Basic thermodynamics

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INTRODUCTION

➢ **What do we consider in thermodynamics: the thermodynamic system**

- A thermodynamic system is a precisely specified macroscopic region of the universe.
- It is limited by boundaries of particular natures, real or not and having specific properties.
- All space in the universe outside the thermodynamic system is known as the surroundings, the environment, or a reservoir.
- Processes that are allowed to affect the interior of the region are studied using the principles of thermodynamics.

➢ **Closed/opened system**

- In open systems, matter may flow in and out of the system boundaries
- Not in closed systems. Boundaries are thus real: walls

➢ **Isolated system**

- Isolated systems are completely isolated from their environment: they do not exchange energy (heat, work) nor matter with their environment.

➢ **Sign convention:**

- Quantities going "into" the system are counted as positive (+)
- Quantities going "out of" the system are counted as negative (-)

INTRODUCTION

➢ **Thermodynamics gives:**

- a macroscopic description of the state of one or several system(s)
- a macroscopic description of their behaviour when they are constrained under some various circumstances

➢ **To that end, thermodynamics:**

- uses macroscopic parameters such as:
  - o the pressure p
  - o the volume V
  - o the magnetization $\hat{M}$
  - o the applied magnetic field $\hat{H}$
- provides some other fundamental macroscopic parameters defined by some general principles (the <u>four laws of thermodynamics</u>):
  - o the temperature T
  - o the total internal energy U
  - o the entropy S...
- expresses the constraints with some relationships between these parameters

INTRODUCTION

➤ **Extensive quantities**
- are the parameters which are proportional to the mass m of the system such as : $V, \hat{M}, U, S...$
  $$\Rightarrow X = m \cdot x$$

➤ **Intensive quantities**
- are not proportional to the mass : $p, T, \hat{H}$ ...

➤ **Thermodynamic equilibrium**
- a thermodynamic system is in thermodynamic equilibrium when there are no net flows of matter or of energy, no phase changes, and no unbalanced potentials (or driving forces) within the system.
- A system that is in thermodynamic equilibrium experiences no changes when it is isolated from its surroundings.
- Thermodynamic equilibrium implies steady state.

  Steady state does not always induce thermodynamic equilibrium

  (ex.: heat flux along a support)

INTRODUCTION

➤ **Quasi-static evolution:**
- It is a thermodynamic process that happens infinitely slowly.
- It ensures that the system goes through a sequence of states that are infinitesimally close to equilibrium.


Example: expansion of a gas in a cylinder

Real evolution   Quasi-static evolution   Continuous evolution

$F = n \cdot F/n$ $F = n \cdot F/n \; (n \to \infty)$
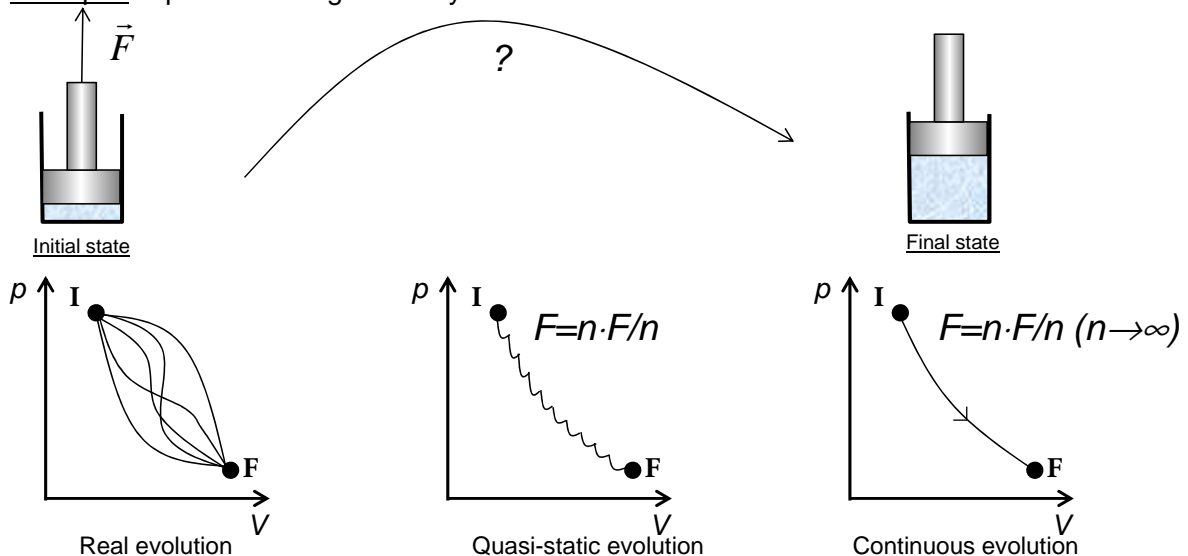
After a perturbation F/n, the time constant to return towards equilibrium (=relaxation time) is much smaller than the time needed for the quasi-static evolution.

INTRODUCTION

➢ Reversible evolution:

- It is a thermodynamic process that can be assessed via a succession of thermodynamic equilibriums ;
- by infinitesimally modifying some external constraints
- and which can be reversed without changing the nature of the external constraints

<u>Example:</u> gas expanded and compressed (slowly) in a cylinder

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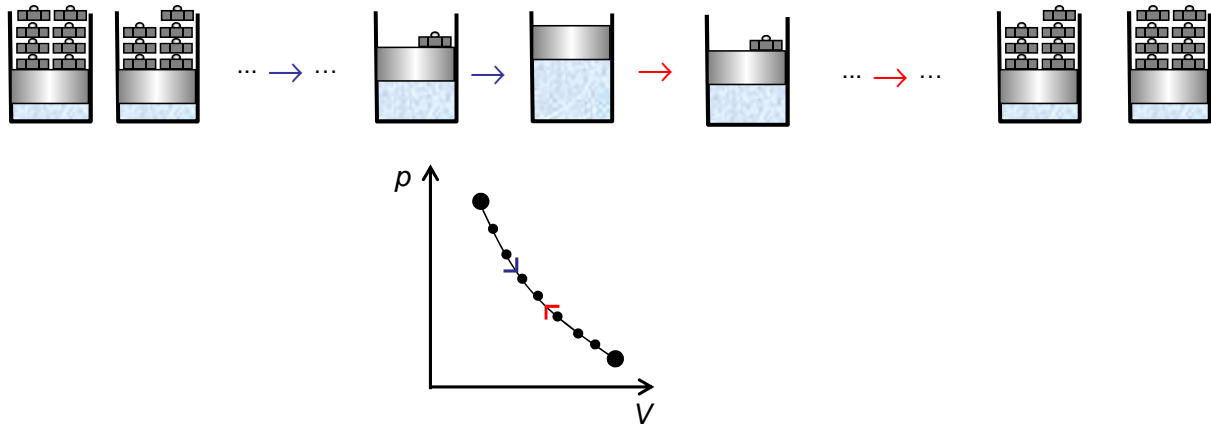
INTRODUCTION

➢ The laws of thermodynamics originates from the recognition that the random motion of particles in the system is governed by general statistical principles

- The statistical weight Ω denotes for the number of possible microstates of a system (ex. position of the atoms or molecules, distribution of the internal energy…)
- The different microstates correspond to (are consistent with) the same macrostate (described by the macroscopic parameters P, V…)
- The probability of the system to be found in one microstate is the same as that of finding it in another microstate
- Thus the probability that the system is in a given macrostate must be proportional to Ω.

A GLANCE AT WORK

➢ Work

- A mechanical work ($W = F \cdot dx$) is achieved when displacements dx or deformations occur by means of a force field

- Closed system:

Considering the gas inside the cylinder, for a quasi-static and reversible expansion or compression:
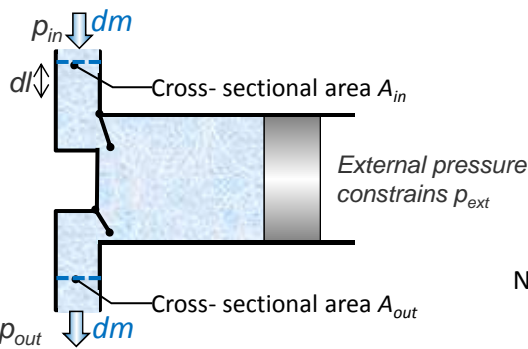

External pressure constrains p_{ext}
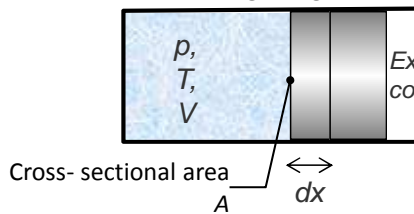
$$\delta W_{epf} = -\frac{F}{A} A dx = -p dV \quad \text{and} \quad W_{epf} = \int -p dV$$

Cross-sectional area A

dx

NB1
- during expansion, $dV > 0$ and $\delta W_{fp} < 0$: work is given to the surroundings
- during compression, $dV < 0$ and $\delta W_{pf} > 0$: work is received from the surroundings
NB2 - Isochoric process: $dV = 0 \Rightarrow \delta W_{pf} = 0$

