilibrium is satisfied & dissipative phenomena are not present, i.e.:

1) It's quasi-static
2) No dissipative effects

} IDEAL

Approximation → huge reservoir

§ REVERSIBLE ADIABATIC SURFACES (6th, check 7th (pdf))

[CARNOT CYCLES & ABSOLUTE TEMPERATURE]

§ CARNOT CYCLE

Ideal simple cycle, for which:

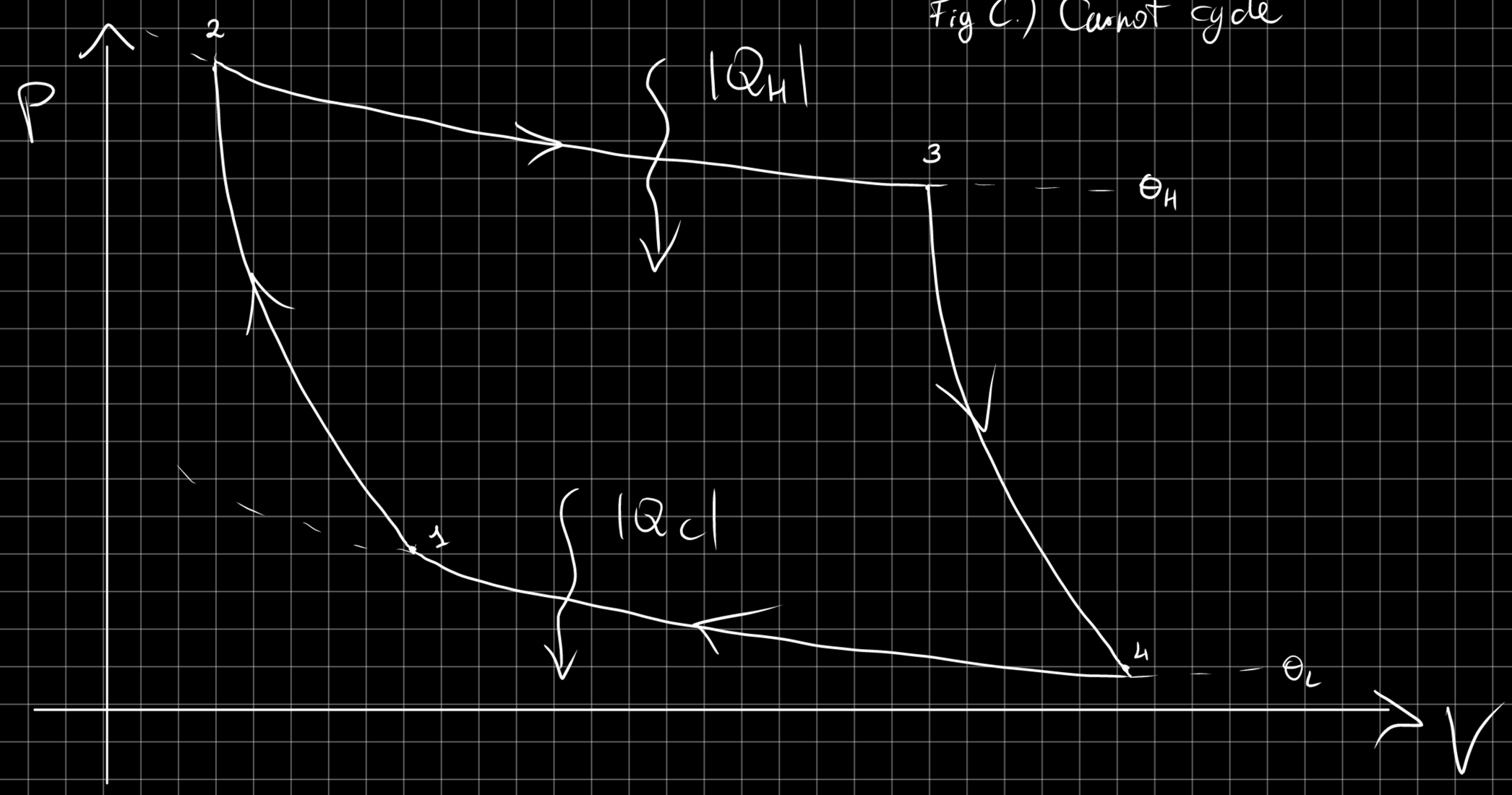
1) All reversible:

1→2) Adiabatic compression from θ_L to θ_H
2→3) Isothermal heat absorption
3→4) Adiabatic expansion from θ_H to θ_L
4→1) Isothermal heat emission at θ_L

All processes reversible; ∴ reversible cycle

e.g.

Fig C.) Carnot cycle

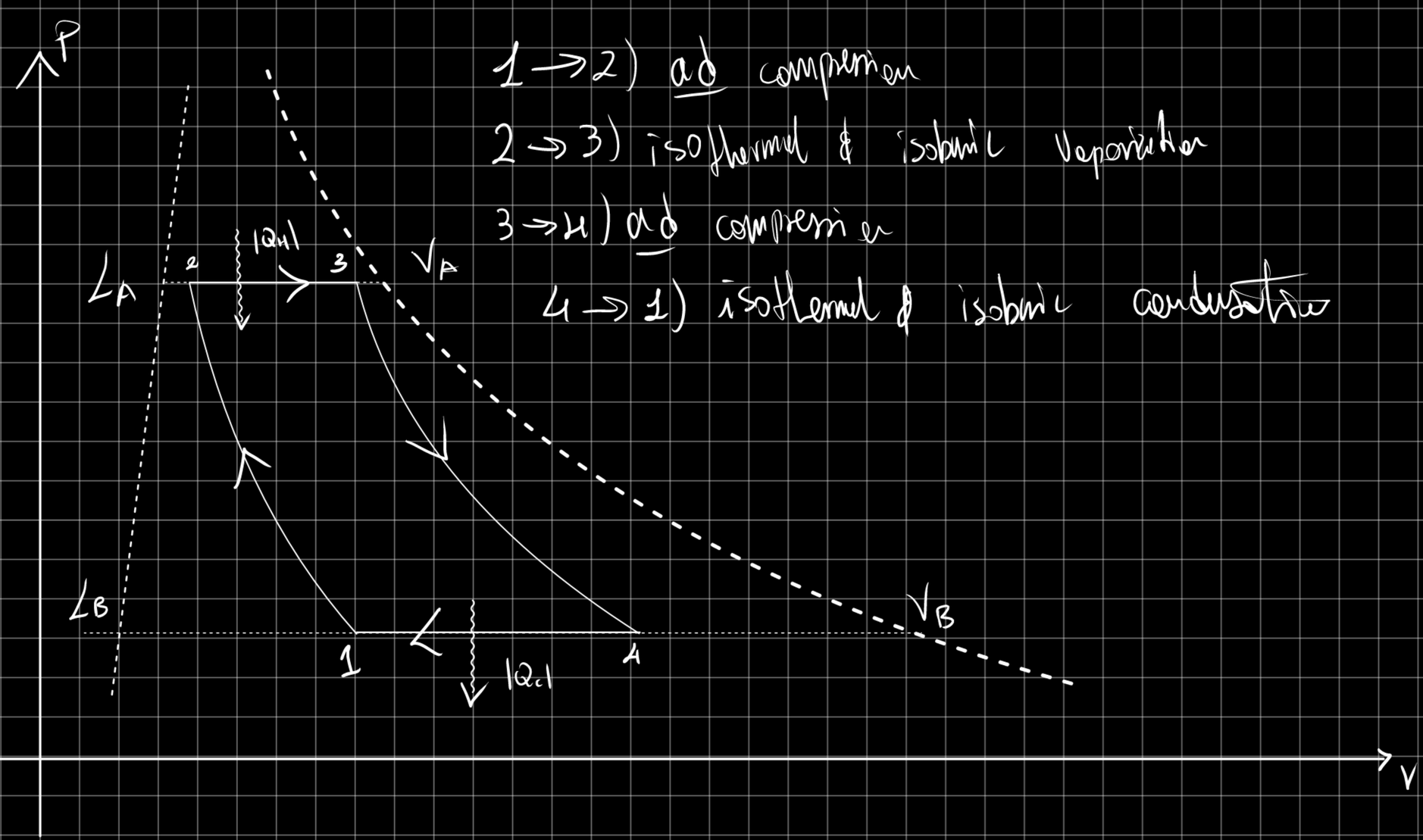


Due to the total reversibility, it's possible to revert the cycle & obtain a Carnot refrigerator

Note that:

$$|Q_H| = |Q_H^R|, \quad |Q_c| = |Q_c^R|, \quad |W| = |W^R|$$

For water, a bi-fasic Carnot cycle (water-steam) has a different shape following the saturation values of (p, V, θ)



1 → 2) ad compression
2 → 3) isothermal & isobaric vaporization
3 → 4) ad compression
4 → 1) isothermal & isobaric condensation

Fig WC) Water Carnot cycle, $L_A V_A$ → isoth/isob vaporization line, $L_B V_B$ → isoth/isob condensation
During vaporization $|Q_H|$ is absorbed from the hot reservoir & during condensation $|Q_c|$ gets emitted to the cold reservoir

CARNOT THEOREM

THM (CARNOT)
No heat engine has a higher efficiency than the Carnot equivalent

Proof.
Take a Carnot engine R & an irreversible engine I we have
R, I, absorb $|Q_H|$, $|Q_H'|$ from hot reservoir
R, I, perform work $|W|$
R, I, emit $|Q_H| - |W|$, $|Q_H'| - |W|$ from cold reservoir

$$\eta_R = \left|\frac{W}{Q_H}\right|, \quad \eta_I = \left|\frac{W}{Q_H'}\right|$$

Assume that $\eta_I > \eta_R$, thus

$$|Q_H| > |Q_H'|$$

Reverse the Carnot engine, and take the work exerted by I, thus:

$$(|Q_H| - |W|) - (|Q_H'| - |W|) = |Q_H| - |Q_H'| > 0$$

But the heat delivered to the hot reservoir is $|Q_H| - |Q_H'|$ $\Rightarrow$ <u>Thus</u>:

$$\eta_I \leq \eta_R$$

<u>Corollary</u>

All Carnot engines b/w two equal reservoir have the same η

Taken R_1 & R_2 2 Carnot engines we have that:

