

1.

TEMPERATURE & 2nd LAW OF THERMODYNAMICS

↳ Macroscopic POV

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

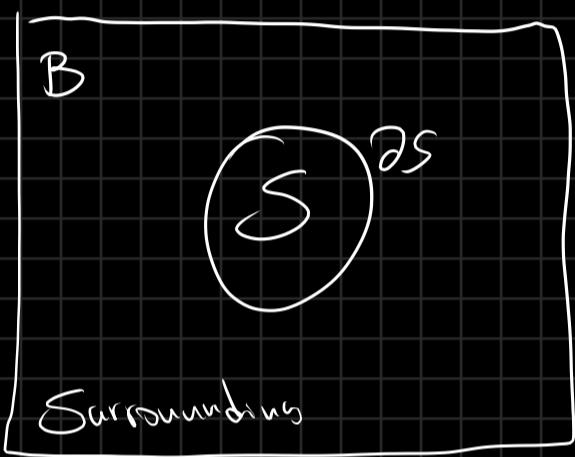
Def. (System)

Region of space or finite portion of matter by means of a closed surface the **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 some



Σ

Fig 1: a system.

$\Sigma \rightarrow$ universe

$S \rightarrow$ system, $B \rightarrow$ Surrounding

$DS \rightarrow$ boundary

System

—
something
interacting

If matter passes through $DS \rightarrow S$ is **OPEN**

If no matter passes through $DS \rightarrow S$ 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 characteristic at molecular or smaller level ($\leq 100\text{Å}$)

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

Taken as an example the contents in a cylinder chamber of an automobile a chemical analysis would find the following behaviour

hydrocarbons + air \longrightarrow combustion products

A statement on the amount of these chemicals describes both $\begin{cases} \text{mass} \\ \text{composition} \end{cases}$

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, small after expansion. In fact a gauge can be used to measure & record change. Another quantity is Temperature

These are **Macroscopic coordinates**

Def (macroscopic coordinates)

Coordinates which

- involve no assumption on structure, fields / radiation
- few in number
- fundamental
- can be (in general) be directly measured

Def (Thermodynamics)

Branch of physics which deals w/ macroscopic properties of ~~systems~~ includes Temperature

Def (Microscopic POV)

A microscopic system is a number N of particles w/ energy states ϵ_i , particles interact 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 ~~all~~ 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

6 OTH 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 $\begin{cases} X \rightarrow \text{ext force (pressure)} \\ Y \rightarrow \text{ext displacement (Volume)} \end{cases}$

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: $\{A, B; \text{systems}\}$

- 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. $|EQ> = (X, Y, X', Y')$

A)
all X', Y' possible
for eq

A) Some X', Y'
possible for eq

A DIABATIC

all X', Y' possible
for eq

B)

DIATHERMIC

Some X', Y' possible
for eq

B)

a) A, B separated by ad
wall

b) A, B separated by
dt wall

In case b, the systems, when \Rightarrow equilibrium, are said to be in Thermal equilibrium
by (Thermal equilibrium)

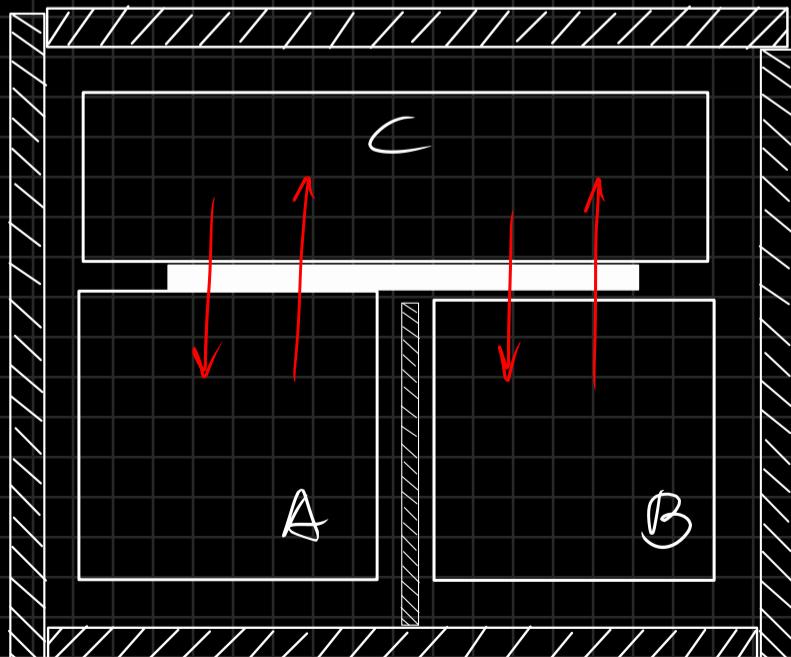
Thermal equilibrium is the state achieved by two or more systems characterized
by restricted values of sys coordinates after they've been in contact through a dt wall.

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

LAW (Qth Thermal law)

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

$$\left\{ \begin{array}{l} A \leftrightarrow C \\ B \leftrightarrow C \end{array} \right. \Rightarrow A \leftrightarrow B$$



$$A \leftrightarrow C$$

$$B \leftrightarrow C$$

$$\therefore A \leftrightarrow B$$

Two systems in thermal equilibrium with a
third one in thermal equilibrium w/ each other

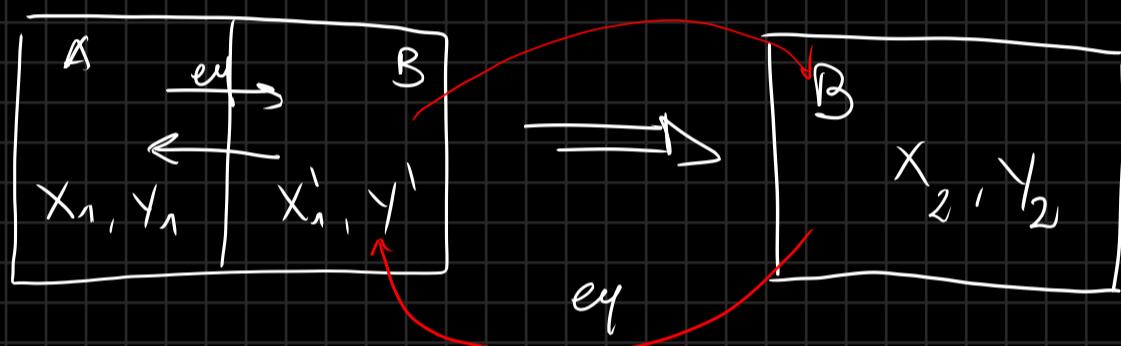
TEMPERATURE

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 relative 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 \exists 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

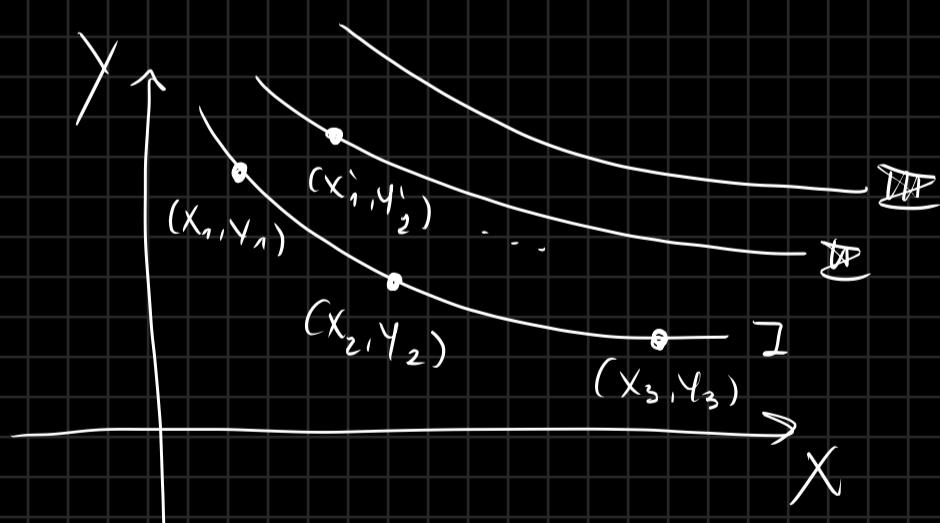


Fig 2.) Representation of isotherm curves of I , II , III in plane (X, Y)

N.B., it's assumed that AT LEAST a portion of the isotherm is continuous. Doing the same analysis on \mathbb{A} by removing B we find isotherms I' , II' , III' in an (X', Y') plane.

By definition, then, $I \leftrightarrow I'$, $\mathbb{I} \leftrightarrow \mathbb{I}'$, $\mathbb{II} \leftrightarrow \mathbb{II}'$, aka corresponding isotherms

We define the TEMPERATURE as the property in common bw/ states in thermal

equilibrium.
 Temperature MUST be scalar \rightarrow defined by a number. For each value T comes
 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
 off thermometers \neq temperature measurement

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

\Rightarrow Take a convenient path in (X, Y) (i.e. $Y = Y_1$) $\therefore \Theta = \Theta(X)$

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

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

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

$\Theta_A \rightarrow$ ABSOLUTE SCALE ($\Theta_A=0 \Rightarrow X=0$) e.g. } Kelvin
 } Rankine

STANDARD GAS FOR THERMOMETRIC EVAL $\rightarrow H_2$

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

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

$$\hookrightarrow a = \frac{273.16 K}{X_{TP}}$$

gen:

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

THUS!

$$\Theta(P) = 273.16 K \frac{P}{P_{TP}} \quad (\text{const. } V) \quad \left. \begin{array}{l} \text{Same goes for} \\ \text{Res., ent} \end{array} \right\}$$

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

NOTATION:

TP: Triple Point (Gas + Liquid + Solid)

NSP: Normal Sublimation Point (Solid \rightarrow Gas)

NMP: Normal Melting Point (Solid \rightarrow Liquid)

TEMPERATURE SCALES FOR IDEAL GASES

LAW (Ideal Gases)

$$PV = nRT \quad \left\{ \begin{array}{l} P \rightarrow \text{Pressure} \\ V \rightarrow \text{Volume} \\ T \rightarrow \text{Temperature} \end{array} \right. \quad \left\{ \begin{array}{l} n \rightarrow \text{mol} \\ R \rightarrow \text{molar gas const.} \end{array} \right.$$

Note, @ const V θ (absolute temp.)

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

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

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

Celsius, Rankine, Fahrenheit scales

- Celsius [Anders Celsius (SWE)]

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15 \quad (\text{defined at NMP H}_2\text{O } \{273.15 \text{ K}\})$$

- Rankine [William Rankine (UK)]

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

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

$$T(^{\circ}\text{F}) = T(R) - 459.67$$

$$\text{Thus: } \left\{ \begin{array}{l} T(^{\circ}\text{F}) = \frac{9}{5} T(\text{K}) - 459.67 \end{array} \right.$$

$$\left. \begin{array}{l} T(R) = \frac{9}{5} (T(^{\circ}\text{C}) + 273.15) \end{array} \right)$$

$$\left\{ \begin{array}{l} T(^{\circ}\text{F}) = \frac{9}{5} (T(^{\circ}\text{C}) + 273.15) - 459.67 \end{array} \right.$$

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

$$\text{Or: } T(^{\circ}\text{F}) = 1.8 T(^{\circ}\text{C}) + 32$$

SIMPLE Systems

\oint Thermo wnic equilibrium

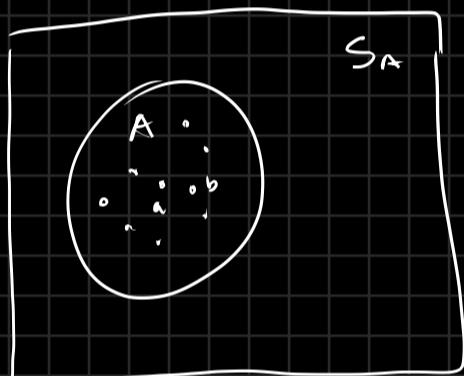
Def (Change of state)

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 \rightarrow balanced forces
- Chemical equilibrium \rightarrow no spontaneous chemical reaction + Mechanical equilibrium
- Thermal equilibrium \rightarrow Chemical + Mechanical eq + no change of words when separated from surroundings w/ dt well
- Thermodynamical equilibrium \rightarrow Mech + Chem + Thermal equilibrium



$$F_{N_m} = \sum_{i=1}^n f_{in} = 0 \Rightarrow \text{Mechanical equilibrium } \textcircled{1}$$

$$a \rightleftharpoons b \text{ or } a \rightleftharpoons a \Rightarrow \text{Chemical eq } \textcircled{2}$$

iff $\partial A / \partial t \Rightarrow$ iff $\textcircled{1} + \textcircled{2}$ & no change \Rightarrow Thermal $\textcircled{3}$

$$\textcircled{1} + \textcircled{2} + \textcircled{3} \Rightarrow \text{Thermodynamical equilibrium } \textcircled{4}$$

In $\textcircled{4}$ no change of state for A or S_A . Describable by macro variables s.t. $\frac{d\theta^i}{dt} = 0$

If $\textcircled{4} \times \Rightarrow$ NON EQUILIBRIUM STATE \Rightarrow NOT DESCRIBABLE W/ THERMODYNAMICS

{ Accelerations $\Rightarrow P_a(x_1) \neq P_a(x_2)$ & $T_A(x_1) \neq T_A(x_2) \Rightarrow \cancel{T_A}, P_a$

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 , P
 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., E , 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)

$$[P] = \text{N/m}^2 = \text{kg/ms}^2 = \text{Pa} = \text{lbf/in}^2 = \text{atm} = \text{mm Hg} = \text{in Hg}$$

$$[V] = \text{m}^3$$

$$[T] = [\Theta] = K$$

PURE SUBSTANCES, pV DIAGRAM

Consider H_2O @ $T = 94^\circ\text{C}$ in a vessel w/ $V \approx 2 \text{ m}^3$ with ad air water will evaporate completely \Rightarrow system in unsaturated vapor. If it's compressed slowly $\Rightarrow p$ rises \Rightarrow saturated vapor (steep graph py 2g 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, $\text{H}_2\text{O}_{(g)}$ is compressible $\rightarrow P_B = P_C$ @ C $\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)}$ (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 ($\text{H}_2\text{O}_{(l)}$ incompressible) therefore

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

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 bw/ liquid & vapour)

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

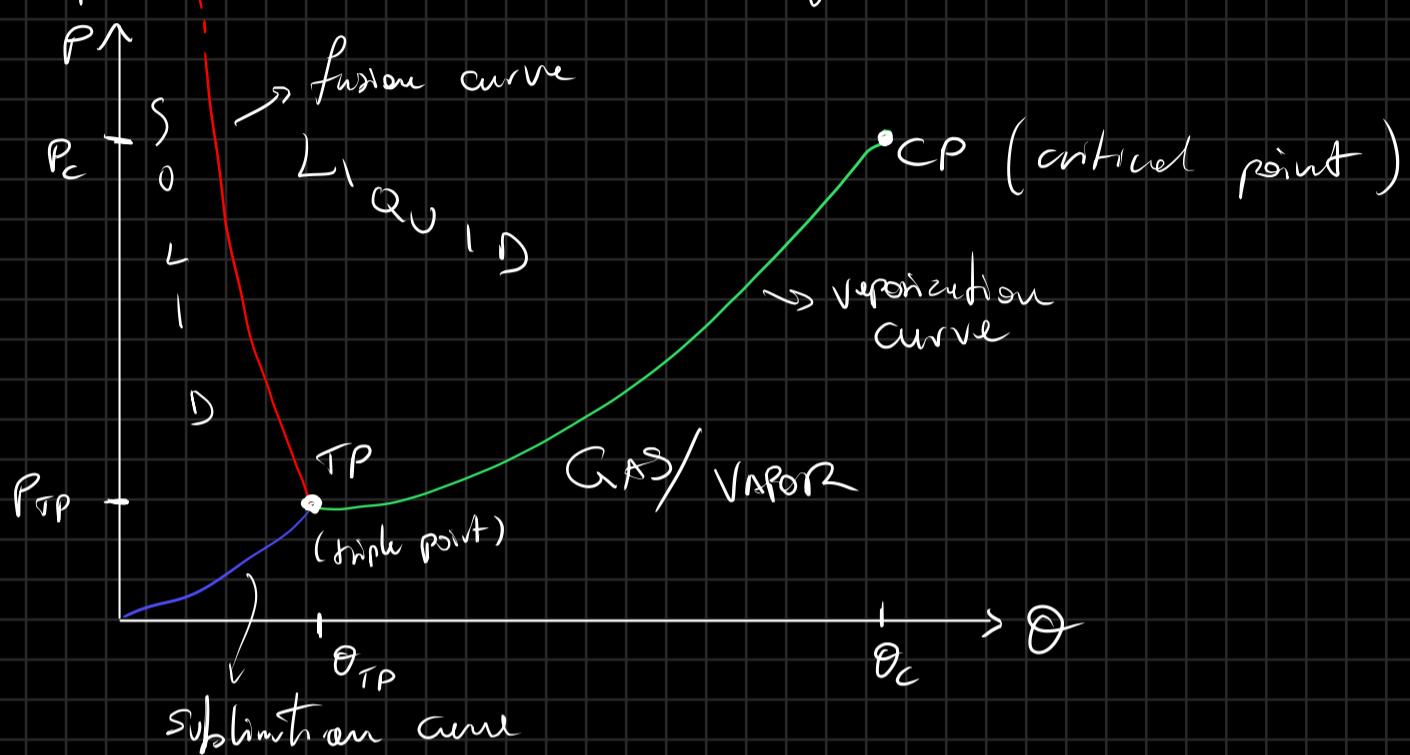
$$(P_c, V_c, T_c)$$

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

↳ P-T (pθ) diagram

$\theta \rightarrow$ ideal gas temp
 $T \rightarrow$ Kelvin temp

Masuring the vapor pressure of a solid until the T_C of 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 only in pθ diagrams.

