Cryogenic Fluids

European Advanced Cryogenics School

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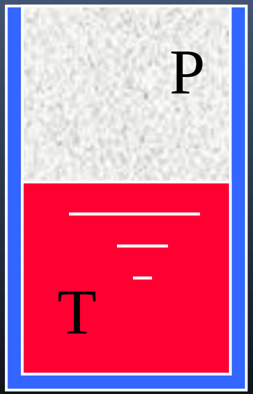
Fluids : basic concepts

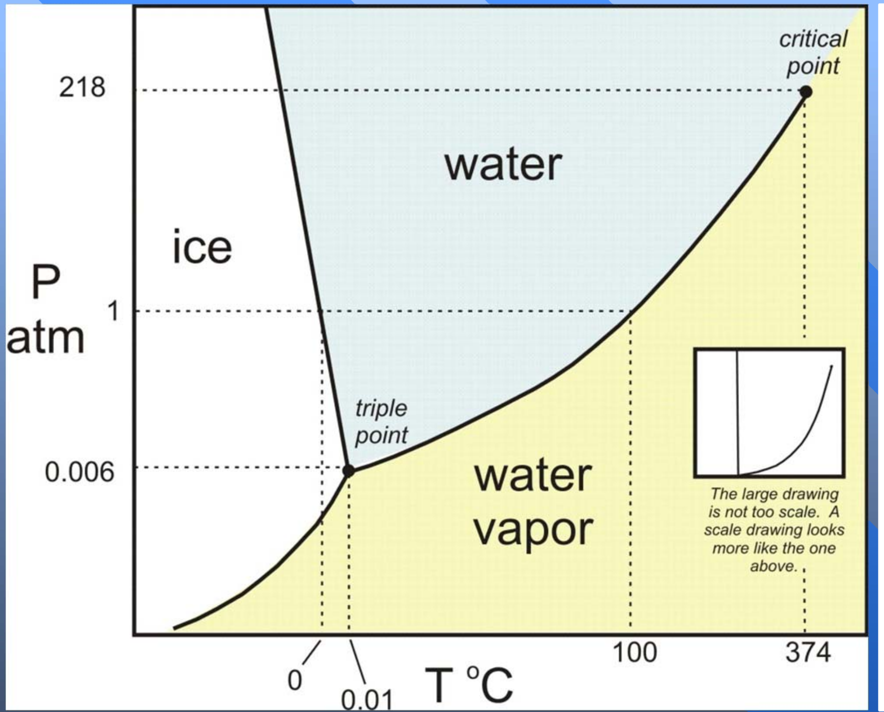
- 3 states of matter: solid / liquid / gas
  - → Influence of temperature and pressure
    - *Example: water*
      - At (constant) atmospheric pressure:
        - if T ↘ : Solidification
        - if T ↗ : Evaporation
      - At constant temperature (20 C) :
        - if P ↘ : Evaporation
        - if P ↗ : Solidification

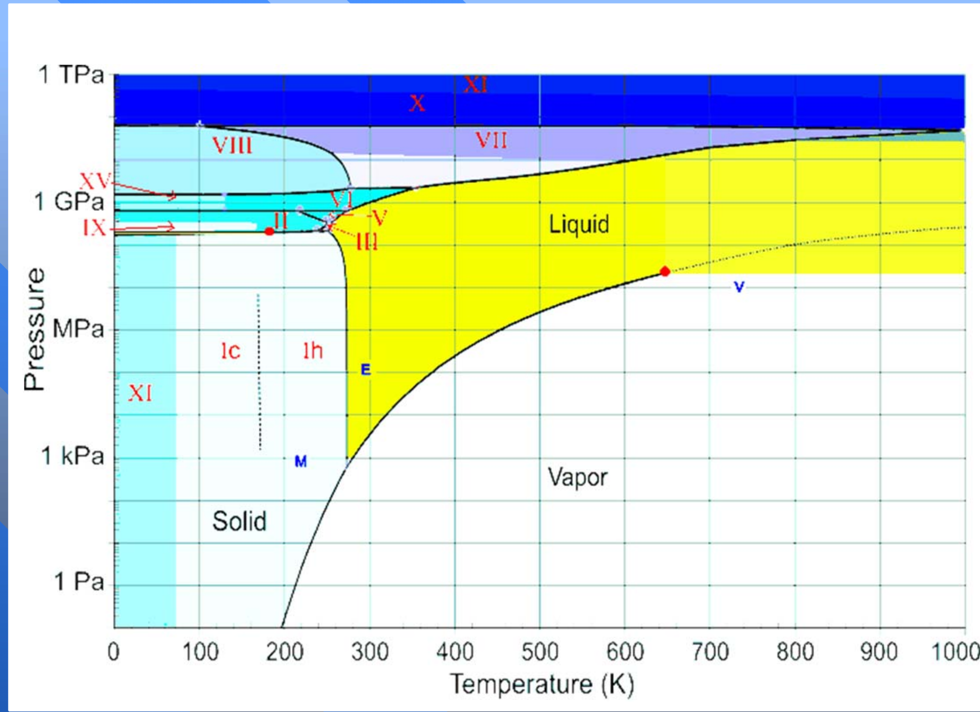
- Liquid state : saturated vapour pressure



- *Liquid boiling at temperature T : in equilibrium with the gas at pressure P. It is a dynamical equilibrium (exchange of atoms)*
- *A well defined pressure corresponds to each temperature :*
  ➔ *saturated vapour pressure*