-) If R_1 drives R_2 backwards

$$\eta_{R_1} \leq \eta_{R_2}$$

-) If R_2 drives R_1 backwards

$$\eta_{R_2} \geq \eta_{R_1}$$

Thus:

$$\eta_{R_1} = \eta_{R_2}$$

§ ABSOLUTE TEMPERATURE SCALE

0th law $\rightarrow$ measurement of temperature (relative)

II th law $\rightarrow$ ABSOLUTE temperature

Using Carnot's theorem, which indicates that η is independent from the substance used we have that if T indicates the absolute temperature, that the cycle goes b/w two reservoirs @ $T_H > T_L$, & gets $|Q_H|$ ($|Q_C|$) absorbed (emitted) w/ efficiency η_R

$$\eta_R = 1 - \left|\frac{Q_L}{Q_H}\right|$$

By definition, we have then that

$$\eta_R = \mathcal{F}(T_H, T_L)$$

Therefore, we can write

$$\left|\frac{Q_H}{Q_L}\right| = \frac{1}{1-\eta_{\phi}(T_H,T_L)} = f(T_H,T_L)$$

Thus taking 3 Carnot engines working bw/ $T_1 > T_3 > T_2$, we have

$$\left|\frac{Q_1}{Q_2}\right| = f(T_1,T_2)$$

$$\left|\frac{Q_1}{Q_3}\right| = f(T_1,T_3)$$

$$\left|\frac{Q_3}{Q_2}\right| = f(T_3,T_2)$$

$$\therefore f(T_1,T_2) = \frac{f(T_1,T_3)}{f(T_2,T_3)}$$

$$\Rightarrow \left|\frac{Q_1}{Q_2}\right| = \frac{\psi(T_1)}{\psi(T_2)} = \frac{T_1}{T_2}$$

Were ψ is a random function. Thus we define the ratio of temperatures as the ratio of heat emitted / absorbed by a Carnot engine bw/ reservoirs @ same temperature.

The defined scale is the <<ABSOLUTE SCALE>> (measured in K (SI) or Ra (imp)). By def:

$$T_{TP} = 273.16\ K$$

Thus:

$$\left|\frac{Q}{Q_{TP}}\right| = \frac{T}{T_P}$$

$$\therefore T = 273.16\ K \left|\frac{Q}{Q_{TP}}\right|$$

Note that

$$\Theta = 273.16\ K \lim_{P_{TP}\to 0}\left(\frac{P}{P_{TP}}\right)$$

Therefore Q becomes a "thermodynamic prop." of the Carnot cycle, & it's independent from the substance use.

Note that, by this definition

$$\left|\frac{Q_L}{Q_H}\right| = \left|\frac{T_L}{T_H}\right|$$

$$\Rightarrow \eta_R = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H}$$

Note also that $\eta_R = 100\% \Rightarrow T_L = 0$ (!)

§ EQUALITY OF IDEAL-GAS & ABSOLUTE TEMP

For a carnot cycle bw/ $\theta = \theta_1$, $\theta = \theta_2$, we have

$$\begin{cases} pV = nR\theta_1 \\ pV = nR\theta_2 \end{cases}$$

For the Ist law

$$đQ = C_V d\theta + p dV \Rightarrow |Q| = \int_{\Delta V} p dV = nR\theta \int_{\Delta V} d\log|V|$$

$$\Rightarrow |Q_1| = nR\theta_1 \log\left|\frac{V_3}{V_2}\right| \quad , |Q_2| = nR\theta_2 \log\left|\frac{V_4}{V_1}\right|$$

Therefore

$$\left|\frac{Q_1}{Q_2}\right| = \frac{\theta_1}{\theta_2} \frac{\log(V_3/V_2)}{\log(V_4/V_1)}$$

Note that also, going from $\theta_1 \to \theta_2$ $đQ = 0$, therefore

$$p dV = nR\theta \, d\log(V) = -C_V d\theta$$

Thus:

$$p dV = -C_V d\theta$$

$$nR\theta \, d\log(V) = -C_V d\theta$$

$$\int d\log(V) = -\frac{C_V}{nR} \int d\log\theta$$

Thus

$$\begin{cases} \log\left(\frac{V_2}{V_1}\right) = \log\left(\frac{V_3}{V_4}\right) \\ \log\left(\frac{V_3}{V_2}\right) = \log\left(\frac{V_4}{V_1}\right) \end{cases}$$

$$\therefore \quad \left|\frac{Q_1}{Q_2}\right| = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \quad \blacksquare$$

$$\{\underline{\theta = T}\}$$

SECOND PRINCIPLE OF THERMODYNAMICS

§ KARATHEODORIS FORMULATION

The mathematical formulation of the IInd principle comes from the Greek mathematician Karathéodoris.

AXIOM

In a neighborhood of an equilibrium state of any number of thermodynamic coordinates there exist states which are inaccessible by REVERSIBLE ADIABATIC PROCESSES (can be derived from KP)

Consider

-) temperature t

-) gen displacement x

-) gen. force y

Then, the first law can be written as

$$đQ = dU - y\,dx$$

If there's an equation of state $f(x,y,t)=0$, then only 2 coords are independent. Said (x,t) the two ind. coordinates, we have $U \equiv U(x,t)$

$$dU = \left(\frac{\partial U}{\partial x}\right)_t dx + \left(\frac{\partial U}{\partial t}\right)_x dt$$

Thus

$$đQ = \left(\frac{\partial U}{\partial x}\right)_t dx + \left(\frac{\partial U}{\partial t}\right)_x dt - y\,dx$$

$$đQ = \left(\frac{\partial U}{\partial t}\right)_x dt + \left[\left(\frac{\partial U}{\partial x}\right)_t - y\right] dx$$

For a reversible adiabatic process

$$đQ = 0$$

$$\therefore \left(\frac{\partial U}{\partial t}\right)_x dt + \left[\left(\frac{\partial U}{\partial x}\right)_t - y\right] dx = 0$$

$$\hookrightarrow \left(\frac{\partial U}{\partial t}\right)_x \frac{dt}{dx} + \left[\left(\frac{\partial U}{\partial x}\right)_t - y\right] = 0$$

Solving for $\frac{dt}{dx}$

$$\frac{dt}{dx} = \left(\frac{\partial U}{\partial t}\right)_x^{-1} \left[y - \left(\frac{\partial U}{\partial x}\right)_t\right]$$

$$\frac{dt}{dx} = \frac{y - (\partial_x U)_t}{(\partial_t U)_x} \Leftarrow \text{only for } đQ = 0 \text{ (ad)}$$

The solutions for $\frac{dt}{dx}$ are the surfaces $\sigma(x,t) = k \in \mathbb{R}$, aka <<adiabatic rev. surfaces>>

Follows directly from the Ist law; for the IInd law we have that <u>All</u> <u>ad</u> rev processes lie

on <u>NON</u> intersecting surfaces $\sigma(x,t)$

Consider a second force y' & second displacement x', where

$$đQ = dU - y\,dx - y'\,dx'$$

Since we have 2 gen forces & displacements, we have 2 EOS

$$\begin{cases} f_1(x,y,t) = 0 \\ f_2(x',y',t) = 0 \end{cases}$$

Thus, only <u>3</u> coordinates are independent, say (x, x', U). Said A an eq state and B an eq. state reachable via a rev. <u>ad</u> process. ⊛ C has the same (x, x') coords of B

Take a third state $C^{⊛}$, and suppose that there's a possible <u>ad</u> <u>rev</u>. process to reach both B & C, i.e.

$$A \xleftrightarrow{ad} B \xleftrightarrow{ad} C$$

Suppose that the process pass through the following cycle

$$\begin{tikzcd} & B \arrow[dl, bend right, "ad"'] \arrow[dd, bend left, "ad"] \\ A \arrow[ur, bend right, "ad"'] \arrow[dr, bend right, "ad"'] & \\ & C \end{tikzcd}$$

Since C has the same coordinates of B, we have that $W = 0$, $\Delta U \neq 0$. From the first law we must have $Q \neq 0$, but since the process is <u>ad</u> it's $W \neq 0$, $Q = 0$!

Due to the reversibility of the ABC cycle we must have that on the full cycle

$$\Delta U_{ABC} = 0$$

$$\therefore Q_{ABC} = W_{ABC} \lightning$$

Thus the cycle violates KP $\Rightarrow$ C is inaccessible through an <u>ad</u> rev process, & the set of accessible processes $\{\sigma(x,t)\} = \mathcal{L}_s$ has $\dim\{\mathcal{L}_s\} < 3 = \dim(\Omega)$, by def, if $\dim\{\Omega\} = n$ (number of ind. coords) we have $\dim\{\mathcal{L}_s\} = n-1$, and all surfaces $\sigma(x,x',t)$ <u>DO NOT</u> <u>INTERSECT</u>

§ INTEGRABILITY OF đQ

Consider again

$$đQ = dU - y\,dx - y'\,dx'$$

where $U \equiv U(x,x',t)$, $y \equiv y(x,x',t)$, $y' \equiv y'(x,x',t)$

Since $\Omega = \text{span}\{\langle x, x', t\rangle\}$ & it's subdivided in surfaces

$$\sigma(x,x',t) = k \in \mathbb{R}$$

We might indicate every point in Ω using (x, x', σ); thus

$$dU(x,x',\sigma) = \left(\frac{\partial U}{\partial x}\right)_{x',\sigma} dx + \left(\frac{\partial U}{\partial x'}\right)_{x,\sigma} dx' + \left(\frac{\partial U}{\partial \sigma}\right)_{x,x'} d\sigma$$

Thus:

$$đQ = \left(\frac{\partial U}{\partial x}\right)_{x'\sigma} dx + \left(\frac{\partial U}{\partial x'}\right)_{x\sigma} dx' + \left(\frac{\partial U}{\partial \sigma}\right)_{xx'} d\sigma - y\,dx - y'\,dx'$$

$$đQ = \left(\frac{\partial U}{\partial \sigma}\right)_{xx'} d\sigma + \left[\left(\frac{\partial U}{\partial x}\right)_{x'\sigma} - y\right] dx + \left[\left(\frac{\partial U}{\partial x'}\right)_{x\sigma} - y'\right] dx'$$

