Introduction à la CRYOGENIE

Ecole DRTBT
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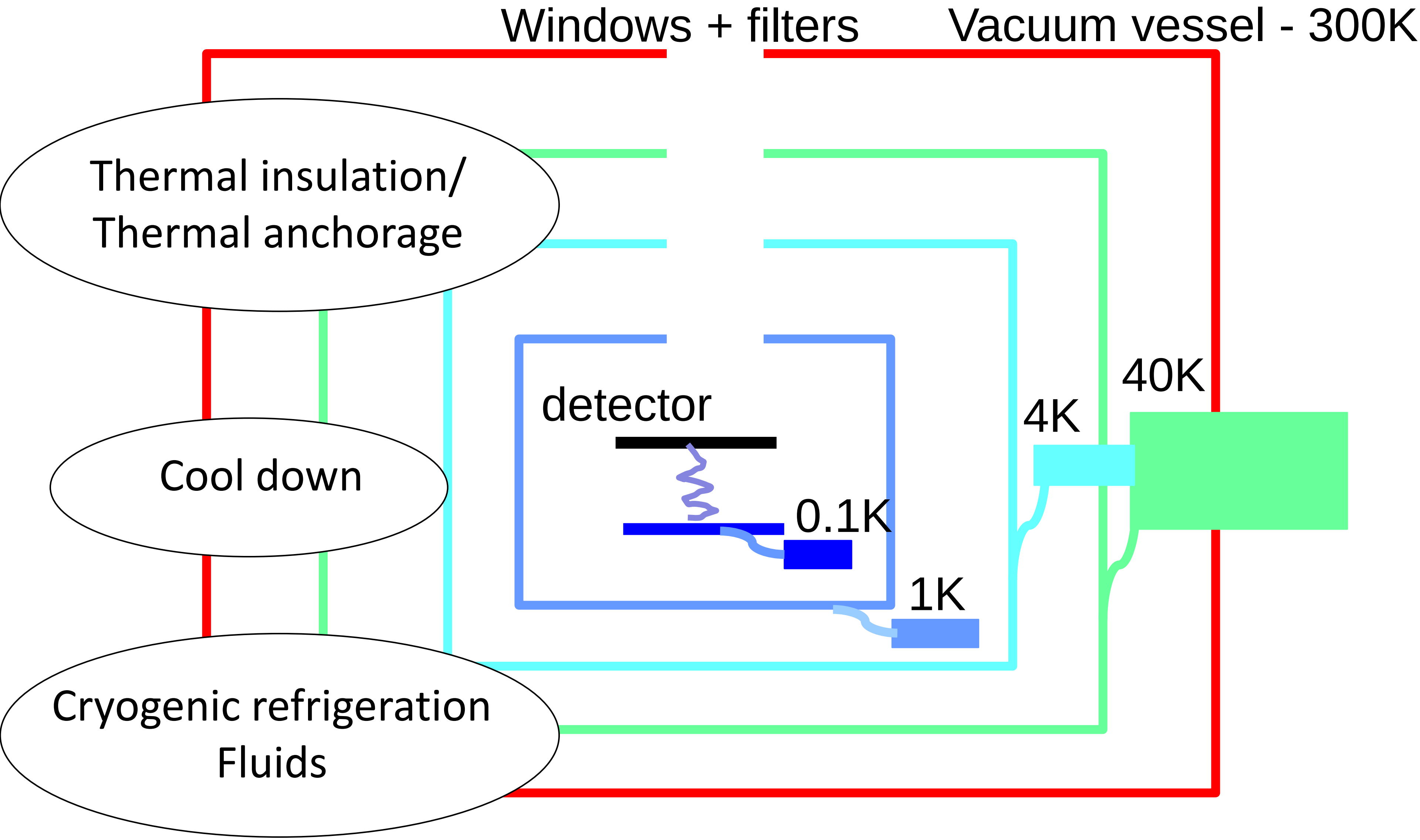
Instrument Layout



Contents

- **Cryogenic refrigeration**
    - Ideal refrigeration systems,
    - Counterflow heat exchanger cycle
    - Regenerative cycle
    - Cryocooler at T < 1K
- **Heat capacities**
    - Anomalous heat capacities
- **Heat transfer**
    - Radiation
    - Conduction

How to produce mechanical or refrigeration power?

- Ideal thermodynamic cycle ⇒ cycle defined by Carnot

  Limit irreversibilities at interfaces ⇒ Isothermal

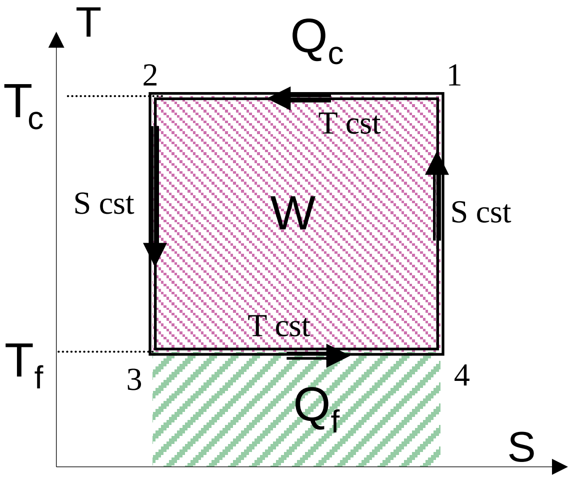
  Reversible transformation ⇒ Isentropic

- Refrigeration

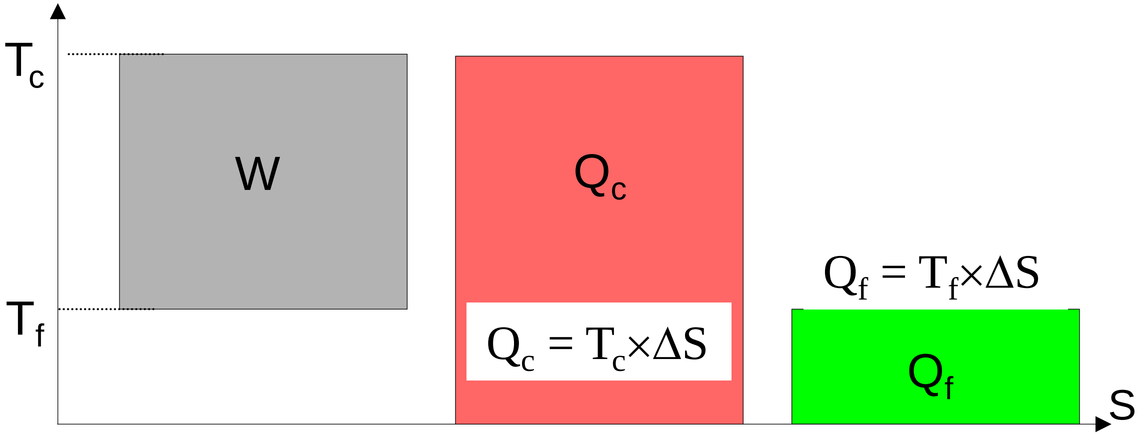
  Producing a cold gas or liquefied, it means carrying out a thermodynamic cycle which, by absorbing work and rejecting heat in a hot source, succeeds in extracting caloric energy from a cold sink.