Phase diagram of Water

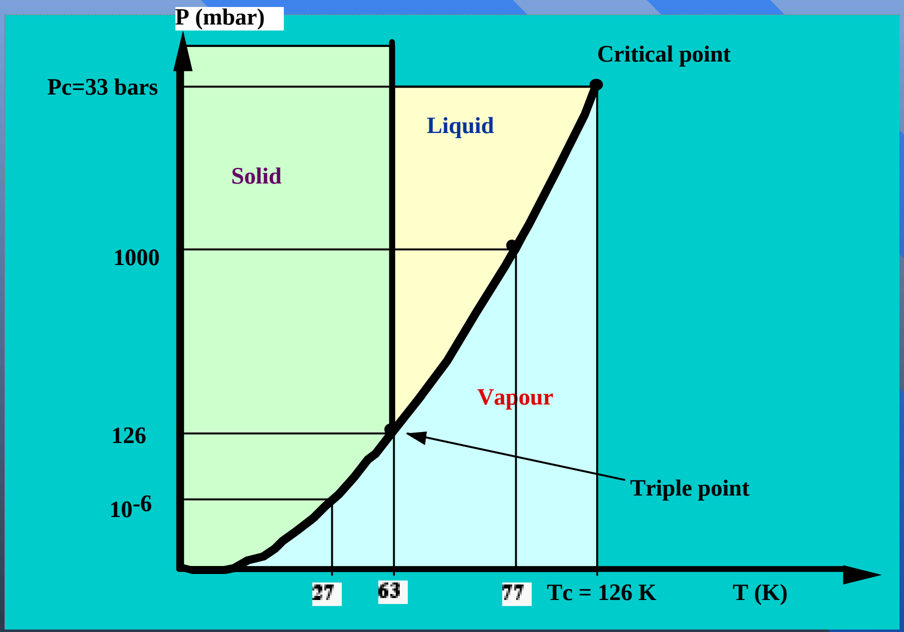


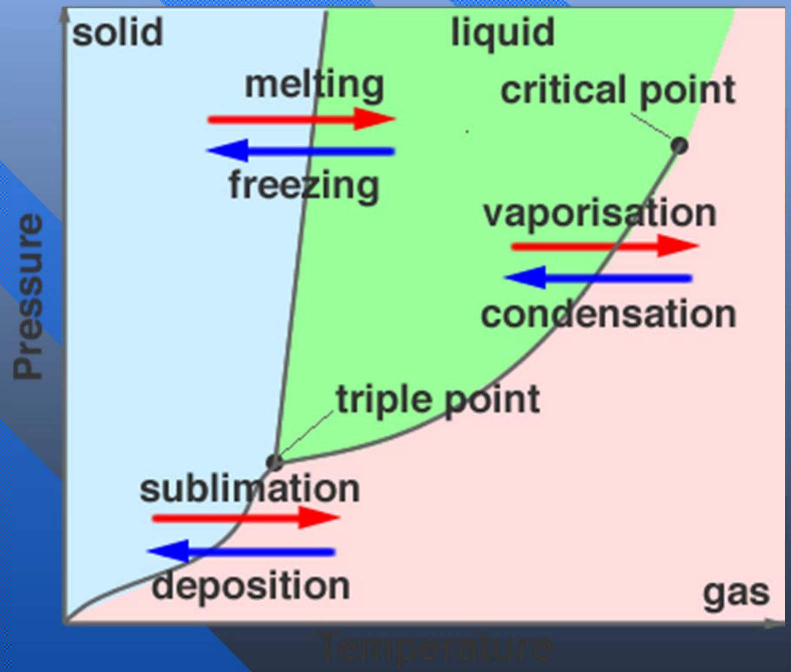


- Triple point: solid-liquid-gas coexistence (thermometry!)
- Solids have a saturated vapour pressure too!
- Critical point ➔ vapour and fluid phases are indistinguishable

Cryogenic fluids (nitrogen, hydrogen, helium, etc…)

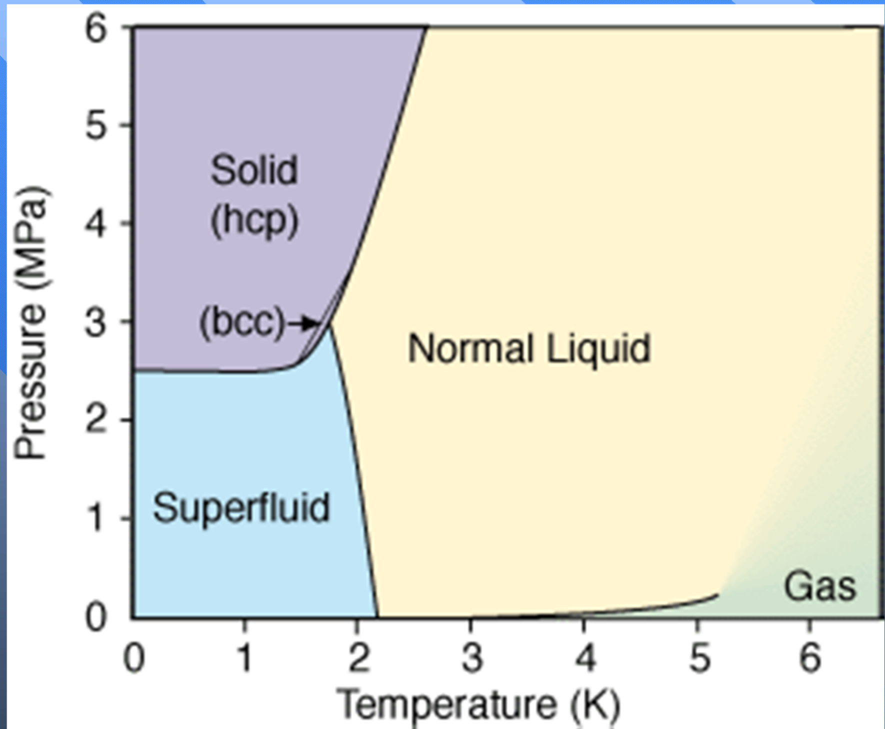
- Nitrogen





- The dependence P = f (T) is a characteristic of the fluid.
- It is tabulated and can be used for thermometer calibration.

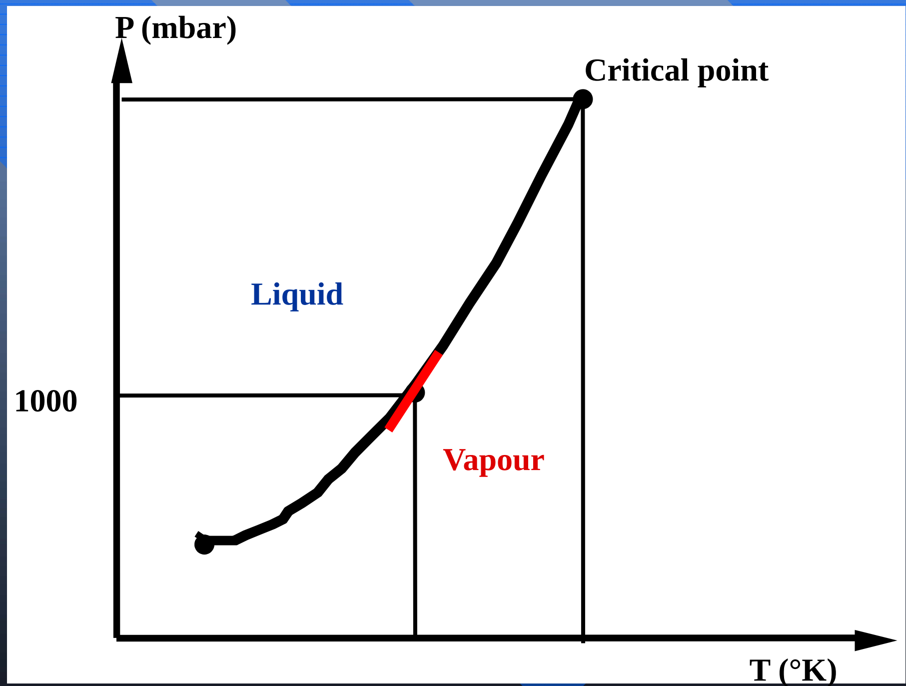
One exception : helium



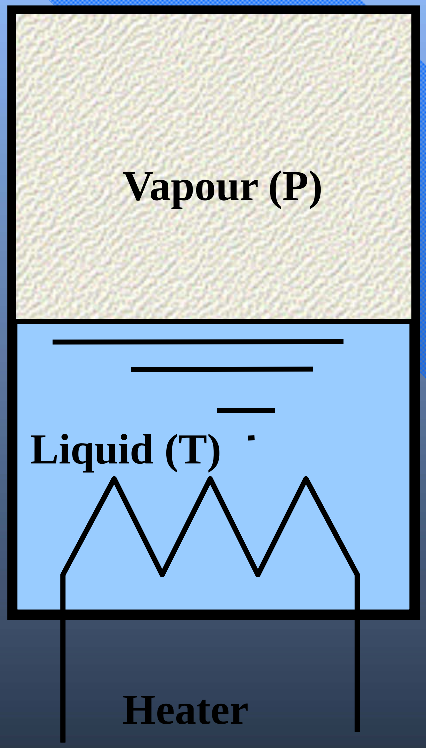
- No solidification at low Pressure !
- solid ➔increase P at low temperatures (T<1K; P>25bar)

Boiling cryogenic fluids

- A cryogenic fluid at atmospheric pressure is always boiling
- And therefore, on the P(T) curve