1) $d\sigma = dx = 0$, $dx' \neq 0$, therefore

$$đQ = \left[\left(\frac{\partial U}{\partial x'}\right)_{x\sigma} - y'\right] dx' = 0$$

$$\therefore \left(\frac{\partial U}{\partial x'}\right)_{x\sigma} = y'$$

2) $d\sigma = dx' = 0$, $dx \neq 0$ imply

$$\left(\frac{\partial U}{\partial x}\right)_{x'\sigma} = y$$

Therefore, if $đQ = 0$ we must have $d\sigma = 0$, & $đQ$ becomes

$$đQ = \left(\frac{\partial U}{\partial \sigma}\right)_{xx'} d\sigma$$

Said $\lambda = \partial_\sigma U$, we have

$$đQ = \lambda(x, x', \sigma)\, d\sigma$$

By definition $d\sigma$ is exact ($\sigma = \int d\sigma$), i.e.

$$\omega = \frac{1}{\lambda} đQ$$

<u>IS INTEGRABLE</u> (λ is an integrating factor for $đQ$)

Consider now 2 adiabatic rev. surfaces σ, $\sigma + d\sigma$. We have that each process connecting these has the same change of σ ($d\sigma$), but different values of λ, because $\lambda \equiv \lambda(\sigma, x, t)$.
For finding the temperature dependence of λ, we consider 2 system in contact w/ a heat reservoir @ temperature t & w/ eachother through a <u>dt</u> wall

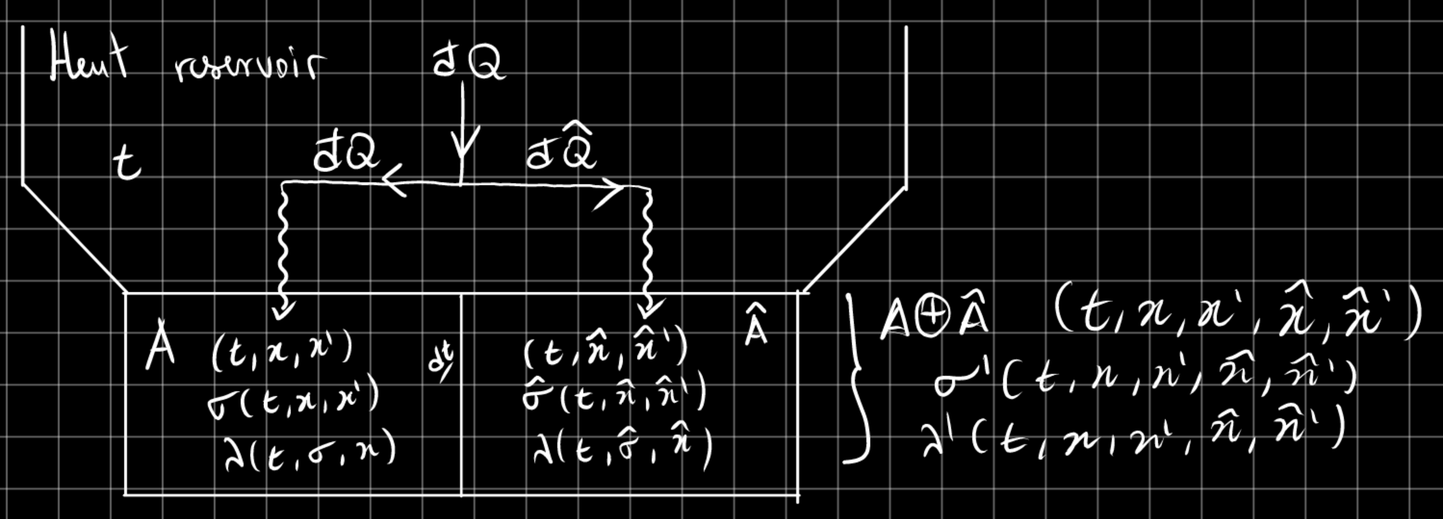


Fig Q) two systems: main (A), reference ($\hat{A}$) & heat reservoir in thermal equilibrium

The main system A & the reference system $\hat{A}$ constitute a coupled system in thermal w/ 5 dof
We have (next page)

A : $đQ$ heat absorption gives change $d\sigma$, with $đQ = \lambda d\sigma$

$\hat{A}$: $đ\hat{Q}$ absorption gives $d\hat{\sigma}$, where $đ\hat{Q} = \hat{\lambda} d\hat{\sigma}$

$A \oplus \hat{A}$: the composite adiabatic surfaces are defined by the function $\hat{\sigma}$ of the composite system

We have $đQ' = \lambda' d\sigma'$, where

$$d\sigma' = \frac{\partial \sigma'}{\partial t} dt + \frac{\partial \sigma'}{\partial x} dx + \frac{\partial \sigma'}{\partial x'} dx' + \frac{\partial \sigma'}{\partial \hat{\sigma}} d\hat{\sigma} + \frac{\partial \sigma'}{\partial \sigma} d\sigma \quad (1)$$

We also have

$$đQ' = đQ + đ\hat{Q} = \lambda d\sigma + \hat{\lambda} d\hat{\sigma} = \lambda' d\sigma'$$

Therefore :

$$d\sigma' = \frac{\lambda}{\lambda'} d\sigma + \frac{\hat{\lambda}}{\lambda'} d\hat{\sigma} \quad (2)$$

We must have then due to (1) & (2)

$$\frac{\partial \sigma'}{\partial t} = \frac{\partial \sigma}{\partial x} = \frac{\partial \sigma}{\partial x'} = 0$$

$$\therefore \begin{cases} \sigma' = \sigma'(\sigma, \hat{\sigma}) \\ \frac{\lambda}{\lambda'} = \frac{\partial \sigma'}{\partial \sigma}, \quad \frac{\hat{\lambda}}{\lambda'} = \frac{\partial \sigma'}{\partial \hat{\sigma}} \end{cases}$$

By definition then, since the ratios depend only on $(\sigma, \hat{\sigma})$, each separate $\lambda \equiv \lambda(t)$

$$\begin{cases} \lambda(t, \sigma) = \phi(t) f(\sigma) \\ \hat{\lambda}(t, \hat{\sigma}) = \phi(t) \hat{f}(\hat{\sigma}) \\ \lambda'(t, \sigma, \hat{\sigma}) = \phi(t) g(\sigma, \hat{\sigma}) \end{cases}$$

With $\phi(t)$ being an arbitrary continuous positive function of only temperature. Therefore

$$đQ = \phi(t) f(\sigma) d\sigma$$

Since $f(\sigma) d\sigma$ is exact, we must have that $\frac{1}{\phi(t)} đQ$ is exact, $\therefore \frac{1}{\phi(t)}$ is an integrating factor for $đQ$.

$\phi(t)$ is universal (!) thus we can define (again) an absolute temperature

§ ABSOLUTE TEMPERATURE II

Consider a system w/ (x, x', t) as independent coordinates. For an exchange of heat b/w the system & a reservoir, we have

$$Q = \phi(t) \int_{\sigma_1}^{\sigma_n} f(\sigma) d\sigma$$

For an isothermal process @ same temperature $t = t_3$ we have

$$Q_3 = \phi(t_3) \int_{[\sigma_1, \sigma_n]} f(\sigma) d\sigma$$

thus

$$\frac{Q}{Q_3} = \frac{\phi(t)}{\phi(t_3)} = \frac{T}{T_3}$$

when T is the Kelvin absolute temperature. Thus, the scale is independent from the system's prop.

If we say $T = T_{TP}$ of water, we can say

$$T_{TP} = 273.16\,K \implies T = 273.16\,\frac{Q}{Q_{TP}}\,K$$

ENTROPY

§ Concept of Entropy

We have seen that

$$đQ = \lambda d\sigma = \varphi(t) f(\sigma) d\sigma$$

Since, for what we have defined for the Kelvin scale

$$\frac{T}{T'} = \frac{đQ}{đQ'} \Rightarrow T \propto \varphi(t)$$

Thus:

$$\frac{1}{T} đQ = \frac{1}{K} f(\sigma) d\sigma, \quad K \in \mathbb{R}$$

We might then define a function S, such that

$$dS = \frac{1}{T} đQ = \frac{1}{K} f(\sigma) d\sigma \quad \{ Q \text{ is transferred REVERSIBLY } \}$$

The function S is known as «ENTROPY», and an entropy change is thus given by

$$\Delta S = \int_{\gamma_R} \frac{1}{T} đQ$$

When with γ_R we indicated a reversible process. Note that only entropy variations are defined (!) as for U

Note that, also, by definition of exact differential, on a reversible cycle η_R we have

$$S_{\eta_R} = \oint_{\eta_R} \frac{1}{T} đQ = \int_{\eta_R} dS = 0 \quad (\text{CLAUSIUS})$$

AKA «Clausius' theorem»

§ IDEAL GASES

With all this, we can say that, for a rev. process.

$$đQ = T dS$$

Plus, the 1st law becomes

$$đQ = c_p dT - V dp$$

$$\hookrightarrow dS = c_p d\log T - \frac{V}{T} dp$$

But

$$pV = nRT \Rightarrow T = \frac{pV}{nR}$$

$$\therefore \; dS = c_p d\log T - nR d\log p$$

And thus, for an ideal gas in a process $\gamma : (T_r, p_r) \to (T, p)$

$$\Delta S = C_p \log\left(\frac{T}{T_r}\right) - nR \log\left(\frac{p}{p_r}\right) \quad *$$

Said $\Delta S = S - S_r$, we have

$$S(p,T) = C_p \log(T) - nR \log(p) - \underbrace{\left(C_p \log(T_r) - nR \log(p_r) - S_r\right)}_{-S_0} \quad *$$

$$S(p,T) = C_p \log T - nR \log p + S_0 \quad *$$

Note that also:

$$đQ = C_v dT + p dV$$

$$\therefore \quad dS = C_v d\log T + nR\, d\log V$$

$$\Rightarrow S(V,T) = C_v \log T + nR \log V + S_0 \quad *$$

§ TS diagrams

We can use entropy as a coordinate itself, building TS diagrams, where we will have

$$Q = \int_{\gamma_R} T\, dS$$

In this plane, we have

1) Rev ad

$$đQ = T\, dS = 0 \Rightarrow dS = 0 \quad \{T \neq 0\}$$

Therefore

$$\boxed{S_{ad} = S_0}$$

2) Infinitesimal quasi static (non ad) process

$$đQ = T\, dS, \quad \frac{đQ}{dT} = T \frac{dS}{dT} \longrightarrow \begin{cases} đQ_V = C_V dT + p dV \\ đQ_p = C_p dT - V dp \end{cases} \begin{cases} dS_V = \frac{C_V}{T} dT + nR\, d\log V \\ dS_p = \frac{C_p}{T} dT - nR\, d\log p \end{cases}$$

$$\begin{cases} dS_V = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad * \\ dS_p = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \end{cases}$$