Ideal refrigeration cycle

Reversed Carnot cycle



1st principle : $Q_c = W + Q_f$



Gaz cycle

- 1-2 : Isothermal compression (heat Q_c is rejected to a high-temperature reservoir)
- 2-3 : Isentropic expansion
- 3-4 : Isothermal expansion (heat Q_f is absorbed from the low-temperature reservoir)
- 4-1 : Isentropic compression

$W = Q_c - Q_f = (T_c - T_f) \times \Delta S$

COP : coefficient of performance

$$COP(carnot) = \frac{Q_f}{W} = \frac{T_f}{T_c - T_f}$$

$$Tf \downarrow \Rightarrow COP \rightarrow 0$$

Ideal refrigeration cycle

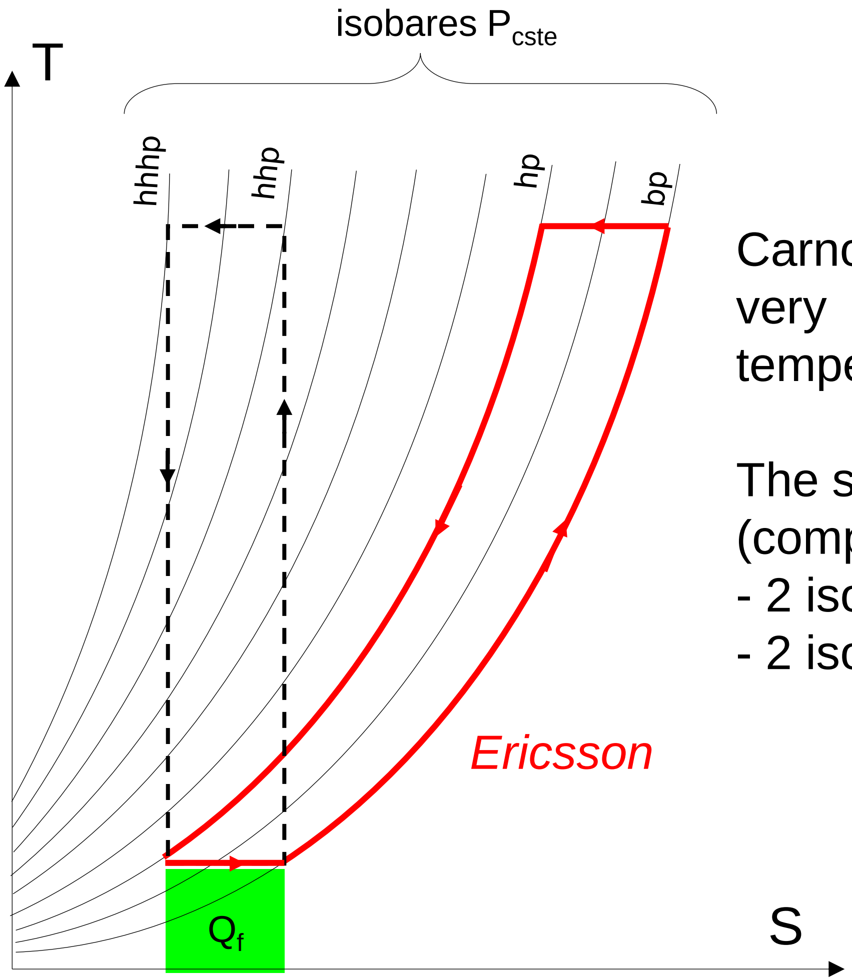
For the cryogenic applications, the efficiency of the cycle is evaluated with 1/COP (work consumed to produce 1W at T_f)

$$\left(\frac{W}{W}\right) = \frac{1}{COP} = \frac{W}{Q_f} = \frac{T_c - T_f}{T_f} = \frac{T_c}{T_f} - 1$$

$\frac{1}{COP}$ Ideal refrigeration cycle

T_c = 300 K	T_f = 0.1K	T_f = 1K	T_f = 4.2K	T_f = 20K	T_f = 40K	T_f = 80K
1/COP (W/W)	2999	299	70	14	6.5	2.75

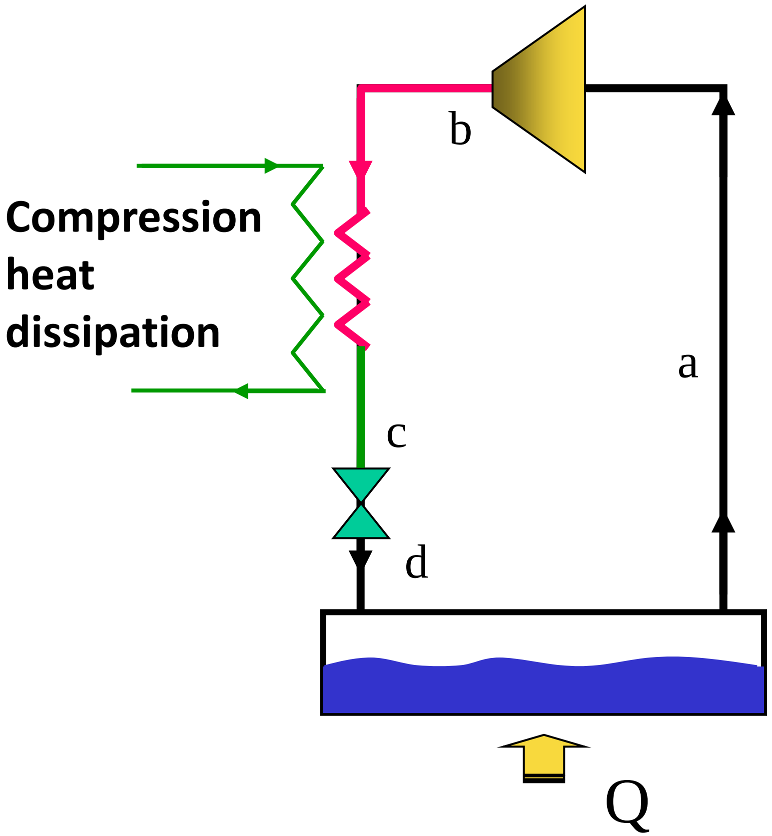
Reversibles cycles

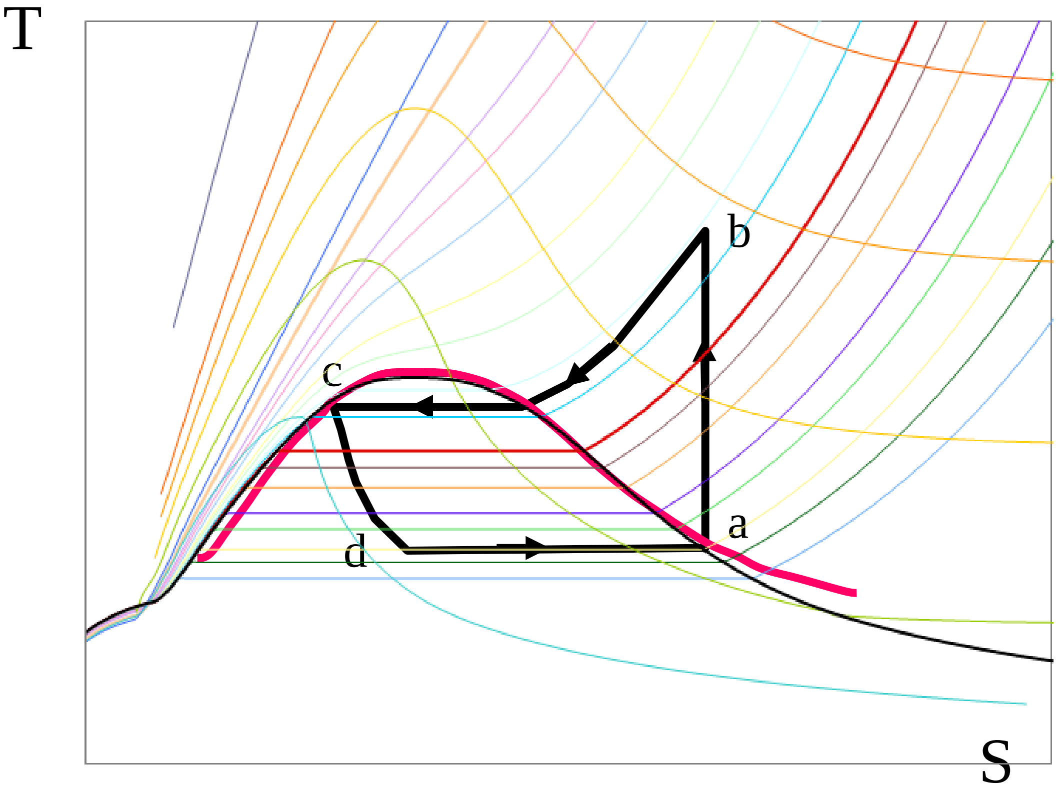


Carnot cycle : Theoretically feasible but very very high pressure necessary! ⇒ high temperature