- Opened system (transfer of matter dm with the surroundings)

p_{in} dm

dl

Cross-sectional area A_{in}

External pressure constrains p_{ext}

Cross-sectional area A_{out}

p_{out} dm

$$\delta W = \delta W_{shaft} + \delta W_{flow}$$

$$\delta W_{flow} = p_{in} A_{in} dl_{in} - p_{out} A_{out} dl_{out} = p_{in} dV_{in} - p_{out} dV_{out}$$

$$= p_{in} v_{in} \delta m_{in} - p_{out} v_{out} \delta m_{out} = [p v \delta v]_{out}^{in}$$

$$\delta W_{shaft} = V dp \qquad \text{(Cf. Slide 12)}$$

NB3- isobaric process: $dp = 0 \Rightarrow \delta W_{shaft} = 0$


FIRST LAW OF THERMODYNAMICS

➢ Internal energy

- It is a function of state such as: $U = \Sigma E_{c,micro} + \Sigma E_{p,micro}$ *(Joules J)*

- It can thus be defined by macroscopic parameters

For example, for a non-magnetic fluid, if p and V are fixed, $U = U(p, V)$ is also fixed

➢ First law of thermodynamics

- Between two thermodynamic equilibriums, we have:

$\delta U = \delta W + \delta Q$ *(for a reversible process: $dU = \delta W + \delta Q$)*

  o Q: exchanged heat
  o W: exchanged work (mechanical, electrical, magnetic interaction…)

- For a cyclic process
(during which the system evolves from an initial state I
to an identical final state F):

$U_I = U_F \Rightarrow \Delta U = U_F - U_I = 0$
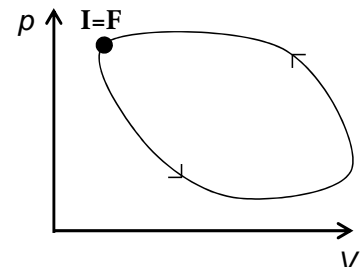
ENERGY BALANCE

➢ Between two thermodynamic equilibriums:

- *The total energy change is given by* $\Delta E = \Delta E_{c,macro} + \Delta E_{p,macro} + \Delta U = W + Q$

- if $\Delta E_{c,macro} = \Delta E_{p,macro} = 0 \Rightarrow \Delta U = W + Q$
  - o if work is only due to external pressure forces: $W_{epf} = \int -p\,dV$

    $\Delta U = W_{epf} + Q,$

  - o and if $V = cst$ (*isochoric process*), $\Delta U = Q$ (*calorimetetry*)

➢ Opened system:

$\Delta E = \Delta E_{c,macro} + \Delta E_{p,macro} + \Delta U = W_{shaft} + W_{flow} + Q$

$\Delta E = \Delta E_{c,macro} + \Delta E_{p,macro} + \Delta U + [pV]_{in}^{out} = W_{shaft} + Q$

- Function of state Enthalpy: $H = U + pV$ (*Joules J*)

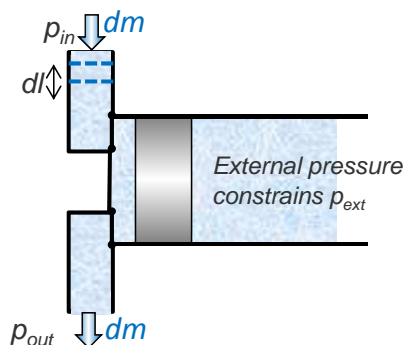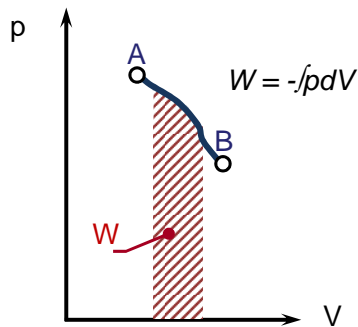$\Rightarrow \Delta E = \Delta E_{c,macro} + \Delta E_{p,macro} + \Delta H = W_{shaft} + Q$

- *if* $\Delta E_{c,macro} = \Delta E_{p,macro} = 0 \Rightarrow \Delta H = W_{shaft} + Q$

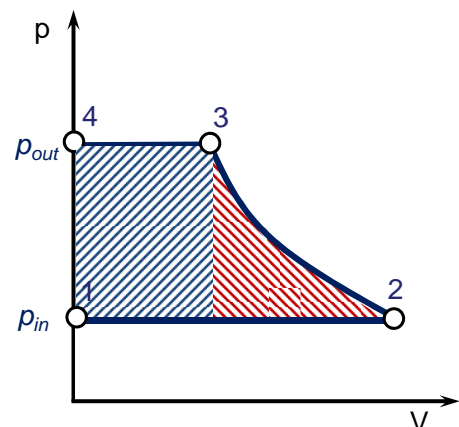 - o and if $p = cste$ (*isobaric process*), $\Delta H = Q$

$$W_{shaft} + Q = \sum_{\text{output boundaries}} mh - \sum_{\text{input boundaries}} mh$$

$$\dot{W}_{shaft} + \dot{Q} = \sum_{\text{output boundaries}} \dot{m}h - \sum_{\text{input boundaries}} \dot{m}h$$

ENERGY BALANCE

$W = -\int p\,dV$

$W_{shaft} = \int v\,dp$

SECOND LAW OF THERMODYNAMICS
➢ Entropy

- Entropy S is a function of state (J/K)
- For a system considered between two successive states: $\Delta S_{syst} = \Delta S = \Delta S^e + S^i$
  - ○ ΔS^e relates to the heat exchange $\Delta S^e = \int \frac{\delta Q}{T}$
  - ○ S^i is an entropy production term: $S^i = \Delta S_{syst} + \Delta S_{surroundings}$
  - ○ For a <u>reversible</u> process, $S^i = 0$; for an <u>irreversible</u> process: $S^i > 0$
  - ○ For an <u>adiabatic</u> ($\delta Q = 0$) and <u>reversible</u> process, $\Delta S = 0 \Rightarrow$ <u>isentropic</u>

### ➢ Entropy of an isolated system (statistical interpretation)

- $\Delta S^e = 0 \Rightarrow \Delta S_{syst} = S^i \geq 0$
- An isolated system is <u>in thermodynamic equilibrium</u> when its state does not change with time and that $S^i = 0$.
- $S = k_B \cdot ln(\Omega)$
  - ○ Ω is the number of observable microstates. It relates to the probability of finding a given macrostate.
  - ○ If we have two systems A and B, the number of microstates of the combined systems is $\Omega_A \cdot \Omega_B \Rightarrow S = S_A + S_B$ the entropy is additive
  - ○ Similarly, the entropy is proportional to the mass of the system (extensive): if $B = m \cdot A$, $\Omega_B = (\Omega_A)^m$ and $S_B = m \cdot [k_B \cdot ln(\Omega_A)] = m \cdot S_A$

SECOND LAW OF THERMODYNAMICS

➢ The principle of increase in entropy:

- The entropy of an isolated system tends to a maximum value at the thermodynamic equilibrium

Example 1: gas in a box

Initial state: $\Omega = \Omega_I$

Final equilibrium state: $\Omega = \Omega_F$
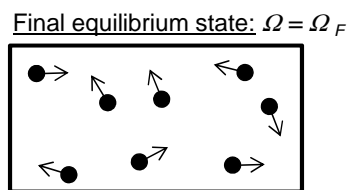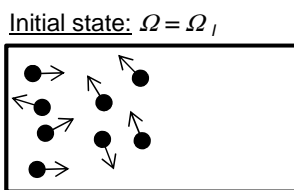
$\Omega_I << \Omega_F$
$\Rightarrow S_I << S_F$

- It thus provides the direction (in time) of a spontaneous change

- If the system is not isolated, we shall have a look at Ω or S of the surroundings and this principle becomes not very convenient to use...

- NB: it is always possible to consider a system as isolated by enlarging its boundaries...