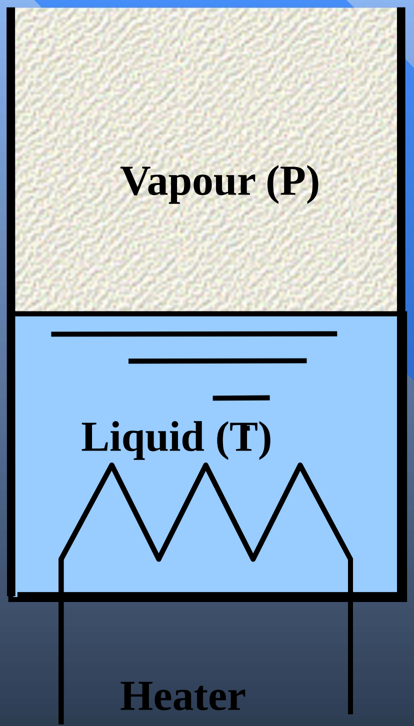


1st transformation



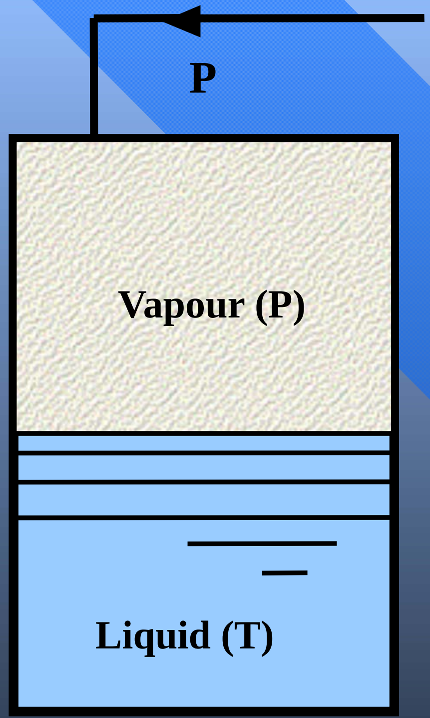
- Heating in a closed vessel
  - P et T will increase following the curve till the critical point.
  - For each value of P , one value of T
- Not recommended!
  - Except in special cases, one never closes the output of a cryogenic reservoir (vent)

2^d transformation



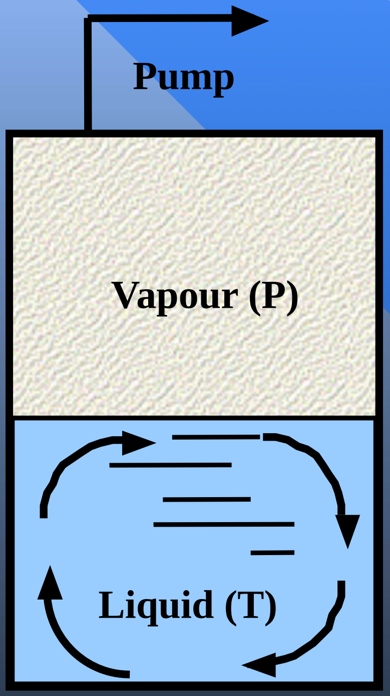
- Heating an open vessel
  - At atmospheric pressure, for instance
- T = Constant (77K for Nitrogen)
- The helium level drops, with production of vapour.

3^d transformation



- Closed vessel, with external supply of gas under pressure
  - (bottle or compressor)
- T increases in principle following the P(T) curve
- In practice, the equilibrium P(T) is not reached instantaneously = stratification within the liquid.
  - Poor thermal conduction
  - Hotter in the upper part

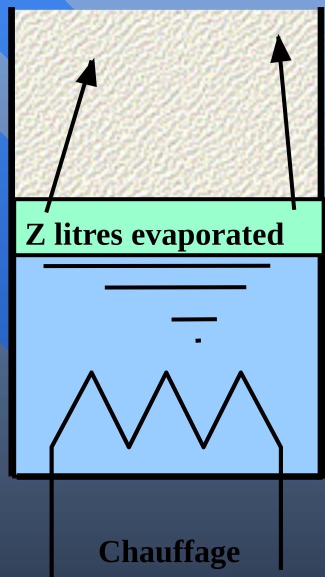
4^{th} transformation



- Closed vessel under depression (vacuum pump)
- T diminishes following P(T)
- At each value of P corresponds a value of T till the triple point.
- In this case : better equilibrium
  - Cold on the top : convection flow

Latent heat of vaporisation

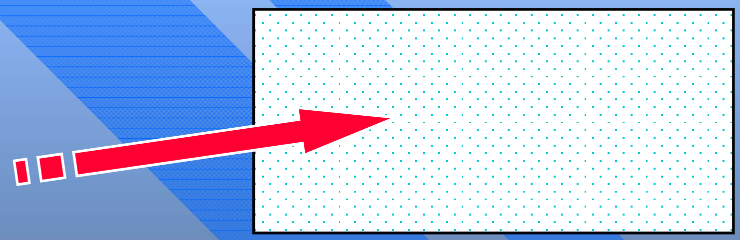
- ➔An important property related to vaporisation
- L_{vap} : Amount of heat needed in order to evaporate a given amount of liquid
    - *Heating : expressed in watts*
    - *Energy supplied = Watts x sec. = Joules*
- L_{vap} characterises the volatility
    - Expressed in : joules / gram
      or joules / litre
    - *More practically : in litres of liquid evaporated per hour for 1 Watt.*
- ➔ Liquid Nitrogen
    - *1 watt evaporates* ***0,022 litre / hour***
- ➔ Liquid Helium : more « volatile »
    - *1 watt evaporates* ***1,4 litre / hour***
- For the same applied power, helium evaporates at a rate 1400/22 = 70 times faster than Nitrogen.



$$Z = \frac{time \times power}{L_{vap}}$$

Ideal Gases

- T >> Liquefaction temperature
  - Standard Volume = 1 Mole
    - *V = 22,4 litres (22400 cm^3)*
    - *T = 0°C (273,15 K)*
    - *P = 1 Bar (10^5 Pa)*



  - For all gases ➔ same number of molecules
    - Na = 6,02 . 10^{23} (Avogadro's number)
  - The masses depend on the gas considered
    - M = molar masse (in grams)
      - *He :* *1 atom / molecule* *M = 4 g*
      - *H_2 :* *2 atoms / molecule* *M = 2 g*
      - *N_2 :* *2 atoms / molecule* *M = 28 g*
  - The density at a given T and P is given by

$$\rho = \frac{M_{(grams)}}{22400} \times \frac{P_{(Pascal)}}{10^5} \times \frac{273{,}15}{T_{(Kelvin)}} \quad (in \;\; g/cm^3)$$

Properties of Cryogenic Fluids

- Boiling temperatures at atmospheric pressure

– Butane :	263 K
– Propane :	230 K
– Freon :	de 140 à 240 K
– CO_2 :	195 K
– Xenon :	165 K
– Krypton :	121 K
– Methane :	111 K
– Argon :	87 K
– Oxygen :	90 K
– CO :	82 K
– Fluor :	85 K
– Nitrogen :	77,3 K
– Neon :	27,2 K
– Deuterium :	23,6 K
– Hydrogen :	20,3 K
– Helium 4 :	4,21 K
– Helium 3 :	3,2 K

« permanent gases » → (Argon through Helium 4)

Interest of liquefying gases :
storage and transportation
(O_2, N_2, He, H_2, Ar, CH_4, …).

Properties of Cryogenic Fluids

- 1 litre of evaporated liquid gives ca. 1000 litres of gas at room temperature and atmospheric pressure, i.e. 1 m^3 (more precisely; from 700 to 800 litres).

- Example : the gas contained in a bottle (O_2, N_2, He)
  (50 litres at 150 bars) ➔ 7,5 m^3 NPT
  - This corresponds to about 10 litres of liquid

10 litres of liquid	Bottle 50 L
~ Ø30 cm / h = 40 cm	Ø 25 cm / h = 1,50 m
weight : a few kg	weight : ~ 60 kg

Liquid Nitrogen

- Nitrogen in air : 80 %
- 1st liquefaction in 1877 (Cailletet)
- Boiling T at atmospheric pressure : *77,4 K*
- Range of temperatures accessible by varying the pressure :
  - from 62 K / 128 mbar to 126 K / 33 bars
- Density : slightly less than water :
  - 800 g/litre at 77 K
- Heat of evaporation :
  - 1 watt evaporates 22,6 cm^3/hour liquid (L_{vap} = 199 j/g)

Liquid Nitrogen

- Thermal conductivity : similar to that of an insulator
  - Comparable to Teflon at 300 K , 1000 times less than Copper
  - k = 1,38 mW/cm.K
- Viscosity : small
  - η = 1500 micropoises
  - 7 times less than water
- Correspondence liquid / gas :
  - 1 L liquid → 700 L gas NTP
- Other applications :
  - Food cooling and conservation
  - Inert : microelectronics, metallurgy, cleaning, …
  - Car industry