The solution: transform the 2 isentropic (compression and expansion) into:
- 2 isobaric (p=cst): Ericsson cycle
- 2 isochoric (V=cst): Stirling cycle

Vapour-compressor cycle

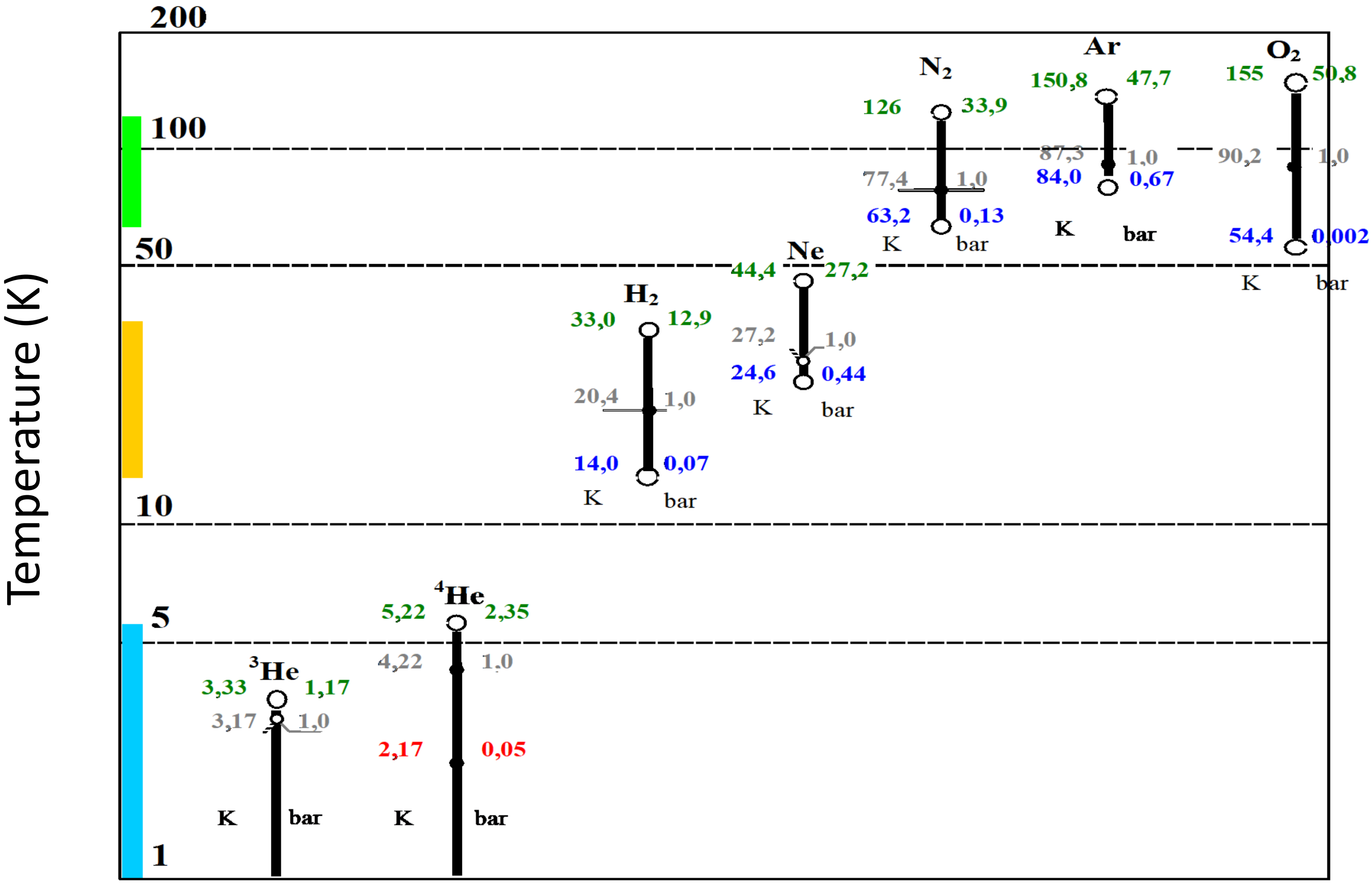




Widely used in “industrial and domestic” refrigeration systems but limited in range by:

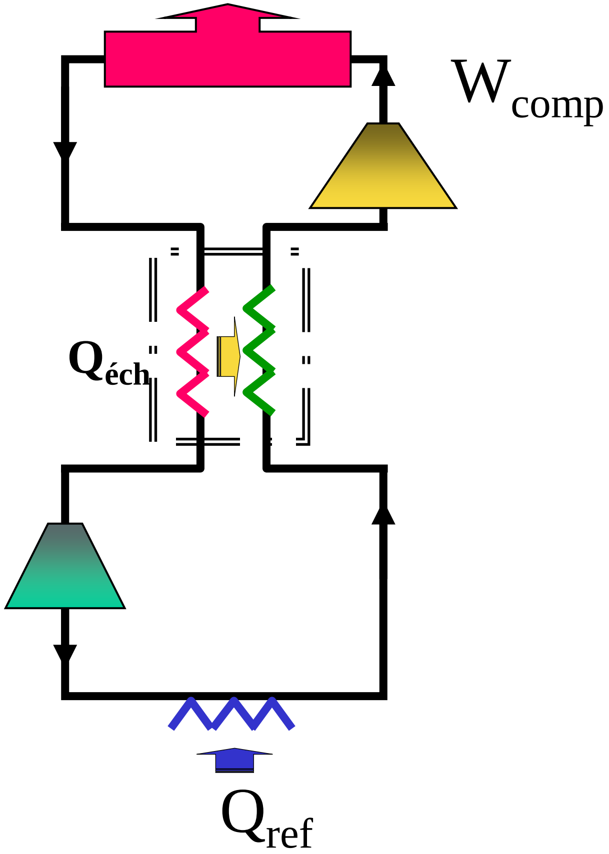
- the small temperature difference achievable in wet steam between the triple and critical points,
- the need for a fluid at saturation temperature close to ambient temperature (compressor).

Domain of existence of cryofluids



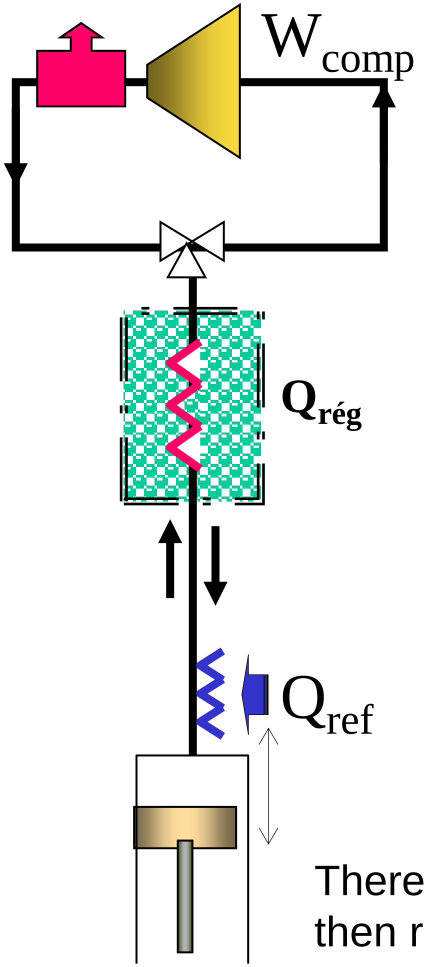
The 2 main kinds of refrigeration gas cycles