* IF C_p, C_V ARE CONSTANT

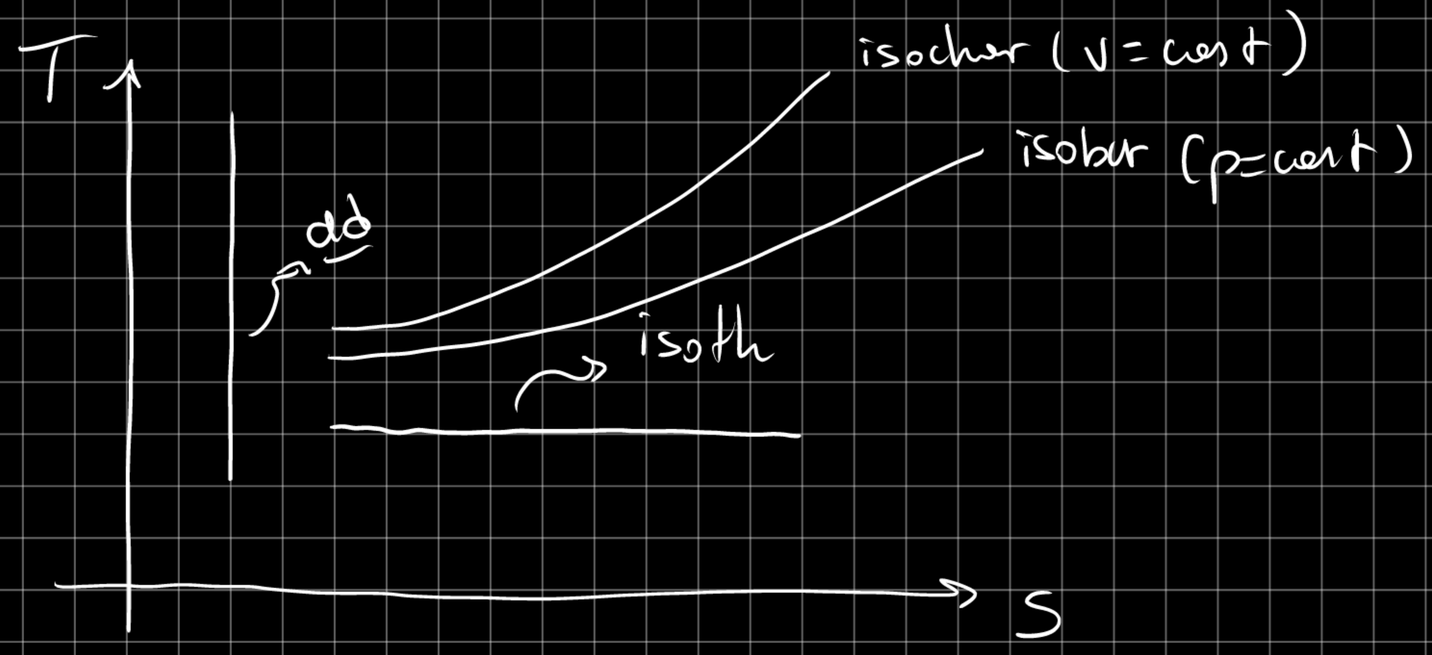
$$\therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}, \quad \frac{\partial S}{\partial V} = -\frac{\partial S}{\partial p} = nR$$

I.e. $C_p = T\left(\frac{\partial S}{\partial T}\right)_V$, $C_V = T\left(\frac{\partial S}{\partial T}\right)_p$

Note that:

ISOENTROPIC $\Longleftrightarrow$ ADIABATIC $\therefore S(p,V,T) = S_0$ (vertical)

ISOTHERMAL $\Rightarrow T(S) = T_0$ (horizontal)



Isobar & isochor processes are easily found noting that

1) Isobar $\Rightarrow dp = 0$, $dS_p = C_p \frac{dT}{T} - V\,dp = C_p \frac{dT}{T}$

$$S_p = C_p \int_A^B \frac{1}{T}\,dT = C_p \log\left(\frac{T_B}{T_A}\right) \quad \{C_p \text{ cost}\}$$

2) Isochor $\rightarrow dV = 0$, $dS_V = C_V \frac{dT}{T} + p\,dV = C_V \frac{dT}{T}$

$$S_V = C_V \int_A^B \frac{1}{T}\,dT = C_V \log\left(\frac{T_B}{T_A}\right) \quad \{C_V \text{ cost}\}$$

Note also that, $C_V < C_p$

For what we said, CARNOT CYCLES ARE ALL RECTANGULAR!

§ ENTROPY & REVERSIBILITY

Said A a system, Σ_A its surrounding, if we define the universe Ω as $\Omega = A \cup \Sigma_A$ we can define the entropy change of the universe as

$$dS_\Omega = dS_A + dS_{\Sigma_A}$$

if the surroundings are a heat reservoir, during a reversible process we have

$$\begin{cases} dS_A = \frac{1}{T}\,đQ \\ dS_{\Sigma_A} = -\frac{1}{T}\,đQ \end{cases} \Rightarrow dS_\Omega = 0$$

$\therefore$ The entropy change of Ω during a rev. process is 0. Called the rev. proc γ_R, we have therefore

$$\Delta S_\Omega = \int_{\gamma_R} dS_A + \int_{\gamma_R} dS_{\Sigma_A} = \int_{\gamma_R} \frac{1}{T} đQ - \int_{\gamma_R} \frac{1}{T} đQ = 0 \quad \blacksquare$$

When the system instead undergoes an IRREVERSIBLE process $\varphi_I : \alpha \to \beta$, w/ α, β being eq. states we have that

$$\Delta S_A = S_\beta - S_\alpha = \int_{\varphi_R} \frac{1}{T} đQ \quad (\text{Not. } \int \to \text{reversible integral})$$

$$\neq \int_{\varphi_I} T^{-1} đQ$$

Where $\varphi_R : \alpha \xrightarrow{R} \beta$ is a reversible process bw, the 2 eq. states. Note that integration over φ_I is NOT DEFINABLE due to the irreversibility of the process

§ IRREVERSIBILITY & Σ §§ MECHANICAL EXTERNAL IRREVERSIBILITY

Consider now specific irreversible processes:

1) ISOTHERMAL TRANSFORMATION OF WORK

Since thermodynamic coordinates don't change (for A), we have

$$\Delta S_A = 0$$

There's a flow of heat Q_A into the reservoir, where $Q_A = W$, thus

$$\Delta S_{\Sigma_A} = \frac{W}{T}$$

Thus

$$\Delta S_\Omega = \frac{W}{T} > 0$$

2) ADIABATIC TRANSFORMATION OF WORK

Consider an <u>ad</u> transformation of W into $\mathcal{U}$, we must have a rise of temperature from T_i, T_f. Since it's <u>ad</u>, from the surroundings we have $Q_{\Sigma_A} = 0$, we therefore must have

$$\Delta S_{\Sigma_A} = 0$$

For the system instead we have

$$\Delta S_A = \int_{T_i}^{T_f} \frac{1}{T} đQ$$

For constant pressure we have $đQ_p = C_p dT$, therefore

$$\Delta S_A = \int_{T_i}^{T_f} \frac{C_p}{T} dT = C_p \log \frac{T_f}{T_i}$$

Thus:

$$\Delta S_\Omega = \Delta S_A = C_p \log \frac{T_f}{T_i} > 0$$

§§ INTERNAL MECHANICAL IRREVERSIBILITY

Consider now a process that transforms $\mathcal{U} \to W \to \mathcal{U}$

-) Free expansion

Here we have $\Delta S_{\Sigma_A} = 0$. We note that $T = \text{const.}$ & $V : V_i \to V_f$. We have

$$\Delta S_A = \int_{V_i}^{V_f} \frac{1}{T} đQ$$

We have: $đQ = p\,dV$, $pV = nRT \Rightarrow p = \frac{nRT}{V} \Rightarrow đQ = nRT\frac{dV}{V}$

Thus:

$$\Delta S_A = nR \int_{V_i}^{V_f} \frac{1}{V} dV = nR \log \frac{V_f}{V_i}$$

$$\therefore \Delta S_\Omega = \Delta S_A = nR \log \frac{V_f}{V_i}$$

§§ EXTERNAL THERMAL IRREVERSIBILITY

-) Heat transfer b/w reservoirs @ T_1 & T_2 w/ $T_1 > T_2$ through A

We have

$$\Delta S_A = 0$$

$$\Delta S_1 = -\frac{Q}{T_1} \quad (Q<0)$$

$$\Delta S_2 = \frac{Q}{T_2}$$

$$\therefore \Delta S_\Omega = \Delta S_1 + \Delta S_2 = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = Q\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

§§ CHEMICAL IRREVERSIBILITY

MADSTONE IN THE GARDEN OF EARTHLY DELIGHTS

THE MOSCOW COUP ATTEMPT FAILURE OF SHORTWAVE RADIO

65 DAYS OF STATIC

ESTHER VENROOY SHIFT COORDINATE POINTS

KISS TAPE RECORDINGS

§ PRINCIPLE OF INCREASE OF ENTROPY

We already saw, that for irreversible processes, that

$$\Delta S_\Omega > 0$$

We now consider ad processes. For a system described by (x, x', T) going from eq. state A to eq. state B adiabatically (IRREVERSIBLE). The entropy change is:

$$\Delta S = S_B - S_A$$

Consider now a rev ad process, bringing T to T' in C of some reservoir, putting it in contact and therefore make it undergo a rev. isothermal process to D until $S_D = S_A$, & a final rev. ad process brings the system back to A

Thus:

$$(S_B - S_A) + (S_D - S_C) = 0$$

If ΔS_{irr} is the irreversible entropy change, we have

$$\Delta S_{irr} = S_C - S_D$$

The only possible heat transfer from the reservoir is during the isothermal process, where

$$Q_{rev} = T'(S_D - S_C)$$

&, from the first principle ($đQ = dU + đW$) we have

1) $A \longrightarrow B$, $B \longrightarrow C$ $đQ = 0$

2) $C \longrightarrow D$ $dU = 0$, $đQ = đW$

$$\therefore Q_{rev} = W_{TOT}$$

From the second law we have that $Q_{rev} \not> 0$, thus $Q_{rev} \leq 0$ and therefore

$$T'(S_D - S_C) = -T\Delta S_{irr} \leq 0$$

$$\therefore \Delta S_{irr} \geq 0$$

If we assume that $\Delta S_{AB} = 0$ then it means the $\exists B \overset{a}{\longleftrightarrow} A$, and since $Q_{TOT} = 0 = W_{TOT}$ then the system and surroundings didn't change in the cycle ↯

$$\therefore \Delta S_{AB} > 0$$

Therefore, in general, <u>for any kind of process</u>

$$\sum_{j\geq 0} \Delta S_j \begin{cases} =0 & \text{reversible process} \\ >0 & \text{irreversible process} \end{cases}$$

§ APPLICATION OF $\Delta S \geq 0$

The fact that, in an irreversible process $\Delta S_\Omega > 0$ can let us discern the behavior of the system analyzed.