↳ P-V-θ SURFACE

Representation of the informations obtained on (p,V,θ) measurements. (Steel fig 2-3, 4, 5)

fig 2-5 shows the P-V-θ surface for water, including 7 triple points (10 known)

④ for the fusion line slope ≥ 0 . Depends if V increases or decreases upon melting, see H_2O .

EQUATIONS OF STATE

IT'S IMPOSSIBLE TO DESCRIBE THE BEHAVIOR OF A SUBSTANCE OVER THE pVθ SURFACE!

There are various equations of state:

1) Low P, gass

$$PV = RD \quad (\text{IDEAL GAS})$$

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

b) R → gas constant

2) $(P, V, \theta) > (P, V, \theta)_T$, adjustable

$$\left\{ \begin{array}{l} PV = \frac{1}{\gamma} RD(1-\epsilon)(V+B) - \frac{A}{V} \quad (\text{BETTLE-BRIDGEMAN}) \\ A = A_0 \left(1 - \frac{a}{V}\right) \\ B = B_0 \left(1 - \frac{b}{V}\right) \\ \epsilon = \frac{c}{V^3} \end{array} \right.$$

3) Empirical

4) From kinetic theory &/ stat mech

$$\left(P + \frac{\alpha}{V}\right)(V - b) = RD \quad (\text{VAN DER WAALS})$$

N.B.

R → "universal gas constant"

DIFFERENTIAL CHANGES OF STATE

IN THERMODYNAMICS

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

1) given a volume V , $dV \ll V$, but dV is big enough to be macroscopic

2) given a pressure P , molecular perturbations dP , then

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

$$\left\{ \begin{array}{l} \left| \frac{dp}{p} \right| \ll 1 \\ \left| \frac{dV}{V} \right| \ll 1 \end{array} \right.$$

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

$$\left\{ \begin{array}{l} V = V(p, \theta) \\ p = p(V, \theta) \end{array} \right. \quad \theta = \theta(p, V)$$

therefore

$$\left\{ \begin{array}{l} dV = \frac{\partial V}{\partial p} dp + \frac{\partial V}{\partial \theta} d\theta \\ dp = \frac{\partial p}{\partial V} dV + \frac{\partial p}{\partial \theta} d\theta \end{array} \right. \quad d\theta = \frac{\partial \theta}{\partial p} dp + \frac{\partial \theta}{\partial V} dV$$

DEFINED

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

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

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

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

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

$$\textcircled{3} \quad 1 \text{ bar} = 10^5 Pa$$

DINI THEOREM (IMPLICIT FUNCTION)

Suppose $f(x,y,z)$ is a function such that, for a given point (x_1, y_1, z_1)

$$1) f(x_1, y_1, z_1) = 0$$

$$2) \nabla f \neq 0$$

$$\text{Then : } f(x,y,z) = f(x(y,z), y(x,z), z(x,y)) \quad \forall (x,y,z) \in B_\epsilon((x_0,y_0,z_0))$$

$$d\alpha = \frac{\partial \alpha}{\partial y} dy + \frac{\partial \alpha}{\partial z} dz, \quad dy = \frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial z} dz, \quad dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy$$

@ (b)

Taken ⑧, ⑪, then

$$\begin{cases} dx = \partial_y y dy + \partial_a x da \\ dy = \partial_x y dx + \partial_a y da \end{cases} \Rightarrow dx = \frac{\partial x}{\partial y} \left(\frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial a} da \right) + \frac{\partial x}{\partial a} da$$

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

$$\textcircled{1} \quad dz = 0 \Rightarrow \frac{\partial x}{\partial y} \frac{\partial y}{\partial x} = 1$$

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

$$\textcircled{2} \quad dx = 0 \Rightarrow \frac{\partial x}{\partial y} \frac{\partial y}{\partial z} = - \frac{\partial x}{\partial z}$$

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

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

$$\begin{cases} \frac{\partial p}{\partial v} \frac{\partial v}{\partial \theta} = - \frac{\partial p}{\partial \theta}, \\ \left\{ \begin{array}{l} \beta = \frac{1}{v} \frac{\partial v}{\partial \theta} \\ \kappa = - \frac{1}{v} \frac{\partial v}{\partial p} = - \frac{1}{v} \left(\frac{\partial p}{\partial v} \right)^{-1} \end{array} \right\} \begin{array}{l} \frac{\partial v}{\partial \theta} = v \beta \\ \frac{\partial p}{\partial v} = - \frac{1}{\kappa v} \end{array} \Rightarrow \left(- \frac{1}{\kappa v} \right) (v \beta) = - \frac{\partial p}{\partial \theta} \end{cases}$$

$$\therefore \Rightarrow \frac{\partial p}{\partial \theta} = \beta_n$$

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 \rightarrow work exerted from the system to the surroundings

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

ONLY EXTERNAL WORK IS SIGNIFICANT (IN THERMODYNAMICS)

Def (Quasi-static process)

INFINITE 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 ad 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, $dW = F \cdot dx$, if the movement happens only in the x -direction, then

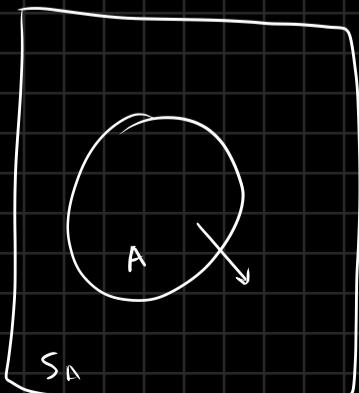
$$\begin{cases} dW = -Fdx \\ F = PS \end{cases}$$

Thus

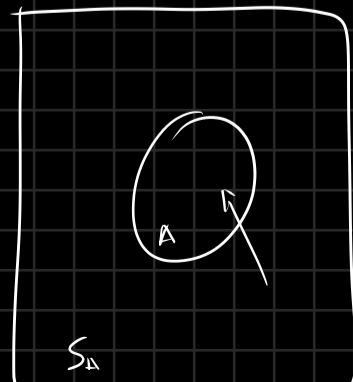
$$dW = -PSdx = -PdV$$

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

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



$$dW < 0$$



$$dW > 0$$

For a quasi-static process going through a transformation $V_i \rightarrow V_f$, 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:

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

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

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

If the path is quasi-static $\rightarrow W_{if} - W_{fi} = 0$

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

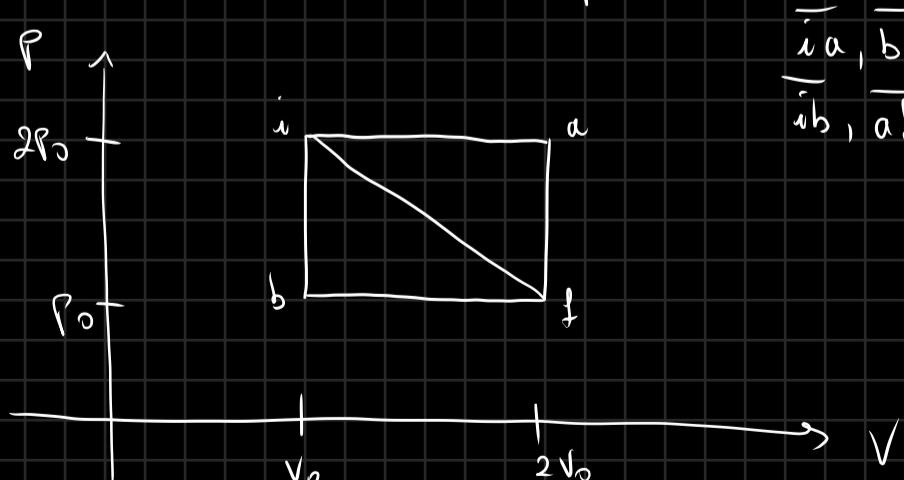
$$[P] = atm = 101.325 kPa$$

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

Thus,

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

Consider now 3 different processes on a pV plane:



$\overline{ia}, \overline{bf}$ \rightarrow isobaric process ($P = \text{const}$)
 $\overline{ib}, \overline{af}$ \rightarrow isochoric process ($V = \text{const}$)

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:

$$\left\{ \begin{array}{l} W_{iuf} = - \int_{iuf} p dV = -2P_0 \int_{iuf} dV = -2P_0 (2V_0 - V_0) = -2P_0 V_0 \\ W_{ibf} = - \int_{ibf} p dV = -P_0 \int_{ibf} dV = -P_0 (2V_0 - V_0) = -P_0 V_0 \neq W_{iuf} (!!) \\ W_{if} = - \int_{if} p dV = - \frac{3}{2}(P_0 V_0) \neq W_{iuf} + W_{ibf} (!!) \end{array} \right.$$

Work depends strictly on intermediate states (path)!

Therefore dW is an inexact differential (d) since $\oint dW \neq \int dW$!

\oint 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 ($\Theta = \text{const}$) compression / expansion

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

{Note that if $\Theta = \Theta(V, p)$ this is not true anymore}

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

$$W = nR\Theta \log\left(\frac{V_f}{V_i}\right) = (2 \cdot 10^3 \text{ mol}) R (273.15 \text{ K}) \log\left(\frac{1}{4}\right) \quad \left\{ \begin{array}{l} n = 2000 \text{ mol} \\ \Theta = 0^\circ\text{C} = 273.15 \text{ K} \\ V_f/V_i = \frac{1}{4} \end{array} \right.$$

Noting that $R = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}$ (Joule / Kelvin-mole) is the ideal gas const., we have

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

$$W = 2 \left(831.4 \right) (273.15) \log\left(\frac{1}{4}\right) \text{ J} \approx 6300000 \text{ J} = 6.3 \text{ MJ}$$

Note that $W > 0 \Rightarrow$ work was done 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

$$\left\{ \begin{array}{l} w = - \int p dV \\ dV = \frac{\partial V}{\partial P} dP + \frac{\partial V}{\partial \Theta} d\Theta \end{array} \right.$$

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:

$$w = - \int_{V_i}^{V_f} p dV = \int_{P_i}^{P_f} \kappa p V dP = \frac{\kappa V}{2} (P_f^2 - P_i^2) = \frac{\kappa V}{2} (1000^2 - 1) \text{ atm}^2$$

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

$$\rho = 8930 \frac{\text{kg}}{\text{m}^3}, \kappa = 7.16 \cdot 10^{-12} \text{ Pa}^{-1}, m = 100 \text{ kg}, P_i = 0 \text{ atm}, P_f = 1000 \text{ atm} = 101.325 \cdot 10^6 \text{ Pa} = 1.013 \cdot 10^8 \text{ Pa}, \text{ we have}$$

$$w = \frac{m \kappa}{2 \rho} (P_f^2 - P_i^2) = \frac{100 \text{ kg} \cdot 7.16 \cdot 10^{-12} \text{ Pa}^{-1}}{2 \cdot 8930 \frac{\text{kg}}{\text{m}^3}} \left((1.013)^2 \cdot 10^{16} \text{ Pa}^2 \right) \approx 0.411 \text{ J.m} = 0.411 \text{ kJ}$$

Pg. 63 (3-13)

+ ch. 4 Pg. 68

§ Composite systems

Consider 2 hydrostatic systems divided by a st wall. The composite 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

$$\delta w = -p dV - p' dV'$$

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

$$\delta w = Y \delta X + Y' \delta X'$$

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

$$\underbrace{f_1(X, Y, \Theta)}_{\substack{\text{Divi theorem} \\ \text{w/ EOS}}} \\ f_2(X', Y', \Theta)$$

1st LAW of THERMODYNAMICS

of 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

Def (Heat, calorimetric)

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

ad wall \rightarrow heat insulator

ct wall \rightarrow heat conductor

of Adiabatic work

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

-) Quasi-static motion of the piston $\rightarrow w = - \int p dV$

-) Non quasi-static motion of the piston \rightarrow **<free expansion>**

$\left. \begin{array}{l} \text{-) Joule effect w/ R} \\ \text{-) EM effects} \end{array} \right\}$

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

Work is path independent $\rightarrow w = \int_{\gamma} p dV = - \int_{\gamma'} p dV \Leftrightarrow \gamma \sim \gamma' : c[a,b] \rightarrow \mathbb{R}_{(P,V,\theta)}^3$

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

$$\text{Thus: } W_{12}(p, V, \theta) = U(p_2, V_2, \theta_2) - U(p_1, V_1, \theta_1) \quad \left\{ \begin{array}{l} > 0 \text{ if work is done ON system} \\ = 0 \text{ if no work is done} \\ < 0 \text{ if work is done FROM system} \end{array} \right.$$

\oint INTERNAL ENERGY FUNCTION

The function $U(p, V, \theta)$, & therefore dU , define the conservation of energy of the system when ad work is done.

It's not needed to know the exact functional shape of U , but just the fact that it exists. Since w/ EOS we have always one coordinate fixed, we have:

$$\left\{ \begin{array}{l} U_1(p, V) \\ U_2(V, \theta) \\ U_3(\theta, p) \end{array} \Rightarrow \begin{array}{l} dU_1 = \frac{\partial U_1}{\partial p} dp + \frac{\partial U_1}{\partial V} dV \\ dU_2 = \frac{\partial U_2}{\partial V} dV + \frac{\partial U_2}{\partial \theta} d\theta \\ dU_3 = \frac{\partial U_3}{\partial \theta} d\theta + \frac{\partial U_3}{\partial p} dp \end{array} \right. \quad \begin{array}{l} \text{Note that } \frac{\partial U_1}{\partial V} \neq \frac{\partial U_2}{\partial V} ! \\ U_1 = U_1(p, V), \quad U_2 = U_2(V, \theta) \end{array}$$

New notation:

$$U(X, Y) \& U(X, \theta) \Rightarrow \left\{ \begin{array}{l} dU = \frac{\partial U}{\partial X} dX + \frac{\partial U}{\partial Y} dY \\ dU = \frac{\partial U}{\partial X} dX + \frac{\partial U}{\partial \theta} d\theta \end{array} \right.$$

For avoiding confusion:

$$\left\{ \begin{array}{l} dU = \left(\frac{\partial U}{\partial X} \right)_Y dX + \left(\frac{\partial U}{\partial Y} \right)_X dY \\ dU = \left(\frac{\partial U}{\partial X} \right)_\theta dX + \left(\frac{\partial U}{\partial \theta} \right)_X d\theta \end{array} \right. \quad \begin{array}{l} \text{There is no confusion b/w } \left(\frac{\partial U}{\partial X} \right)_Y \& \left(\frac{\partial U}{\partial X} \right)_\theta \\ \text{read as "pdV of U wrt X at const \theta or Y"} \end{array}$$

\oint IS + LAW OF THERMODYNAMICS

Consider a system, on which we perform two experiments

- 1) change of state $i \rightarrow f$ adiabatically
- 2) change of state $i \rightarrow f$ non ad

For ①, we know that

$$W_{ad} = \Delta U_{if}$$

while for ②

$$W_{non} \neq \Delta U_{if}$$

but, since Energy is conserved \rightarrow energy has been transferred via other means which are not work \rightarrow heat (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 ΔU & W is heat, indicated by Q . Thus

$$Q = \Delta U - W \Rightarrow \Delta U = Q + W$$

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) $\Delta E_{\text{tot}} = 0$
- 3) Q is ENERGY IN TRANSIT by means of $\Delta \theta \neq 0$ (Joule, 1840-1843)

CONCEPT OF HEAT

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

$$Q = \int_{t_1}^{t_2} \frac{dQ}{dt} dt$$

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

Q , as work, depends on the path \rightarrow 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

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

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

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

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:

$$dU = \delta Q + \delta W \quad (\text{1st, diff})$$

If the process is quasi-static, then $dU = dU(p, V, \Theta)$, $\delta W = \delta W(p, V, \Theta)$. If the system is also hydrostatic, then

$$\delta W = -pdV$$

$$\therefore dU(p, V, \Theta) = \delta Q - p(V, \Theta)dV$$

Heat capacity & measurements

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

The average heat capacity is known, then, as:

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

The heat capacity is then defined as:

$$c = \frac{\delta Q}{\delta \Theta}$$

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

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

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

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

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

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

where M is the molar mass. By def., the number of moles in m_A mass of substance A is

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

The specific heat (molar) is then

$$c = \frac{C}{n} = \frac{1}{n} \frac{\delta Q}{\delta \Theta}, [c] = \frac{J}{mol K}$$

Note that $C \leq 0$ or also $C = \infty$ depending on the process.