Counterflow heat exchanger cycle



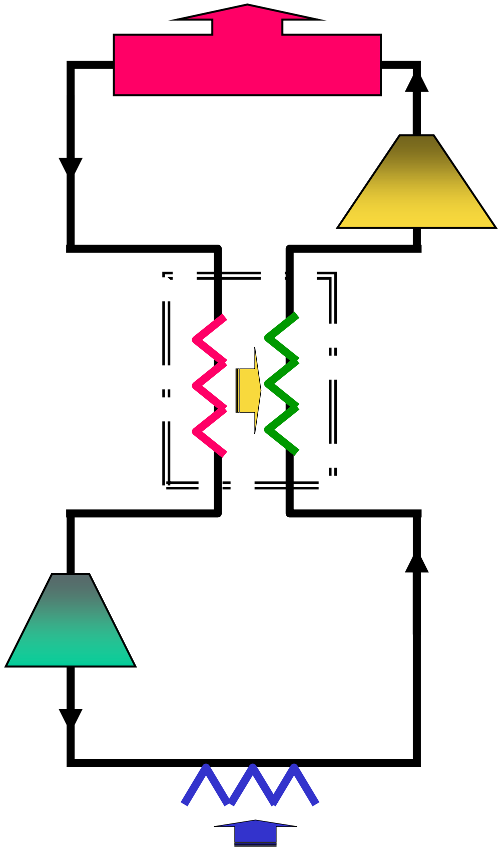
Permanent exchange between the ascending and descending branches (recovery of frigories)

Regenerative cycle

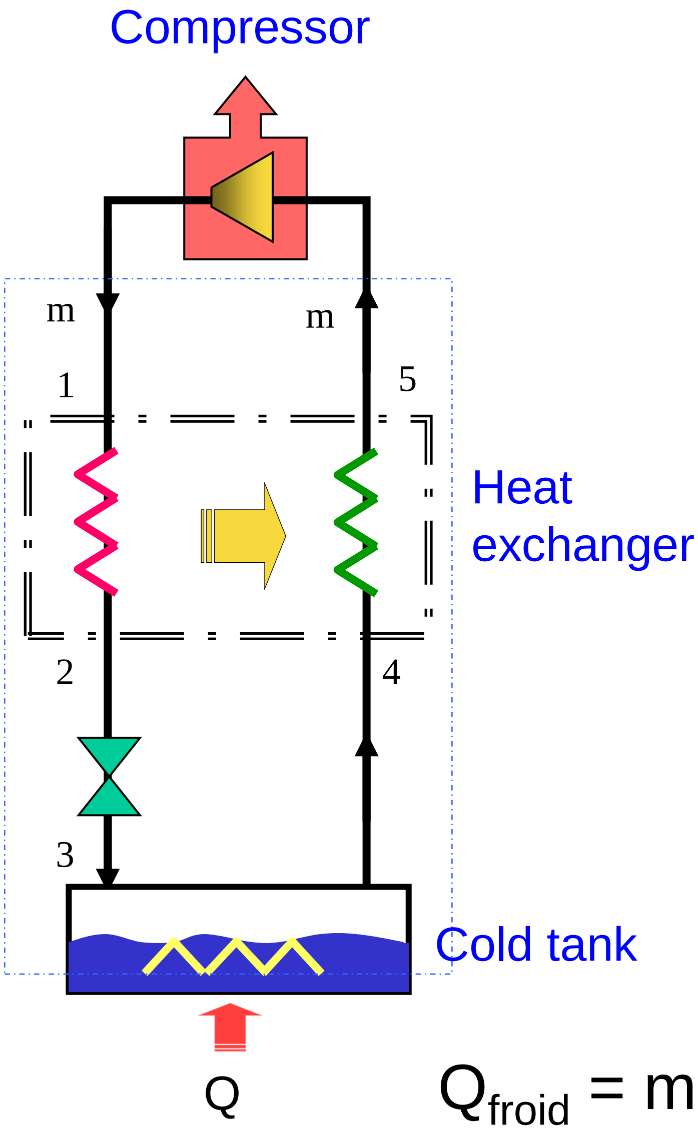


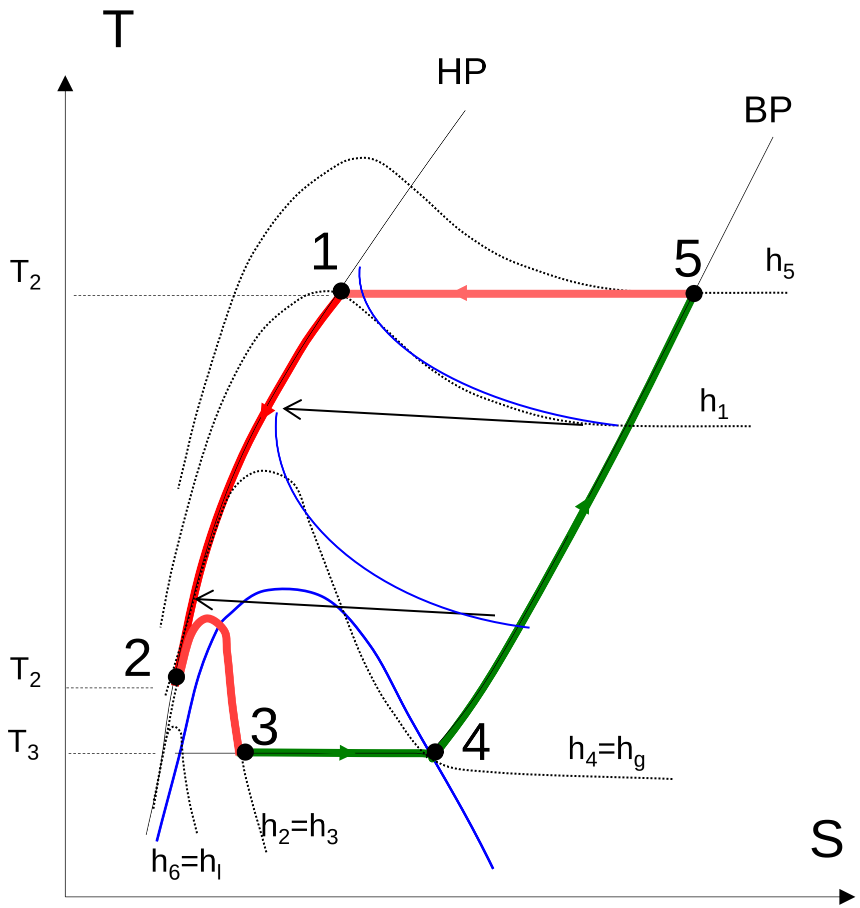
There is alternate storage then release of heat in the regenerator