Consider a heat engine performing a generic cycle bw T_H & T_L, absorbing Q from T_H & emitting $Q-W$ @ T_L, then:

$$\Delta S_\Omega = \Delta S_H + \Delta S_L = \left(-\frac{Q}{T_H}\right) + \left(\frac{Q_L}{T_L}\right)$$

$$\therefore \Delta S_\Omega = \frac{Q-W}{T_L} - \frac{Q}{T_H} = Q\left(\frac{1}{T_L} - \frac{1}{T_H}\right) - \frac{W}{T_L} \geq 0$$

$$\therefore T_L Q\left(\frac{1}{T_L} - \frac{1}{T_H}\right) \geq W$$

$$\Rightarrow W \leq Q\left(1 - \frac{T_L}{T_H}\right)$$

$$\therefore \exists \max\{W\} = W_{max} = Q\left(1 - \frac{T_L}{T_H}\right)$$

Note that

$$1 - \frac{T_C}{T_H} = \eta_C \quad \text{(Carnot efficiency)}$$

Thus:

$$W \leq \eta_C Q$$

Remembering that $\eta = \frac{W}{Q}$ we have again Carnot's <u>theorem</u>

$$\eta \leq \eta_C$$

$$\eta = \eta_C \Rightarrow \Delta S_\Omega = 0$$

Analogously, for a refrigerator bw T_H & T_L (*) we have / (*) Q <u>FROM</u> A, $Q+W$ to rcs (In one cycle)

$$\begin{cases} \Delta S_A = S_H - S_L \\ \Delta S_Q = \frac{Q+W}{T_H} \end{cases} \Rightarrow \Delta S_\Omega = S_H - S_L + \frac{Q+W}{T_H} \geq 0$$

Then, rearranging

$$-S_2 + S_1 - \frac{Q}{T_H} \leq \frac{W}{T_H}$$

$$\therefore \underline{T_H(S_1 - S_2) - Q \leq W}$$

Therefore, $\exists \min\{W\} = W_{min} = T_H(S_1 - S_2) - Q$ (minimum cost of operation)

THERMODYNAMIC POTENTIALS

Def (Enthalpy)

By definition, the enthalpy function (H) is defined as follows

$$H = U + pV$$

Hence

$$dH = dU + pdV + Vdp$$

But, for ideal gases

$$đQ = dU + pdV$$

$$\therefore \; dH = đQ + Vdp \Rightarrow H \equiv H(T, p)$$

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

FOR AN ISOBARIC PROCESS ($p = cost \Rightarrow dp = 0$)

$$dH = đQ \Rightarrow \Delta H = Q$$

Or, by definition from the PDE:

$$\begin{cases} \frac{\partial H}{\partial T} = C_p \\ dH = đQ \end{cases} \Rightarrow H(T) = \int C_p dT$$

Rewriting $đQ = TdS$, we also have

$$dH = TdS + Vdp = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

$$\Rightarrow \begin{cases} \frac{\partial H}{\partial S} = T \\ \frac{\partial H}{\partial p} = V \end{cases}$$

Note:

$$\begin{cases} dU = đQ - đW = TdS - pdV \\ dH = đQ + Vdp = TdS + Vdp \end{cases} \quad \begin{cases} \left(\frac{\partial U}{\partial S}\right)_V = T, \; \left(\frac{\partial U}{\partial V}\right)_S = -p \\ \left(\frac{\partial H}{\partial S}\right)_p = T, \; \left(\frac{\partial H}{\partial p}\right)_S = V \end{cases}$$

$dU \rightarrow V \equiv const$ $\quad \begin{cases} dU = C_V(T)dT \\ dH = C_p(T)dT \end{cases}$; $\quad \Delta U = \int C_V dT$

$dH \rightarrow p \equiv const$ $\quad \Delta H = \int C_p dT$

Def (Hemholtze Free energy)

By definition:

$$\begin{cases} F = U - TS \\ dF = dU - TdS - SdT \\ dU = TdS - pdV \end{cases} \Big\} dF = \cancel{TdS} - \cancel{TdS} - SdT - pdV$$

$$\therefore dF = -SdT - \underset{(đW)}{\underset{\shortparallel}{pdV}}$$

$\Rightarrow$ For an isothermal process ($dT = 0$)

$$\begin{cases} dF = -pdV = đW \\ \Delta F = -\int pdV \end{cases}$$

Note that, by definition:

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

Def (Gibbs function)

$$G = H - TS$$

$$\left.\begin{array}{l} dG = dH - TdS - SdT \\ dH = TdS + Vdp \end{array}\right\} \rightarrow dG = Vdp - SdT$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_p = -S, \left(\frac{\partial G}{\partial p}\right)_S = V$$

In particular, if a process is isothermal, isobaric & reversible (fusion, sublimation, vaporization)

$$dT = dp = 0$$

$$\therefore dG = 0 \Rightarrow G(p, T) = \text{const}$$

RECAP: ($đQ = TdS$, Ideal gases $\Rightarrow đW = -pdV$)

INTERNAL ENERGY	ENTHALPY	FREE ENERGY
$U \equiv U(S,V)$	$H \equiv H(S,p)$	$F \equiv F(T,V)$
Ist) $dU = TdS - pdV$	$dH = TdS + Vdp$	$dF = -SdT - pdV$
V) $\frac{\partial U}{\partial S} = T$, $\frac{\partial U}{\partial V} = -p$	$\frac{\partial H}{\partial S} = T$, $\frac{\partial H}{\partial p} = V$	$\frac{\partial F}{\partial T} = -S$, $\frac{\partial F}{\partial V} = -p$

GIBBS

$G \equiv G(T,p)$

Ist) $dG = -SdT + Vdp$

V) $\frac{\partial G}{\partial T} = -S$, $\frac{\partial G}{\partial p} = V$

Special cases

Isochoric process ($dV = 0$) ⓐ

$\therefore dU = TdS$, $\int_A^B dU = T\Delta S = Q$

Reversible isothermal & isochoric ⓒ

($dS = dT = dV = 0$)

$\therefore dF = 0$, $F = \text{const.}$

Isobaric process ($dp = 0$) ⓑ

$\therefore dH = TdS$, $\int_A^B dH = T\Delta S = Q$

Reversible isothermal & isobaric ⓓ

($dS = dT = dp = 0$)

$\therefore dG = 0$, $G = \text{const.}$

ⓐ $\boxed{dU = TdS}$, $dH = TdS + Vdp$, $dF = -SdT$, $dG = -SdT + Vdp$ (isochoric process)

ⓑ $dU = TdS - pdV$, $\boxed{dH = TdS}$, $dF = -SdT - pdV$, $dG = -SdT$ (isobaric process)

ⓒ $dU = 0$, $dH = Vdp$, $\boxed{dF = 0}$, $dG = Vdp$ (chemical reactions)

ⓓ $dU = -pdV$, $dH = 0$, $dF = -pdV$, $\boxed{dG = 0}$ (phase transitions)

ADIABATIC (ISOENTROPIC) processes ($dS = 0$)

$\boxed{dU = -pdV}$, $dH = Vdp$, $dF = -SdT - pdV$, $dG = -SdT + Vdp$ (adiabatic process)

Thm (Stokes $\mathbb{R}^2$)

Let $\omega \in \Lambda(\mathbb{R}^2)$, $\omega = M(x,y)\,dx + N(x,y)\,dy$, then if

$$d\omega = dM \wedge dx + dN \wedge dy = 0$$

$dM = \frac{\partial M}{\partial x}dx + \frac{\partial M}{\partial y}dy$, $dN = \frac{\partial N}{\partial x}dx + \frac{\partial N}{\partial y}dy$ $\quad$ * if $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$

Then ω is exact*, thus $\exists f \in C^2(\mathbb{R}^2)$ s.t.

$$df = \omega$$

Where, since $df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy \Rightarrow \frac{\partial f}{\partial x} = M(x,y)$, $\frac{\partial f}{\partial y} = N(x,y)$

<u>Proof</u>

$$d\omega = \left(\frac{\partial M}{\partial x}dx + \frac{\partial M}{\partial y}dy\right)\wedge dx + \left(\frac{\partial N}{\partial x}dx + \frac{\partial N}{\partial y}dy\right)\wedge dy$$

By def. $dx \wedge dx = dy \wedge dy = 0$, $dx \wedge dy = -dy \wedge dx$

$$\therefore d\omega = \frac{\partial M}{\partial y}dy \wedge dx + \frac{\partial N}{\partial y}dx \wedge dy$$

$$\left[\, d\omega = \left(\frac{\partial N}{\partial y} - \frac{\partial M}{\partial x}\right)dx \wedge dy \,\right]$$

$\therefore$ ω exact $\Rightarrow \frac{\partial N}{\partial y} = \frac{\partial M}{\partial x}$, & therefore $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ $(f \in C^2)$ &

$$\omega = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = df \quad \blacksquare$$

<u>Thm</u>

Let $f \in C^2(\mathbb{R}^3)$, $f \equiv f(x,y,z)$ & $x \equiv x(y,z)$, $y \equiv y(x,z)$, $z \equiv z(x,y)$, then:

$f \equiv f(x,y)$ or $f \equiv f(x,z)$ or $f(y,z)$, &

$x \equiv x(f,y)$, $x \equiv x(f,z)$ ...

$$\begin{cases} dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy \\ dy = \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz \end{cases} \Rightarrow dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f \left[\left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz\right]$$

$$\therefore dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right]df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)dz$$

But, $dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)dz$

+1 pg

$$\begin{cases} dx = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right] df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f dz \\ dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)_f dz \end{cases}$$

$$\therefore \underbrace{\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z = \left(\frac{\partial x}{\partial f}\right)_z}_{??} \; ; \; \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f = \left(\frac{\partial x}{\partial z}\right)_f$$

(Già risolto ma sul libro è sbagliato??)