Liquid Oxygen

- Oxygen in air : 20 %
- Boiling T at atmospheric pressure : 90,2 K
- Range of temperatures accessible by varying the pressure :
  - From 54,4 K / 1,2 mbar to 154 K / 50 bars
- Density : somewhat larger than water :
  - 1140 g/litre at 90 K
- Heat of evaporation :
  - 1 watt evaporates 15 cm^3/hour liquid

Liquid Oxygen

- Seldom used in Cryogenics (only calibrations)
- Danger : avoid contact with oil, grease
- Correspondence liquid / gas :
  - 1 L liquid ➔ 800 L gas NPT
- Other applications :
  - Steel, cutting, combustion (furnaces)
  - Medical, space, …

Liquid Hydrogen

- The lightest gas (balloons)
- Danger = flammable
- Boiling T at atmospheric pressure : *20,2 K* *(Dewar 1898)*
- Range of temperatures accessible by varying the pressure :
  - from 13,8 K / 70 mbar to 33 K / 12,7 bars
- Density : the lightest liquid : (rockets)
  - 70 g/litre at 20 K
- Heat of evaporation : L_{vap} = 445 J/g
  - 1 watt evaporates 115 cm^3/hour liquid (5 times more than nitrogen)

Liquid Hydrogen

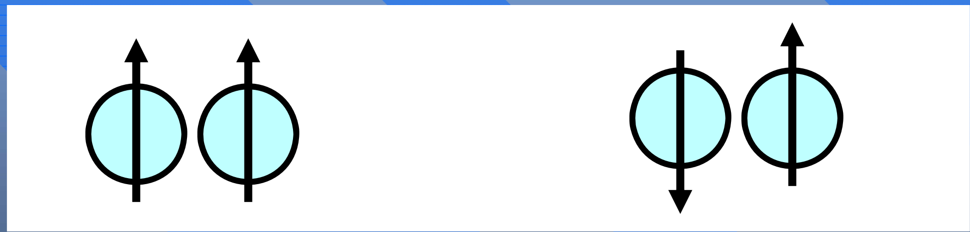
- Thermal conductivity : similar to that of an insulator
  - like LN2 ➔ k = 1,18 mW/cm/K
- Viscosity : 70 times smaller than water

  ➔ η = 140 micropoises
- Correspondence liquid / gas :
  - 1 L liquid ➔ 780 L gas NPT
- Other applications :
  - Rocket fuel (Ariane 4 and 5)
  - Industry of micro components (inert atmosphere), chemistry, …

Liquid Hydrogen

- 2 isotopes : Deuterium and Tritium
- In H_2 : 2 spin orientations are possible

Ortho Para



- In equilibrium :
  - 300 K → 75% of ortho and 25% of para
  - 20 K → 0,2% of ortho and 99,8% of para
- Transformation ortho → para exothermal and slow
  - Catalyser to accelerate the transformation
  - Releases 450 J/g
  - Liquefaction without catalyser = large % of ortho → large evaporation in the storage dewar.

Liquid Neon

- Noble gas: 10 times more expensive than Helium
- Boiling T at atmospheric pressure : *27 K*
- Range of temperatures accessible by varying the pressure :
  - from 24,5 K / 425 mbar to 44,5 K / 27,8 bars
- Density :
  - 1210 g/litre at 27 K
- Heat of evaporation :
  - 1 watt evaporates 35 cm^3/hour liquid

Liquid Neon

- Thermal conductivity : similar to that of an insulator
- Viscosity : small, 8 times less than water
- Correspondence liquid / gas :
  - 1 L liquid ➔ 1350 L gas NTP
- Other applications :
  - Light tubes

Liquid Argon

- Boiling T at atmospheric pressure : *87,3 K*
- Range of temperatures accessible by varying the pressure :
  - from 83,8 K / 690 mbar to 150,9 K / 50 bars
- Density :
  - 1400 g/litre at 87 K
  - Gas NPT = 1,78 g/litre → **heavier than air !**
- Heat of evaporation :
  - 1 watt evaporates 16 cm^3/hour liquid

Liquid Argon

- Thermal conductivity : similar to that of an insulator
  - Like nitrogen
- Viscosity : rather low, 4 times less than water
- Correspondence liquid / gas :
  - 1 L liquid ➔ 784 L gas NTP
- Other applications :
  - Inert atmosphere, welding
  - Industry of micro components (inert atmosphere)

Physical constants for the GAS state

	Molar Mass **M** (grams)	Densiy NTP **ρ** (g/cm^3)	Viscosity **η** (micropoises)	Thermal Conductivity **k** (mW/cm.K)	Heat capacity of gaz **Cp** (j/g.K)
Nitrogen (N_2)	28	1,25 . 10^{-3}	69 to 100 K 180 to 300 K	0,09 to 100 K 0,26 to 300 K	1,04 from 100 K to 300 K
Oxygen (O_2)	32	1,43 . 10^{-3}			
Hydrogen (H_2)	2	9,0 . 10^{-5}	10 to 20 K 90 to 300 K	0,15 to 20 K 1,8 to 300 K	10,4 to 20 K 10,8 to 80 K 14,5 to 300 K
Helium 4 (^{4}He)	4	1,78 . 10^{-4}	14 to 5 K 85 to 80 K 200 to 300 K	0,1 to 4,2 K 1,5 to 300 K	5,2

Helium

- 2 stable isotopes : ^{4}He = abundant
  ^{3}He = rare and expensive
- Helium 4 (^{4}He):
- Discovered in :
  - 1868 = astronomical observation (chromosphere)
  - 1895 = on earth (in air: 1/250 000) (Ramsay)
  - 1905 = in natural gas, in the USA
- The hardest gas to liquefy!
  (1908 in Leyden, Kamerlingh Onnes)

Helium 4 gas

- World consumption = 35 millions of m^3 / year
- Rare gas - Price ~ 8 Euros /m^3 NTP
- In natural gas wells : 0,1 à 0,5 %
- USA, Poland, Russia, Algeria
- Other applications :
  - Balloons, diving
  - Inert atmosphere, welding
  - Pressurisation (rockets), spatial and nuclear engineering
  - Leak detection

Liquid ^{4}He

- Boiling T at atmospheric pressure : *4,2 K*
- Range of temperatures accessible by varying the pressure :
  - from 1 K / 0,1 mbar to 5,2 K / 2,26 bars
- Density :
  - 125 g/litre at 4,2 K
- Heat of evaporation :
  - L_{vap} = 20,9 J/g ➔ very low
  - 1 watt evaporates 1400 cm^3/hour liquid (65 times more than nitrogen)
- Correspondence liquid / gas :
  - 1 L liquid ➔ 750 L gas NTPtriple)

Helium 3

- Available since the 60's : produced by nuclear reaction
  - $^{6}Li + n \rightarrow {}^{4}He +$ Tritium
  - Tritium $\rightarrow {}^{3}He + \beta$
  - Half-life of Tritium = 12 years
  - Strategic (military industries)
  - Very expensive : Price ~ 3000 Euros (2011) /litre of gas NTP !
- Applications :
  - Low temperatures < 1 K
    - ^{3}He liquid at 10^{-3} mbar $\rightarrow$ T = 0,3 K
    - Mixtures $^{3}He/^{4}He$: a few mK
  - Medical imaging (polarised gas)
  - Neutron detectors