Counterflow heat exchanger cycle



Linde – Hampson cycle

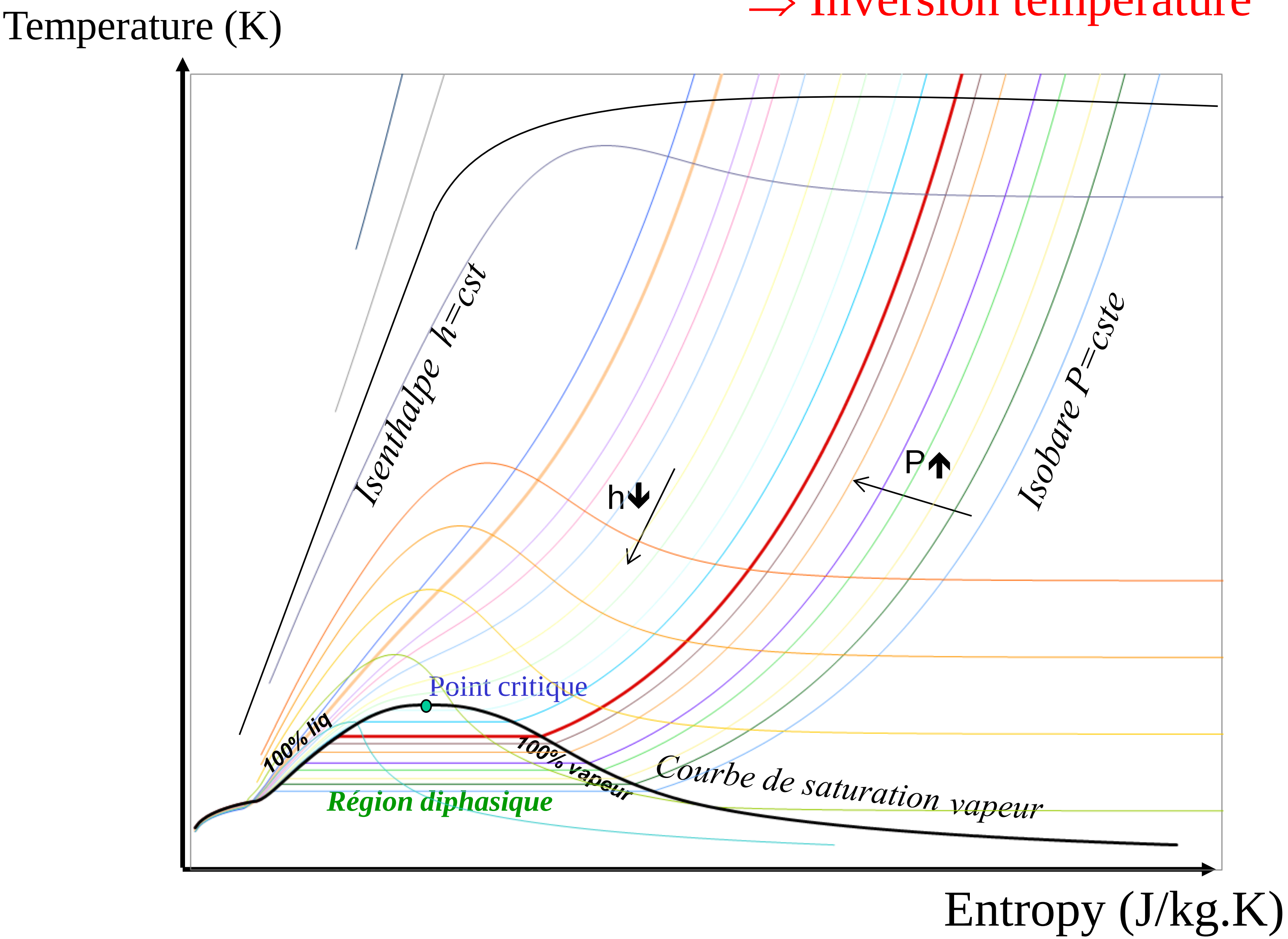




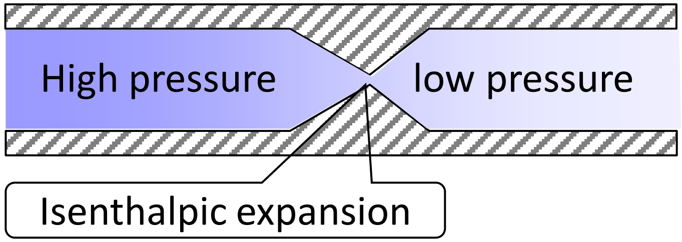
$$Q_{froid} = m\,(h5 - h1)$$

T – S diagram

⇒ Inversion temperature



Joule-Thomson expansion



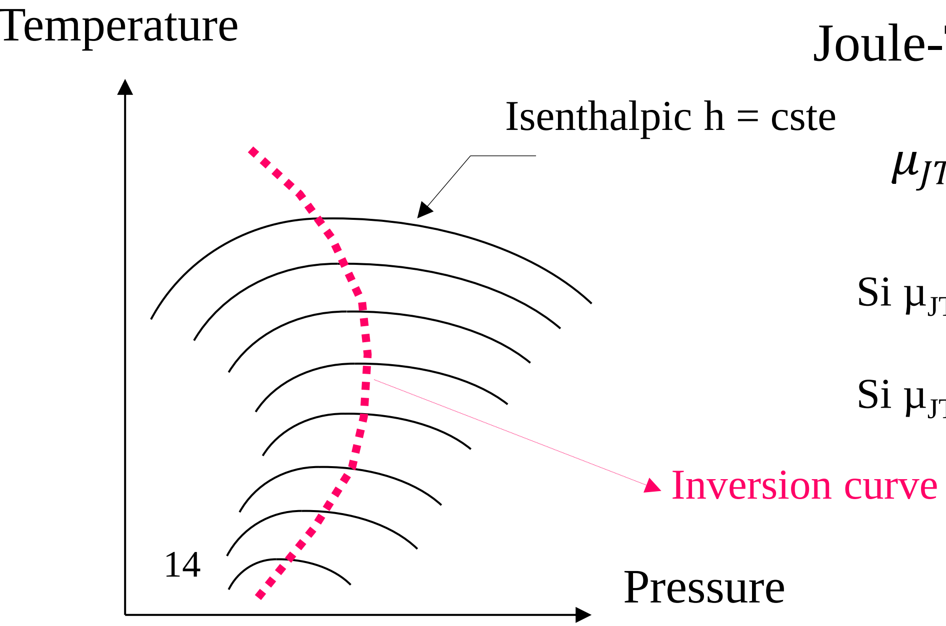
Isenthalpic expansion ⇒ dh = 0 et dT ?

$$dh = C_p dT + (V + k)dp \qquad \frac{dT}{dp} = ?$$

$$k = -T\left(\frac{\partial V}{\partial T}\right)_p$$

$$dh = C_p dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_p\right)dp = 0 \qquad \alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$dT = -\frac{V}{C_p}\left(1 - \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p\right)dp = \frac{V}{C_p}(\alpha_v T - 1)dp = \mu_{JT} . dp$$