§ MAXWELL RELATIONS

Four functions (potentials):

INTERNAL ENERGY : $\mathcal{U}$

ENTHALPY : $\mathcal{H} = \mathcal{U} + pV$

Hemholtz free energy : $\mathcal{F} = \mathcal{U} - TS$

Gibbs function : $G = \mathcal{H} - TS$

Any of these can be described by any combination of two of (p, V, T).

e.g.:

$\mathcal{U} \equiv \mathcal{U}(V,T)$ & $S \equiv S(V,T)$, but also $\mathcal{U} \equiv \mathcal{U}(S,V)$

In general, take $(p, V, T, S, \mathcal{U}, \mathcal{H}, F, G)$ can be expressed as functions of any two other

Consider a system undergoing a rev. qs. process

1. $d\mathcal{U} = đQ - pdV = TdS - pdV$

2. $d\mathcal{H} = d\mathcal{U} + pdV + Vdp = TdS + Vdp$

3. $dF = d\mathcal{U} - TdS - SdT = -SdT - pdV$

4. $dG = d\mathcal{H} - TdS = Vdp - TdS$

All the differentials are exact, we have

$$d\mathcal{U} = TdS - pdV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$d\mathcal{H} = TdS + Vdp \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dF = -SdT - pdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$dG = Vdp - SdT \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

§ TdS EQUATIONS (pg. 221)

The entropy S of a pure substance can be evaluated as function of T, V, thus

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

Thus:

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV = đQ$$

It follows then that

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{đQ}{dT}\right)_V$$

$$\therefore \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Thus

Maxwell III rd

$$\boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \quad (1ST\ TdS)$$

Instead, if $S \equiv S(T, P)$ we have

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP = đQ$$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{đQ}{dT}\right)_P = C_P$$

$$\boxed{TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP} \quad (2nd\ TdS)$$

Also, $S \equiv S(P, V)$, then:

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV$$

For an isochoric rev. process we have

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP = C_V dT = đQ$$

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

For an isobaric rev. process

$$TdS = T\left(\frac{\partial S}{\partial V}\right)_P dV = C_P dT = đQ$$

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

$$\therefore \quad \boxed{TdS = C_V\left(\frac{\partial T}{\partial p}\right)_V dp + C_p\left(\frac{\partial T}{\partial V}\right)_p dV} \quad (3\text{rd } TdS)$$

§§ APPLICATIONS

1 mol of Van der Waals gas undergoes a rev. isothermal expansion from $v_i \to v_f$
How much heat was transferred?

$$\left(p - \frac{a}{v^2}\right)(v-b) = RT \quad (EOS)$$

$$Tds = c_v dT + \left(\frac{\partial p}{\partial T}\right)_v T dv \quad (1\text{st } TdS)$$

The process is isothermal, thus $c_v dT = 0$, thus

$$Tds = \left(\frac{\partial p}{\partial T}\right)_v T dv$$

But

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

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

Thus

$$Tds = \frac{RT}{v-b} dv = đQ$$

$$Q = RT\int_{v_i}^{v_f} \frac{1}{v-b} dv = RT \log(v-b)\Big|_{v_i}^{v_f} = RT \log\left(\frac{v_f - b}{v_i - b}\right)$$

$$\therefore Q = RT \log\left(\frac{v_f - b}{v_i - b}\right)$$

-) Consider a reversible isothermal change of pressure

$$TdS = C_p dT - \left(\frac{\partial V}{\partial T}\right)_p dp \quad (\text{IInd})$$

$$đQ = TdS = -\frac{\partial V}{\partial T} dp$$

$$\therefore Q = -T\int \frac{\partial V}{\partial T} dp$$

Noting that the volumetric expansivity is $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, we have $\left(\frac{\partial V}{\partial T}\right)_p dp = \beta V dp$

$$\therefore Q = -T\int \beta V dp$$

For a solid or liquid $\frac{\partial \beta}{\partial p} = \frac{\partial V}{\partial p} \simeq 0$, thus

$$Q = -T\overline{V\beta}\,\Delta p$$

where $\overline{V}, \overline{\beta}$ are the average values

During the compression, also:

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\therefore TdS = -T\left(\frac{\partial V}{\partial T}\right)_p dp$$

q

$$đW = -pdV$$

$T = \text{const} \Longrightarrow W = -\int\left(\frac{\partial V}{\partial T}\right)_p p\,dp$, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \Rightarrow \frac{\partial V}{\partial T} p\,dp = -\kappa p V dp$

$$W = -\int \kappa p V dp$$

Again, $\frac{\partial \kappa}{\partial p} = \frac{\partial V}{\partial p} = 0$,

$$\therefore W = -\frac{\overline{\kappa}}{2}\overline{V}\left(p_f^2 - p_i^2\right)$$

-) rev. ad. (iso S) change of pressure

$$TdS = C_p dT - \left(\frac{\partial V}{\partial T}\right)_p T dp$$

But $dS = 0$, thus

$$C_p dT = \left(\frac{\partial V}{\partial T}\right)_p T dp \Rightarrow \frac{C_p}{T} dT = \left(\frac{\partial V}{\partial T}\right)_p dp$$

Since

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V$$

$$dT = \frac{\beta V T}{C_p} dp$$

therefore

$$\Delta T = \int \frac{\beta V T}{C_p} dp \simeq \frac{\overline{\beta V T}}{C_p}\Delta p$$

§ ENERGY EQUATIONS

For an infinitesimal rev. process bwt two eq. states, we have

$$dU = TdS - pdV$$

i.e.

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

but $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p}$$ (1st energy eq)

Note that, for ideal gases:

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

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p(V,T) = 0 \quad \therefore U \equiv U(T) + U_0 \quad \boxtimes$$

For 1 mol of Van der Waals gas:

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

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$\therefore dU = C_V dT + \frac{a}{V^2} dV$$

$$\& \quad U(T,V) = \int C_V(T)\,dT - \frac{a}{V} + U_0$$

The second equation gives us the dependency on pressure. Thus

$$\left.\begin{aligned} dU &= TdS - pdV \\ \left(\frac{\partial U}{\partial p}\right)_T &= T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T \end{aligned}\right\} \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{\therefore \left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T} \quad \text{(2nd Energy eq)}$$

§ Heat - Capacity Equations

We know:

$$\begin{cases} TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp & \text{Ist } TdS \\ TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV & \text{IInd } TdS \end{cases}$$

Thus, equating the

$$C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$(C_p - C_V)\, dT = T\left[\left(\frac{\partial p}{\partial T}\right)_V dp + \left(\frac{\partial V}{\partial T}\right)_p dV\right]$$

$$\& \quad dT = \frac{T}{C_p - C_V}\left[\left(\frac{\partial p}{\partial T}\right)_V dp + \left(\frac{\partial V}{\partial T}\right)_p dV\right]$$

By definition, $T \equiv T(p, V)$, thus

$$dT = \left(\frac{\partial T}{\partial p}\right)_V dp + \left(\frac{\partial T}{\partial V}\right)_p dV$$

$$\therefore \begin{cases} \left(\frac{\partial T}{\partial p}\right)_V = \frac{T}{C_p - C_V}\left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial V}\right)_p = \frac{T}{C_p - C_V}\left(\frac{\partial V}{\partial T}\right)_p \end{cases} \Rightarrow C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V$$

Note also that

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

$$\boxed{\therefore C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T}$$

$$\begin{cases} (\partial_V p)_T < 0 \Rightarrow C_p \geq C_V \\ C_p(0) = C_V(0) \\ C_p = C_V \text{ iff } \left(\frac{\partial V}{\partial T}\right)_p = 0 \end{cases}$$

Note also that:

$$\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T^{-1}, \quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{\kappa V}, \quad \left(\frac{\partial V}{\partial T}\right)_p^2 = V^2\beta^2$$

$$\therefore C_p - C_V = \frac{\beta V T}{\kappa}$$

From the TdS I & II we have for an isoentropic process

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp = 0$$

$$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV = 0$$

$$\therefore \begin{cases} C_p dT = T\left(\frac{\partial V}{\partial T}\right)_p dp \\ C_V dT = -T\left(\frac{\partial p}{\partial T}\right)_V dV \end{cases}$$

Solving for $\frac{C_p}{C_V}$ we have

$$\frac{C_p}{C_V} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V^{-1} \left(\frac{\partial p}{\partial V}\right)_S = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_S$$

$$\therefore \frac{C_p}{C_V} = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_S$$

Defined the adiabatic compressibility κ_S as

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

We have

$$\frac{C_p}{C_V} = \frac{V\kappa}{V\kappa_S} = \frac{\kappa}{\kappa_S} = \gamma$$

RECAP.

$$\begin{cases} \begin{cases} TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV & (TdS\ I) \\ TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp & (TdS\ II) \end{cases} \\ TdS = C_V\left(\frac{\partial T}{\partial p}\right)_V dp + C_p\left(\frac{\partial T}{\partial V}\right)_p dp \quad (TdS\ III) \\ \begin{cases} \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p & (U\ I) \\ \left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T & (U\ II) \end{cases} \\ \begin{cases} C_p - C_V = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right) & (C\ I) \\ \gamma = \frac{C_p}{C_V} = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_S = \frac{\kappa}{\kappa_S} & (C\ II) \end{cases} \end{cases}$$