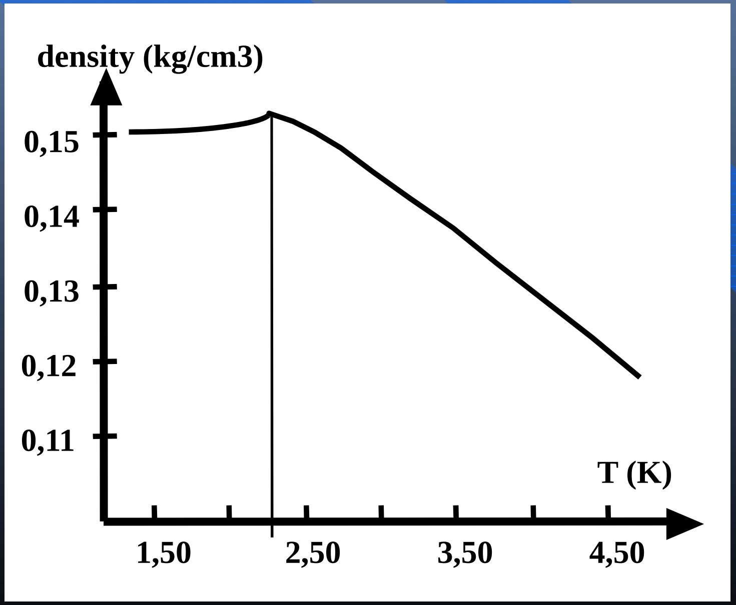
Helium 3

- Boiling T at atmospheric pressure : *3,2 K*
- Range of temperatures accessible by varying the pressure :
  - from 0,3 K / 10^{-3} mbar to 3,33 K / 1,16 bars
- Density : 59 g/litre at 300 K
- Heat of evaporation :
  - 1 watt evaporates ~ 3 litres/hour liquid (2 times more than ^{4}He)
- Correspondence liquid / gas :
  - 1 L liquid ➔ 460 L gas NTP

^{4}He = a special liquid

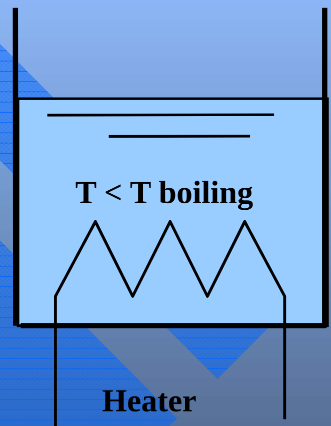
- Properties are not "classical"
- Quantum mechanics
- Seen already in early studies :

➔ Discontinuity of physical constants at T = 2,17 K

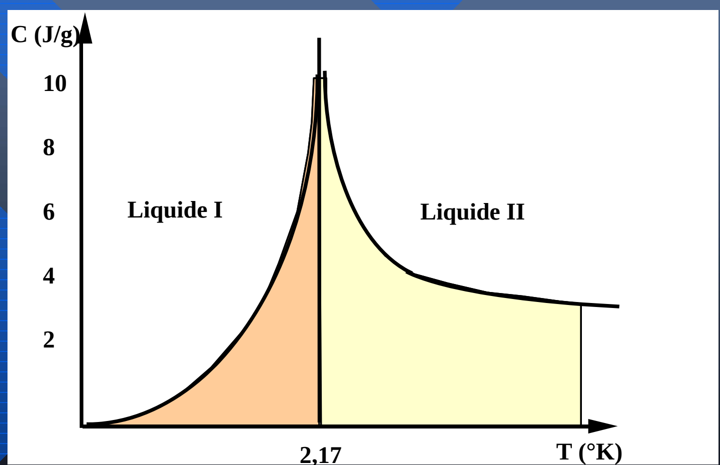


^{4}He : Heat capacity (C)

- C is the amount of heat needed to increase the temperature by 1 °K for a given amount of matter.
  - *≠ heat of evaporation*
  - *Units :   J / g .K   or cal / g .K*



- For helium :
  - At 4,2 K : like water
    - C = 4,18 J / g / °K
  - Cooling : discontinuity at 2,17 K
    - C : ↗ and then ↘
  - Lambda Point
    - 2,17 K
    - Pressure : 50 mbar
    - 2 phases (helium I and II)

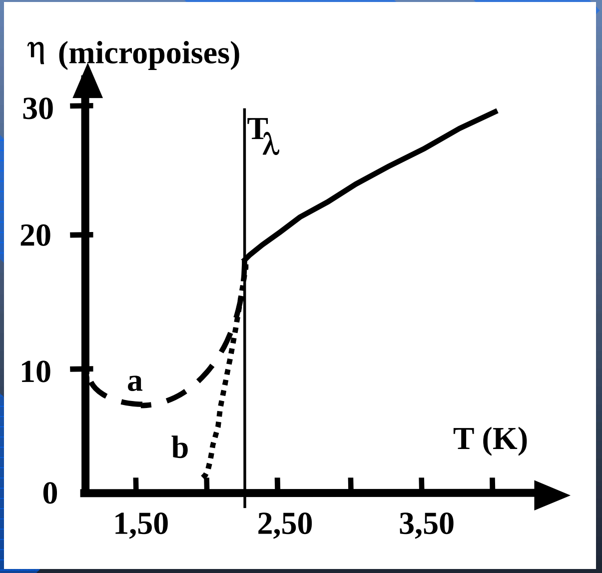


Liquid ^{4}He : Heat capacity (C)

- $C_{hélium.}$ is very large
  - ➔ from 4 to 8 J/g.K
- As a comparison :
  - Copper at 4,2 K : C_{copper} = 10^{-4} J/g.K
    - *$C_{helium.}$ / C_{copper} = 40 000 !*
  - Copper at 300 K : C_{copper} = 0,4 J/g.K
    - *$C_{hélium}$ / C_{copper} = 10 !*
- Large thermal inertia of helium with respect to metals
  - Also true for other cryogenic fluids

^{4}He : Viscosity (η)

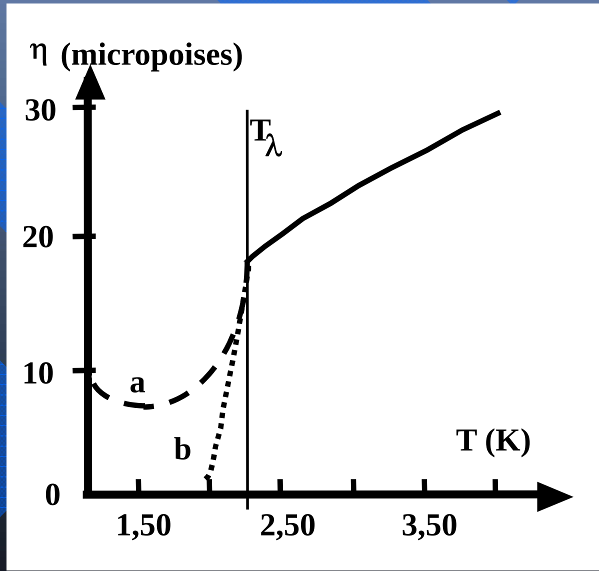
- Viscosity (η)
  - Above de T_λ : liquid I
    - *Small viscosity*
      - 60 times less than N_2 et 400 times less than H_2O
      - About 30 micropoises
  - Below T_λ : liquid II (T < 2,17 K)
    - *Superfluid Helium : superflow*
    - *Unusual properties*



^{4}He : Viscosity (η)

- Below T_λ, η depends on the kind of measurement
  - a) damping of disk oscillations in the liquid
    - *Viscosity remains above 5 micropoises*
  - b) Flow in narrow slits (10^{-3} à 10^{-4} mm) (Kapitza)
    - *Large flow even with small ΔP*
    - *Difficult to measure*
    - *Flow independent on P*
    - *η lower than 10^{-3} micropoises*

➔ SUPERFLUID Liquid



^{4}He : Viscosity (η)