Joule-Thomson coefficient μ_{JT}

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{V}{C_p}(\alpha_v T - 1)$$

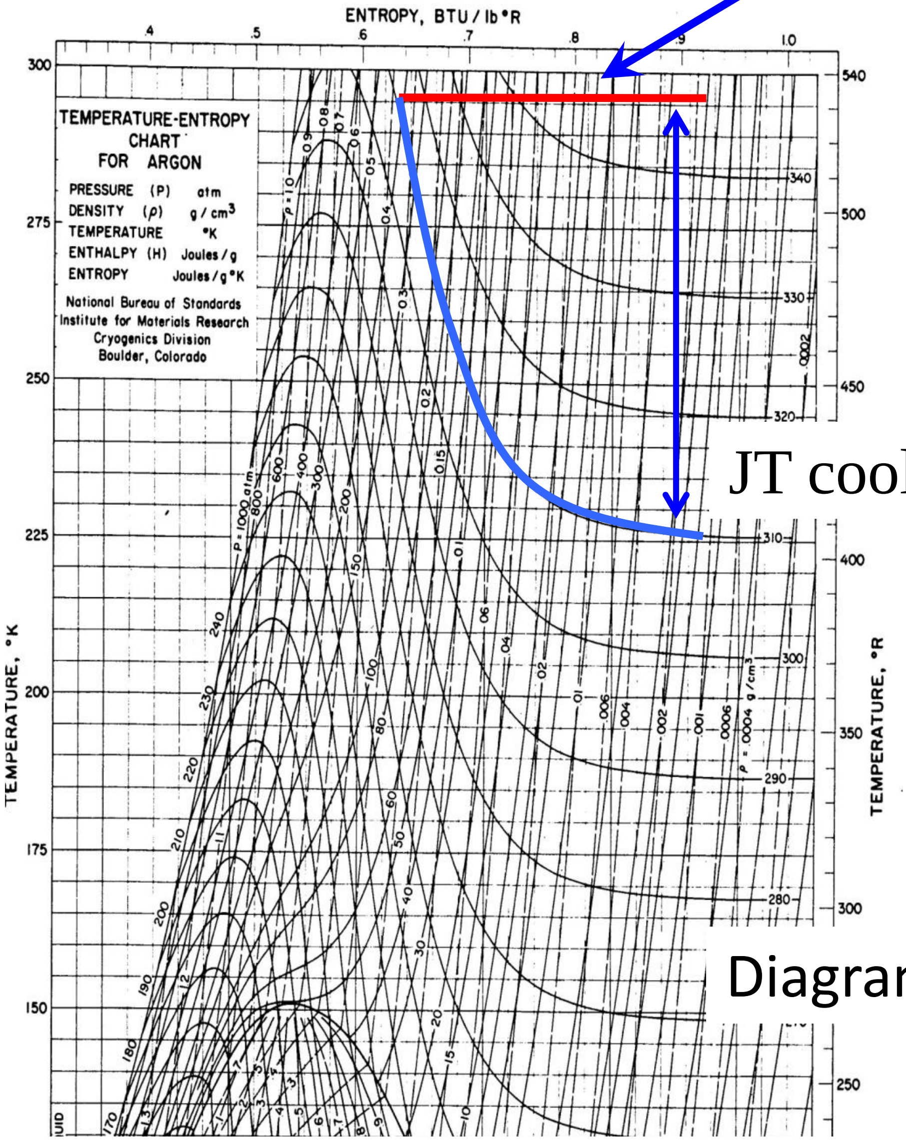
Si $\mu_{JT} > 0$ ⇒ expansion and T↓

Si $\mu_{JT} < 0$ ⇒ expansion and T↑

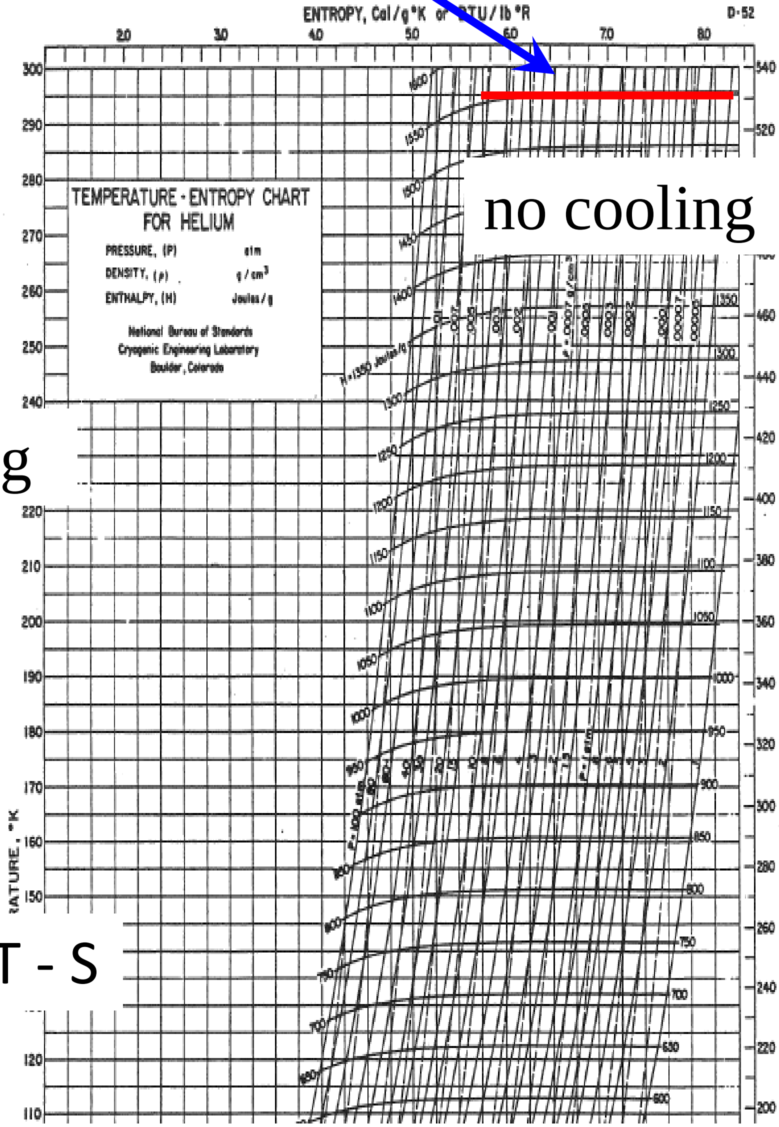
⚠ Perfect gas ⇒ $\mu_{JT} = 0$

Joule-Thomson expansion

Isothermal compression + JT expansion



JT cooling



no cooling

Diagram T - S

Joule-Thomson expansion

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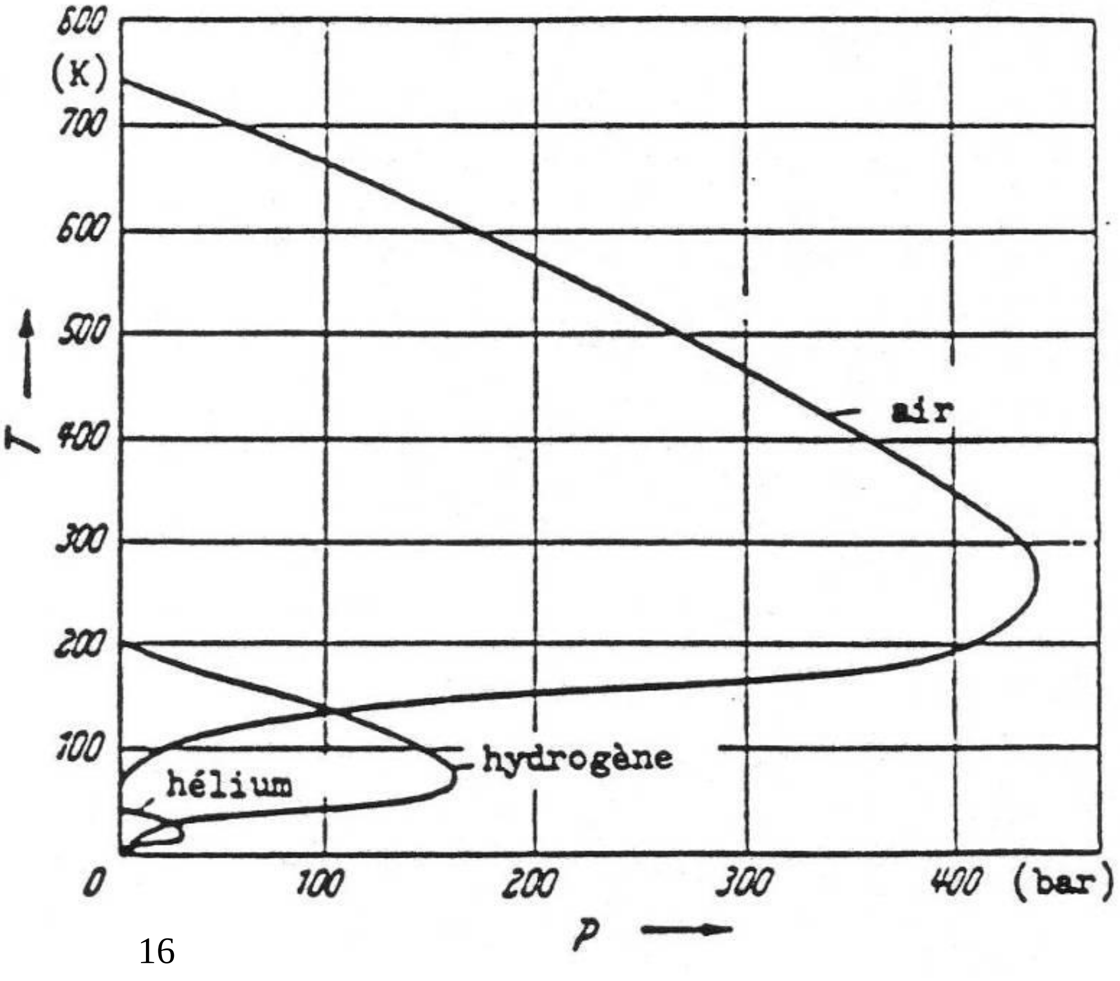
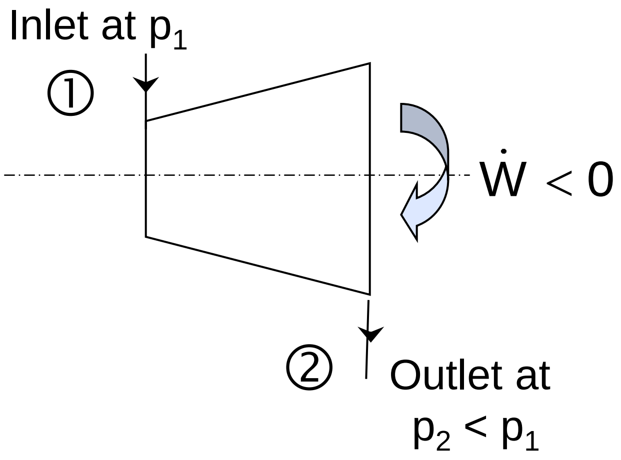
Inversion curve