For a hydrostatic system it has two specific values

$$\left\{ \begin{array}{l} C_p(p, \theta) = \left(\frac{\partial Q}{\partial \theta} \right)_p \approx C_p \text{ (heat capacity at } p=\text{const}) \\ C_v(v, \theta) = \left(\frac{\partial Q}{\partial \theta} \right)_v \approx C_v \text{ (heat capacity at } v=\text{const}) \end{array} \right.$$

↳ DEFINITION OF CALORIES

Def (calorie)

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

1) for $\Delta \theta = 1^\circ C$, $\theta_i = 14.5^\circ C$, $\theta_f = 15.5^\circ C$ per unit mass of water

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

↳ Equations of a hydrostatic system

As we determined before, for a hydrostatic system

$$du = dQ - pdV$$

$$dQ = du + pdV$$

Thus, choosing coordinates (θ, V)

$$\left\{ \begin{array}{l} du = \left(\frac{\partial u}{\partial \theta} \right)_V d\theta + \left(\frac{\partial u}{\partial V} \right)_\theta dV \\ dQ = \left(\frac{\partial u}{\partial \theta} \right)_V d\theta + \left(\frac{\partial u}{\partial V} \right)_\theta dV + pdV \end{array} \right.$$

Thus:

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

$$\boxed{\frac{\partial Q}{\partial \theta} = \left(\frac{\partial u}{\partial \theta} \right)_V + \left[\left(\frac{\partial u}{\partial V} \right)_\theta + p \right] \frac{dV}{d\theta}} \quad \text{1st Law}$$

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

$$\left(\frac{\partial Q}{\partial \theta} \right)_V = \left(\frac{\partial u}{\partial \theta} \right)_V = C_V (!)$$

b) $p = \text{const}$

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

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

$$\left(\frac{\partial Q}{\partial \theta}\right)_P = C_V + \beta V \left[\left(\frac{\partial U}{\partial V}\right)_\theta + P \right] = C_P$$

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

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

f 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 $M > m$, with m being the system's mass.

\therefore A finite amount of heat transfer will not bring an appreciable change on the larger body.

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

Def (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 IS a change of state $(P_1, V_1, \theta_1)_R \rightarrow (P_2, V_2, \theta_2)_R$, but it's NEGLIGIBLE

$$(P_1, V_1, \theta_1)_R \approx (P_2, V_2, \theta_2)_R$$

Any quasi-static proc of a system in contact with a reservoir IS ISOTHERMAL

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:

$$\left(\frac{\partial Q}{\partial \theta}\right)_P = C_P \Rightarrow Q_P = \int_{\theta_i}^{\theta_f} C_P d\theta$$

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

$$Q_P = C_P \Delta \theta \quad (\text{isobaric process})$$

If instead $V = \text{const}$

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

$C_V(\theta) \approx C_V$, 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 t . We have

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

Combining $\Delta x \rightarrow 0$, $t \rightarrow 0$, we have

$$\frac{dQ}{dt} = -kA \frac{d\theta}{dx} \quad \begin{array}{l} \text{Thermal conductivity} \\ \text{---} \\ Q > 0 \Rightarrow x > 0 \end{array}$$

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

$$R \left\{ \begin{array}{l} \gg 0 \text{ thermal conductor} \\ = 0 \text{ perfect insulator} \\ \ll 1 \text{ thermal insulator} \end{array} \right.$$

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

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

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 metals the heat lost through the insulation is then evaluated by subtracting the heat supplied by the electrode & heat which enters in the water

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

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

If $\Delta\theta \ll 1$ then $k = \langle k \rangle_0$

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

Note Hunt

-) impurities in metal change radius by κ . Eg. tube Cu w/ As impurities

$$\kappa_{\text{Cu}} \approx 3 \kappa_{\text{Cu, no}}$$

-) Continuous heating or changes in pressure change κ

-) $\kappa_{(e)} < \kappa_{(s)}$

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

-) Non metallic solids behave like liquids

-) For metals $\kappa(\theta_1) > \kappa(\theta_2) \leq \kappa_{\max}$

-) $\frac{\partial \kappa}{\partial P} \approx 0$ for gases, & limiting pressure $P_{\text{e, gas}} \ll P_{\text{atm}}$, $\frac{\partial \kappa}{\partial \theta} > 0$

IDEAL GASES

EOS OF A GAS

Gases are the best behaved thermometric substances since

$$\lim_{P \rightarrow 0} \left(\frac{P}{P_{TP}} \right) \rightarrow \text{is independent from the gas nature}$$

With this definition, we have

$$\Theta = 273.15 \lim_{P \rightarrow 0} \left(\frac{P}{P_{TP}} \right) K \quad (\text{IDEAL GAS TEMPERATURE})$$

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

$$P\nu = \sum_{n=0}^{\infty} \frac{a_n}{\nu^n}, \quad a_n = (A, B, C, \dots)$$

The coefficients a_n are known as << Vinel coefficients >>, and $a_i \equiv a_i(\Theta, \dots)$

For $0 \text{ atm} < P < 40 \text{ atm}$ we have that

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

It is found that

$$\lim_{P \rightarrow 0} (P\nu) = A(\Theta)$$

Thus, since

$$\begin{aligned} \Theta &= 273.16 \lim_{P \rightarrow 0} \left(\frac{P}{P_{TP}} \right)_{V,n} K \\ \Rightarrow \Theta &= 273.16 \lim_{P \rightarrow 0} \left(\frac{P\nu}{P_{TP}\nu} \right) K = 273.16 \frac{\lim(P\nu)}{\lim(P_{TP})} K \end{aligned}$$

I.e.:

$$\lim_{P \rightarrow 0} (P\nu) = \frac{\lim(P\nu)_{TP}}{273.16} \Theta$$

We then define the << UNIVERSAL GAS CONSTANT >>

$$R = \frac{\lim(P\nu)_{TP}}{273.16} \text{ K} \approx 8.31441 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Thus, finally

$$\lim_{P \rightarrow 0} (P\nu) = nR\Theta = A(\Theta)$$

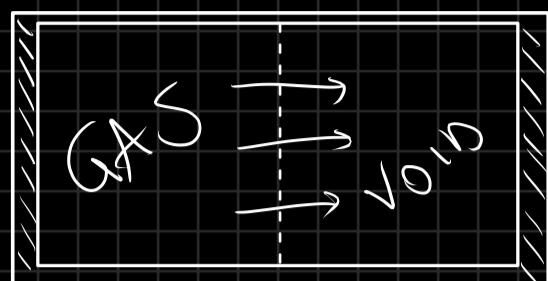
And the vinel expansion becomes

$$\frac{P\nu}{R\Theta} = 1 + \sum_{n=1}^{\infty} \frac{a_n}{\nu^n}$$

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

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

From the first law then

$$dU = \delta Q + \delta W = 0$$

$$\therefore U = U_0$$

In general tho

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

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 $P \rightarrow 0$ we have

$$\begin{aligned} pV &= nR\theta \\ \left(\frac{\partial U}{\partial P}\right)_\theta &= 0 \end{aligned}$$

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

$$\left(\frac{\partial u}{\partial v}\right)_\theta = -\frac{P}{v} \left(\frac{\partial v}{\partial p}\right)_\theta = 0$$

Thus

$$u(p, v, \theta) \equiv u(\theta)$$

FOR AN IDEAL GAS u depends only on θ . Now, for the 1st Law

$$\begin{cases} \delta Q = \delta U - \delta W \\ \delta W = -pdV \Rightarrow \delta Q = \frac{\partial U}{\partial \theta} d\theta + pdV \\ \delta U = \frac{\partial U}{\partial \theta} d\theta = C_V d\theta \end{cases}$$

$$\boxed{\delta Q = C_V d\theta + pdV} \quad \text{1st Law (IDEAL)}$$

For all equilibrium states we have

$$pV = nR\theta$$

Thus, in a quasi-static process

$$d(pV) = pdV + Vdp = nRd\theta$$

$$\therefore pdV = nRd\theta - Vdp$$

$$\delta Q = (C_V + nR)d\theta - Vdp$$

Therefore

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

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

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

Therefore

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

$$\begin{cases} \delta Q = C_V d\theta + pdV \\ \delta Q = C_p d\theta - Vdp \end{cases}$$

Also

Determination of C_p & C_v

1) ALL GASES (constant 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) MONATOMIC GASES {He, Ne, ...}

a) $C_V \approx \frac{3}{2}R$

b) $C_p = C_V + R \approx \frac{5}{2}R$

c) $\gamma = \frac{C_p}{C_V} \approx \frac{5}{3}$

3) DIATOMIC GASES {H₂, O₂, N₂, ...}

a) $C_V \approx \frac{5}{2}R$

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

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

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:

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

§ QUASI-STATIC ADIABATIC PROCESSES

From the first law, we have

$$\left\{ \begin{array}{l} \delta Q = C_V d\theta + PdV \\ \delta Q = C_P d\theta - Vdp \end{array} \right.$$

In an adiabatic process $\delta Q = 0$, thus

$$\left\{ \begin{array}{l} PdV = -C_V d\theta \\ Vdp = C_P d\theta \end{array} \right.$$

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

$$\int \frac{dp}{P} = -\gamma \int \frac{dV}{V}$$

Considering that $\gamma \approx \text{const}$, we have finally

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

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

$$\therefore PV^\gamma = \text{const.}$$

$PV^\gamma = \text{const}$ 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 ,

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

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

of 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 1st law we 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 1st law that

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

This process continues till $p = p_{\text{atm}}$, 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 $|Q_H| > |Q_C| \neq |W| \neq 0 \Rightarrow$ 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

$$\left\{ \begin{array}{l} \Delta U = Q_T + W_T = 0 \\ Q_T = |Q_H| - \underbrace{|Q_C|}_{\text{coming back}} \\ W_T = |W| \end{array} \right.$$

Thus

$$|W| = |Q_H| - |Q_C|$$

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

$$\eta = 100\% \text{ iff } |Q_C| = 0 \quad (\text{no heat transfer from the system})$$

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

-) Internal combustion engine (gasoline, diesel)
-) External combustion engine (Stirling, steam)

external combustion \rightarrow heat source outside the system

internal combustion \rightarrow 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:

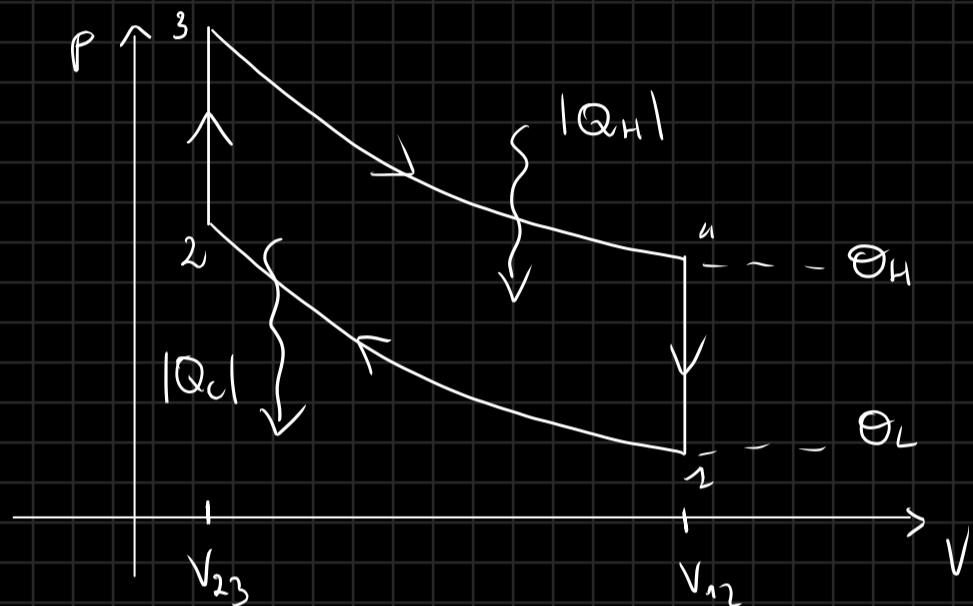


Fig. Stirling cycle

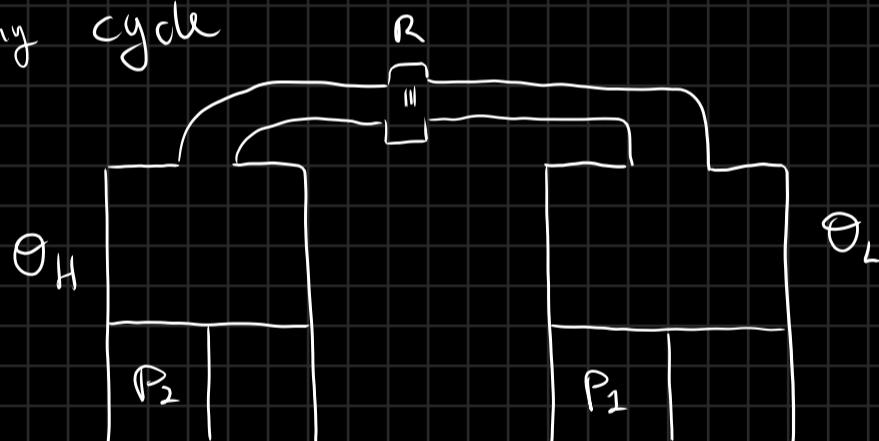


Fig. Stirling engine. $R \rightarrow$ regenerator

$1 \rightarrow 2$: isothermal compression of the gas in P_1 @ θ_L w/ $\dot{Q} = -|Q_L|$

$2 \rightarrow 3$: isochoric heating of gas (P_1 up, P_2 down, $V = \text{const.}$) release of $|Q_R|$ to R

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

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

At the end $\rightarrow -|Q_L| \xrightarrow{1 \rightarrow 2} |Q_R| \xrightarrow{2 \rightarrow 3} |Q_H| \xrightarrow{3 \rightarrow 4} -|Q_R|$

$$\therefore Q_T = |Q_H| - |Q_L| = |W| \quad (\text{ideal system})$$

§ ICE

- Six processes (strokes)

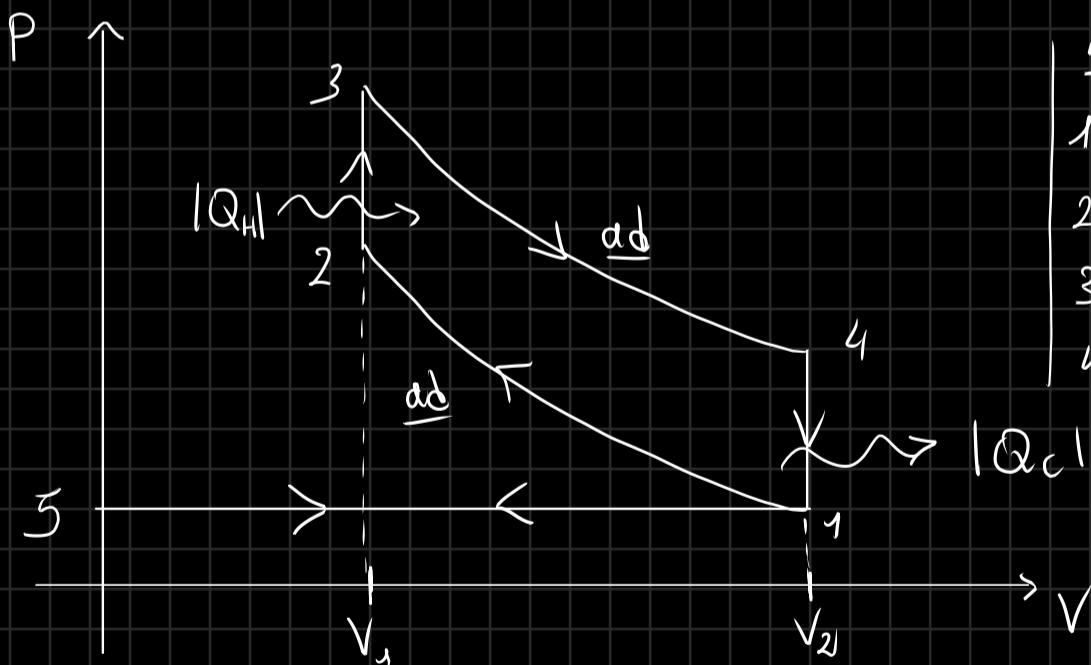
- 1) Intake (get a mix of fuel & air)
- 2) Compression
- 3) Ignition (spark, high θ & high P)
- 4) Power (expansion)
- 5) Valve exhaust (expansion to colder outside)
- 6) Exhaust stroke (piston pushes out)

IDEAL ICE : OTTO ENGINE (DIESEL)

Approximations:

-) Working substance: air, ideal gas
-) Quasi-static processes
-) No friction

§ AIR-STANDARD OTTO CYCLE



5 → 1 isobaric intake ($V_5=0, V_1$)
 1 → 2 adiabatic compression
 2 → 3 isochoric heating
 3 → 4 adiabatic expansion
 4 → 1 isochoric cooling
 1 → 5 isobaric exhaust

$5 \rightarrow 1$, increase of moles to n_1 $\partial P_1, \Theta_1$

$$P_1 V = b R \Theta_1$$

$1 \rightarrow 2$, adiabatic compression, heating from Θ_1 to Θ_2

$$P_1 V_1^\gamma = P_2 V_2^\gamma ; P_2 = \frac{n R \Theta_2}{V_2} \Rightarrow \Theta_1 V_1^{\gamma-1} = \Theta_2 V_2^{\gamma-1}$$

$2 \rightarrow 3$ isochoric heating, absorption of $|Q_H|$ from reservoirs Θ_2, Θ_3