- Explanation = 2 fluids (TISZA)
  - Helium II ➔ mixture of normal ρ_n and superfluid ρ_s component .
  - Superfluid:
    - *Entropy = 0*
    - *Viscosity = 0*
  - Only the normal component carries entropy.
- Oscillating Disc
  - Measures viscosity of normal fluid
- Slits
  - Measures η of superfluid component

$$\rho = \rho_n + \rho_s$$

$$\frac{\rho_n}{\rho} = 1 \quad at \quad T_\lambda$$

$$\frac{\rho_s}{\rho} = 1 \quad at \quad 0 \ K$$

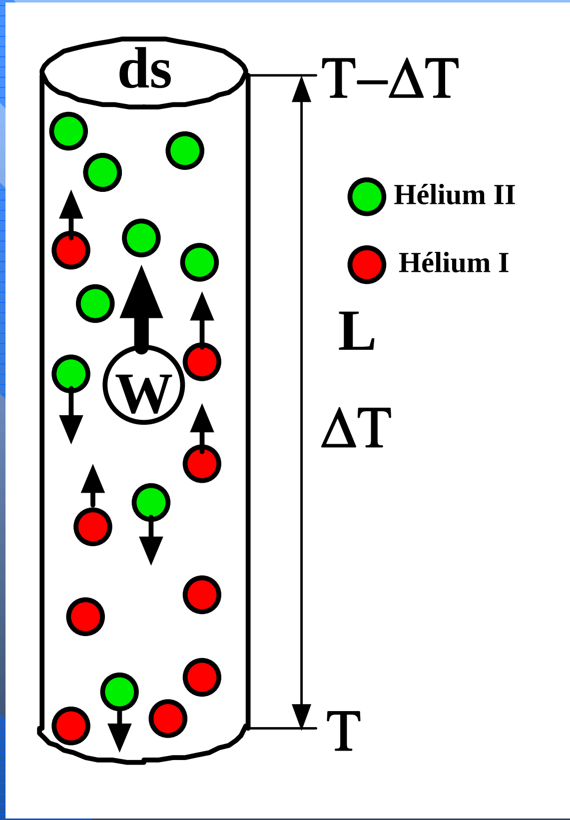
^{4}He : Thermal conductivity (k)

- Liquid helium I
  - *Liquid ^{4}He - I is an insulator (better than Teflon)*
  - *k = 4 times smaller than LN2*
  - *k = 0,27 mW/cm.K*

- Liquid helium II (superfluid)
  - *k becomes very large (8000 W/cm.K at 1,9K !!)*
  - *About 1000 times better than copper*
  - *By far the best thermal conductor near T_λ*
- Consequence : in a superfluid helium bath
  - *No gradient between top and bottom of Dewar (no stratification).*
  - *No bubbles (associated to ΔT)*
- Large conductivity and heat capacity : application for magnets.

^{4}He : Thermal conductivity (k)

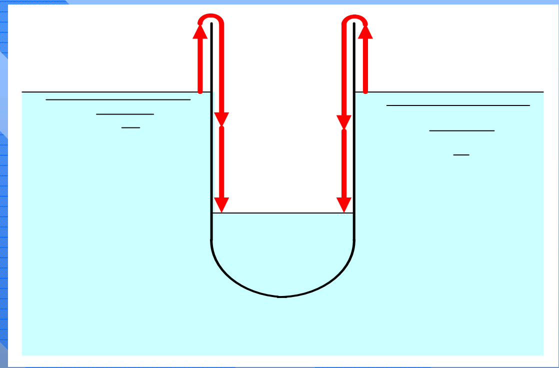
- 2-fluids model
  - Gradient of temperature ?
  - Displacement of x superfluid atoms
    - *From cold to hot parts*
    - *Larger concentration in cold places*
  - No accumulation
    - ➔ *displacement in opposite direction of the normal atoms*
    - *Entropy transport*
  - Heat is transported by dynamical flow
    - *≠ transfer of energy*
    - *Large apparent conductivity*
  - Limits :
    - *If heat flux is large*
    - *Interactions in the normal fluid*
    - *Flux max. ~ W/cm² for ΔT ~ a few 0,1 K*

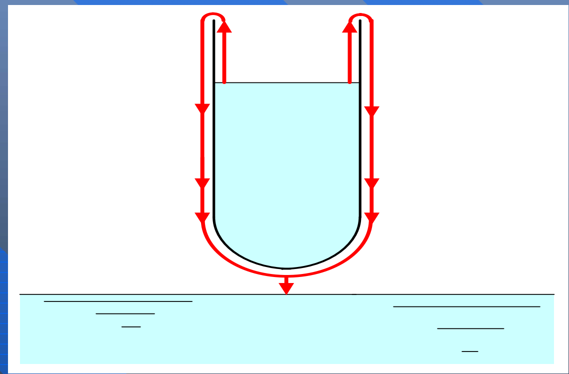


$$W = k\frac{ds}{L}\Delta T$$

^{4}He : superfluid film

- 2 experiments
  - Figure 1 : reservoir fills
  - Figure 2 : reservoir empties
  - ➔ In both cases a film has formed giving rise to a flow of liquid
    - ➔ ROLLIN FILM
- Properties of the film
  - Flows from cold to hot places
  - Evaporates at the hot point (T_λ)
    - *Consequences :*
      - Climbs along the cryostat's neck
      - Climbs along pumping lines
      - Heat leaks and reduced performance of refrigerators
    - *Need of film-burners or diaphragms at T ~ 1 K*





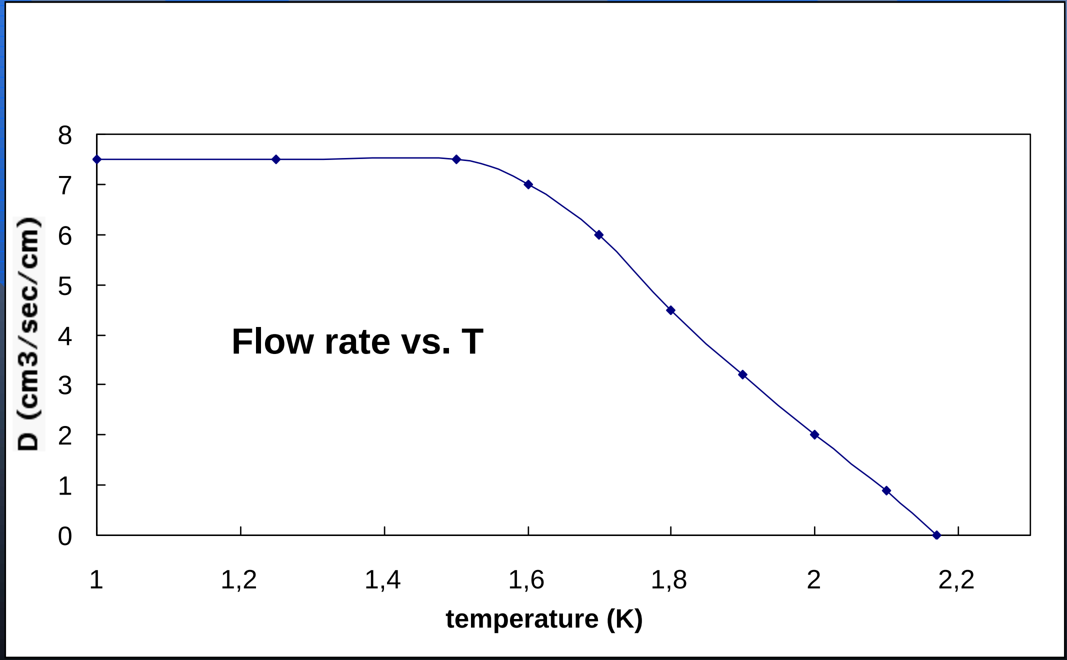
^{4}He : superfluid film

- Flow rate
  - Proportionnal to the smallest perimeter seen
  - Thin film = 30 nm
  - Displacement velocity
    - *25 cm/sec (~ 1 km/h)*

$$\frac{Flow\ \ rate}{Perimeter} = 25 \times 30.10^{-9} = 7{,}5.10^{-5} \quad cm^3/\sec.cm$$