TEMPERATURE AND THE ZEROTH LAW OF THERMODYNAMICS

➢ **Temperature:**

- Thermodynamic temperature: $T = \left(\dfrac{\partial U}{\partial S}\right)_V$

➢ **Zeroth law of thermodynamics:**

- Considering two closed systems:
  - A at T_A
  - B at T_B
  - having constant volumes *(δW=0)*
  - not isolated one from each other

    $\Rightarrow$ energy (heat) *δU(=δQ)* can flow from *A* to *B (or from B to A)*

$A \cup B$
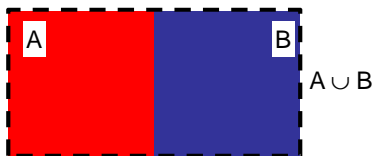
- Considering the isolated system A $\cup$ B: $\quad \delta S^e = \left(\dfrac{\partial S_A}{\partial U_A}\right)_V \delta U - \left(\dfrac{\partial S_B}{\partial U_B}\right)_V \delta U$

- At the thermodynamic equilibrium: $\quad \delta S^e = \dfrac{1}{T_A}\delta Q - \dfrac{1}{T_B}\delta Q$

  ΔS= ΔS^e + S^i = 0 + 0 = 0 and thus T$_A$=T$_B$
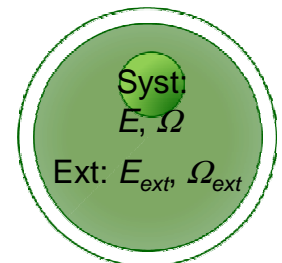

THIRD LAW OF THERMODYNAMICS

➢ **Boltzmann distribution:**

The probability that the system *Syst* has energy *E* is the probability that the rest of the system *Ext* has energy E_0-*E*

$\Rightarrow$ *ln Ω(E$_0$-E) = 1/k$_B$ S , S=f(E$_{ext}$=E$_0$-E)*

Syst:
E, Ω

Ext: E_{ext}, Ω_{ext}

S_0 = Syst $\cup$ Ext:
$E_0=E+E_{ext}, \Omega_0=\Omega\Omega_{ext}$

As *E << E$_0$*, $\quad \ln \; \Omega(E - E_0) = \dfrac{1}{k_B}S(E_0) - \dfrac{1}{k_B}E\left(\dfrac{\partial S}{\partial E_0}\right)_{E=0}$

And as $\left(\dfrac{\partial S_{ext}}{\partial E_0}\right)_{E=0} = \dfrac{1}{T}$, $\quad \ln \; \Omega(E - E_0) = \Omega(E_0) - \dfrac{E}{k_B T}$

$$\Omega(E - E_0) = cst \cdot e^{\left(-\frac{E}{k_B T}\right)} \quad \text{(as T→0, state of minimum energy)}$$

➢ **Zeroth law of thermodynamics:**

- A the absolute zero of temperature, any system in thermal equilibrium must exists in its lowest possible energy state

- Thus, if *Ω= 1* (the minimum energy state is unique) as *T→0, S = 0*

- An absolute entropy can thus be computed

EQUATIONS of STATE

➤ Relating entropy to variable of states

- *U* and *S* are functions of state ; therefore:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \text{ , for a reversible process}$$

$$dU = TdS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \Rightarrow \quad p = -\left(\frac{\partial U}{\partial V}\right)_S \quad \Rightarrow \quad \boxed{dU = TdS - pdV} \qquad dS = \frac{p}{T}dV + \frac{1}{T}dU$$

The relation between *p*, *V* and *T* is called <u>the equation of state</u>

➤ Ideal gas

$$\frac{p}{T} = n\frac{N_A k_B}{V} = \frac{nR}{V} = \frac{mR}{M_{mol}V} = \frac{mr}{V} \text{ ,}$$

n : number of moles (mol)

$pv = rT$

$N_A = 6.022 \cdot 10^{23} \, mol^{-1}$: the Avogadro's number

$k_B = 1.38 \cdot 10^{-23} \, J \cdot K^{-1}$: the Boltzmann's constant

$R = 8.314 \, J \cdot mol^{-1} \cdot K^{-1}$: the gas constant
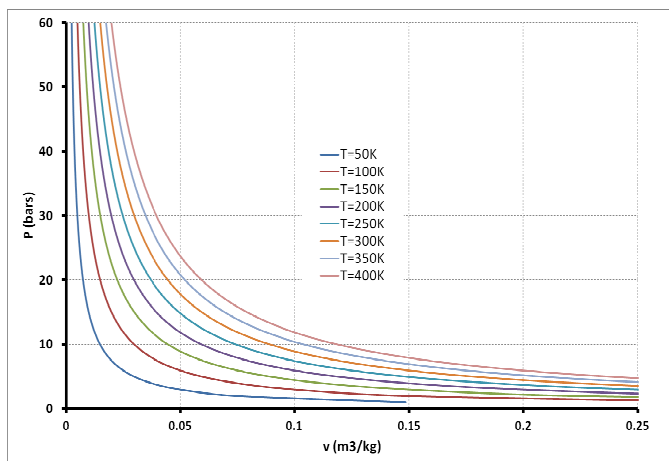
➤ Van der Waals equation

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

a: effect of the attractions between the molecules
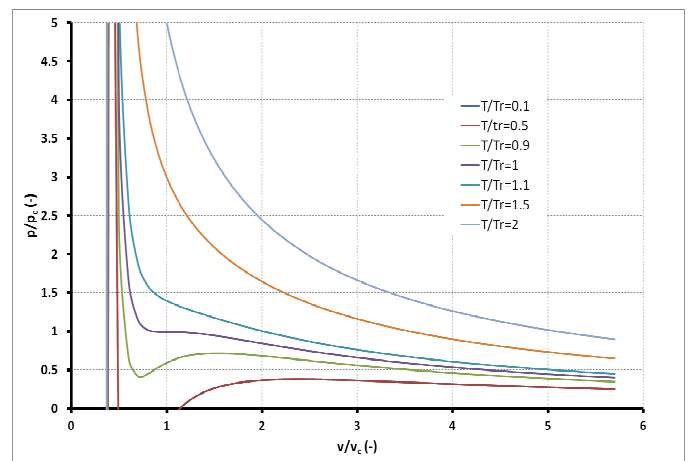
b: volume excluded by a mole of molecules

Other models for the equations of state exist

P, V DIAGRAM

Isotherms of the ideal gas

Isotherms of a Van der Waals gas

HEAT CAPACITIES

- The amount of heat that must be added to a system <u>reversibly</u> to change its temperature is the heat capacity C, $C = \delta Q / dT$ (J/K)

- The conditions under which heat is supplied must be specified: $C_i = \left(\dfrac{\delta Q}{dT} \right)_i = T \left(\dfrac{\partial S}{\partial T} \right)_i$

  NB: specific heat (J·kg^{-1}· K^{-1}): $c_i = T \left(\dfrac{\partial s}{\partial T} \right)_i$

  - at constant pressure: $C_p = T \left(\dfrac{\partial S}{\partial T} \right)_p \Rightarrow S(T, p) = \displaystyle\int_0^T \dfrac{C_p}{T} dT$

  $$ C_p = \left(\dfrac{\partial H}{\partial T} \right)_p \Rightarrow \boxed{\Delta H = \int C_p dT} \text{ (known as sensible heat)} $$

  - at constant volume: $C_V = T \left(\dfrac{\partial S}{\partial T} \right)_V \Rightarrow S(T, V) = \displaystyle\int_0^T \dfrac{C_V}{T} dT$

  $$ C_V = \left(\dfrac{\partial U}{\partial T} \right)_V \Rightarrow \boxed{\Delta U = \int C_V dT} \text{ (known as sensible heat)} $$

- Ratio of heat capacities: $\boxed{\gamma = \dfrac{C_p}{C_V} = \left(\dfrac{\partial V}{\partial p} \right)_T \left(\dfrac{\partial V}{\partial p} \right)_S^{-1}}$

- Mayer's relation: $C_p - C_V = T \left(\dfrac{\partial p}{\partial T} \right)_V \left(\dfrac{\partial V}{\partial T} \right)_p \Rightarrow \boxed{C_p - C_V = nR}$ for an ideal gas

  $$ \boxed{C_p = n \dfrac{R}{\gamma - 1} \text{ and } C_p = n \dfrac{\gamma R}{\gamma - 1}} $$

USE OF THERMODYNAMIC RELATIONS
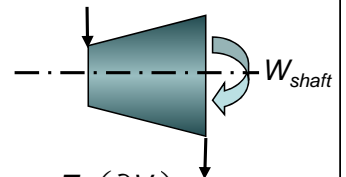
➤ Maxwell relations

- As if $Z = Z(x,y)$, $P = P(x,y)$, $Q = Q(x,y)$ and $dZ = Pdx + Qdy$, we can write:

$$ \left(\dfrac{\partial P}{\partial x} \right)_y = \left(\dfrac{\partial Q}{\partial y} \right)_x $$

- then: $\left(\dfrac{\partial T}{\partial V} \right)_S = -\left(\dfrac{\partial p}{\partial S} \right)_V$; $\left(\dfrac{\partial T}{\partial p} \right)_S = \left(\dfrac{\partial V}{\partial S} \right)_p$; $\left(\dfrac{\partial p}{\partial T} \right)_V = \left(\dfrac{\partial S}{\partial V} \right)_T$; $\left(\dfrac{\partial S}{\partial p} \right)_T = -\left(\dfrac{\partial V}{\partial T} \right)_p$

➤ Adiabatic expansion of gas:

During adiabatic expansion of a gas in a reciprocating engine or a turbine (turbo-expander), work is extracted and gas is cooled.

W_{shaft}

For a reversible adiabatic expansion: $\left(\dfrac{\partial T}{\partial p} \right)_S = -\left(\dfrac{\partial T}{\partial S} \right)_p \left(\dfrac{\partial S}{\partial p} \right)_T = \left(\dfrac{\partial T}{\partial S} \right)_p \left(\dfrac{\partial V}{\partial T} \right)_p = \dfrac{T}{C_p} \left(\dfrac{\partial V}{\partial T} \right)_p$
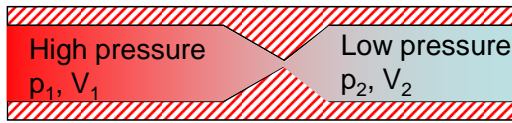
As $C_p > 0$ and $(\partial V / \partial T)_p > 0 \Rightarrow (\partial T / \partial p)_S > 0$. Thus, $dp < 0 \Rightarrow dT < 0$.