§ THERMAL EXPANSIVITY

Said L_1, L_2, L_3 as the smallest lengths of a rectangle containing the system we then have

$$V = L_1 L_2 L_3$$

$$\frac{\partial V}{\partial T} = L_1 L_2 \frac{\partial L_3}{\partial T} + L_1 \frac{\partial L_2}{\partial T} L_3 + \frac{\partial L_1}{\partial T} L_2 L_3$$

Said $\alpha_i = \frac{\partial L_i}{\partial T}$ the linear expansivity in the i-th direction, then

$$\beta = \frac{1}{V}\frac{\partial V}{\partial T} = \frac{1}{L_1 L_2 L_3}\left(\frac{\partial V}{\partial T}\right) = \alpha_1 + \alpha_2 + \alpha_3$$

PHASE TRANSITIONS

ch. 10 pg. 245

§ FIRST ORDER TRANSITIONS

Melting, vaporization & sublimation → Ist order $\begin{cases} p, T \text{ const.} \\ S, V \text{ variable} \end{cases}$

Consider n moles of material in phase i w/ entropy $S_{(i)}$ & volume $V_{(i)}$ transition to a new phase $S_{(f)}$, $V_{(f)}$. Said x the fraction of i transformed to f, then:

$$\begin{cases} S = n_0(1-x)S_{(i)} + n_0 x S_{(f)} \\ V = n_0(1-x)V_{(i)} + n_0 x V_{(f)} \end{cases}$$

If the transition is rev. then $\exists$ latent heat λ def. as

$$\lambda = T(S_{(f)} - S_{(i)})$$

Since $dg = vdp - Tds$, we have

$$s = -\left(\frac{\partial g}{\partial T}\right)_p, \quad v = \left(\frac{\partial g}{\partial s}\right)_p$$

<u>Def</u> (Ist order transition)

$$g(T,S) \in C^0$$
$$\Delta S \neq 0, \ \Delta V \neq 0$$

Since $dp = dT = 0$, we have

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p = \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \infty$$

For the II TdS we have

$$TdS = c_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

Hence

$$T(S_{(f)} - S_{(i)}) = \lambda = T\frac{dp}{dT}(V_{(f)} - V_{(i)})$$

$$\boxed{\frac{dp}{dT} = \frac{\lambda}{T\Delta V}} \quad \text{(Clapeyron eq.)}$$

Note that also, since $g_{(i)} = g_{(f)}$ we have

$$dg_{(i)} = dg_{(f)}$$

$$\therefore V_{(i)}dp - S_{(i)}dT = V_{(f)}dp - S_{(f)}dT$$

$$\Rightarrow \Delta V dp = \Delta S dT$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\lambda}{T}\frac{1}{\Delta V} = \frac{\lambda}{T\Delta V}$$

§ FUSION

Fusion is the phase transition (s) → (l). The best method is to supply electrical energy at a constant rate ($\mathcal{E}I$).

The resulting graph has a line @ $T = T_M$ (melting temperature) long $\Delta\tau$.

Therefore, for n moles of solid

$$\lambda_F = \frac{1}{n}\mathcal{E}I\Delta\tau$$

Also

$$\Delta S = \frac{\lambda_F}{T_M}$$

An empirical formula for evaluating melting curves was found by F.E. Simon & G. Glatzel

$$P - P_{TP} = a\left[\left(\frac{T}{T_{TP}}\right)^c - 1\right]$$

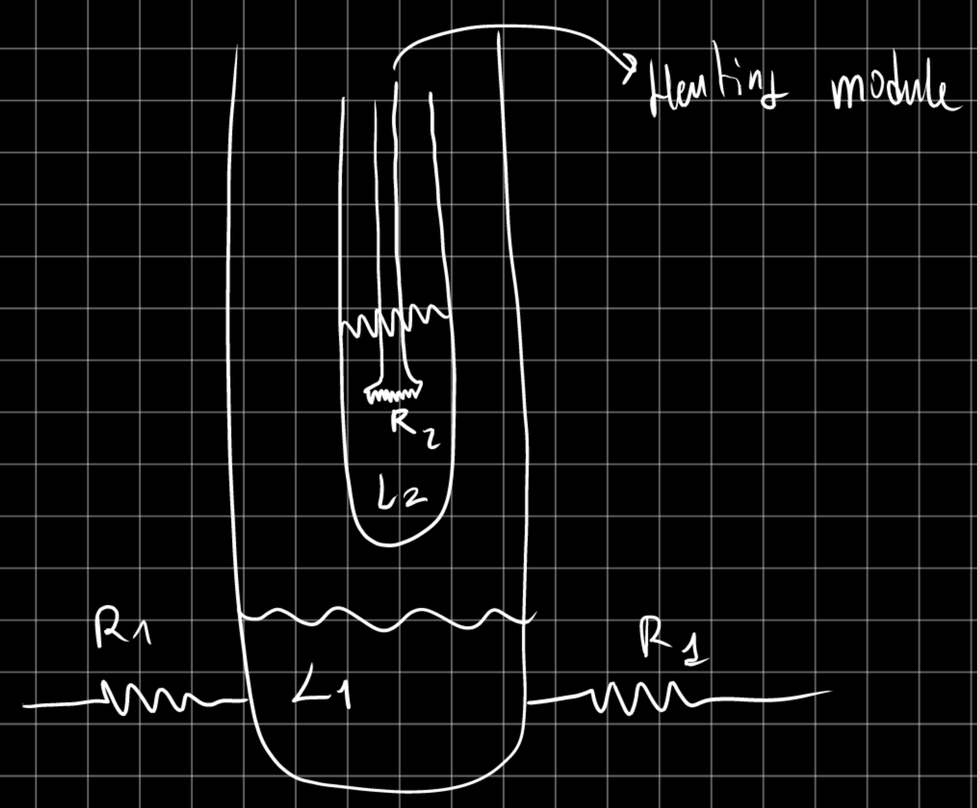
(P_{TP}, T_{TP}) are the TP coordinates & a, c are parameters depending on the substance

§ VAPORIZATION

1st order transition (l) → (g). For liquids @ human temperatures, usually

$$250\,K < T_F < 550\,K$$

λ_V is usually measured with calorimeters like the one in figure:



The simple liquid L_2 is contained in a small vessel containing a heating module. The surrounding vessel is a temperature mixture of air & the vapor of an already studied liquid L_2 which is kept at boiling point together w/ L_2 using adequate pressures and temperatures using the heating module R_1 ...

The latent heat is found to be

$$\lambda_V = \frac{\mathcal{E}I\tau}{n}$$

In general we have from Clayperon's eq.

$$\begin{cases} \dfrac{\lambda_v}{T_c}\dfrac{T}{p(v_f-v_i)} = 5.4 \leftarrow \text{experimental} \\[2ex] \dfrac{dp}{p}\dfrac{T^2}{dT} = \dfrac{\lambda_v T}{p(v_f-v_i)} = \dfrac{\lambda_v}{T_c}\dfrac{T T_c}{p(v_f-v_i)} \leftarrow \text{empirical} \end{cases}$$

Since $\dfrac{\lambda_v}{T_c}\dfrac{T}{p(v_f-v_i)} = 5.4 \Rightarrow \dfrac{dp}{p}\dfrac{T^2}{dT} = 5.4\,T_c \Rightarrow \dfrac{1}{p}dp = 5.4\,T_c\dfrac{dT}{T^2}$

Integrating from T_0 to T_c we have

$$\log\left(\frac{P(T_c)}{P(T_0)}\right) = -5.4\,T_c\,\frac{1}{T}\Big|_{T_0}^{T_c}$$

$$\log\left(\frac{P_c}{P_0}\right) = -5.4\,T_c\left(\frac{1}{T_c}-\frac{1}{T_0}\right)$$

If we're far from $T_c \Rightarrow v_i \simeq 0$, $v_f = \dfrac{RT}{p}$, $\lambda_v \simeq$ const. thus:

$$\frac{dp}{dT} = \frac{\lambda_v}{RT/p} = \frac{\lambda_v p}{RT}$$

$$\int_{P_0}^{P_c}\frac{1}{p}\,dp = \frac{\lambda_v}{R}\int_{T_0}^{T_c}\frac{1}{T^2}\,dT$$

$$\log\left(\frac{P_c}{P_0}\right) = -\frac{\lambda_v}{R}\left(\frac{1}{T_c}-\frac{1}{T_0}\right) \simeq \text{const.} - \frac{\lambda_v}{RT}$$

$$\therefore \frac{\lambda_v}{R} \simeq 5.4\,T_c$$

§ SUBLIMATION

For sublimation, $v_f = v'''$, $v_i = v'$ ($v''' \to \frac{V}{n}\big|_{gas}$, $v' \to \frac{V}{n}\big|_{solid}$)

$$\frac{dP}{dT} = \frac{\lambda_s}{T(v'''-v')}$$

v''' volume of an ideal gas $\rightarrow v''' = \dfrac{RT}{P} \gg v' \Rightarrow v'''-v' \approx v'''$

$$\therefore \frac{dP}{dT} = \frac{\lambda_s}{pTv'''} = \frac{\lambda_s}{pRT^2}$$

$$\therefore \lambda_s = \frac{dP}{P}\frac{T^2}{dT}R = -R\frac{d\log(P)}{d\left(\frac{1}{T}\right)}$$

$$\therefore \log(P) \simeq -\frac{A}{T} + B.$$ A, B depend on material

From Enthalpy we have

1) $dh = Tds + vdp$

From TdS (ii) we get

$$Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$\therefore\ dh = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp + v\,dp$$

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp \quad ; \left[\left(\frac{\partial v}{\partial T}\right)_p = \beta v\right]$$

$$dh = c_p dT + \left[v - v\beta\right] dp$$

$$\Delta h' = c_p \Delta T + \int [v - v\beta]\, dp$$

If $i = (p=0, T=0)$, for gaseous pre sublimation then:

$$h' - h'_0 = \int_0^T c_p dT + \cancel{\int_0^p v - v\beta\, dp} \to 0$$

$$h' - h'_0 = \int c'_p dT$$

For an ideal gas

$$dh''' = c_p''' dT \Rightarrow h''' = \int c_p''' dT$$

$$\therefore\ \lambda_s = \Delta h_{III,I} = h''' - h' = \int c'_p dT - \int c_p''' dT + h'''_0 - h'_0$$

$$\therefore\ \lambda_0 = h'''_0 - h'_0 \quad (T \to 0) \to \text{latent heat of sublimation at } 0K$$

$$h'_0 = h(T=0)$$

If $c_p' \equiv c_p(T)$, $c_p''' = c_p'''(T)$

$$\left[\lambda_s = \int_0^T c'_p dT - \int_0^T c_p''' dT + \lambda_0\right] \quad (K \in Q_s)$$