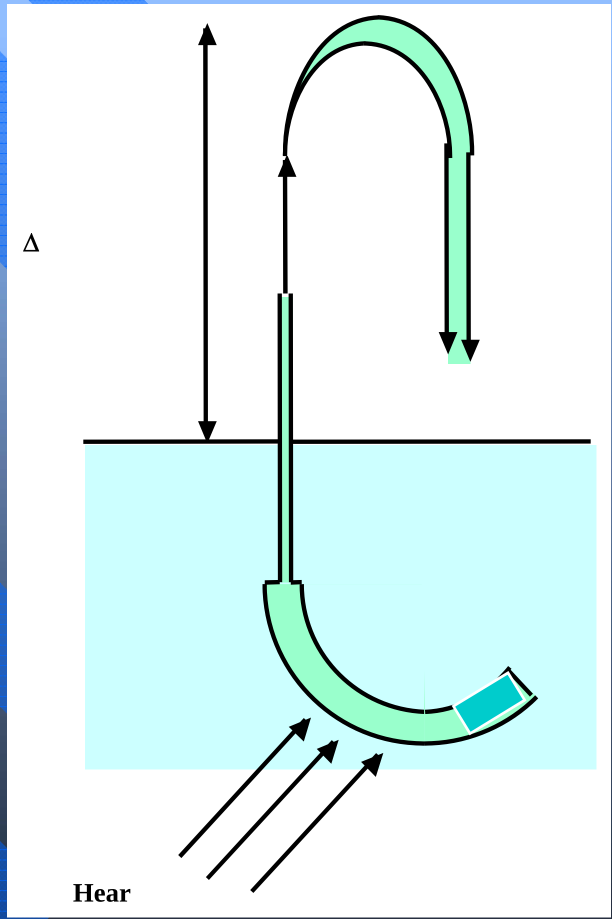
$$i.e.\quad \frac{Flow\ \ rate}{Périmètre} = 0{,}27 \quad cm^3/hour\ \ !!$$

  - For bad surfaces (metals) ➔ *10 times !
  - Independent on the level difference



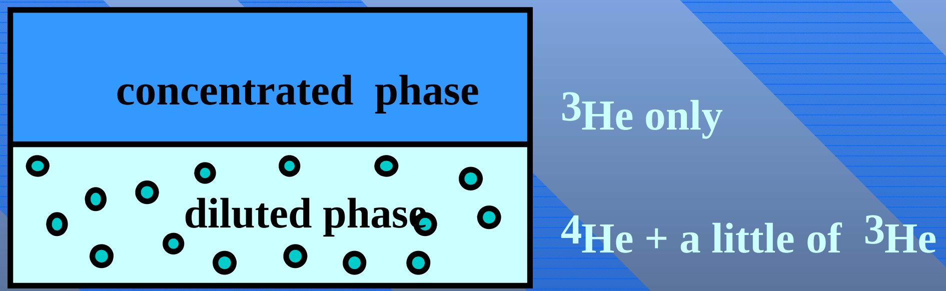
^{4}He : fountain effect

- Fine powder = superleak (alumina)
- Only superfluid component flows
- Liquid helium fountain can reach one meter!
- Explanation :
  - *Heat input*
    - Superfluid ➔ normal conversion
  - *Flow of superfluid towards the hot point (osmotic pressure)*
  - *Normal Fluid « pushed » towards the top of the capillary ➔ fountain effect*
- Direct conversion of thermal energy in kinetic energy



Mixtures $^3He/^4He$

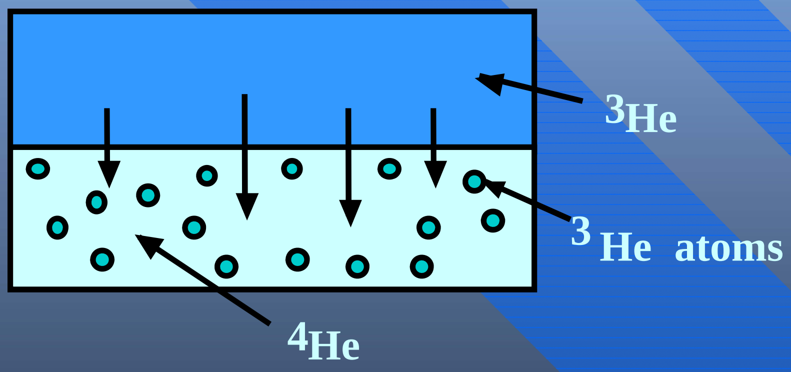
- At T > 0,8 K : the liquids are miscible (like water and alcohol)
- At T < 0,8 K : separation in 2 phases (like water and oil)

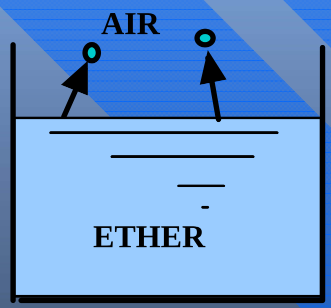


- In the lower phase : ^3He diluted in ^4He = diluted phase
  - *The concentration of ^3He depends on temperature*
    - 0,5 K → ~ 20 % ^3He
    - T ~ 0 K → ~ 6,4 % ^3He
    - Even at low temperatures, there is a finite solubility of ^3He in ^4He
- In the upper phase : concentrated ^3He (no ^4He)
- ^4He is superfluid in the diluted phase

Mixtures $^4He/^3He$: dilution

- Equivalent to the evaporation of a liquid in the presence of another gas : ether in air ➔ cooling
- But upside-down!



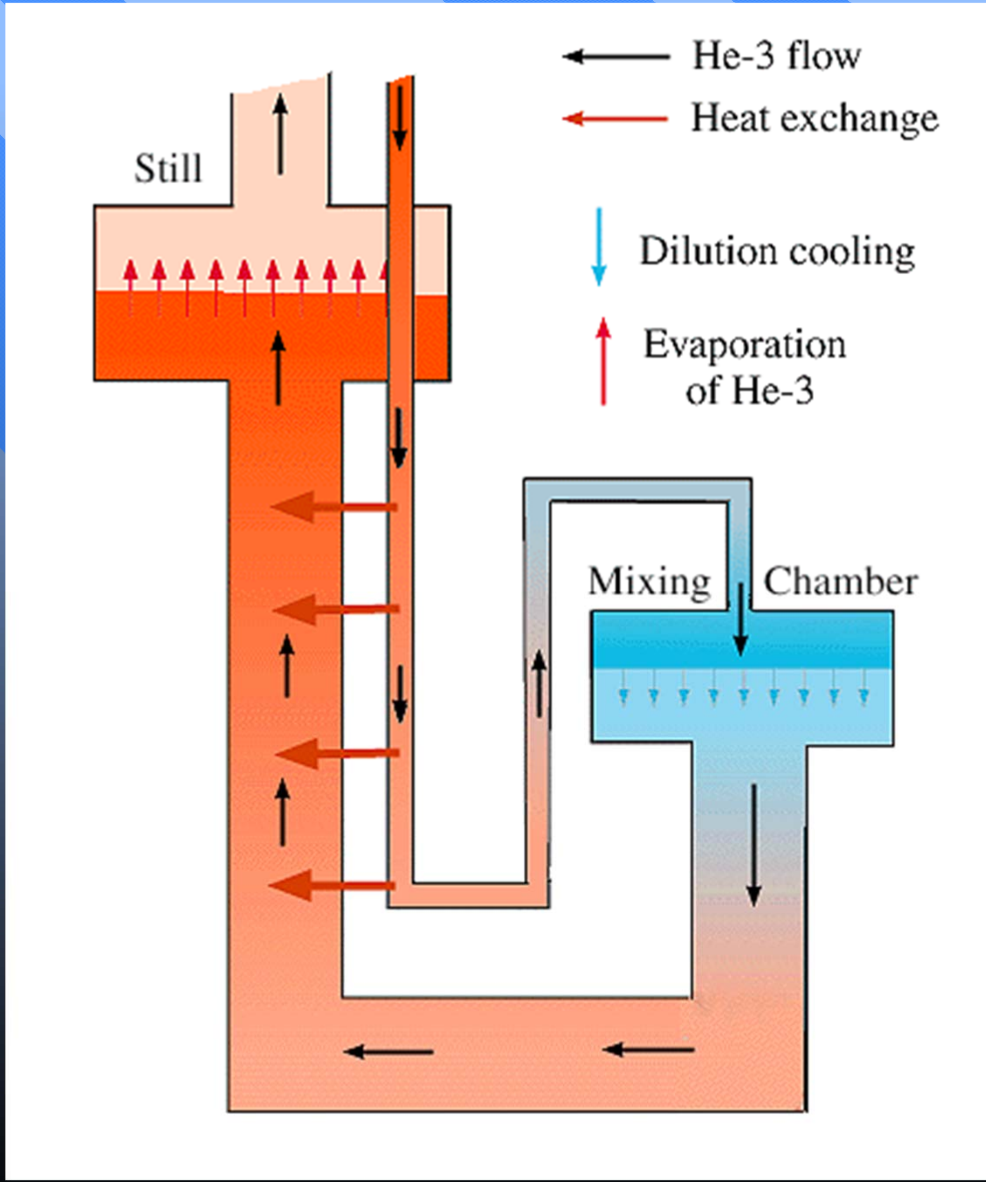


- Continuous refrigeration

  ➔ circulation of ^3He from concentrated to diluted phases
- With a careful design, refrigeration down to mK temperatures