Gaz	T° inversion maximum (K)
O_2	**760**
Ar	**720**
N_2	**620**
Air	**740**
Ne	**250**
H_2	**200**
He	**40**

Isentropic expansion

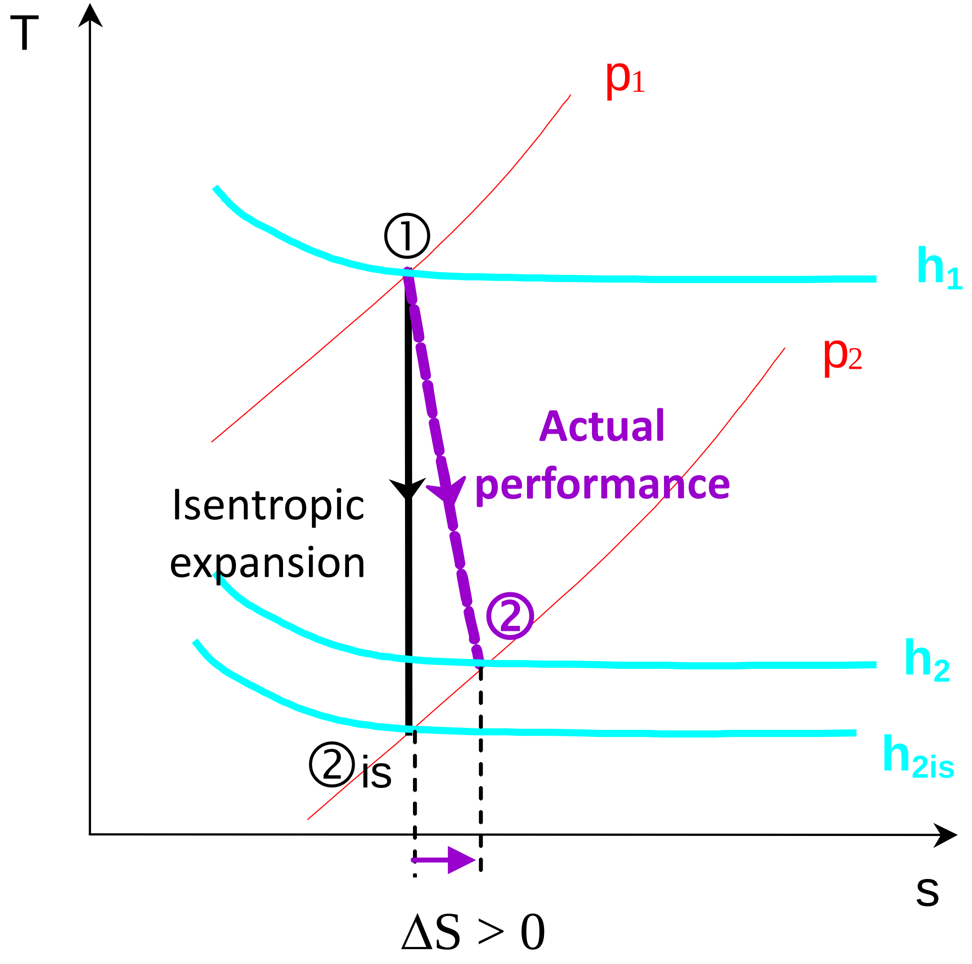
adiabatic reversible expansion through a turbine



1st principle: $\dot m(h_2 - h_1) = \dot W < 0$

2nd principle: $\dot m(s_2 - s_1) = \dot S^i > 0$

Extraction of work
Temperature decreases

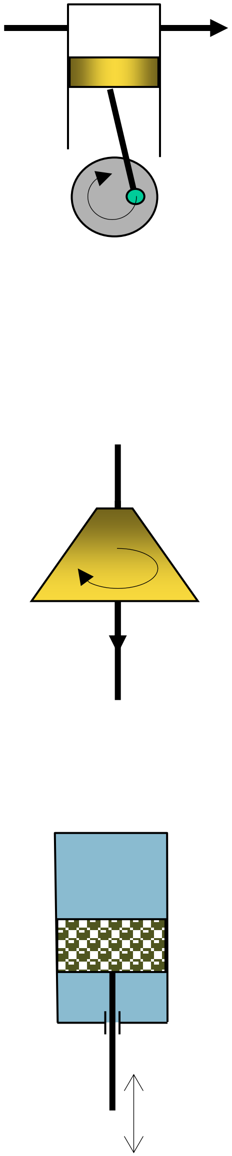


$$\begin{cases} |\dot W| < |\dot W_{is}| \\ T_2 > T_{2is} \end{cases}$$

Isentropic efficiency

$$\eta_{is} = \frac{\dot W_{réel}}{\dot W_{is}} = \frac{h_2 - h_1}{h_{is} - h_1}$$

Isentropic expansion



Generally approached with recovery of external work (piston, turbine) for high expansion rates.

$$\delta Q = TdS = C_P dT + k dp = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \qquad k = -T\left(\frac{\partial V}{\partial T}\right)_p$$

$$dT = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p dp = \frac{V\alpha_v T}{C_p} dp \qquad \alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\frac{dT}{dp} = \frac{V\alpha_v T}{C_p}$$

$$\mu_{\Delta S=0} = \left(\frac{\partial T}{\partial P}\right)_S > 0$$

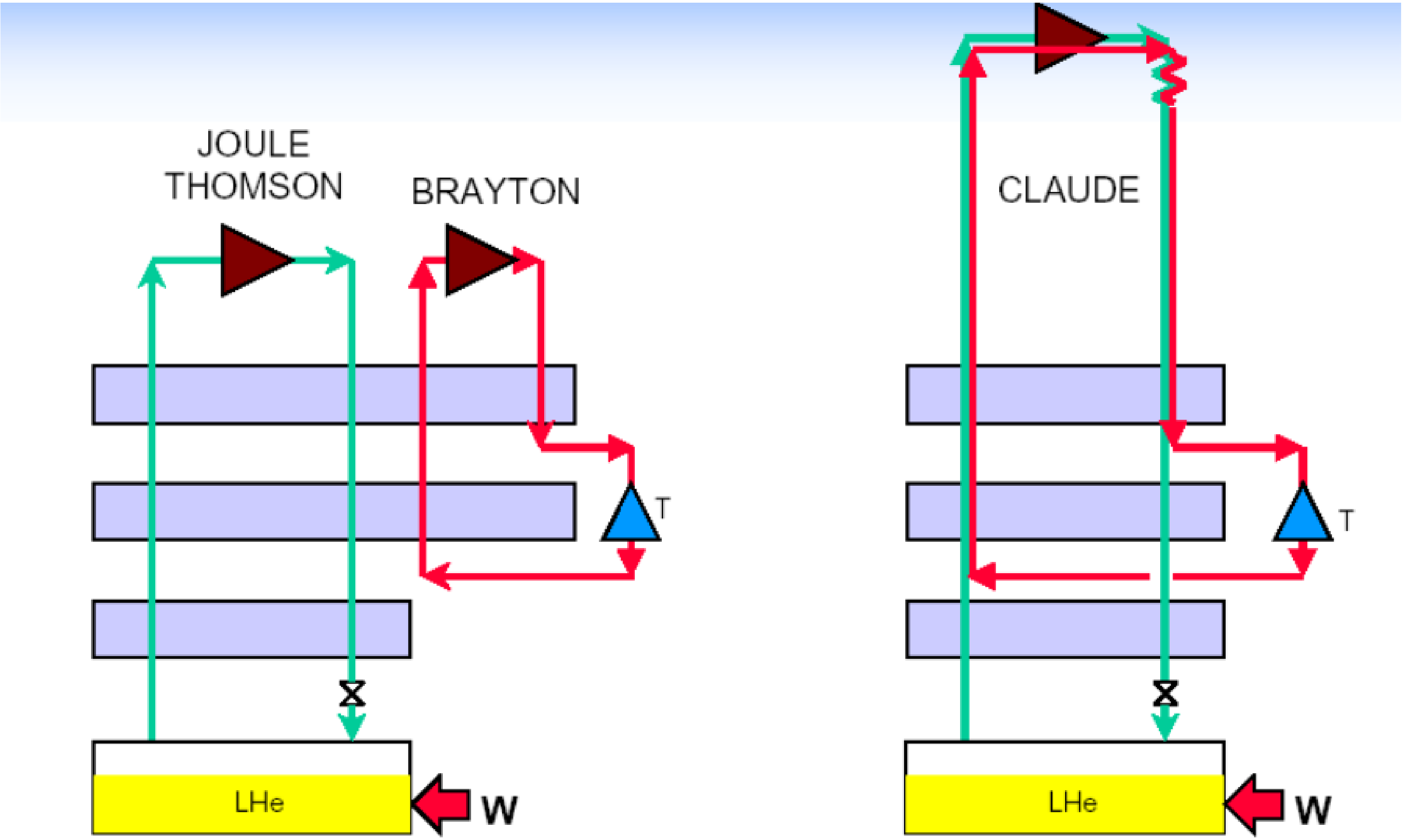
The temperature variation is always negative and greater in an isentropic expansion than in an isenthalpic expansion (JT).