This is << Kirchhoff's equation for sublimation >>

§ VAPOR PRESSURE CONSTANT

Vapor in equilibrium w/ a solid is considered as a real gas, then Clapeyron's equation remains

$$\frac{dp}{p} = \frac{\lambda_s}{RT^2} dT$$

From Reals

$$\lambda_s = \int_0^T c_p''' dT - \int_0^T c'_p dT + \lambda_0$$

But, $c_p''' = C''' + C_i'''(T)$, where $C''' = \begin{cases} \frac{5}{2}R & \text{monoatomic} \\ \frac{7}{2}R & \text{biatomic} \end{cases}$ gas & $C_i'''(T)$ is due to

internal DOF of the molecules. note $C_i'''(T) \to 0$ $\begin{cases} T \to 0 \\ C''' = \frac{3}{2} R \end{cases}$

Thus:

$$s_s = s_0 + C''' T + \int_0^T C_i'''(T)\, dT - \int_0^T C_p'(T)\, dT$$

& thus, since

$$\frac{dP}{P} = \frac{s_s}{RT^2} dT$$

$$\frac{dP}{P} = \frac{s_0}{RT^2} + \frac{C'''}{RT} + \frac{1}{RT^2}\left[\int_0^T C_i'''(T)\, dT - \int_0^T C_p'(T)\, dT\right]$$

Integrating

$$\log(P) = \frac{C'''}{R}\log(T) - \frac{s_0}{RT} + \frac{1}{R}\int_0^T \frac{1}{T}\int_0^T C_i'''(T)\, dT\, dT - \frac{s_0}{R}\int_0^T \frac{1}{T}\int_0^T C_p'(T)\, dT\, dT + k$$

If the vapour is monoatomic, $C_p'''(T) = \frac{5}{2} R$, thus

$$\log(P) = \frac{5}{2}\log(T) - \frac{s_0}{RT} - \frac{1}{R}\int_0^T \frac{1}{T}\int_0^T C_p'(T)\, dT\, dT + k$$

Measurement:

a) $10^{-1}\,Pa < p < 10^5\,Pa \to$ direct measurement (static)

b) Langmuir evaporation $\to$ weigh solid, measure surface S, flux rate of collisions

$$\left.\frac{dN_c}{dt}\right|_{eq} = P\sqrt{\frac{1}{2\pi N k_B T}} \qquad M \to \text{solid mass}$$

$$\& \quad \frac{1}{S}\frac{dM}{dt} = P\sqrt{\frac{M_{mo}}{2\pi R T}} \qquad M_{mo} \to \text{molecular mass}$$

b) Knudsen effusion $\to$ Langmuir but vapor passes a known hole of surf. S & gets trapped in a cold trap.
After a time T, we have that

$$\left\langle \frac{dM}{dt} \right\rangle = \frac{M_{CT}}{T} \qquad M_{CT} \to \text{mass in cold trap after condensation}$$

errors b/w 5% & 10%

Main formula:

$$\log(P) = A - \frac{B}{T} + CT + D\log(T) \qquad \begin{cases} A, B, C, D \\ \text{parameters} \end{cases}$$

experimentally it has been found that

$$\lambda_0 \approx \frac{3}{5}\frac{c_V(0)}{\beta}$$

(c'è bisogno che scrivo il conto (forse - check))

STATISTICAL MECHANICS

§ KINETIC THEORY

Consider an ideal gas, as we've seen from macroscopic thermodynamics, the equation of state is found empirically as

$$pV = nRT$$

We analyze now what are ideal gases from the microscopic POV using "Kinetic theory" using the following rules:

1) Any small sample of gas consists of an enormous number of particles (N)

a) If m is the mass of the single molecule then, the mass of the gas is

$$M = Nm$$

b) If $\mathcal{M}$ is the molar mass (molecular weight / kg / Kmol), then the number of moles is

$$n = \frac{Nm}{\mathcal{M}} = \frac{M}{\mathcal{M}}$$

c) For a <u>single</u> mole ($n=1$) we have

$$1 = \frac{Nm}{\mathcal{M}} \Rightarrow N = \frac{\mathcal{M}}{m} = N_A = 6.022 \cdot 10^{23}\ mol^{-1}$$

$$(6.0225 \cdot 10^{23}\ mol^{-1})$$

c') In general

$$N_A = \frac{N}{n}$$

2) All molecules can be approximated to small spheres in perpetual random motion

3) The molecules exert NO ATTRACTION OR REPULSIONS b/w eachother (no interaction) except with collisions

4) Collisions are perfectly elastic & zones of collisions w/ walls can be considered flat

4a) For a collision

, i.e. $\underline{v}' = \underline{v}_\perp$, $\Delta \underline{v} = -2\underline{v}_\perp$

5) When there is no external field $\rightarrow$ molecules distributed UNIFORMLY

5a) the molecular density $\frac{N}{V}$ is <u>constant</u> thus:

$$dN = \frac{N}{V} dV$$

5b) Note also that dV is big enough to let $dN \gg 1$

6) No preferred directions

7) Different speeds in general, & $v \ll c$.

7a) if there are dN_v particles w/ $v \in [v, v+dv]$, at equilibrium $dN_v = \text{const}$.

Consider a generic velocity vector $\underline{v}$, due to the absence of a preferred direction we can say that

$$d^3N_{\underline{v}} = \frac{1}{4\pi} dN_v d\Omega = \frac{1}{4\pi} \sin\theta \, d\varphi \, d\theta \, dN_v \quad \text{(No preferred direction)}$$

Consider all incoming particles to the solid angle $\frac{d\Omega}{4\pi}$ region. We know that they lie inside a cylinder long $v\,d\tau$, where τ is the time w/o collisions. that volume is then

$$dV = v \cos\theta \, d\tau \, dS$$

where dS is a small area of the vessel. If the total volume is V, then only dV/V will be inside the cylinder, therefore the number of molecules striking dS is

$$N_{c_{dA}} = d^3N_{\underline{v}} \frac{dV}{V} \quad \text{(No preferred location)}$$

Also collisions are elastic, thus, if P is the momentum of the particle & ΔP its change

$$\Delta P = -2mv\cos\theta$$

& the <u>total</u> change of momentum can be seen as:

$$\Delta P_{tot} = \underbrace{\left(\frac{1}{4\pi} dN_v d\Omega\right)}_{\#\text{ w/ } v \text{ in } d\Omega} \underbrace{\left(\frac{v}{V} \cos\theta \, d\tau \, dS\right)}_{\text{fraction of } \# \text{ striking } dS} \underbrace{\left(-2mv\cos\theta\right)}_{\Delta P}$$

the total change of momentum ON THE SECTOR dS of the wall IS THE PRESSURE (From newton II $\dot{\underline{P}} = m\underline{a}$), thus, for dN_v molecules

$$\Delta P_{tot} = \frac{1}{4\pi} dN_v \sin\theta \, d\theta \, d\varphi \, \frac{v}{V} \cos\theta \, d\tau \, dS \, (-2mv\cos\theta)$$

$$\Delta P_{tot} = \frac{mv^2}{4\pi V} \sin\theta \cos^2\theta \, d\theta \, d\varphi \, d\tau \, dS \, dN_v$$

But, $\int \frac{\Delta P_{tot}}{d\tau \, dS} = dp_v$, thus

$$dp_v = \frac{mv^2}{4\pi V} dN_v \int_0^{2\pi} d\varphi \int_{-\pi/2}^{\pi/2} \cos^2\theta \sin\theta \, d\theta$$

But

$$\int_{-\pi/2}^{\pi/2} \cos^2\theta \sin\theta \, d\theta = 2 \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta$$

Therefore

$$dp_v = \frac{mv^2}{2\pi V} dN_v \int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta = -\frac{mv^2}{2\pi} dN_v \int_0^{2\pi} d\varphi \int_1^0 \cos^2\theta \, d(\cos\theta)$$

$$dp_v = \frac{mv^2}{V} dN_v \left(\frac{1}{3} \cos^3\theta \right)_0^1 = \frac{mv^2}{3} dN_v$$

Integrating for all particles w/ velocity v we have

$$p = \frac{m}{3V} \int v^2 dN_v = \frac{1}{3V} m N \langle v^2 \rangle \, , \quad \langle v^2 \rangle = \frac{1}{N} \int_{\mathbb{R}} v^2 dN_v$$

<u>But</u> $\frac{1}{2} m \langle v^2 \rangle = \langle \epsilon \rangle$ (no field, expected kinetic energy (total) per molecule)

$$pV = \frac{2}{3} N \langle \epsilon \rangle = \frac{2}{3} \underbrace{N \left(\frac{1}{2} m \langle v^2 \rangle \right)}_{\langle \epsilon \rangle}$$

Thus, from the empirical EOS

$$pV = \frac{2}{3} N \langle \epsilon \rangle = nRT$$

$$pV = \frac{2}{3} N_A \langle \epsilon \rangle = RT$$

$$\therefore \langle \epsilon \rangle = \frac{3}{2} \frac{R}{N_A} T$$

Defined the BOLTZMANN CONSTANT K_B as

$$K_B = \frac{R}{N_A}$$

We get

$$\langle \epsilon \rangle = \frac{3}{2} K_B T$$

with

$$K_B = \left(\frac{1}{6.0225} \cdot 10^{-23} \, mol \right) \left(8.3143 \, \frac{J}{K mol} \right) = 1.3805 \cdot 10^{-23} \, \frac{J}{K}$$

Also,

$$pV = \frac{2}{3} N \langle \epsilon \rangle = \frac{2}{3} N \left(\frac{3}{2} k_B T \right) = N k_B T$$

or

$$p = \frac{N}{V} k_B T = \rho_{mol} k_B T \quad \left\{ \rho_{mol} = \frac{N}{V}, \text{ mol. density} \right\}$$