$3 \rightarrow 4$ adiabatic expansion w/ cooling from Θ_3 to Θ_4

$$\begin{cases} \Theta_3 V_3^{\gamma-1} = \Theta_4 V_4^{\gamma-1} \\ V_3 = V_2, V_4 = V_1 \end{cases} \Rightarrow \Theta_3 V_3^{\gamma-1} = \Theta_4 V_4^{\gamma-1}$$

$4 \rightarrow 1$ isochoric cooling, emission of $|Q_C|$ to external reservoirs Θ_4, Θ_1

$1 \rightarrow 5$ isoburnic exhaust, $V \cdot V_1 \rightarrow 0, n \cdot n_1 \rightarrow 0, \Theta = \Theta_1$ (const)

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

Note:

Thus heat absorption at $2 \rightarrow 3$, $|Q_H|$ & emission at $4 \rightarrow 1$ of $|Q_C|$

$2 \rightarrow 3$) By definition

$$|Q_H| = \int_{\Theta_2}^{\Theta_3} C_V d\Theta = C_V (\Theta_3 - \Theta_2) > 0$$

$4 \rightarrow 1$)

$$|Q_C| = \int_{\Theta_4}^{\Theta_1} C_V d\Theta = C_V (\Theta_1 - \Theta_4) < 0$$

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 ad processes $1 \rightarrow 2$ & $3 \rightarrow 4$ ($V_1 = V_2, V_3 = V_4$)

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

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

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

$$\eta = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{1}{3} = \frac{2}{3} \approx 67\%$$

AIR STANDARD DIESEL ENGINE (Pg 143)

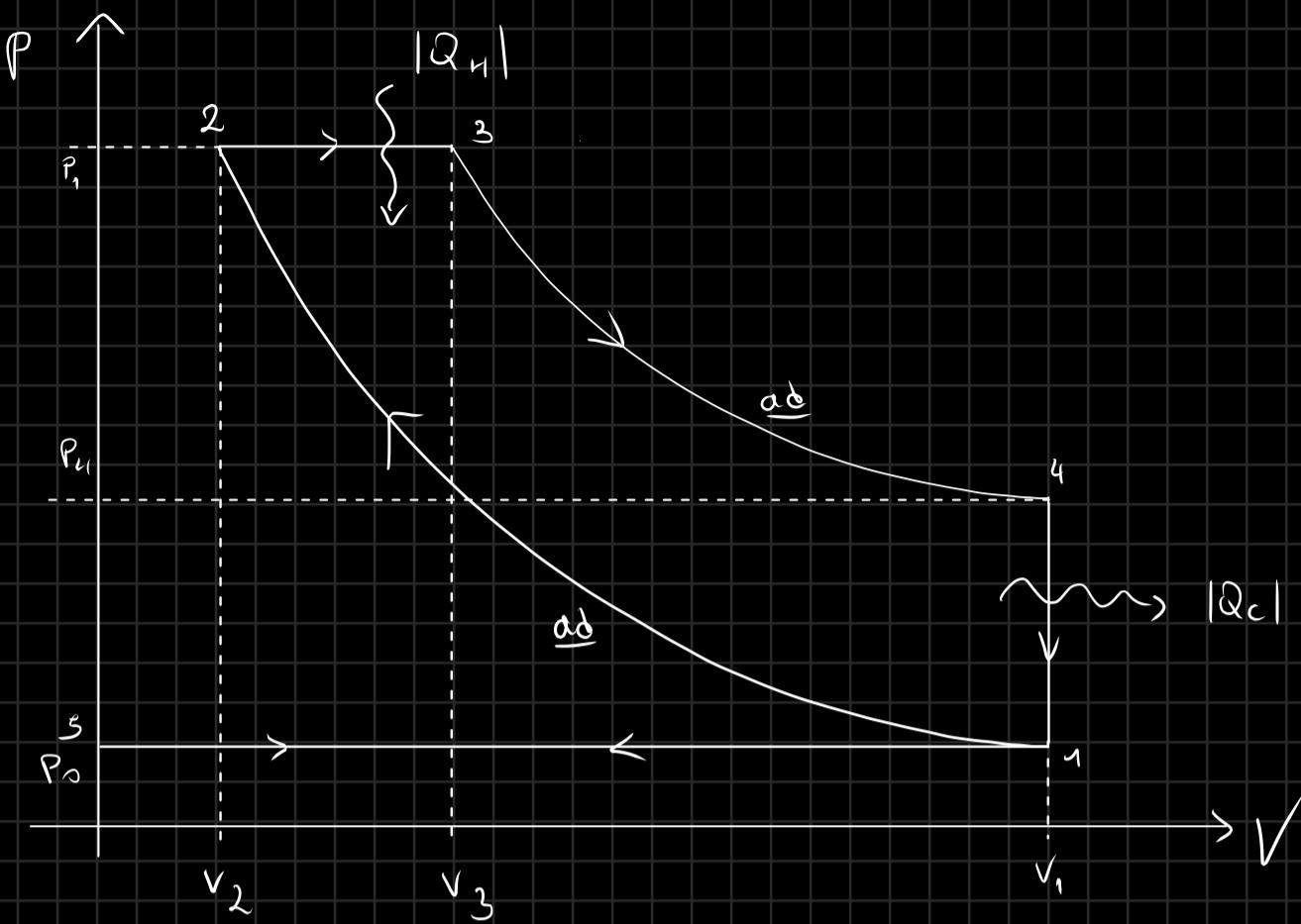


Fig. (Diesel) Air-standard diesel cycle

5 → 1) Air intake (isoboric expansion, 0 → V₁, 0 → n)

1 → 2) Adiabatic compression until combustion (P₀ → P₁, V₁ → V₂)

2 → 3) Isobaric increase of temperature (V₂ → V₃) |Q_H|

3 → 4) Adiabatic expansion (P₁ → P_n, V₃ → V₁)

4 → 1) Isochoric decrease of temperature (P_n → P₀) |Q_C|

4 → 5) exhaust (V₁ → 0, n → 0)

ex.: find η

$$-\eta = 1 - \frac{|Q_C|}{|Q_H|}$$

1) ∫Q ≠ 0 in only 2 → 3, 4 → 1 dQ ≈ C_v dθ

$$\therefore |Q_H| = C_v \left| \int_{\theta_2}^{\theta_3} d\theta \right| ; |Q_C| = C_v \left| \int_{\theta_1}^{\theta_n} d\theta \right|$$

2) 1 → 2) change of temperature θ₁ → θ₂, 3 → 4) + θ₃ → θ₄

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

$$\begin{cases} P_1 V_3 = nR \theta_3 \\ P_n V_1 = nR \theta_n \end{cases} \quad \left. \begin{cases} P_1 = nR \theta_3 / V_3 \\ P_n = nR \theta_n / V_1 \end{cases} \right\} \therefore \theta_3 V_3^{r-1} = \theta_n V_n^{r-1}$$

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

$$\begin{cases} \theta_1 V_1^{\gamma-1} = \theta_2 V_2^{\gamma-1} \\ \theta_3 V_3^{\gamma-1} = \theta_4 V_4^{\gamma-1} \end{cases}; \eta = 1 - \left| \frac{Q_C}{Q_H} \right| = 1 - \frac{\theta_4 - \theta_1}{\theta_3 - \theta_2}$$

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

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

if it is a simple machine
Cit. M.W. Zemansky pg 145

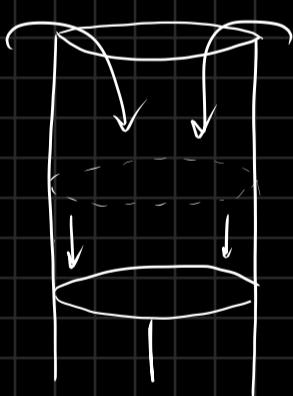
F) $\eta = 1 - \frac{1}{\gamma} \frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}}$

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

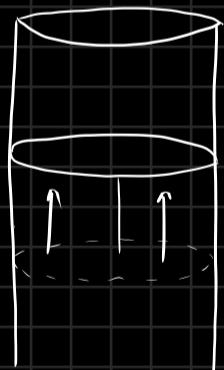
$$r_C = 15, r_E = 5, \gamma = \frac{3}{2}$$

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

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



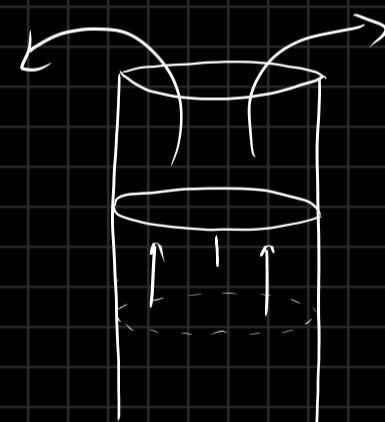
$5 \rightarrow 1$
intake
stroke



$1 \rightarrow 2$
compression
stroke



$2 \rightarrow 3$
 $3 \rightarrow 4$
isochoric heat
increase
(ignition)
+ adiabatic
expansion



$4 \rightarrow 1$
 $1 \rightarrow 5$
isochoric
heat decrease
+ exhaust
stroke

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-Planck 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

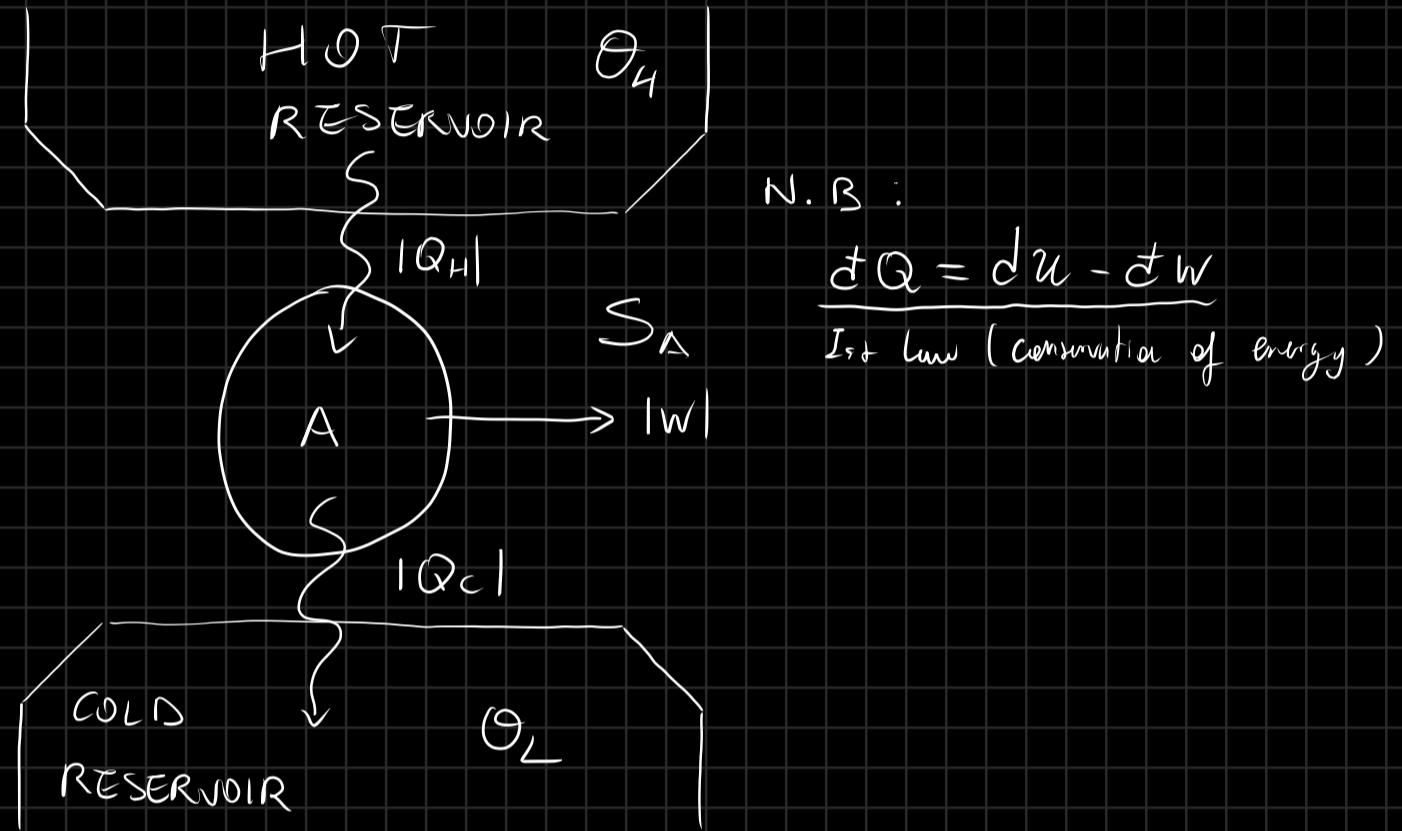


Fig IIa) Schematization of thermodynamic heat conversion into work

Everything that has been found in experiment can be reduced 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 $\nexists \Theta_H$ (Q_H), 2) $Q_C < Q_H$ is emitted $\nexists \Theta_L$, 3) W is done to surroundings

Opposite cycle \rightarrow Absorption higher $\nexists \Theta_L$ & emission $\nexists \Theta_H$ + W {REFRIGERATOR}

A Stirling cycle can be reversed

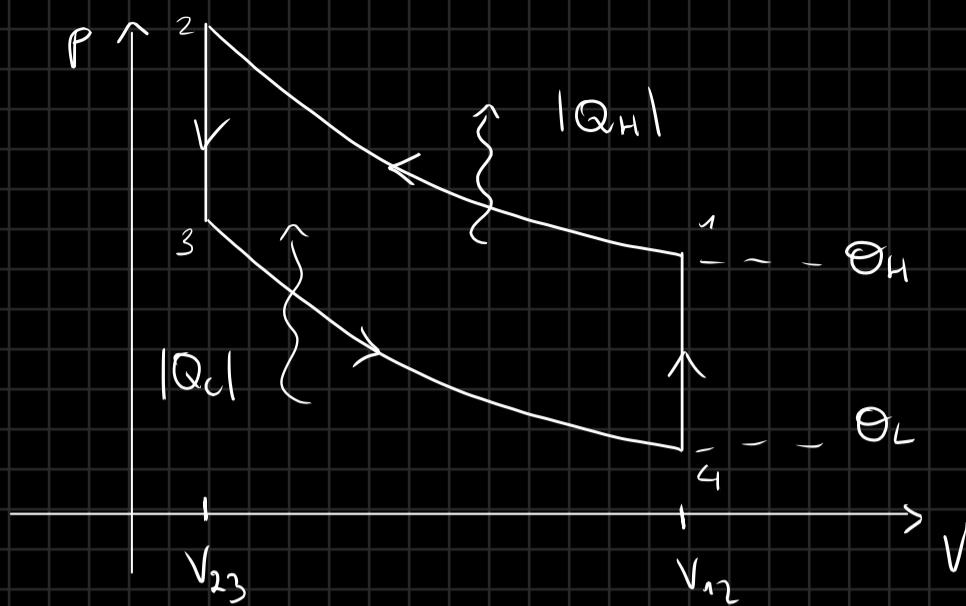


Fig SR) Stirling refrigerator cycle

1 → 2) Isothermal compression @ Θ_H , emission of $|Q_H|$ from hot reservoir

2 → 3) Isochoric cooling (real emits $|Q_R|$ to reservoir)

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 refrigeration are in Fig. RS

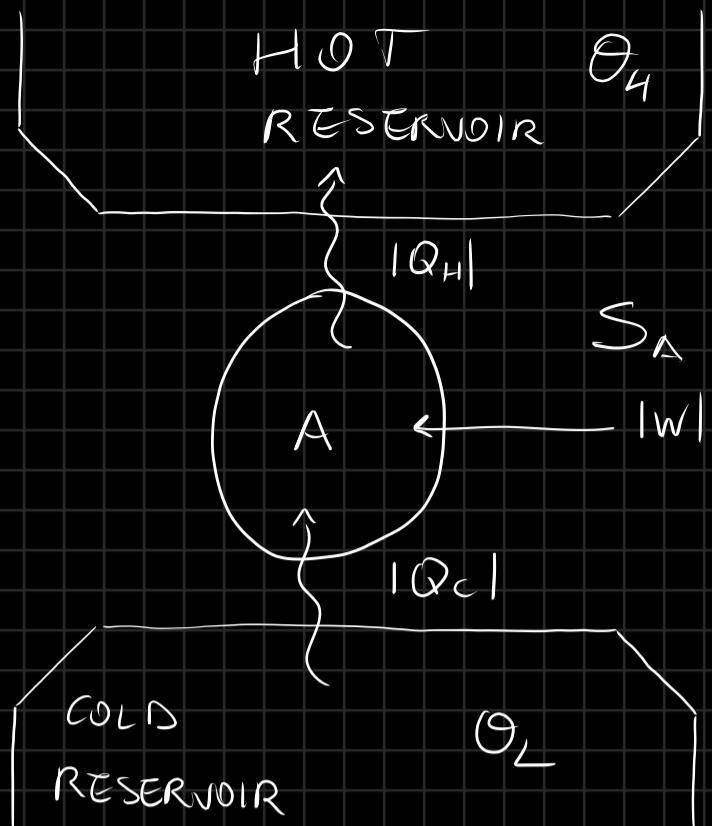


Fig RS) Refrigerator scheme. Note the inversion of work from "done to" to "done from".
The negative statement was given by Kelvin:

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

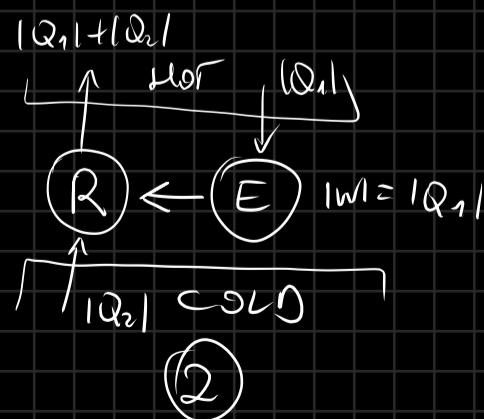
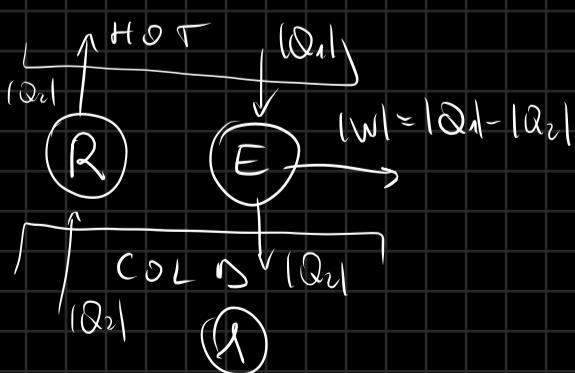
1) Consider a refrigerator for which $w = 0$ (violates Clausius) that transfers $|Q_2|$ from a cold to a hot reservoir.