  (2 to 4 mK in the best dilution refrigerators)

Schematic view of a dilution refrigerator



^{4}He = a special liquid

- Very dense vapour
    - *Liquid at 4,2 K ➔ 125 g/litre*
    - *Vapour at 4,2K ➔ 17 g/litre ➔ factor 7,5 (180 for Nitrogen)*
- Consequence on the amount of matter in an empty devwar at 4,2 K :
  100 litres of vapour at 4,2 K = 10 m^3 of gas NTP
- Large enthalpy of the vapour
    - *Heating vapour from 4 K to 300 K*

      ➔ recovering frigories!.

      – Example : 1 kg of copper from 300 to 4,2 K

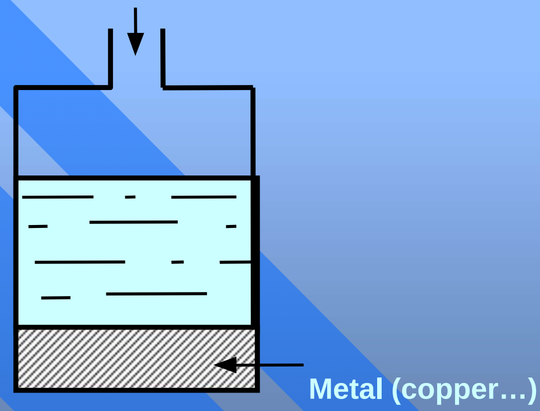
      – Without recovering the gas enthalpy : 30 litres of helium

      – recovering the gas enthalpy : only 0,4 litres needed

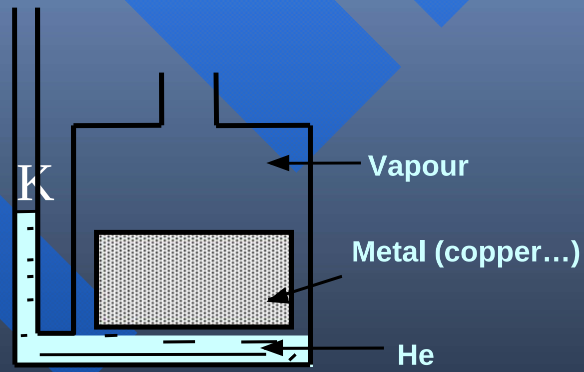
      – Precooling with Liquid Nitrogen, this is not so critical :
      0,5 litres without / 0,2 litres with gas enthalpy recovery.

Amount evaporated for cooling:

- Without using the gas enthalpy
  - To cool down 1 kg of copper starting at 300 K
    ➔ 30 litres of liquid helium
  - Pre-cooling with liquid Nitrogen
    From 77 to 4,2 K ➔ 2,5 litres of liquid He



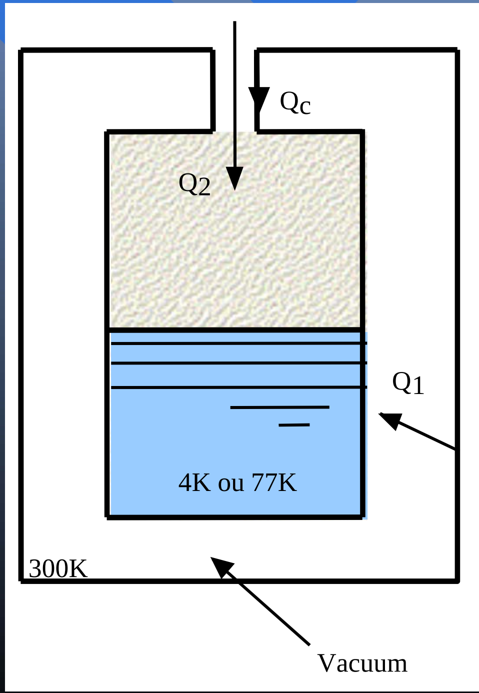
- Using the gas enthalpy
  - Ex : transferring from below
  - To cool down 1 kg of copper from 300 to 4,2 K
    ➔ 0,5 litres of liquid He
    maximum use of gas enthalpy!



- Between these two approaches = litres / kg
  - Important that transfer is slow and from below
  - LN2 pre-cooling is important

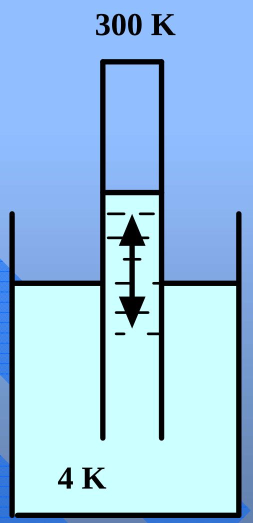
Storage of cryogenic fluids

- Usually called "cryostats" or « Dewar »
  - Heat reaches the fluid by different ways: :
    - conduction by the neck   Qc
    - radiation   Q1 + Q2
  - These sources of heating can be calculated, expressed in watts, and thus the evaporated amount (losses) :
    - Losses in litres / hour   = N_{watt} x 1,4 for helium
      = N_{watt} x 0,022 for Nitrogen

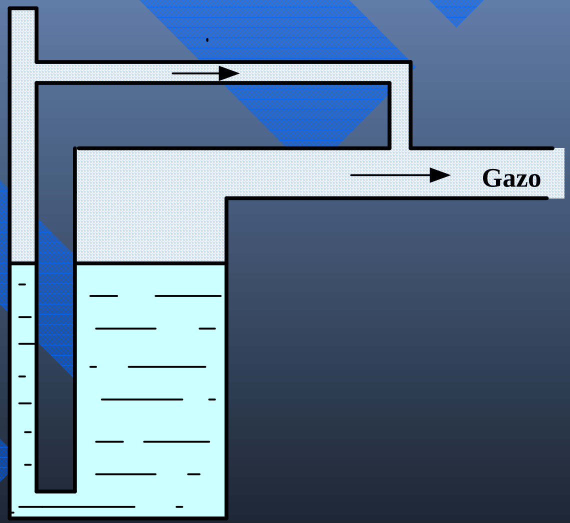


- Typical losses :
  - 1 storage 100 litres helium :   0,030 watt
    ➔ i.e. 1 litre / day
  - 1 helium laboratory cryostat :   0,1 to 1 watt
    ➔ i.e. ~ 10 litres / day
  - 1 LN2 cryostat :   ~ a few 10 watt
    ➔ i.e. 5 litres / day

TACONIS EFFECT



- Thermo-acoustic oscillations.
- tube closed at the top immersed in liquid helium.
- Self-maintained phenomenon
- Evaporation ~ 0,1 l/h to more than 10 l/h !!



- Solution :
  - *Avoid this geometry*
  - *Or, if unavoidable :*
    - Foresee a connection to recovery
    - Anti-oscillantion damp volume (100 litres)
    - Diaphragms

Thanks!