⇒ Adiabatic expansion always leads to a cooling.

USE OF THERMODYNAMIC RELATIONS

➢ Joule-Kelvin (Joule-Thomson) expansion:

A flowing gas expands through a throttling valve from a fixed high pressure to a fixed low pressure, the whole system being thermally isolated

High pressure p_1, V_1 — Low pressure p_2, V_2

$$\Delta U = W \Rightarrow U_1 + p_1 V_1 = U_2 + p_2 V_2$$
$$H_1 = H_2$$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{C_p}\left[\left(\frac{\partial S}{\partial p}\right)_T + V\right] = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \frac{1}{C_p}(\alpha T - 1)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \text{is the coefficient of thermal expansion}$$

o for the ideal gas: $\alpha T = 1 \Rightarrow (\partial T/\partial p)_H = 0 \Rightarrow$ isenthalpic expansion does not change T

o for real gas:

o $\alpha T > 1 \Rightarrow (\partial T/\partial p)_H > 0$ below a certain $T \Rightarrow$ there is cooling below the inversion temperature

o $\alpha T < 1 \Rightarrow (\partial T/\partial p)_H < 0$ above a certain $T \Rightarrow$ there is heating above the inversion temperature
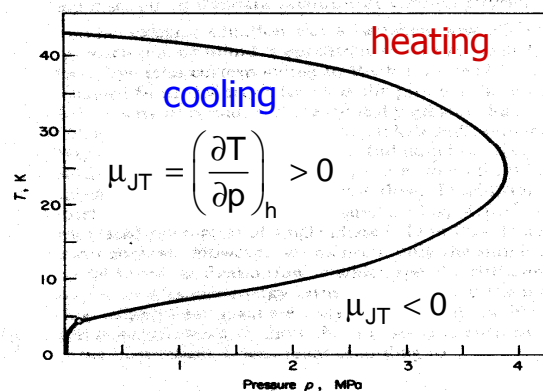

USE OF THERMODYNAMIC RELATIONS

➢ Joule-Kelvin (Joule-Thomson) expansion:

• Inversion temperature:

For helium (He^4):

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_h > 0$$

$$\mu_{JT} < 0$$
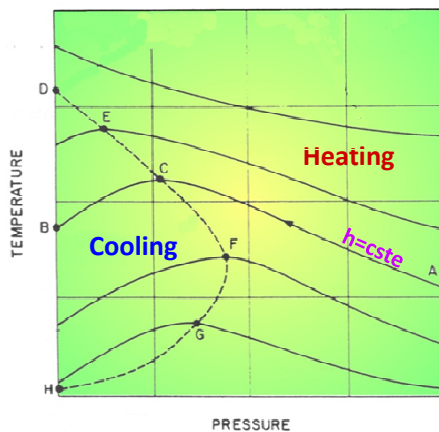
The maximum inversion temperature is about 43K

• In helium liquefier (or refrigerator), the gas is usually cooled below the inversion temperature by adiabatic expansion (and heat transfer in heat exchangers) before the final liquefaction is achieved by Joule-Thomson expansion.

• Nitrogen and oxygen have inversion temperatures of 621 K (348 °C) and 764 K (491 °C).

THERMODYNAMIC REVERSIBLE PROCESSES for an ideal gas

Type of state change	ISOCHORIC	ISOBARIC	ISOTHERMAL	ADIABATIC	POLYTROPIC
Feature	$v = cst$	$p = cst$	$t = cst$	$\delta q = 0$	
p-v diagram					
Eq.	$\dfrac{p_B}{p_A} = \dfrac{T_B}{T_A}$	$\dfrac{v_B}{v_A} = \dfrac{T_B}{T_A}$	$p_A v_A = p_B v_B = RT_A = cst$	$p_A v_A^{\gamma} = p_B v_B^{\gamma} = cst$ $\gamma = c_p / c_v$	$p_A v_A^{n} = p_B v_B^{n} = cst$
Heat (J/kg)	$q_{AB} = u_B - u_A = \int_{T_A}^{T_B} c_V dT$ $= c_V(T_B - T_A)$	$q_{AB} = h_B - h_A = \int_{T_A}^{T_B} c_p dT$ $= c_p(T_B - T_A)$	$q_{AB} = rT \ln \dfrac{v_B}{v_A}$	$q_{AB} = 0$	$q_{AB} = \dfrac{p_B v_B - p_A v_A}{\gamma - 1} + p_A v_A \ln \dfrac{v_B}{v_A}$
Work (J/kg)	$w_{AB} = 0$	$w_{AB} = -p(v_B - v_A)$ $= c_p(T_B - T_A)$	$w_{AB} = p_A v_A \ln \dfrac{v_B}{v_A} = p_A v_A \ln \dfrac{p_A}{p_B}$	$w_{AB} = \dfrac{r}{\gamma - 1}(T_B - T_A)$ $= \dfrac{p_A v_A}{\gamma - 1}\left[1 - \left(\dfrac{p_B}{p_A}\right)^{\frac{\gamma-1}{\gamma}} \right]$	$w_{AB} = \dfrac{p_B v_B - p_A v_A}{n - 1} \; n \neq 1$
Δu (J/kg)	$u_B - u_A = c_V(T_B - T_A)$	$u_B - u_A = c_V(T_B - T_A)$	$u_B - u_A = 0$	$w_{AB} = c_V(T_2 - T_1)$ $= \dfrac{p_B v_B - p_A v_A}{\gamma - 1}$	
Δs (J/kg)	$s_B - s_A = c_V \ln \dfrac{p_B}{p_A}$	$s_B - s_A = c_p \ln \dfrac{T_B}{TA}$ $= c_p \ln \dfrac{v_B}{v_A}$	$s_B - s_A = r \ln \dfrac{v_B}{v_A}$	$s_B - s_A = 0$	$\Delta s_{AB} = r \dfrac{\gamma - n}{\gamma - 1} \ln \dfrac{v_B}{v_A}$

HEAT MACHINES

➤ General principle
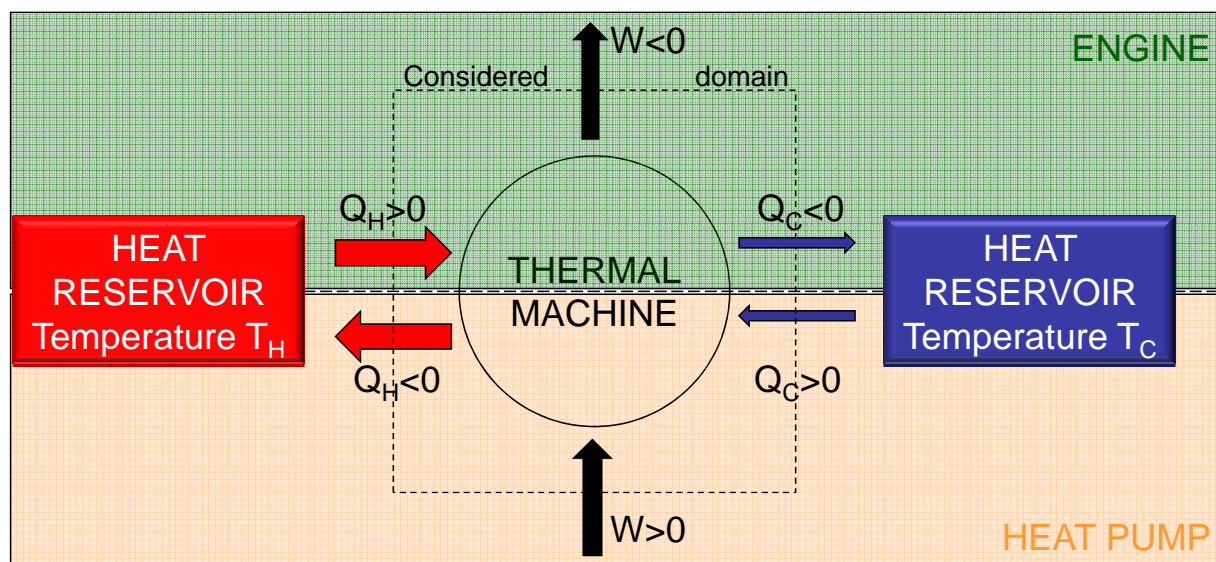
NB: in the case of a heat pump, if Q_2 is the useful heat transfer (from the cold reservoir) then the heat pump is a refrigerator.
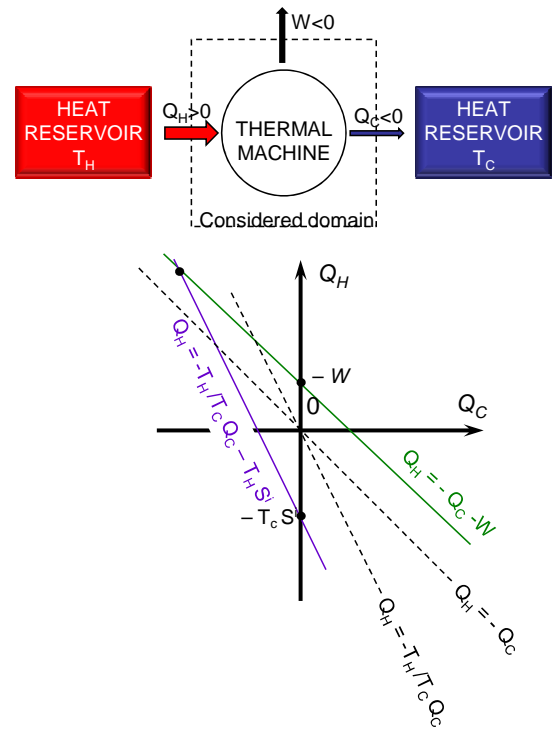
- Over one cycle:
  - o Energy balance (1st law): $\Delta U = U_1 - U_1 = 0 = W + Q_C + Q_H$
  - o Entropy balance (2nd law): $\Delta S = 0 = \Delta S^e + S^i = Q_C / T_c + Q_H / T_H + S^i \geq 0$