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 $|Q_{cl}| = 0$ ($\neg KP$). 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.

Schemm:



Therefore:

$$\text{Clausius} \equiv \text{Kelvin-Planck} \quad (\text{Ex Ch 7 P. 158})$$

REVERSIBILITY & ABSOLUTE TEMPERATURE

Def (Local & Auxiliary surroundings)

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

Def (Reversibility)

Consider a process from a state A to a state B.

If in $A \rightarrow B$ Q heat is transferred & W is made, if in going $B \rightarrow A$ 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 $\oplus \Delta Q$

↳ 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 complete restoration to the initial state, Q heat must be extracted from the reservoir & completely converted into work

→ Violation of Kelvin-Planck

∴ Irreversible process

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

→ Violation of Kelvin-Planck

All the processes exhibit dissipative effects are irreversible.

If work is dissipated into internal energy

→ EXTERNAL MECHANICAL IRREVERSIBILITY

INTERNAL IRREVERSIBILITY

INTERNAL ENERGY \rightarrow MECHANICAL ENERGY \rightarrow 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 \rightarrow No local surroundings

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

- 1) No friction (quasi-static) \rightarrow Work from external machine
- 2) Since $W > 0, Q < 0 \& Q = -W \quad \nexists$
 \rightarrow VIOLATION OF KELVIN-PLANCK

EXTERNAL 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
 \rightarrow Violation of Clausius

\therefore EXTERNAL THERMAL IRREVERSIBILITY

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

CHEMICAL IRREVERSIBILITY

SPOONTANEOUS 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

\rightarrow ALL CHEMICALLY IRREVERSIBLE

\rightarrow ALL NATURAL SPONTANEOUS PROCESSES ARE IRREVERSIBLE

-) violation of thermodynamical equilibrium
-) Perse 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 dissipation effects

Approximatively \rightarrow huge reservoir

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

CARNOT CYCLES & ABSOLUTE TEMPERATURE

§ CARNOT CYCLE

Ideal simple cycle, for which:

- 1) All reversible:

$1 \rightarrow 2$) Adiabatic compression from θ_L to θ_H

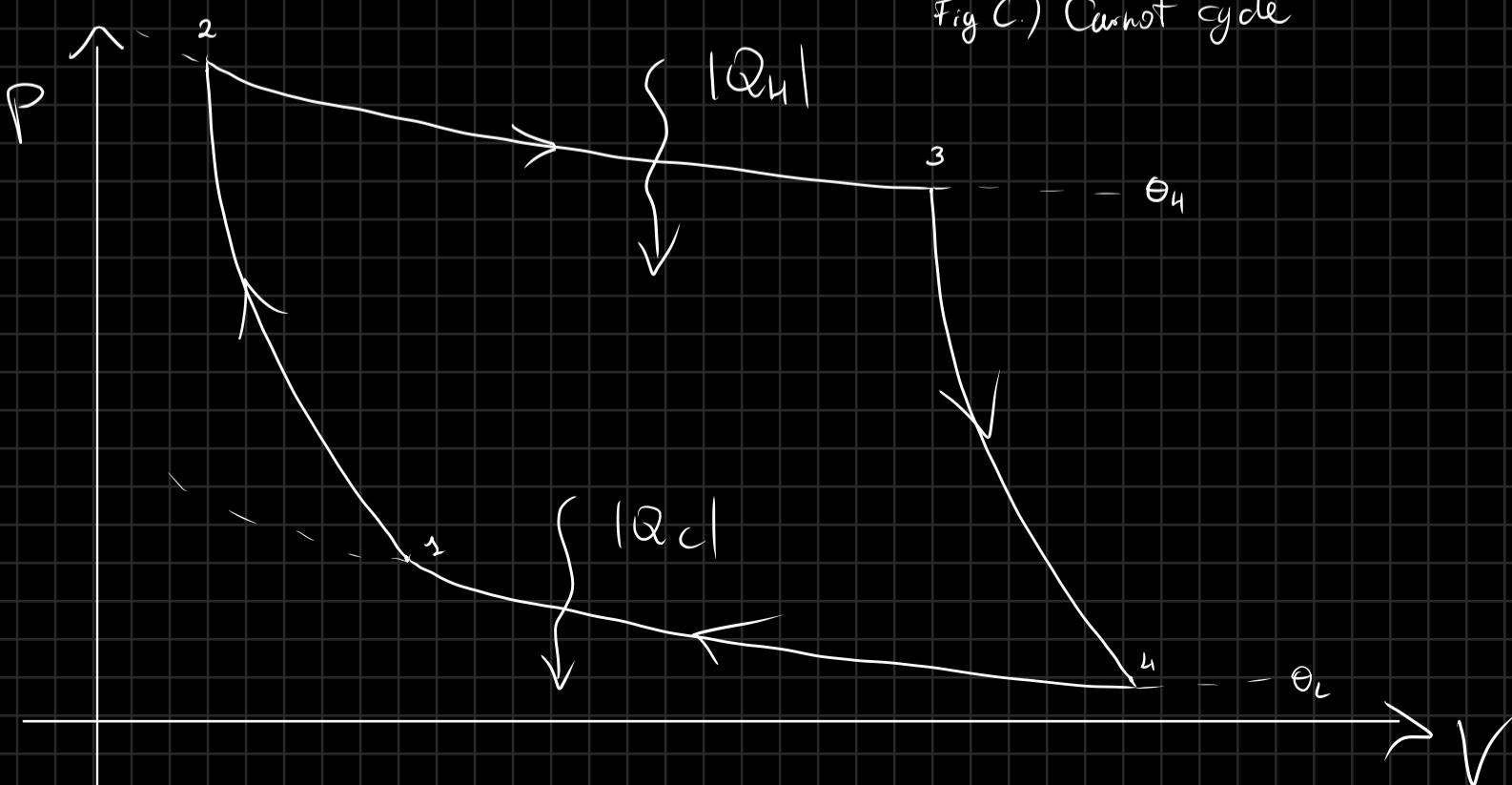
$2 \rightarrow 3$) Isothermal heat absorption

$3 \rightarrow 4$) Adiabatic expansion from θ_H to θ_L

$4 \rightarrow 1$) Isothermal heat emission at θ_L

All processes reversible; \therefore reversible engine

e.g.



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

Note that:

$$|Q_H| = |Q_H^R|, |Q_C| = |Q_C^R|, |W| = |W^R|$$

For water, a bi-fluid Carnot cycle (water-Steam) has a different shape following the saturation values of (P, V, δ)

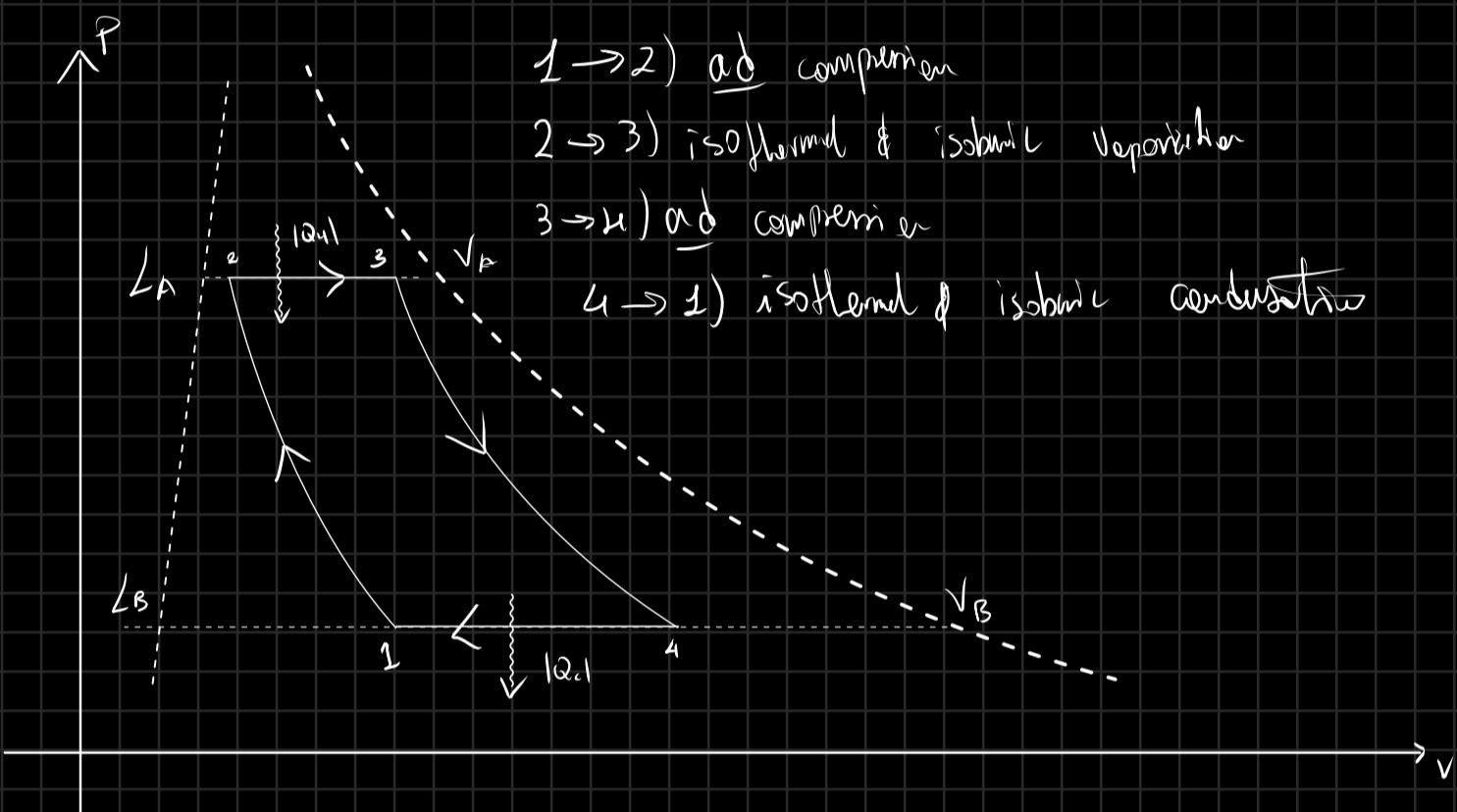


Fig WC) Water-Carnot cycle, $L_A V_A \rightarrow$ isoth/ isob vaporization line, $L_B V_B \rightarrow$ isoth/ isob condensation

During vaporization $|Q_H|$ is absorbed from the hot reservoir & during condensation $|Q_C|$ gets emitted to the cold reservoir

CARNOT THEOREM

Theorem (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

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

Assume that $\eta_I > \eta_R$, thus

$$|Q_H| > |Q'_H|$$

Reverse the Carnot engine, and take the work emitted 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 Thus.

$$\eta_I \leq \eta_R$$

Corollary

All Carnot engines b/w two equal reservoirs 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)

1st 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, then the cycle goes b/w two reservoirs @ $T_H > T_L$, & gets $|Q_H|$ ($|Q_L|$) absorbed (emitted) w/ efficiency η_R

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

By definition, we have that

$$\eta_R = \varphi(T_H, T_L)$$

Therefore, we can write

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

Thus taking 3 Carnot engine working b/w $T_1 > T_3 > T_2$, we have

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

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

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

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

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

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

The defined scale is the **ABSOLUTE SCALE** (measured in K (SI) or Rn (imp)). By def.

$$T_{\text{ref}} = 273.16 \text{ K}$$

Thus :

$$\left| \frac{Q}{Q_{\text{ref}}} \right| = \frac{T}{T_{\text{ref}}}$$

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

Note that

$$\Theta = 273.16 \text{ K} \lim_{P_{\text{ref}} \rightarrow 0} \left(\frac{P}{P_{\text{ref}}} \right)$$

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 b/w $\theta = \theta_1, \theta = \theta_2$, we have

$$\left\{ \begin{array}{l} pV = nR\theta_1 \\ pV = nR\theta_2 \end{array} \right.$$

For the 1st law

$$\delta Q = C_V d\theta + pdV \Rightarrow |Q| = \int_{V_1}^{V_2} pdV = nR\theta \int_{V_1}^{V_2} d\log(V)$$

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

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 $\theta_1 \rightarrow \theta_2$ $\delta Q = 0$, Hence

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

Thus :

$$pdV = -C_V d\theta$$

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

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

Thus

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

$$\therefore \left| \frac{Q_1}{Q_2} \right| = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \quad \boxed{\text{Q.E.D}}$$

$$\underbrace{\left\{ \theta = T \right\}}$$

SECOND PRINCIPLE OF THERMODYNAMICS

KARATHEODORIS FORMULATION

The mathematical formulation of the 2nd principle comes from the Greek mathematician Karathodoris.

Axiom

In a neighbourhood 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

$$dQ = du - ydx$$

If this is an equation of state $f(x, y, t) = 0$, then only 2 variables 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

$$dQ = \left(\frac{\partial u}{\partial x}\right)_t dx + \left(\frac{\partial u}{\partial t}\right)_x dt - ydx$$

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

For a reversible adiabatic process

$$dQ = 0$$

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

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

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

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

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

The solutions for $\frac{dt}{dx}$ are the surfaces $\sigma(x, t) = k \in \mathbb{R}$, aka *coadiabatic surfaces*

Follers directly from the 1st law; for the 2nd law we have that all adiab processes lie

on now intersecting surfaces $\sigma(n, t)$

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

$$\delta Q = dU - ydn - y'dn'$$

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

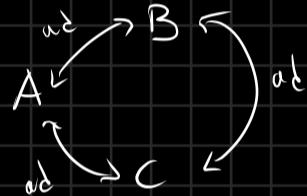
$$\begin{cases} f_1(n, y, t) = 0 \\ f_2(n', y', t) = 0 \end{cases}$$

Thus, only 3 coordinates are independent, say (n, n', U) . Said A an eq state and B an eq state reachable via a rev. proc. ^(*) C has the same (n, n') coords of B

Take a third state C^(*), and suppose that there's a possible ad rev. proc to reach both B & C, i.e.

$$A \xleftarrow{\text{ad}} B \xleftarrow{\text{ad}} C$$

Suppose that the process passes through the following cycle



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 ad it's $W=0$, $Q=0$!

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

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

$$\therefore Q_{ABC} = W_{ABC} \stackrel{?}{=} 0$$

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

f INTEGRABILITY OF δQ

Consider again

$$\delta Q = dU - ydn - y'dn'$$

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

Since $\mathcal{L} = \text{span}\{n, n', t\}$ & it's subdivided in surfaces

$$\sigma(n, n', t) = \int_{\mathbb{R}} g(R)$$

We might indicate every point in \mathcal{L} using (n, n', σ) ; then

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

Thus:

$$\delta Q = \left(\frac{\partial u}{\partial n} \right)_{n=0} dn + \left(\frac{\partial u}{\partial n'} \right)_{n'=0} dn' + \left(\frac{\partial u}{\partial \sigma} \right)_{\sigma=0} d\sigma - y dn - y' dn'$$

$$dQ = \left(\frac{\partial u}{\partial \sigma} \right)_{n,n'} d\sigma + \left[\left(\frac{\partial u}{\partial n} \right)_{n=0} - y \right] dn + \left[\left(\frac{\partial u}{\partial n'} \right)_{n'=0} - y' \right] dn'$$

1) $d\sigma = dn = 0$, $dn' \neq 0$, then have

$$dQ = \left[\left(\frac{\partial u}{\partial n'} \right)_{n=0} - y' \right] dn' = 0$$

$$\therefore \left(\frac{\partial u}{\partial n'} \right)_{n=0} = y'$$

2) $d\sigma = dn = 0$, $dn \neq 0$ imply

$$\left(\frac{\partial u}{\partial n} \right)_{n=0} = y$$

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

$$dQ = \left(\frac{\partial u}{\partial \sigma} \right)_{n,n'} d\sigma$$

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

$$dQ = \lambda(n, n', \sigma) d\sigma$$

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

$$\omega = \frac{1}{\lambda} dQ$$

IS INTEGRABLE (λ is an integrating factor for dQ)

Consider now 2 adiabatic r.w. 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 , between $\lambda = \lambda(\sigma, n, t)$.

For finding the temperature dependence of λ , we consider 2 systems in contact w/ a heat reservoir (2) at temperature t & w/ each other through a dt wall

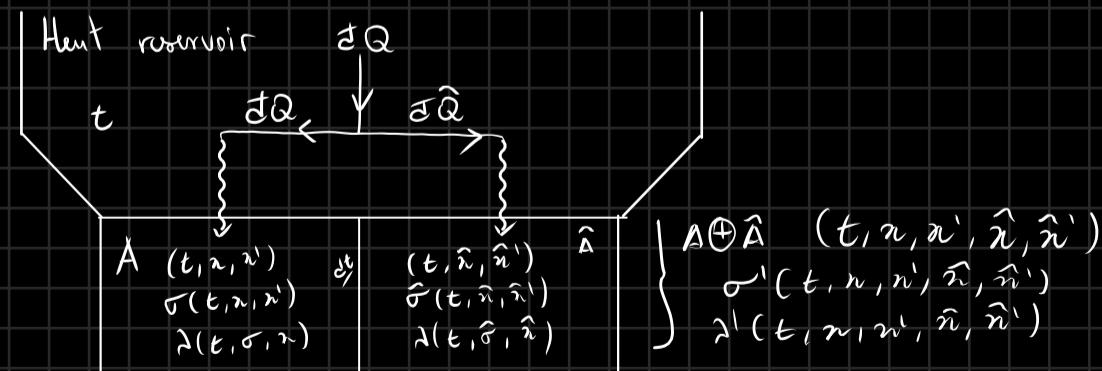


Fig Q) two systems: main (A), reference (\hat{A}) & heat reservoir in thermal equilibrium

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

A : ∂Q heat absorption gives change $d\sigma$, with $\partial Q = \lambda d\sigma$

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

A + \hat{A} : the composite adiabatic surfaces are defined by the function σ' of the composite system

We have $\partial Q = \lambda' d\sigma'$, 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

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

Therefore :

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

We must have this 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 $\lambda = \lambda(t)$

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

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

$$\partial Q = \phi(t) f(\sigma) d\sigma$$

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

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

ϕ ABSOLUTE TEMPERATURE II

Consider a system w/ (n, n', t) as independent coordinates. For an exchange of heat b/w the system

& a reservoir, we have

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

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

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

thus

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

where T is the Kelvin absolute temperature. thus, the scale is independent from the system's prop.

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

$$T_{\text{TP}} = 273.16 \text{ K} \Rightarrow T = 273.16 \frac{Q}{Q_{\text{TP}}} \text{ K}$$

ENTROPY

Concept of Entropy

We have seen that

$$\oint dQ = \lambda d\sigma = \oint \psi(t) f(\sigma) d\sigma$$

Since, for what we have defined for the Kelvin scale

$$\frac{T}{T'} = \frac{\oint dQ}{\oint dQ} \Rightarrow T \propto \psi(t)$$

thus:

$$\frac{1}{T} \oint dQ = \frac{1}{k} \int f(\sigma) d\sigma, \quad k \in \mathbb{R}$$

We might now define a function S , such that

$$dS = \frac{1}{T} \oint dQ = \frac{1}{k} \int f(\sigma) d\sigma \quad \left. \begin{array}{l} \text{if } Q \text{ is transformed REVERSIBLY} \\ \text{if } T \end{array} \right\}$$

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

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

Where 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 γ_R we have

$$S_{\gamma_R} = \oint \frac{1}{T} \oint dQ = \int_{\gamma_R} dS = 0 \quad (\text{CLAUSSUS})$$

aka "Clausius' theorem"

IDEAL GASES

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

$$dQ = T dS$$

thus, the 1st law becomes

$$\left. \begin{array}{l} \oint dQ = C_p dT - V dp \\ \int dS = C_p d \ln T - \frac{V}{T} dp \end{array} \right\}$$

But

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

$$\therefore dS = C_p d \ln T - nR d \ln p$$

And thus, for an ideal gas in a process $\gamma: (\tau_r, p_r) \rightarrow (\tau, p)$

$$\Delta S = C_p \log\left(\frac{\tau}{\tau_r}\right) - nR \log\left(\frac{p}{p_r}\right) *$$

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

$$S(p, \tau) = C_p \log(\tau) - nR \log(p) - \underbrace{(C_p \log(\tau_r) - nR \log(p_r) - S_r)}_{-S_0} *$$

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

Note that also:

$$dQ = C_v dT + pdV$$

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

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

TS diagrams

We can view Entropy as a coordinate itself, building TS diagram, where we will have

$$Q = \int_{\tau_r}^{\tau} T dS$$

In this plane, we have

1) Rev ad

$$dQ = T dS = 0 \Rightarrow dS = 0 \quad \{T \neq 0\}$$

Then here

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

2) infinitesimal quasi static (non adiabatic) process

$$\begin{aligned} dQ = T dS, \quad \frac{dQ}{dT} = T \frac{dS}{dT} &\rightarrow \begin{cases} dQ_V = C_v dT + pdV \\ dQ_P = C_p dT - Vdp \end{cases} \quad \begin{cases} dS_V = \frac{C_v}{T} dT + nR d \log V \\ dS_P = \frac{C_p}{T} dT - nR d \log p \end{cases} \\ &\quad \oplus \end{aligned}$$

$$\begin{cases} dS_V = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ dS_P = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \end{cases} \quad \oplus$$

* IF C_p, C_v ARE CONSTANT

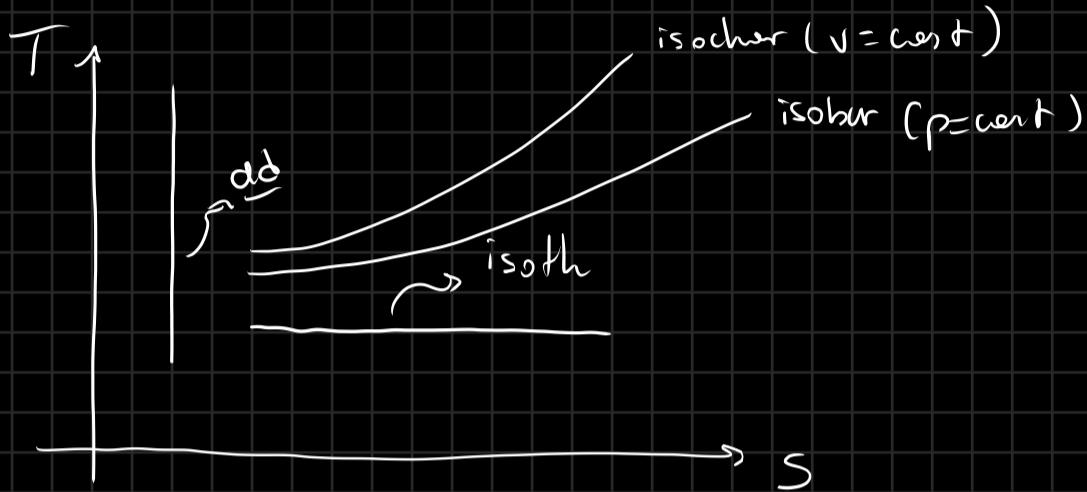
$$\therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}, \quad \frac{\partial S}{\partial V} = -\frac{\partial S}{\partial P} = nR$$

$$\text{I.e. } C_P = T \left(\frac{\partial S}{\partial T} \right)_V, \quad C_V = T \left(\frac{\partial S}{\partial T} \right)_P$$

Note that:

ISOENTROPIC \Leftrightarrow ADIABATIC $\therefore S(P, V, T) = S_0$ (Vertical)

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



Isotherm & isobar processes are easily found noting that

$$1) \text{ Isotherm } \Rightarrow dP=0, \quad dS_P = C_P \frac{dT}{T} - V \frac{dP}{P} = C_P \frac{dT}{T}$$

$$S_P = C_P \int_A^B \frac{1}{T} dT = C_P \log\left(\frac{T_B}{T_A}\right) \quad \left\{ C_P \text{ const} \right\}$$

$$2) \text{ Isochor } \rightarrow dV=0, \quad dS_V = C_V \frac{dT}{T} + P \frac{dV}{V} = C_V \frac{dT}{T}$$

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

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 surroundings, 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

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

∴ The entropy change of Σ during a rev. procn is 0. Called the rev. proc V_R , we have therefore

$$\Delta S_{\Sigma} = \int_{V_R} dS_A + \int_{V_R} dS_{\Sigma_A} = \int_{V_R} \frac{1}{T} dQ - \int_{V_R} \frac{1}{T} dQ = 0 \quad \square$$

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

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

$$= \int_{\varphi_I} T^{-1} dQ$$

where $\varphi_R : \alpha \xrightarrow{\text{R}} \beta$ is a reversible procn b/w the 2 eq. states. Note that integration over φ_I is NOT DEFINABLE due to the irreversibility of the procn

§ IRREVERSIBILITY & § § MECHANICAL EXTERNAL IRREVERSIBILITY

Consider now specific irreversible procnms:

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,

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

2) ADIABATIC TRANSFORMATION OF WORK

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

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

For the system instead we have

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

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

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

Thus:

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

INTERNAL MECHANICAL IRREVERSIBILITY

Consider how a process that transforms $U \rightarrow W \rightarrow U$

-) Free expansion

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

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

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

Thus:

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

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

EXTERNAL THERMAL IRREVERSIBILITY

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

We have

$$\Delta S_A = 0$$

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

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

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

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

K7SS TAPE RECORDINGS

PRINCIPLE OF INCREASE OF ENTROPY

We already saw, that for irreversible processes, that

$$\Delta S_{irr} > 0$$

We now consider ad process. For a system described by (n, v, T) going from eq. state A to eq. state B adiabatically (IRREVERSIBLE). The entropy change is:

$$\Delta S = S_B - S_A \quad \text{in C}$$

Consider now a rev ad proc., bringing T to T' , of some reservoir, putting it in contact and therefore make it undergo a rev. isothermal proc. to D until $S_D = S_A$, & a final rev. ad proc. 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 proc., where

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

&, from the first principle ($dQ = dU + dW$) we have

$$1) A \rightarrow B, B \rightarrow C \quad dQ = 0$$

$$2) C \rightarrow D \quad dU = 0, \quad dQ = dW$$

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

From the second law we have that $Q_{rev} \neq 0$, 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 $B \xrightleftharpoons{Q=0} A$, 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, for any kind of process

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

§ APPLICATION OF $\Delta S \geq 0$

The fact that, in an irreversible process $\Delta S_{\text{irr}} > 0$ 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:

$$\Delta S_{\text{irr}} = \Delta S_u + \Delta S_L = \left(-\frac{Q}{T_H} \right) + \left(\frac{Q_L}{T_L} \right)$$

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

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

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

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

Note that

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

Then:

$$W \leq \eta_C Q$$

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

$$\eta \leq \eta_C$$

$$\eta = \eta_C \Rightarrow \Delta S_{\text{irr}} = 0$$

Analogously, for a refrigerator bw T_H & T_L we have / ∇Q from A, $Q+W$ to res
(In sum cycle)

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

Then, rearranging

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

$$\therefore \underbrace{T_H(S_1 - S_2) - Q}_{\text{minimum cost of operation}} \leq W$$

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,

$$H = U + PV$$

then from

$$dH = dU + PdV + Vdp$$

But, for ideal gases

$$dQ = dU + PdV$$

$$\therefore dH = dQ + Vdp \Rightarrow H \equiv H(T, P)$$

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

FOR AN ISOBARIC PROCESS ($P = \text{const} \Rightarrow dp = 0$)

$$dH = dQ \Rightarrow \Delta H = Q$$

Or, by definition from the PDE:

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

Rewriting $dQ = TdS$, we also have

$$\begin{aligned} dH &= TdS + Vdp = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dp \\ \Rightarrow \begin{cases} \frac{\partial H}{\partial S} = T \\ \frac{\partial H}{\partial P} = V \end{cases} \end{aligned}$$

Note: $\begin{cases} dU = dQ - dW = TdS - pdV \quad \left(\frac{\partial U}{\partial S} \right)_V = T, \quad \left(\frac{\partial U}{\partial V} \right)_S = -P \\ dH = dQ + Vdp = TdS + Vdp \quad \left(\frac{\partial H}{\partial S} \right)_P = T, \quad \left(\frac{\partial H}{\partial P} \right)_S = V \end{cases}$

$$dU \rightarrow V = \text{const} \quad \int dU = C_V(T) dT \quad \Delta U = \int C_V dT$$

$$dH \rightarrow P = \text{const} \quad \int dH = C_P(T) dT \quad \Delta H = \int C_P dT$$

Def (Helmholtz Free energy)

By definition:

$$\left\{ \begin{array}{l} F = U - TS \\ dF = dU - TdS - SdT \\ dU = TdS - pdV \end{array} \right\} \rightarrow dF = TdS - TdS - SdT - pdV$$

(dw)

$$\therefore dF = - SdT - pdV$$

⇒ For an isothermal process ($dT = 0$)

$$\left\{ \begin{array}{l} dF = - pdV = dw \\ \Delta F = - \int pdV \end{array} \right.$$

Note that, by definition:

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

Def (Gibbs function)

$$\begin{aligned} G &= H - TS \\ dG &= dH - TdS - SdT \\ dH &= TdS + Vdp \end{aligned} \rightarrow dG = Vdp - SdT$$

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P = - S, \quad \left(\frac{\partial G}{\partial P}\right)_S = V$$

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: ($dQ = TdS$, Ideal gases $\Rightarrow dW = -pdV$)

INTERNAL ENERGY

$$U \equiv U(S, V)$$

$$\text{Ist}) \quad dU = TdS - pdV$$

$$\nabla) \quad \frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -p$$

ENTHALPY

$$H \equiv H(S, P)$$

$$dH = TdS + Vdp$$

$$\frac{\partial H}{\partial S} = T, \quad \frac{\partial H}{\partial P} = V$$

FREE ENERGY

$$F \equiv F(T, V)$$

$$dF = -SdT - pdV$$

$$\frac{\partial F}{\partial T} = -S, \quad \frac{\partial F}{\partial V} = -p$$

GIBBS

$$G \equiv G(T, P)$$

$$\text{Ist}) \quad dG = -SdT + Vdp$$

$$\nabla) \quad \frac{\partial G}{\partial T} = -S, \quad \frac{\partial G}{\partial P} = V$$

Special Cases

Isochoric process B ($dV = 0$) ①

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

Isobaric process B ($dp = 0$) ②

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

Reversible isothermal & isochoric ③

$$(dS = dT = dV = 0)$$

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

Reversible isothermal & isobaric ④

$$(dS = dT = dp = 0)$$

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

① $\boxed{dU = TdS}$, $dH = TdS + Vdp$, $dF = -SdT$, $dG = -SdT + Vdp$ (isochoric process)

② $dU = TdS - pdV$, $\boxed{dH = TdS}$, $dF = -SdT - pdV$, $dG = -SdT$ (isobaric process)

③ $\boxed{dU = 0}$, $dH = Vdp$, $\boxed{dF = 0}$, $dG = Vdp$ (chemical reactions)

④ $dU = -pdV$, $\boxed{dH = 0}$, $dF = -pdV$, $\boxed{dG = 0}$ (phase transitions)

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

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

Thm ($\text{Sdokw } \mathbb{R}^2$)

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

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

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

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

$$df = \omega$$

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

Proof

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

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

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

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

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

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

Thm

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

$f = f(x,y)$ or $f = f(x,z)$ or $f = f(y,z)$, &

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

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

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

+1 pg

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

$$\therefore \underbrace{\left(\frac{\partial z}{\partial x} \right)_y + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z}_{??} = \left(\frac{\partial z}{\partial x} \right)_y ; \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial z} \right)_x = \left(\frac{\partial z}{\partial y} \right)_x \quad \left(\text{Già visto ma sul libro è} \right. \\ \left. \text{Scritto ??} \right)$$

MAXWELL RELATIONS

Four functions (potentials):

INTERNAL ENERGY: \mathcal{U}

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

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

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

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

E.g.

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

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

Consider a system undergoing a rev. adiabatic process

$$1. d\mathcal{U} = \cancel{\partial Q} - PdV = TdS - PdV$$

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

$$3. d\mathcal{F} = d\mathcal{U} - TdS - SdT = -SdT - PdV$$

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

If all the differentials are exact, we have

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

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

$$d\mathcal{F} = -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$d\mathcal{G} = Vdp - SdT \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

TdS EQUATIONS (pg. 221)

The entropy S of a pure substance can be evaluated as function of $T, V, \text{ and } P$

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

Thus:

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

It follows then that

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

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

Also

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

Maxwell Mhd

Instead, if $S = S(T, P)$ we have

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

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

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

Also, $S = S(P, V)$, 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. procn we have

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

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

For an isobaric rev. procn

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

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

$$TdS = C_V \left(\frac{\partial T}{\partial P} \right)_V dP + C_P \left(\frac{\partial T}{\partial V} \right)_P dV \quad (3rd TdS)$$

Applications

1 mol of Van der Waals gas undergoes a rev. isothermal expansion from $V_i \rightarrow V_f$
How much heat was transferred?