HEAT MACHINES

➤ Engine cycle:

- $Q_H + Q_C = -W$
- $Q_H = -Q_C - W$
- $Q_H = -T_H/T_C \cdot Q_C - T_H \cdot S^i$
- If $-W > 0$ (work being given by the engine)

  and if $T_H > T_C$

  then $Q_H > 0$ and $Q_C < 0$

➤ Engine efficiency:

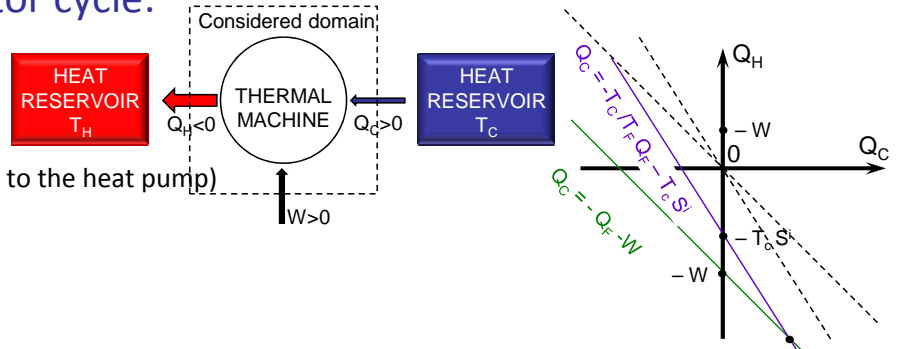- $\eta = \dfrac{|W|}{Q_H} = \dfrac{-W}{Q_H} = \dfrac{Q_H + Q_C}{Q_H} = 1 + \dfrac{Q_C}{Q_H}$

- As $\quad \dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H} - \dfrac{T_C S^i}{Q_H}$,
  $\qquad \boxed{\eta = 1 - \dfrac{T_C}{T_H} - \dfrac{T_C S^i}{Q_H} \leq 1 - \dfrac{T_C}{T_H} < 1} \quad \left(S^i \geq 0\right)$

HEAT MACHINES

➤ Heat pump or refrigerator cycle:

- $Q_H + Q_C = -W$
- $Q_H = -Q_C - W$
- $Q_H = -T_H/T_C \cdot Q_C - T_H \cdot S^i$
- If $-W < 0$ (work being provided to the heat pump)

  and if $T_H > T_C$

  then $Q_H < 0$ and $Q_C > 0$

➤ Heat pump efficiency:

- Coefficient of perfomance: $COP_{Heating} = \dfrac{|Q_H|}{W} = \dfrac{-Q_H}{W} = \dfrac{-Q_H}{-Q_H - Q_C} = \dfrac{1}{1 + Q_C/Q_H}$

- As $\quad \dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H} - \dfrac{T_C S^i}{Q_H}$,
  $\qquad \boxed{COP_{Heating} = \dfrac{1}{1 - \dfrac{T_C}{T_H} - \dfrac{T_C S^i}{Q_H}} \leq \dfrac{1}{1 - \dfrac{T_C}{T_H}}} \quad \left(S^i \geq 0\right)$

➤ Refrigerator efficiency:

- Coefficient of perfomance: $COP_{Cooling} = \dfrac{Q_F}{W} = \dfrac{Q_F}{-Q_H - Q_C} = \dfrac{1}{-1 - Q_H/Q_C}$

- As $\quad \dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H} - \dfrac{T_C S^i}{Q_H}$,
  $\qquad \boxed{COP_{Cooling} = \dfrac{1}{\dfrac{T_C}{T_H} - 1 + \dfrac{T_C S^i}{Q_H}} \leq \dfrac{1}{\dfrac{T_H}{T_C} - 1}}$
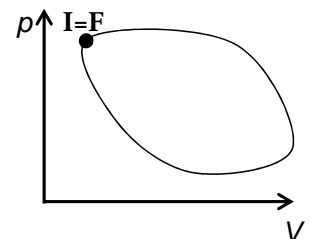
HEAT MACHINES

➤ Sources of entropy production and destruction of exergy:

- Heat transfer (with temperature difference)
- Friction due to moving solid solid components
- Fluid motions (viscous friction, dissipative structures)
- Matter diffusion
- Electric resistance (Joule effect)
- Chemical reactions

HEAT MACHINES

➤ The Carnot cycle

- Cyclic process:

  upon completion of the cycle there has been no net change in state of the system

- Carnot cycle: 4 reversible processes

  o 2 isothermal processes (reversibility means that heat transfers occurs under very small temperature differences)

  o 2 adiabatic processes (reversibility leads to isentropic processes)

  o 1st law of thermodynamics over cycle: $\Delta U = U_1 - U_1 = 0 = W + Q_{12} + Q_{34}$

Carnot cycle: engine case
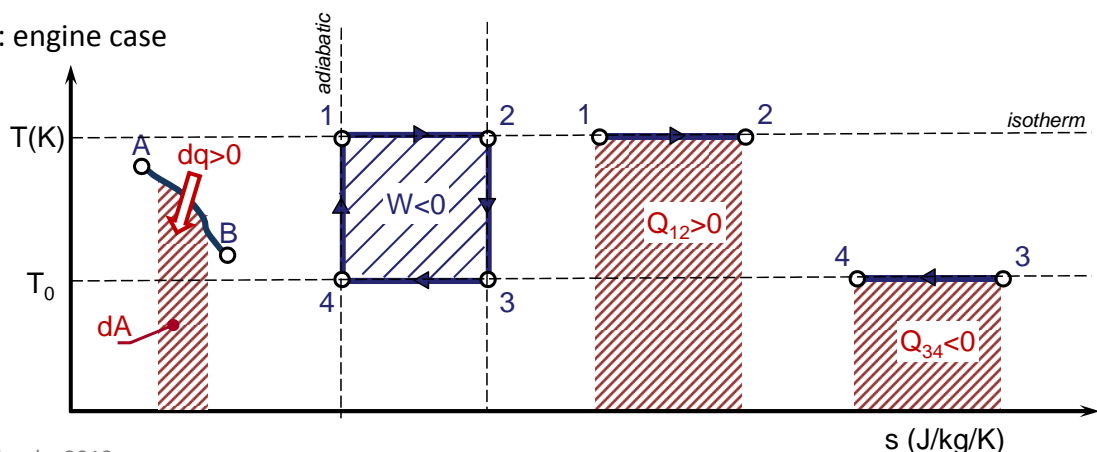
HEAT MACHINES

➤ The Carnot cycle

- **Efficiency of a Carnot engine:**

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

- **Coefficient of performances of Carnot heat pump:**

$$COP_{Heating} = \frac{T_H}{T_H - T_C}$$

- **Coefficient of performances of Carnot refrigerator:**

$$COP_{Heating} = \frac{T_C}{T_H - T_C}$$

➤ Comparison of real systems relatively with the Carnot cycle

relative efficiencies and coefficients of performance

- **Relative efficiencies:**
  - o Engine:

$$\eta_r = \frac{\eta}{\eta_C} = 1 - \frac{T_C S^i}{Q_H\left(1 - \frac{T_C}{T_H}\right)}$$
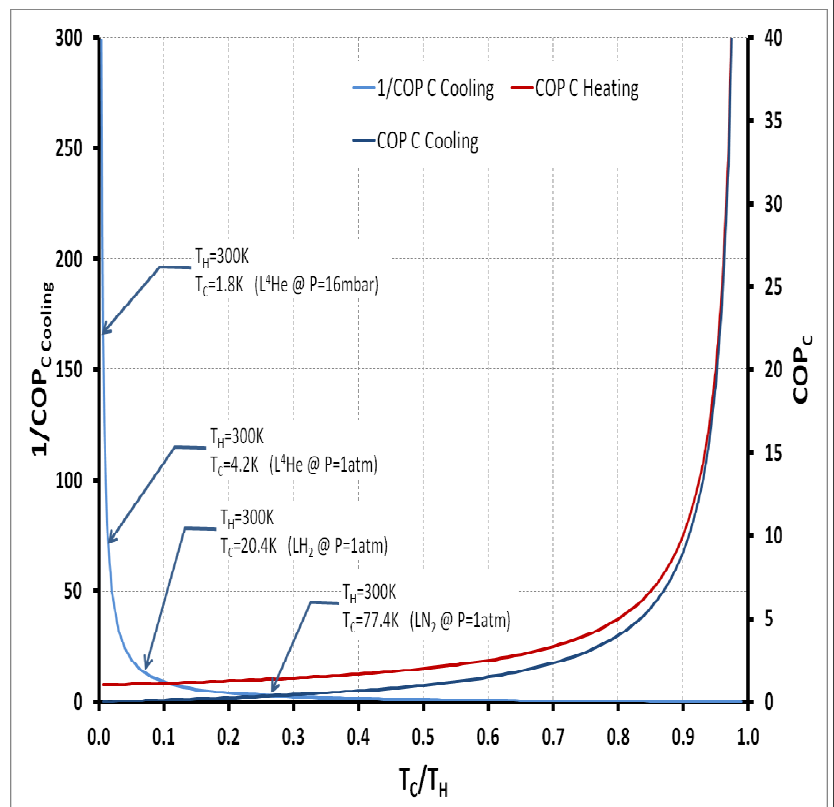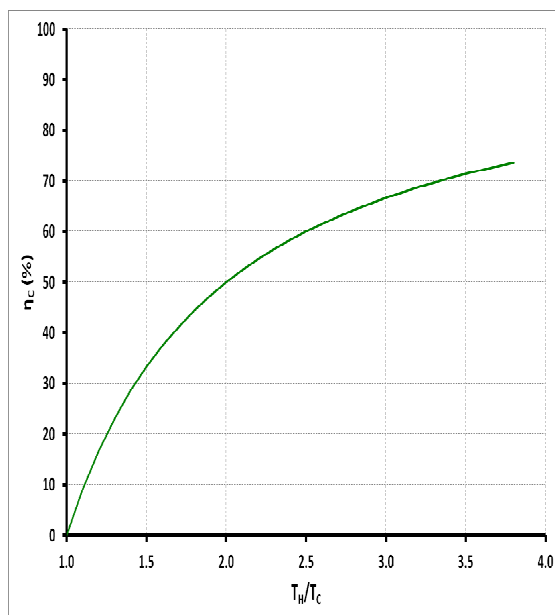
  - o Heat pump and refrigerator:

$$COP_{r\,Heating} = \frac{COP_{Heating}}{COP_{C\,Heating}} = \frac{1 - \frac{T_C}{T_H}}{1 - \frac{T_C}{T_H} - \frac{T_C S^i}{Q_C}}$$

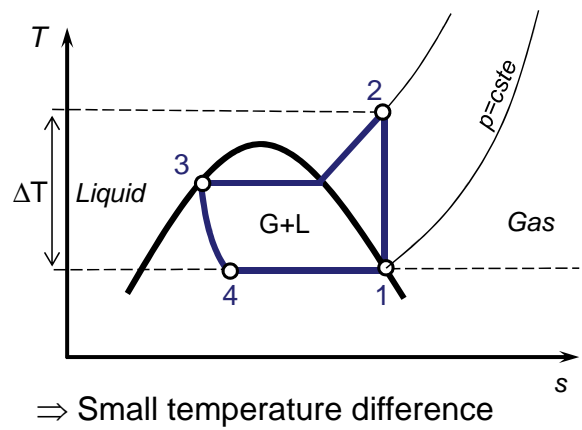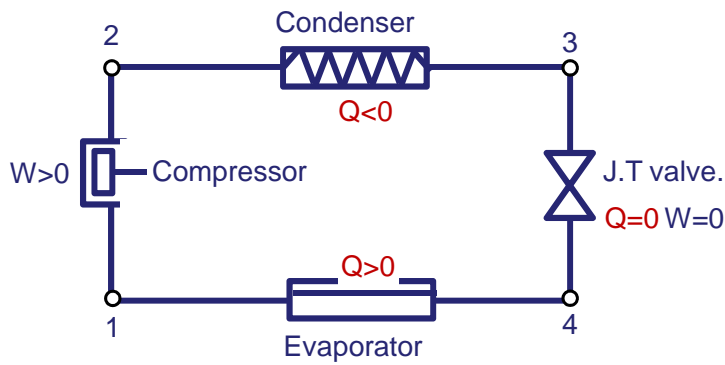$$COP_{r\,Cooling} = \frac{1 - \frac{T_C}{T_H}}{1 - \frac{T_C}{T_H} - \frac{T_C S^i}{Q_H}}$$

HEAT MACHINES

➤ Carnot efficiency and coefficient of performance

HEAT MACHINES

➢ Vapour compression

$\Rightarrow$ Small temperature difference

- the COP of a vapour compression cycle is relatively good compared with Carnot cycle because:
  - o vaporization of a saturated liquid and liquefaction of saturated vapour are two isothermal process (NB: heat is however transfered irreversibely)
  - o isenthalpic expansion of a saturated liquid is sensitively closed to an isentropic expansion

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EXERGY

- Heat and work are not equivalent: they don't have the same "thermodynamic grade" :
  - o (Mechanical, electric…) work can be integrally converted into heat
  - o Converting integrally heat into work is impossible (2nd law)
- Energy transfers implies a direction of the evolutions:
  - o Heat flows from hot to cold temperatures;
  - o Electric work from high to low potentials;
  - o Mass transfers from high to low pressures…
- Transfers are generally irreversible.
- Exergy allows to "rank" energies by involving the concept of "usable " or "available" energy which expresses
  - o the potentiality of a system (engine) to produce work without irreversibility evolving towards equilibrium with a surroundings at $T_{REF}=T_a$ (ambiant)
  - o the necessary work to change the temperature of a system (refrigerator) compared to the natural equilibrium temperature of this system with the surroundings (T_a).

$$Ex = \int \delta Q \left(1 - \frac{T_a}{T} \right)$$ Equivalent work of the transferred heat $\qquad Ex = W$

$$\boxed{Ex = H - T_a S}$$

EXERGY

➤ **Exergetic balance of opened systems:**

$$\Delta Ex = \Delta H - T_a \Delta S = W_{shaft} + Q\left(1 - \frac{T_a}{T}\right) - T_a S^i \qquad T_a S^i \geq 0 \; ;$$

Usuable work and potentially usuable work is given by the exergetic change

Usable energy is maximum if the system has no irreversibility: $T_a S^i = 0$.

➤ **Exergetic balance of closed systems:**

$$\Delta U - T_a \Delta S = W + Q\left(1 - \frac{T_a}{T}\right) - T_a S^i$$

➤ **Exergetic balance of heat machines (thermodynamic cycles):**

$$0 = W + Q\left(1 - \frac{T_a}{T}\right) - T_a S^i$$

➤ **Exergetic efficiency:**

$$\eta_{exergetic} = \frac{\text{Equivalent work of service}}{\text{Equivalent work of supply}} \qquad \eta_{exergetic} = \frac{\Delta Ex \; real}{\Delta Ex \; rev}$$

MAXWELL THERMODYNAMIC RELATIONS

As $dU = TdS - pdV$

➤ **ENTHALPY**

- $H = U + pV$ $\Rightarrow$ $dH = TdS + Vdp$

➤ **HELMHOTZ FREE ENERGY**

- $F = U - TS$ $\Rightarrow$ $dF = -pdV - SdT$

➤ **GIBBS FREE ENERGY**

- $G = U - TS + pV$ $\Rightarrow$ $dG = -SdT + Vdp$

FREE ENERGY AND EXERGY

- Considering an isothermal ($T=T_0$) and reversible thermodynamic process:
  - $dU = \delta W + T_0 dS \Rightarrow \delta W = dU - T_0 dS = dF$
  - the work provided (<0) by a system is equal to the reduction in free energy
  - Here (reversible process) it is the maximum work that can be extracted ;

- Similarly, for an opened system:
  - $dH = \delta W_{shaft} + T_0 dS \Rightarrow \delta W_{shaft} = dH - T_0 dS = dG$
  - the maximum work (other than those due to the external pressure forces) is equal to the reduction of Gibbs free energy.