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

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

The proc is isothermal, thus $C_V dT = 0$, hence

$$TdS = \left(\frac{\partial P}{\partial T} \right)_V T dV$$

But

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

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b}$$

Thus

$$TdS = \frac{RT}{V-b} dV = dQ$$

$$Q = RT \int_{V_i}^{V_f} \frac{1}{V-b} dV = RT \log(V-b) \Big|_{V_i}^{V_f} = RT \log \left(\frac{V_f - b}{V_i - b} \right)$$

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

-) Consider a reversible isothermal change of pressure

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

$$dQ = TdS = - \frac{\partial V}{\partial T} dP$$

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

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 $\frac{\partial \beta}{\partial P} = \frac{\partial V}{\partial P} \approx 0$, thus

$$Q = -T \bar{V} \beta \Delta P$$

Where $\bar{V}, \bar{\beta}$ are the average values

During the compression, also:

$$TdS = Cp dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

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

q

$$\delta W = -PdV$$

$$T = \text{const} \implies W = - \int \left(\frac{\partial V}{\partial T} \right)_P P dP, \quad \kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \Rightarrow \frac{\partial V}{\partial T} P dP = -\kappa P V dP$$

$$W = - \int \kappa P V dP$$

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

$$\therefore W = -\frac{\kappa}{2} \bar{V} (P_f^2 - P_i^2)$$

-) rev. ad. (isot S) change of pressure

$$TdS = Cp dT - \left(\frac{\partial V}{\partial T} \right)_P T dP$$

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

$$\Delta T = \int \frac{\beta V T}{C_P} dP \approx \frac{\beta \bar{V} T}{C_P} \Delta P$$

ENERGY EQUATIONS

For an infinitesimal rev. process b/w two eq. states, we have

$$dU = TdS - pdV$$

L.e.

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

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

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - p} \quad (1st \text{ energy eq})$$

Note that, for ideal gases:

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p(V, T) = 0 \quad \therefore U = U(T) + U_0 \quad \text{Ans}$$

For 1 mol of Van der Waals gas:

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

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$\therefore dU = C_V dT + \frac{a}{V^2} dV$$

$$\& U(T, V) = \int C_V(T) dT - \frac{a}{V} + U_0$$

The second equation gives us the dependency on pressure. Thus

$$\left. \begin{aligned} dU &= TdS - pdV \\ \left(\frac{\partial U}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T - p \left(\frac{\partial V}{\partial P}\right)_T \end{aligned} \right\} \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{\therefore \left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T} \quad (\text{2nd Energy eq})$$

\oint 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 them

$$C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$(C_p - C_v) dT = T \left[\left(\frac{\partial P}{\partial T}\right)_V dP + \left(\frac{\partial V}{\partial T}\right)_P dV \right]$$

$$\therefore dT = \frac{T}{C_p - C_v} \left[\left(\frac{\partial P}{\partial T}\right)_V dP + \left(\frac{\partial V}{\partial T}\right)_P dV \right]$$

By definition, $T \equiv T(p, V)$, thus

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

$$\begin{cases} \left(\frac{\partial T}{\partial P}\right)_V = \frac{T}{C_p - C_v} \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial V}\right)_P = \frac{T}{C_p - C_v} \left(\frac{\partial V}{\partial T}\right)_P \end{cases} \Rightarrow C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

Note also that

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

$$\boxed{\therefore C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T} \quad \begin{cases} \left(\frac{\partial V}{\partial P}\right)_T < 0 \Rightarrow C_p \geq C_v \\ C_p(0) = C_v(0) \\ C_p = C_v \text{ iff } \left(\frac{\partial V}{\partial T}\right)_P = 0 \end{cases}$$

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 isentropic process

$$TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dp = 0$$

$$TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV = 0$$

$$\begin{cases} C_p dT = T \left(\frac{\partial V}{\partial T} \right)_P dp \\ \therefore C_v dT = -T \left(\frac{\partial P}{\partial T} \right)_V dV \end{cases}$$

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

$$\left\{ \begin{array}{l} TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \quad (\text{TdS I}) \\ TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_P dp \quad (\text{TdS II}) \\ TdS = C_v \left(\frac{\partial T}{\partial P} \right)_V dP + C_p \left(\frac{\partial T}{\partial V} \right)_P dp \quad (\text{TdS III}) \\ \left\{ \begin{array}{l} \left(\frac{\partial u}{\partial v} \right)_r = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (u \text{ I}) \\ \left(\frac{\partial u}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial P} \right)_T \quad (u \text{ II}) \end{array} \right. \\ \left\{ \begin{array}{l} C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_S \quad (C \text{ I}) \\ \gamma = \frac{C_p}{C_v} = \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_S = \frac{\kappa}{\kappa_s} \quad (C \text{ II}) \end{array} \right. \end{array} \right.$$

§ THERMAL EXPANSIVITY

Suppose L_1, L_2, L_3 as the smallest lengths of a rectangle containing the system we have

$$V = L_1 L_2 L_3$$

$$\frac{\partial V}{\partial T} = L_1 L_2 \frac{\partial L_3}{\partial T} + L_1 L_3 \frac{\partial L_2}{\partial T} + L_2 L_3 \frac{\partial L_1}{\partial T}$$

Suppose $\alpha_i = \frac{\partial L_i}{\partial T}$ 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

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FIRST ORDER TRANSITIONS

Melting, vaporization & sublimation \rightarrow 1st 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:

$$\begin{cases} S = n_0(1-x)S_{(i)} + n_0xS_{(f)} \\ V = n_0(1-x)V_{(i)} + n_0xV_{(f)} \end{cases}$$

If the transition is rev. then λ latent heat ΔH as

$$\lambda = T(S_{(f)} - S_{(i)})$$

Since $dg = Vdp - Tds$, we have

$$S = -\left(\frac{\partial g}{\partial T}\right)_P, \quad V = \left(\frac{\partial g}{\partial p}\right)_T$$

Def (1st order transition)

$$g(T, S) \in C^0$$

$$\Delta S \neq 0, \Delta V \neq 0$$

Since $dp = dT = 0$, we have

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = k = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \infty$$

For the $\int Tds$ 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

$$dg_{(i)} = dg_{(f)}$$

$$\therefore V_{(i)}dp - S_{(i)}dT = V_{(f)}dp - S_{(f)}dT$$

$$\Rightarrow \Delta V dp = \Delta S dT$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\lambda}{T} \frac{1}{\Delta V} = \frac{\lambda}{T\Delta V}$$

f Fusion

Fusion is the phase transition $(s) \rightarrow (l)$. The heat method is to supply electrical energy at a constant rate ($E I$).

The resulting graph has a line @ $T = T_m$ (melting temperature) along ΔT .

Further, for n moles of solid

$$\lambda_F = \frac{1}{n} EI \Delta T$$

Also

$$\Delta S = \frac{\lambda_F}{T_m}$$

An empirical formula for evaluating melting curves was found by F.E.Simon & G.Glatzel

$$P - P_{TP} = a \left[\left(\frac{T}{T_{TP}} \right)^c - 1 \right]$$

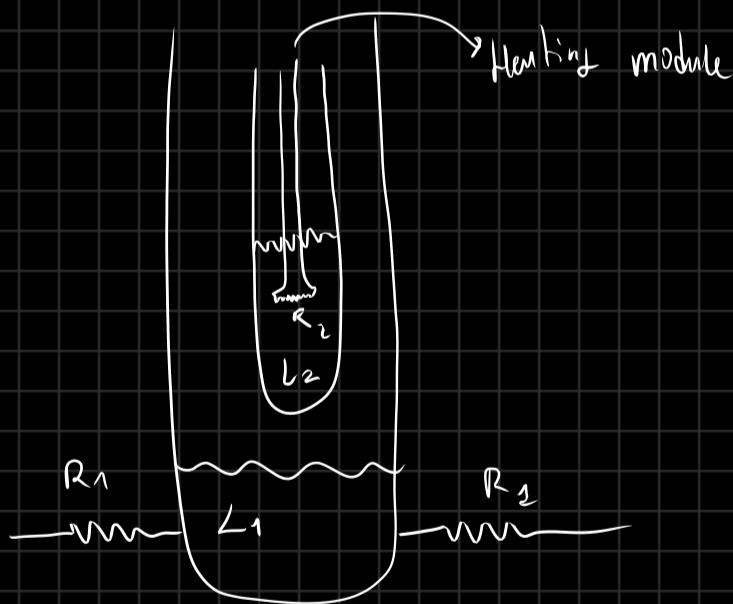
(P_{TP}, T_{TP}) are the TP coordinates & a, c are parameters depending on the substance

f VAPORIZATION

1st order transition $(l) \rightarrow (g)$. For liquids @ human temperatures, usually

$$250K < T_f < 550K$$

λ_v is usually measured with calorimeters like the one in figure:



The sample 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 standard liquid L_1 which is kept at boiling point together w/ L_2 using adequate pressures and temperatures along the heating module R_1 ...

The latent heat is found to be

$$\lambda_v = \frac{EI\Delta T}{n}$$

In general we have from Clapeyron's eq.

$$\left\{ \begin{array}{l} \frac{\partial V}{T C} \frac{T}{P(V_f - V_i)} = 5.4 \leftarrow \text{experimental} \\ \frac{\partial P}{T} \frac{T^2}{\partial T} = \frac{\partial V}{P(V_f - V_i)} = \frac{\partial V}{T C} \frac{T^2 C}{P(V_f - V_i)} \leftarrow \text{empirical} \end{array} \right.$$

$$\text{Since } \frac{\partial V}{T C} \frac{T}{P(V_f - V_i)} = 5.4 \Rightarrow \frac{\partial P}{T} \frac{T^2}{\partial T} = 5.4 T_C \Rightarrow \frac{1}{P} dP = 5.4 T_C \frac{dT}{T^2}$$

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 integrate from T_C $\Rightarrow V_i \approx 0, V_f = \frac{RT}{P}, \lambda_v \approx \text{const.}$ thus:

$$\frac{dP}{dT} = \frac{\partial V}{R T / P} = \frac{\partial V P}{R T}$$

$$\int_{P_0}^{P_C} \frac{1}{P} dP = \frac{\partial V}{R} \int_{T_0}^{T_C} \frac{1}{T} dT$$

$$\log \left(\frac{P_C}{P_0} \right) = - \frac{\partial V}{R} \left(\frac{1}{T_C} - \frac{1}{T_0} \right) \approx \text{const.} - \frac{\partial V}{R T}$$

$$\therefore \frac{\partial V}{R} \approx 5.4 T_C$$

§ SUBLIMATION

For sublimation, $V_f = V'''$, $V_i = V'$ ($V''' \rightarrow V''|_{\text{gas}}, V' \rightarrow V''|_{\text{solid}}$)

$$\frac{dP}{dT} = \frac{\lambda_s}{T(V''' - V')}$$

V''' volume of an ideal gas $\rightarrow V''' = \frac{RT}{P} \gg V' \Rightarrow V''' - V' \approx V'''$

$$\therefore \frac{dP}{dT} = \frac{\lambda_s}{P T V'''} = \frac{\lambda_s}{P R T^2}$$

$$\therefore \lambda_s = \frac{dP}{P} \frac{T^2}{dT} R = -R \frac{d \log(P)}{d(\frac{1}{T})}$$

$$\therefore \log(P) \approx -\frac{A}{T} + B . \quad A, B \text{ depend on material}$$

From Enthalpy we have

$$1) dh = T ds + V dp$$

From TDS (ii) we get

$$Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

$$\therefore dh = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp + v dp$$

$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp ; \left[\left(\frac{\partial v}{\partial T} \right)_p = \beta v \right]$$

$$dh = c_p dT + [v - v\beta] dp$$

$$\Delta h = c_p \Delta T + \int [v - v\beta] dp$$

If $i = (P=0, T=0)$, for generic pre sublimation then:

$$h - h_0 = \int_0^T c_p dT + \int_0^P v - v\beta dp$$

$$h - h_0 = \int c_p dT$$

For an ideal gas

$$dh^m = c_p^m dT \Rightarrow h^m = \int c_p^m dT$$

$$\therefore \lambda_s = \Delta h_{m,i} = h^m - h^i = \int c_p^m dT - \int c_p^i dT + h_0^m - h_0^i$$

$$\therefore \lambda_0 = h_0^m - h_0^i \quad (T \rightarrow 0) \rightarrow \text{latent heat of sublimation at } 0K$$

If $c_p^i \equiv c_p(T)$, $c_p^m = c_p^i(T)$

$$\left[\lambda_s = \int_0^T c_p^i dT - \int_0^T c_p^i dT + \lambda_0 \right] \quad (\text{neglecting } \lambda_0)$$

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 becomes

$$\frac{dp}{P} = \frac{\lambda_s}{RT^2} dT$$

$$\lambda_s = \int_0^T c_p^i dT - \int_0^T c_p^i dT + \lambda_0$$

But, $c_p^i = C^m + C_i^m(T)$, where $C^m = \begin{cases} \frac{5}{2} R & \text{monatomic} \\ \frac{7}{2} R & \text{diatomic gas} \end{cases}$ & $C_i^m(T)$ is due to

internal DOF of the molecules. note $C_i'''(T) \rightarrow 0$ $\left\{ \begin{array}{l} T \rightarrow 0 \\ C''' = \frac{5}{2} R \end{array} \right.$

Thus:

$$dS = d\Omega + C'''T + \int_0^T C_i'''(T) dT - \int_0^T C_p'(T) dT$$

& Thus, since

$$\frac{dp}{P} = \frac{dS}{RT^2} dT$$

$$\frac{dp}{P} = \frac{d\Omega}{RT^2} + \frac{C'''}{RT} + \frac{1}{RT^2} \left[\int_0^T C_i'''(T) dT - \int_0^T C_p'(T) dT \right]$$

Integrating

$$\log(P) = -\frac{C'''}{R} \log(T) - \frac{d\Omega}{RT} + \frac{1}{R} \int_0^T \frac{1}{T} \int_0^T C_i'''(T) dT dT - \frac{1}{R} \int_0^T \frac{1}{T} \int_0^T C_p'(T) dT dT + k$$

If the vapour is monatomic, $C_p'''(T) = \frac{5}{2} R$, thus

$$\log(P) = \frac{5}{2} \log(T) - \frac{d\Omega}{RT} - \frac{1}{R} \int_0^T \frac{1}{T} \int_0^T C_p'(T) dT dT + k$$

Measurement:

a) $10^{-1} \text{ Pa} < p < 10^5 \text{ Pa} \rightarrow$ direct measurement (static)

b) Langmuir evaporation \rightarrow weigh solid, measure surface S , then rate of collisions

$$\left. \begin{aligned} \frac{dN_c}{dt}_{\text{ley}} &= P \sqrt{\frac{1}{2\pi N k_B T}} \\ \frac{1}{S} \frac{dN}{dt} &= P \sqrt{\frac{M_{\text{m}}}{2\pi RT}} \end{aligned} \right\} \begin{aligned} M &\rightarrow \text{solid mass} \\ M_{\text{m}} &\rightarrow \text{molecular mass} \end{aligned}$$

b) Knudsen effusion \rightarrow Langmuir but vapor passes a known hole of surf. S & gets trapped in a cold trap

After a time T , we have that

$$\left\langle \frac{dN}{dt} \right\rangle = \frac{M_{\text{c}}}{T} \quad M_{\text{c}} \rightarrow \text{mass in cold trap after condensation}$$

errors b/w 5% & 10%

Arrhenius formula:

$$\log(P) = A - \frac{B}{T} + C\tau + D \log(T) \quad \left\{ \begin{array}{l} A, B, C, D \\ \text{parameters} \end{array} \right.$$

expand initially if has been found that

(i.e. begins the second part of chapter (check))

$$\gamma_0 \approx \frac{3}{5} \frac{C_v(0)}{P}$$

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 one ideal gases form the microscopic POV using "Kinetic Theory" among 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 M is the molar mass (molecular weight / kg / Kmol), then the number of moles;

$$n = \frac{Nm}{M} = \frac{M}{m}$$

- c) For a single mole ($n=1$) we have

$$1 = \frac{Nm}{M} \Rightarrow N = \frac{M}{m} = N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$$
$$(6.0225 \cdot 10^{23} \text{ mol}^{-1})$$

- 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/ each other (no interaction) except with collisions
- 4) Collisions are perfectly elastic & zaws of collision w/ walls can be considered flat
- 4a) For a collision  \simeq  , i.e. $v' = v_{\perp}$, $\Delta v = -2v_{\perp}$
- 5) When there is no external field \rightarrow molecules distributed uniformly

5a) the molecular density $\frac{N}{V}$ is constant 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 v , due to the absence of a preferred direction we can say first

$$d^3 N_v = \frac{1}{4\pi} dN_v d\Omega = \frac{1}{4\pi} \sin\theta d\phi d\theta dN_v \quad (\text{No preferred direction})$$