- In these cases, all energy is **free** to perform useful work because there is no entropic loss

DIRECTION OF SPONTANEOUS CHANGE

- Spontaneous change of a thermally isolated system, :
  - $\Rightarrow$ increase of entropy
  - $\Rightarrow$ at thermodynamic equilibrium, entropy is a maximum

- For non isolated system:
  - System in thermal contact with its surroundings
    - Assumptions:
      - heat flow from the surroundings to the system
      - surroundings EXT at $T=Text=cst$ (large heat capacity)
    - $\Delta S_{total} = \Delta S + \Delta S_{ext} \geq 0$
    - $\delta S_{ext} = -\delta Q / T_{Ext}$
    - For the system: $\delta U = \delta Q$ and thus $\delta(U - T_0 S) \leq 0$
    - Thus spontaneous change (heat flow) is accompanied by a reduction of $U - T_0 S$
      At equilibrium, this quantity must tend to a minimum
      Therfore, in equilibrium, the free energy $F = U - TS$ of the system tends to a minimum
  - System in thermal contact with its surroundings and held at constant pressure:
    - The Gibbs free energy $E - TS + pV$ tends to a minimum at equilibrium
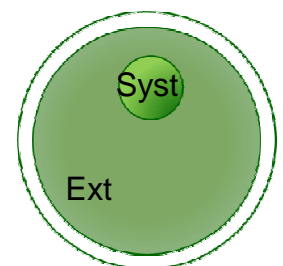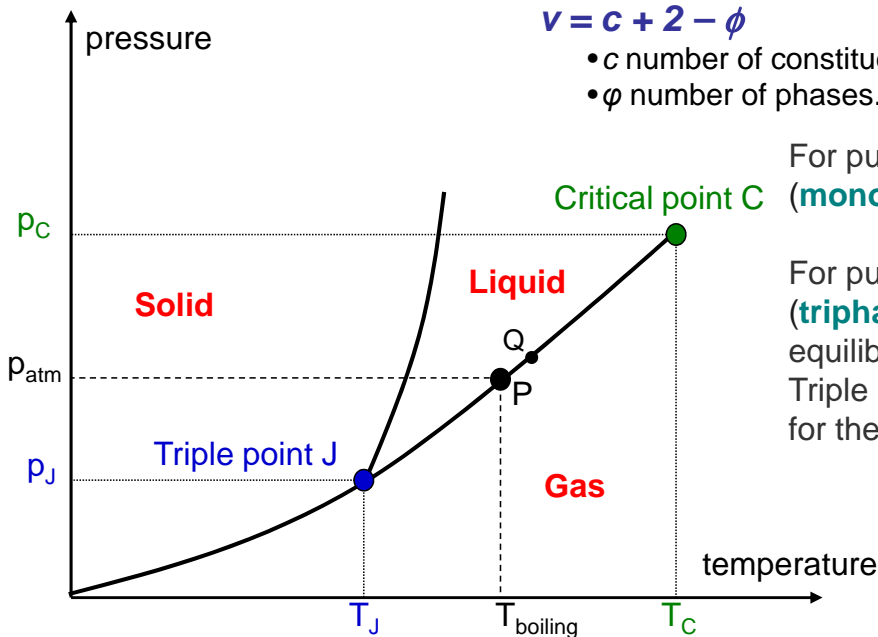
PHASE EQUILIBRIA

➢ States of matter:
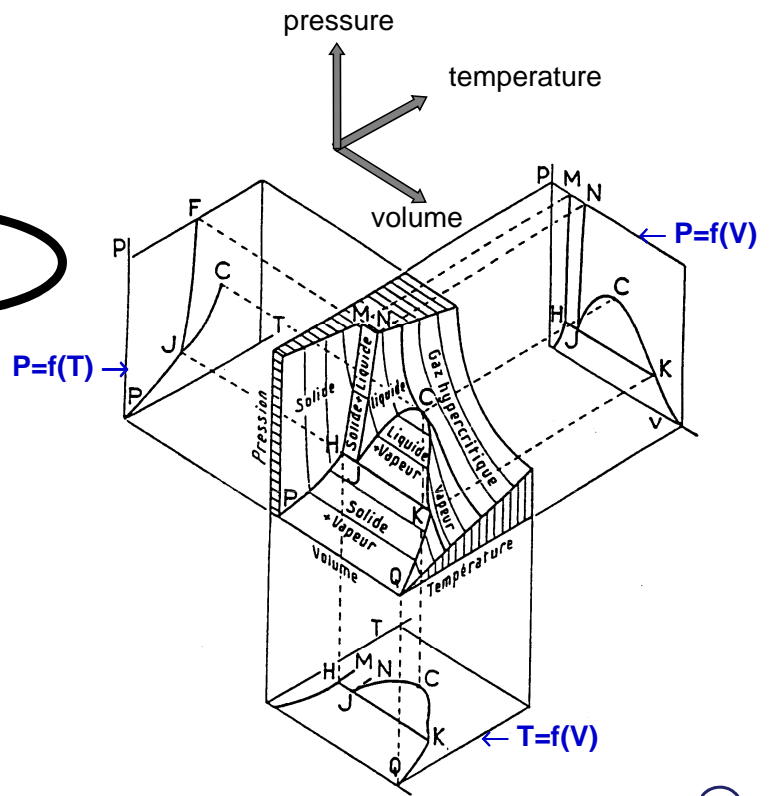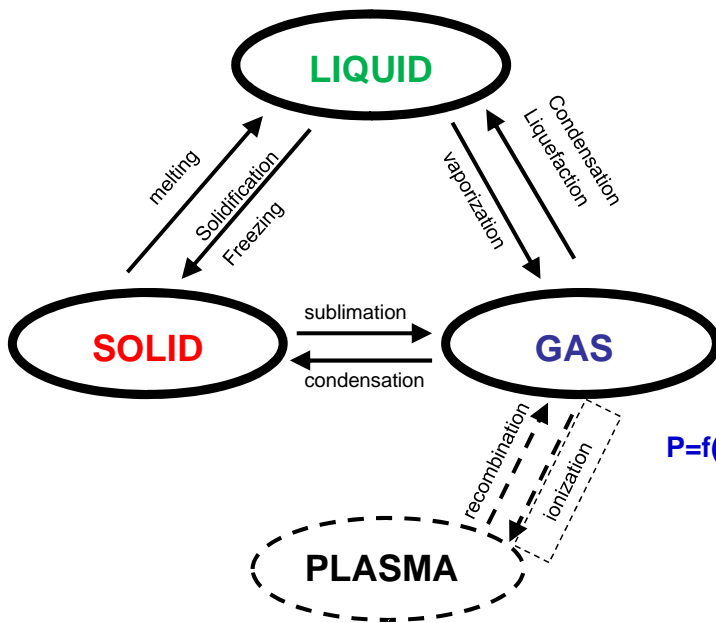
PHASE DIAGRAM: p-T DIAGRAM

Gibbs' phase rule: gives the number of degrees of freedom (number of independent intensive variables)

$$v = c + 2 - \phi$$

- c number of constituents (chemically independent)
- φ number of phases.

For pure substance in a single phase (**monophasic**): $v = 2$

For pure substance in three phases (**triphasic**: coexistence of 4 phases in equilibrium): $v = 0$
Triple point T_J, p_J: metrologic reference for the temperature scale

For a pure substance in two phases (**biphasic**) (point P) : $v = 1$
　　　saturated vapour tension: pressure of the gas in equilibrium with the liquid

PHASE EQUILIBRIA

- Considering point P: gas and liquid phases coexisting at p and T *(constant)*
  - The equilibrium condition is that $G \rightarrow$ minimum
  - Considering a small quantity of matter δm transferring from the liquid to the gas phase
  - The change in total Gibbs free energy is: $(g_{gas}-g_{liq})\cdot\delta m \Rightarrow$ minimum for $g_{gas}=g_{liq}$
- Considering a neighbouring point Q on the saturated vapour tension curve:

$$g_{gas}(Q) = g_{gas}(P) + \left(\frac{\partial g_{gas}}{\partial p}\right)_T dp + \left(\frac{\partial g_{gas}}{\partial T}\right)_p dT = g_{gas}(P) + v_{gas}dp - s_{gas}dT$$

and
$$g_{liq}(Q) = g_{liq}(P) + \left(\frac{\partial g_{liq}}{\partial p}\right)_T dp + \left(\frac{\partial g_{liq}}{\partial T}\right)_p dT = g_{liq}(P) + v_{liq}dp - s_{liq}dT$$

$$\Rightarrow \quad 0 = (v_{gas} - v_{liq})dp - (s_{gas} - s_{liq})dT$$

- The slope of the saturated vapour tension curve is thus given by:

$$\boxed{\frac{dp}{dT} = \frac{(s_{gas} - s_{liq})}{(v_{gas} - v_{liq})} = \frac{L_{vap}}{T(v_{gas} - v_{liq})}}$$ which is the Clausius-Clapeyron equation
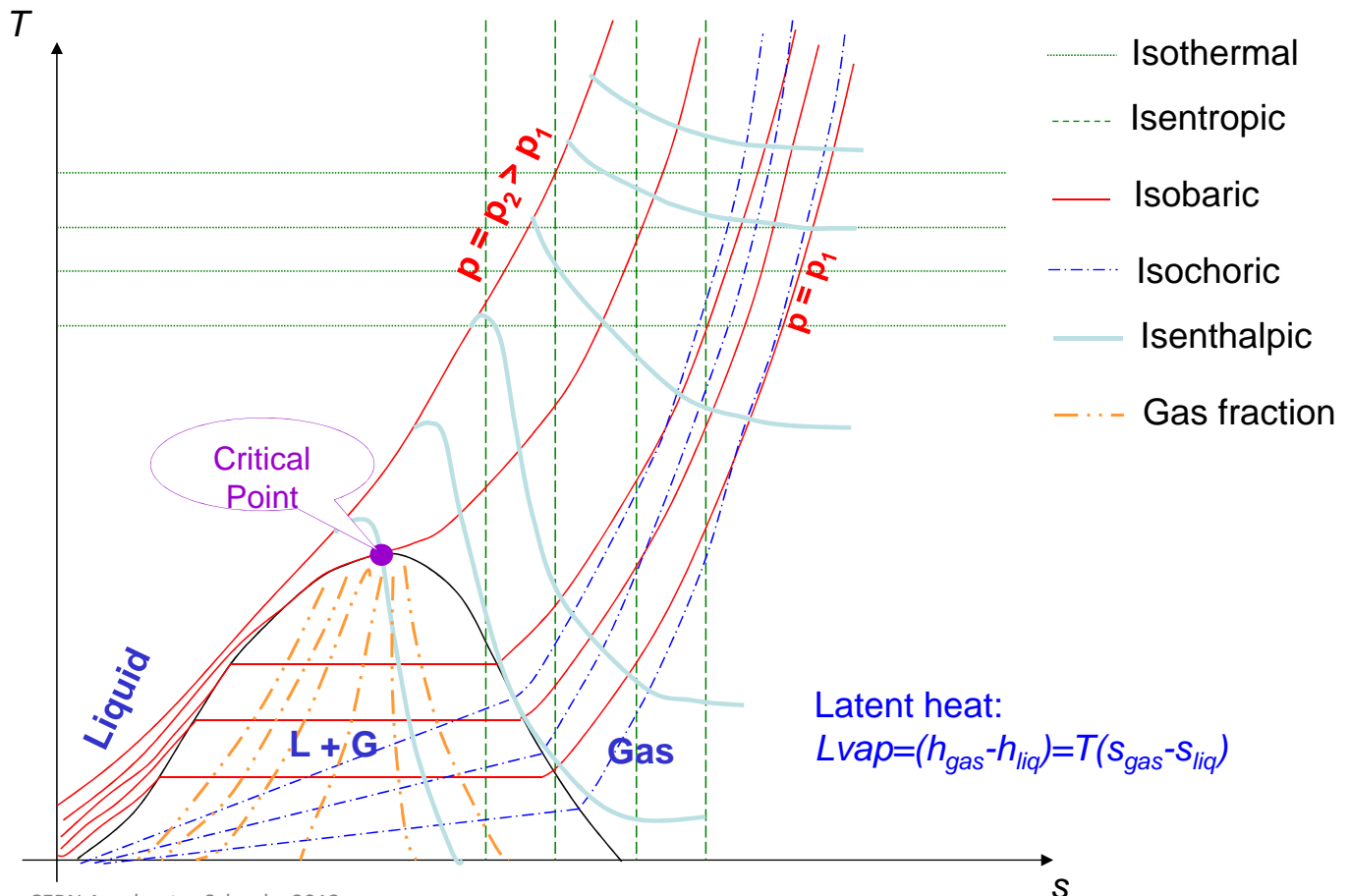
L_{vap} (>0 as ΔS>0) is the specific latent heat for the liquid $\rightarrow$ gas transition (vaporization).

$$\Delta H = Q = m\cdot L_{vap}$$

L_{vap} It is the heat required to transform 1kg of one phase to another (at constant T and p).

NB1- Critical point: $L_{vap} \rightarrow 0$ as $(p,T) \rightarrow (p_C, T_C)$; NB2- At the triple point: $L_{vap}=L_{melt}=L_{sub}$

T-s DIAGRAM

T

Isothermal
Isentropic
Isobaric
Isochoric
Isenthalpic
Gas fraction

$p = p_2 > p_1$

$p = p_1$

Critical Point

Liquid

L + G

Gas

Latent heat:
$L_{vap}=(h_{gas}-h_{liq})=T(s_{gas}-s_{liq})$

s

THERMODYNAMICS OF MAGNETIC MATERIALS

- Magnetic material placed within a coil:
  - i is the current being established inside the coil
  - e is the back emf induced in the coil by the time rate of change of the magnetic flux linkage
  - energy fed into the system by the source of current: $\int i \cdot e \cdot dt$
  - Considering the magnetic piece:
    - applied magnetic field: $\hat{H}$
    - magnetization: $\hat{M}$

    $$\stackrel{\shortparallel}{\int \mu_0 \hat{H} \cdot d\hat{M}}$$

  - $\mu_0 \hat{H} d\hat{M} = \delta W$: reversible work done on the magnetic material ($\hat{H} \equiv -p$ and $\mu_0 \hat{M} \equiv V$).
  - The applied magnetic field $\hat{H}$ is generated by the coil current only and not affected by the presence of the magnetic material.
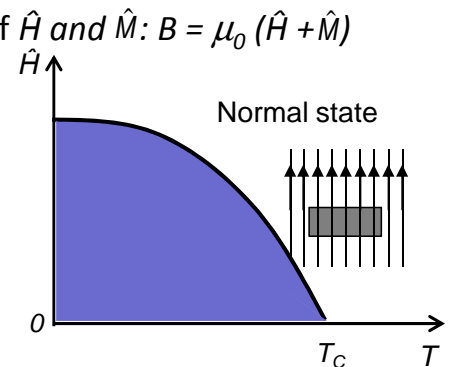 - The magnetic induction B is given by the superposition of $\hat{H}$ and $\hat{M}$: $B = \mu_0 (\hat{H} + \hat{M})$
  - For a type I superconductor in Meissner state ($\hat{H} < \hat{H}_c$):
    $B = \mu_0 (\hat{H} + \hat{M}) = 0$, $\hat{M} = -\hat{H}$ and thus $\delta W = -\mu_0 \hat{H} d \hat{H}$
  - For type I superconductor:
  application of a large magnetic field leads to a phase transition from superconducting to normal states

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THERMODYNAMICS OF MAGNETIC MATERIALS

➢ Type I superconductor phase transition:

- Similarly with the liquid-gas phase transition, along the phase boundary, equilibrium (constant $\hat{H}$ and T) implies that the total magnetic Gibbs free energy is minimum and thus that $\hat{G} = U - TS - \mu_0 \hat{H} M$ <u>is equal</u> in the two phases:

- As $d\hat{G} = -SdT - \mu_0 M d\hat{H}$, in the Meissner state ($\hat{H} < \hat{H}_c$) we have:

$$\hat{G}_s(H,T) = \hat{G}_s(0,T) - \int_0^{\hat{H}} \mu_0 \hat{M} d\hat{H} = \hat{G}_s(0,T) + \int_0^{\hat{H}} \mu_0 \hat{H} d\hat{H} = \hat{G}_s(0,T) + \frac{1}{2}\mu_0 \hat{H}^2$$

- In normal state, the magnetic Gibbs free energy is practically independent of $\hat{H}$ as the material is penetrated by the field: $\hat{G}_n(H,T) = \hat{G}_n(0,T) = \hat{G}_n(T)$

- Therefore, the critical field $\hat{H}_C$ of the superconductor (phases coexistence) is given by:

$$\hat{G}_n(T) - \hat{G}_s(0,T) = \frac{1}{2}\mu_0 \hat{H}_C^2$$

- Analogy of the Clausius-Clapeyron equation: $\dfrac{d\hat{H}_C}{dT} = \dfrac{L}{T\mu_0 \hat{M}_C} = -\dfrac{L}{T\mu_0 \hat{H}_C}$
  - As $\hat{H}_c \to 0$, $d\hat{H}_c/dT$ tends to a finite value. Thus as $\hat{H}_c \to 0$, $L \to 0$.
  - In zero applied magnetic field, no latent heat is associated with the superconducting to normal transition

THERMODYNAMICS OF MAGNETIC MATERIALS

➢ **First and second-order transitions:**

- **First-order phase transition is characterized by a discontinuity in the first derivatives of the Gibbs free energy** (higher order derivatives discontinuities may occur).

    o Ex. : liquid → gas transition:
    $$\frac{dp}{dT} = \frac{(s_{gas} - s_{liq})}{(v_{gas} - v_{liq})} = \frac{L_{vap}}{T(v_{gas} - v_{liq})}$$

        o discontinuity in $S = -(\partial G/\partial T)_p$. Latent heat is involved in the transition.
        o Discontinuity in $(\partial G/\partial V)_T$

- **Second-order phase transition has no discontinuity in the first derivatives but has in the second derivatives of the Gibbs free energy**

    o Ex. : liquid → gas transition at the critical point:

        o as v_{gas}-v_{liq} → 0 and dp/dT is finite, L_{vap} → 0 ⇒ s_{gas}-s_{liq} → 0 and $S = -(\partial G/\partial T)_p$ is continuous
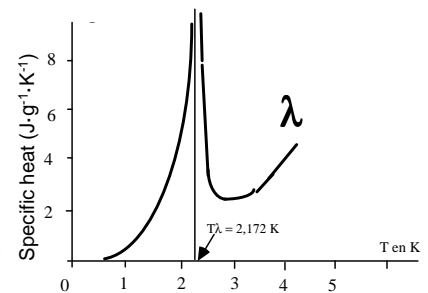
    o Ex.: He I → He II (superfluid) transition:

        o heat capacity: $C_p = T(\partial S/\partial T)_p = -T(\partial^2 G/\partial^2 T)_p$
          (as $dG = -SdT + Vdp$)
          heat capacity is not continuous

    o Type I superconductor → normal transition if
      no magnetic field is applied (⇒ discontinuity in C_p)

- NB: higher order transition exists

The image is a plot of specific heat with a lambda point labeled Tλ = 2,172 K

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- VINEN W. F., *A survey of basic thermodynamics*, CAS, Erice, Italy May (2002).

Thank you for your attention