Consider all incoming particles to the solid angle $\frac{d\Omega}{4\pi}$ per sec. We have that they lie inside a cylinder long $v dt$, where t is the time w/o collision. That volume is then

$$dV = \sqrt{cos\theta} d\tau dS$$

Here 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

$$N_{coll} = d^3 N_v \frac{dV}{V} \quad (\text{No preferred location})$$

Also collisions are elastic, thus, if P is the momentum of the particle & ΔP its change

$$\Delta P = -2mV \cos\theta$$

& the total change of momentum can be seen as:

$$\Delta P_{tot} = \left(\frac{1}{4\pi} dN_v d\Omega \right) \left(\frac{v}{V} \cos\theta d\tau dS \right) (-2mV \cos\theta)$$

~~* w/ V in dΩ | fraction of * striking dS | ΔP~~

The total change of momentum on the sector dS of the wall is THE PRESSURE
(From Newton II $\vec{F} = m\vec{a}$), thus, for dN_v molecule

$$\Delta P_{tot} = \frac{1}{4\pi} dN_v \sin\theta d\phi \frac{v}{V} \cos\theta d\tau dS (-2mV \cos\theta)$$

$$\Delta P_{tot} = \frac{mV^2}{4\pi V} \sin\theta \cos^2\theta d\phi d\theta d\tau dS dN_v$$

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

$$dP_V = \frac{mv^2}{2\pi V} dN_V \int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta = -\frac{mv^2}{2\pi} dN_V \int_0^{2\pi} d\varphi \int_1^0 \cos^2 \theta d(\cos \theta)$$

$$dP_V = \frac{mv^2}{2\pi} dN_V \left(\frac{1}{3} \cos^3 \theta \right)_0^{\pi/2} = \frac{mv^2}{3} dN_V$$

Integrating for all particles w/ velocity v we have

$$P = \frac{m}{3V} \int v^2 dN_V = \frac{1}{3V} m N \langle v^2 \rangle, \langle v^2 \rangle = \frac{1}{N} \int_R v^2 dN_V$$

But $\frac{1}{2} m \langle v^2 \rangle = \langle \epsilon \rangle$ (no field, expected kinetic energy (total) per molecule)

$$PV = \frac{2}{3} N \langle \epsilon \rangle = \frac{2}{3} N \underbrace{\left(\frac{1}{2} m \langle v^2 \rangle \right)}_{\langle \epsilon \rangle}$$

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

$$k_B = \left(\frac{1}{6.0225} \cdot 10^{-23} \text{ mol} \right) \left(8.3143 \frac{\text{J}}{\text{K mol}} \right) = 1.3805 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$$

Also,

$$PV = \frac{2}{3} N \langle E \rangle = \frac{2}{3} N \left(\frac{3}{2} k_B T \right) = N k_B T$$

di

$$P = \frac{N}{V} k_B T = f_{\text{mol}} k_B T \quad \left\{ f_{\text{mol}} = \frac{N}{V}, \text{ mol. density} \right\}$$

Teoria classica dei gas (Saini)

Postulati

1. $N \gg 1$
2. $V_{\text{mol}} \approx 0, m_{\text{mol}} \neq 0$
3. $U_{\text{int}} = 0$
4. Moto casuale
5. Corpi perfetti
6. $dE = 0, \Delta E_{\text{int}} \neq 0$
7. Urto elastico $d^3 p = 0$

Per definizione $Nk_B = PV \Rightarrow PV = Nk_B T$

$$U_{\text{int}} = 0 \Rightarrow E_{\text{tot}} = \sum_{i=1}^N \frac{1}{2} m_i v_i^2, m_i = m \forall i \neq j = 1, \dots, N \Rightarrow E = \frac{N}{2} m \langle v^2 \rangle$$

Poiché il moto è casuale $\langle v_i^2 \rangle = \langle v_j^2 \rangle \rightarrow \langle v_i^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

Supponi $v_x = v_y = 0 \rightarrow 1D, V = v_x$

La probabilità di trovare una molecola con velocità $v_x \in [v_x, v_x + dv_x]$ è data da $\text{pdf}(v_x)$

$$P(dv_x) = \text{pdf}(v_x) dv_x$$

Dove, per def.

$$\int_R \text{pdf}(v_x) dv_x = 1 \quad (\text{normalizz.})$$

Nota:

$$\mathbb{E}(x) = \langle x \rangle = \int_R x \text{pdf}(x) dx$$

Risultato

$$\langle v_x \rangle = \int_R v_x \text{pdf}(v_x) dv_x = 0$$

$$\langle v_x^2 \rangle = \int_R v_x^2 \text{pdf}(v_x) dv_x \neq 0$$

Urto elastico

Considera partita elastica: $P = mv_2, dp = 0 \Rightarrow P_1 = mv_1, P_2 = -mv_2, \Delta P_{12} = -2mv_x$

$$P = \frac{F}{S} = \frac{1}{S} \frac{\Delta P_{12}}{\Delta t_{12}}$$

Supponiamo che la pallina percorre $L = 2l$ prima e dopo l'urto $\Rightarrow \Delta t_{12} = \frac{L}{v_x} = \frac{2l}{v_x}$

particolare

$$F_n = \frac{\Delta P_{n2}}{\Delta t_{n2}} = -\frac{2mV_n}{\pi l/V_n} = -\frac{mV_n^2}{l}$$

poiché il volume del cubo con lati l è l^3 , la sop $S = l^2$

$$P = \frac{F_n}{S} = \frac{1}{l^2} \frac{mV_n^2}{e} = \frac{mV_n^2}{l^3} = \frac{mV_n^2}{V}$$

pertanto, considerate N particelle

$$\rho V = Nm \langle V_n^2 \rangle = Nk_B T$$

$$\therefore \langle V_n^2 \rangle = \frac{k_B T}{m} = \frac{1}{3} \langle V^2 \rangle$$

Cioè, per equipartizione

$$\langle V^2 \rangle = \frac{3k_B T}{m}$$

è la vel. quadratica media è

$$\sqrt{\langle V^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$$

$$\rho V = Nm \langle V_n^2 \rangle \Rightarrow \rho = \frac{Nm \langle V_n^2 \rangle}{V} = \frac{N}{V} \cdot \frac{n \langle V^2 \rangle}{3} = \frac{2}{3} \frac{N}{V} \frac{1}{2} m \langle V^2 \rangle = \frac{2}{3} \frac{N}{V} \in$$

$$\rho V = Nk_B T = \frac{2}{3} N \epsilon \Rightarrow k_B T = \frac{2}{3} \epsilon \Rightarrow \epsilon = \frac{3}{2} k_B T \quad \left. \begin{array}{l} \text{EQUIPART. ENERGIA} \\ \epsilon = E/N \end{array} \right\} E = N\epsilon$$

$$\text{Nota che se ho più DOF} \Rightarrow \langle V_n^2 \rangle = \frac{\langle V^2 \rangle}{f} \Rightarrow E = \frac{f}{2} k_B T \quad (f = \# \text{DOF})$$

Nota che:

$$\rho V = \frac{1}{3} Nm \langle V^2 \rangle \rightarrow \rho = \frac{1}{3} \frac{N}{V} m \langle V^2 \rangle = \frac{2}{3} \frac{N}{V} E = \frac{2}{3} \rho_N E$$

$$\rho_N = \frac{N}{V}, [\rho_N] = \text{m}^{-3} \quad (\text{densità numerica di particelle})$$

Calore e $\frac{f}{2} k_B T$

Per definizione:

$$dQ = nCdT = dU = d\left(\frac{3}{2} Nk_B T\right) = \frac{3}{2} Nk_B dT$$

$$C_V = \frac{1}{h} \left(\frac{dQ}{dT} \right)_V = \frac{3}{2} \frac{Nk_B}{N} = \frac{3}{2} N_A N k_B = \frac{3}{2} N_A k_B = \frac{3}{2} R$$

$$\text{In gen. } U = \frac{f}{2} Nk_B T \Rightarrow C_V = \frac{f}{2} N_A k_B = \frac{f}{2} R$$

Forma funzionale di $\text{pdf}(V_i)$

In 3 dimensioni, ho

$$P(d^3v) = \text{pdf}(v) d^3v$$

poiché moto isotropo, e $\langle v_i \rangle = \langle v_j \rangle \Rightarrow \text{pdf}(v) = \prod_{i=1}^3 \text{pdf}(v_i)$

$$P(d^3v) = \text{pdf}(v_x) \text{pdf}(v_y) \text{pdf}(v_z) dv_x dv_y dv_z$$

Uzendo i logen fun

$$\log \left[\text{pdf}(\underline{v}) \right] = \sum_{i=1}^3 \log \left[\text{pdf}(v_i) \right]$$

$$\therefore \frac{\partial}{\partial v_i} \text{pdf}(\underline{v}) = \frac{d}{dv_i} \text{pdf}(v_i)$$

$$\text{press } V = \|\underline{v}\| = (v_i v_i)^{1/2}$$

$$\frac{\partial}{\partial v_i} = \frac{\partial}{\partial V} \frac{\partial V}{\partial v_i} = \frac{\partial}{\partial v_i} (v_i v_i)^{1/2} \frac{\partial}{\partial V} = \left(\frac{1}{2} \frac{2v_i}{(v_i v_i)^{1/2}} \right) \frac{\partial}{\partial v_i} = \frac{v_i}{V} \frac{\partial}{\partial v_i}$$

$$\therefore \frac{v_i}{V} \frac{\partial}{\partial V} \log \left[\text{pdf}(\underline{v}) \right] = \frac{\partial}{\partial v_i} \log \left[\text{pdf}(v_i) \right]$$

Risolviamo ED

$$\frac{1}{V} \frac{\partial}{\partial V} \log \left[\text{pdf}(\underline{v}) \right] = \frac{1}{v_i} \frac{\partial}{\partial v_i} \log \left[\text{pdf}(v_i) \right]$$

$$\therefore \left\{ \frac{1}{V} \frac{\partial}{\partial V} \log \left[\text{pdf}(\underline{v}) \right] = -b \right.$$

$$\left. \frac{1}{v_i} \frac{\partial}{\partial v_i} \log \left[\text{pdf}(v_i) \right] = -b \rightarrow \int d \log \left[\text{pdf}(v_i) \right] = \int -b v_i dv_i \right.$$

$$\therefore \log \left[\text{pdf}(v_i) \right] = -\frac{b}{2} v_i^2 + \log(c)$$

$$\text{pdf}(v_i) = C e^{-\frac{b}{2} v_i^2}$$

Staviamo costanti:

1) Normalizzazione

$$\int_{\mathbb{R}} \text{pdf}(v_i) dv_i = C \int_{\mathbb{R}} e^{-\frac{b}{2} v_i^2} dv_i$$

Poiché

$$\int_{\mathbb{R}} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad a = \frac{b}{2}$$

$$\int_{\mathbb{R}} \text{pdf}(v_i) dv_i = C \sqrt{\frac{2\pi}{b}} = 1 \Rightarrow C = \sqrt{\frac{b}{2\pi}}$$

$$\text{pdf}(v_i) = \sqrt{\frac{b}{2\pi}} e^{-\frac{b}{2} v_i^2}$$

$$\text{Ma}, \quad \text{da} \quad \epsilon = \frac{3}{2} k_B T = \frac{3}{2} m \langle v_i^2 \rangle \rightarrow \langle v_i^2 \rangle = \frac{k_B T}{m} \quad \left\{ a = \frac{b}{2} \right\}$$

$$e \quad \langle v_i^2 \rangle = \sqrt{\frac{a}{\pi}} \int_{\mathbb{R}} v_i^2 e^{-av_i^2} dv_i = \sqrt{\frac{a}{\pi}} \int_{\mathbb{R}} \frac{\partial}{\partial a} (e^{av_i^2}) dv_i = \sqrt{\frac{a}{\pi}} \frac{\partial}{\partial a} \int_{\mathbb{R}} e^{-av_i^2} dv_i = \sqrt{\frac{a}{\pi}} \frac{\partial}{\partial a} \sqrt{\frac{\pi}{a}} = -\sqrt{\frac{a}{\pi}} \sqrt{\pi} \frac{a^{-3/2}}{-2} = \frac{a^{-3/2} a^{1/2}}{2} = \frac{1}{2a}$$

$$\therefore \frac{1}{2a} = \frac{1}{b} = \frac{k_B T}{m} \Rightarrow b = \frac{m}{k_B T}$$

$$\therefore \text{pdf}(v_i) = C e^{-\frac{b}{2} v_i^2} = \sqrt{\frac{b}{2\pi}} e^{-\frac{b}{2} v_i^2} = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{m}{2k_B T} v_i^2}$$

$$\Rightarrow \text{pdf}(\underline{v}) = \prod_{i=1}^3 \text{pdf}(v_i) = \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{1}{2k_B T} m \langle v^2 \rangle \right) \quad (\text{XYZ})$$

Possiamo trovare anche le altre due relazioni nel goni

$$\langle |V_a| \rangle = \sqrt{\frac{m}{2\pi k_B T}} \int_{R_+}^{\infty} V_a e^{-\frac{1}{2} \frac{mv^2}{k_B T}} dV_a = \sqrt{\frac{2m}{\pi k_B T}} \left(\frac{k_B T}{m} \int_{R_+}^{\infty} e^{-\alpha} d\alpha \right) = \frac{k_B T}{m} \sqrt{\frac{2m}{\pi k_B T}} = \sqrt{\frac{2k_B T}{\pi m}} \quad \checkmark$$

$$\langle V \rangle = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{R^3} V \exp\left(-\frac{1}{2} \frac{mv^2}{k_B T}\right) dV = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{R^3} V^3 \exp\left(-\frac{1}{2} \frac{mv^2}{k_B T}\right) dV \int d\Omega$$

$$\int_{R^3} V^3 \exp\left(-\frac{1}{2} \frac{mv^2}{k_B T}\right) dV = \int_{R^3} V^3 \exp(-\alpha V^2) dV = \int_{R^3} V \frac{\partial}{\partial \alpha} \exp(-\alpha V^2) dV = \int_{R^3} \frac{\partial}{\partial \alpha} \left(V \exp(-\alpha V^2) \right) - \frac{\partial V}{\partial \alpha} \exp(-\alpha V^2) dV = \frac{\partial}{\partial \alpha} \int_{R^3} V \exp(-\alpha V^2) dV$$

$$\frac{\partial}{\partial \alpha} \int_{R^3} V \exp(-\alpha V^2) dV = \frac{1}{2} \frac{\partial}{\partial \alpha} \int_{R^3} \exp(-\alpha z^2) dz = -\frac{1}{2} \frac{\partial}{\partial \alpha} \left(\frac{1}{\alpha} \exp(-\alpha z^2) \right) \Big|_{R^3} = -\frac{1}{2} \frac{\partial}{\partial \alpha} \left(\frac{1}{\alpha} \right) = \frac{1}{2} \frac{1}{\alpha^2}$$

$$\therefore \int_{R^3} V^3 \exp(-\alpha V^2) dV = \frac{1}{2\alpha^2} = \frac{1}{2} \left(\frac{1}{2} \frac{m}{k_B T} \right)^{-2} = \frac{1}{2} \frac{4k_B^2 T^2}{m^2} = 2 \left(\frac{k_B T}{m} \right)^2$$

$$\langle V \rangle = 8\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \left(\frac{k_B T}{m} \right)^2 = \frac{8\pi}{(2\pi)^{3/2}} \sqrt{\frac{k_B T}{m}} = 2^{3/2} \sqrt{\frac{k_B T}{\pi m}} = \sqrt{\frac{8k_B T}{\pi m}} \quad \checkmark$$

$$pdf(V) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{2} \frac{mv^2}{k_B T}} V^2$$

$$\max\{P(v)\} \Rightarrow \max\{pdf(v)\} \rightarrow \frac{\partial}{\partial v} pdf(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \left[(2v) - \frac{mv^3}{k_B T} \right] e^{-\frac{1}{2} \frac{mv^2}{k_B T}} = 0 \quad \therefore P_{\max}(v) \Rightarrow v_m = \sqrt{\frac{2k_B T}{m}} \quad \checkmark$$

Sezione d'urto

Preso molecule diam. d. Prendo sezione circolare r=d $\Rightarrow S = \pi d^2$, allora,

$$\sqrt{S} = \langle V \rangle \pi d^2 = \langle V \rangle S$$

$$\text{Il numero d'urto } Z_e = \frac{N}{V} V_S \rightarrow Z_e = \frac{N}{V} \langle V \rangle \pi d^2$$

Nota: Va usata $\underline{\underline{V_{rel}}}$, dove $m \rightarrow \frac{m}{2} = \mu$

$$\langle V_{rel} \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} = \sqrt{\frac{16k_B T}{\pi m}}$$

$$Z_e = \frac{N}{V} \langle V_{rel} \rangle \pi d^2 = \frac{N \pi d^2}{V} \left(\sqrt{\frac{16k_B T}{\pi m}} \right)$$

Def. Cammino libero medio λ con $\frac{\langle v \rangle}{Z_e} = \frac{N}{V} \sqrt{2} \langle V \rangle \pi d^2$

$$\lambda = \frac{N \pi d^2}{V} \sqrt{\frac{16k_B T}{\pi m}}$$

$$\text{Poischi } pV = Nk_B T \rightarrow \frac{N}{V} = \frac{p}{k_B T} \Rightarrow \lambda = p \frac{\pi d^2}{k_B T} \sqrt{\frac{16k_B T}{\pi m}} = p d^2 \sqrt{\frac{16\pi}{m k_B T}} = p d^2 \sqrt{\frac{\pi}{m k_B T}}$$