Claude cycle

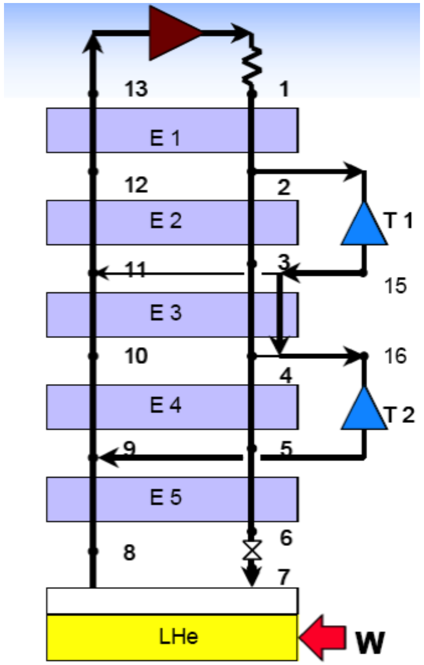
- Coupling of a Brayton cycle with a Joule-Thomson cycle

⇒ Claude cycle for the liquefaction of air or helium

- Operation in pure liquefier (liquid extraction), in refrigerator (closed cycle) or mixed



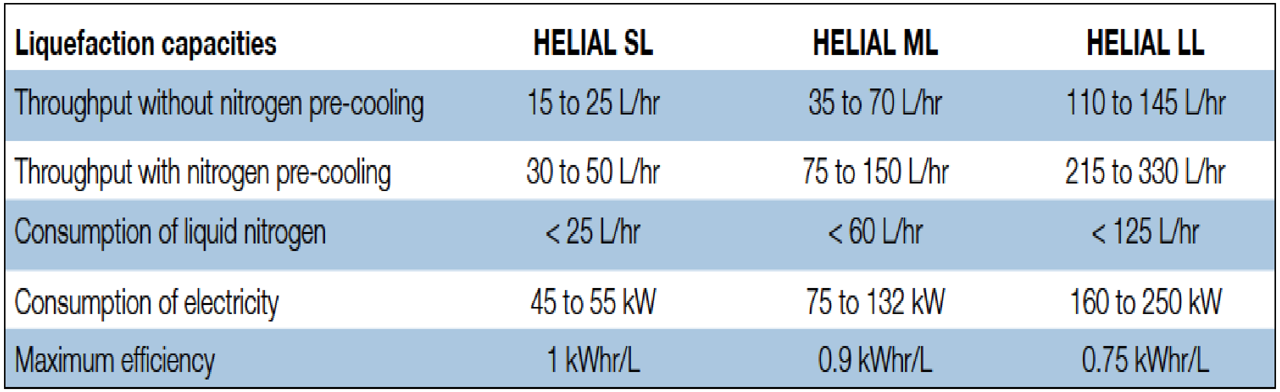
Examples of small helium refrigerator



1/COP

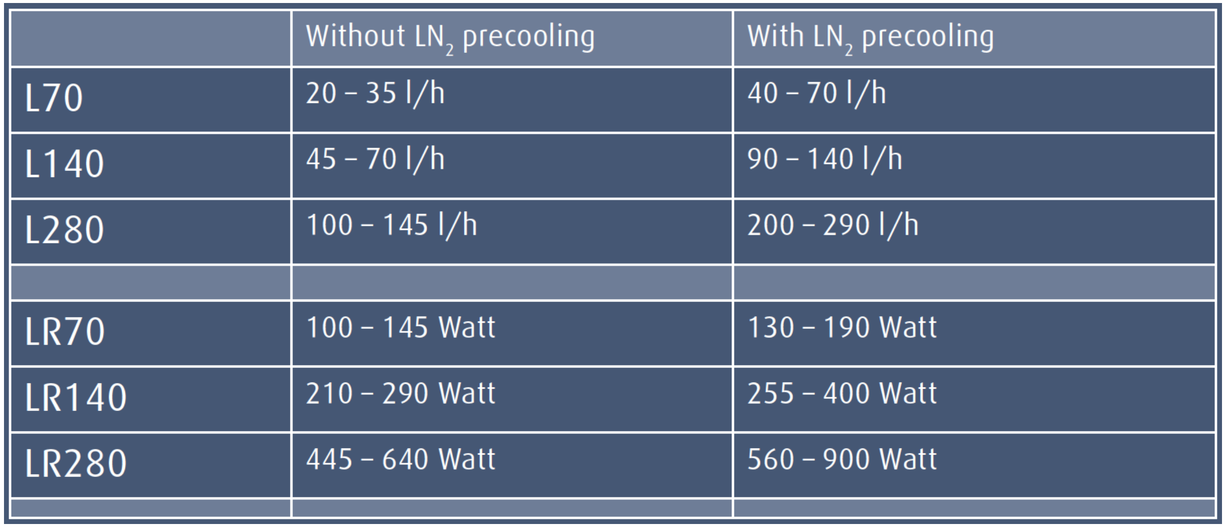
> 500 W/W

Air Liquide document



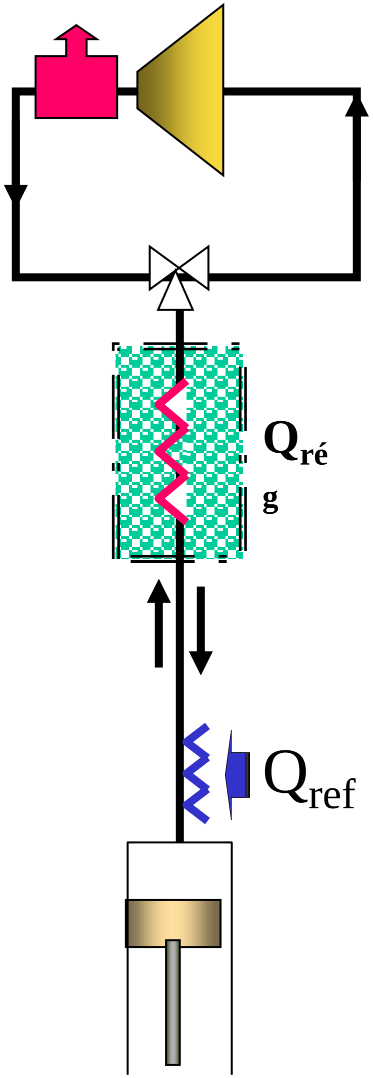
Liquefaction capacities	HELIAL SL	HELIAL ML	HELIAL LL
Throughput without nitrogen pre-cooling	15 to 25 L/hr	35 to 70 L/hr	110 to 145 L/hr
Throughput with nitrogen pre-cooling	30 to 50 L/hr	75 to 150 L/hr	215 to 330 L/hr
Consumption of liquid nitrogen	< 25 L/hr	< 60 L/hr	< 125 L/hr
Consumption of electricity	45 to 55 kW	75 to 132 kW	160 to 250 kW
Maximum efficiency	1 kWhr/L	0.9 kWhr/L	0.75 kWhr/L

Linde Kryotechnik document



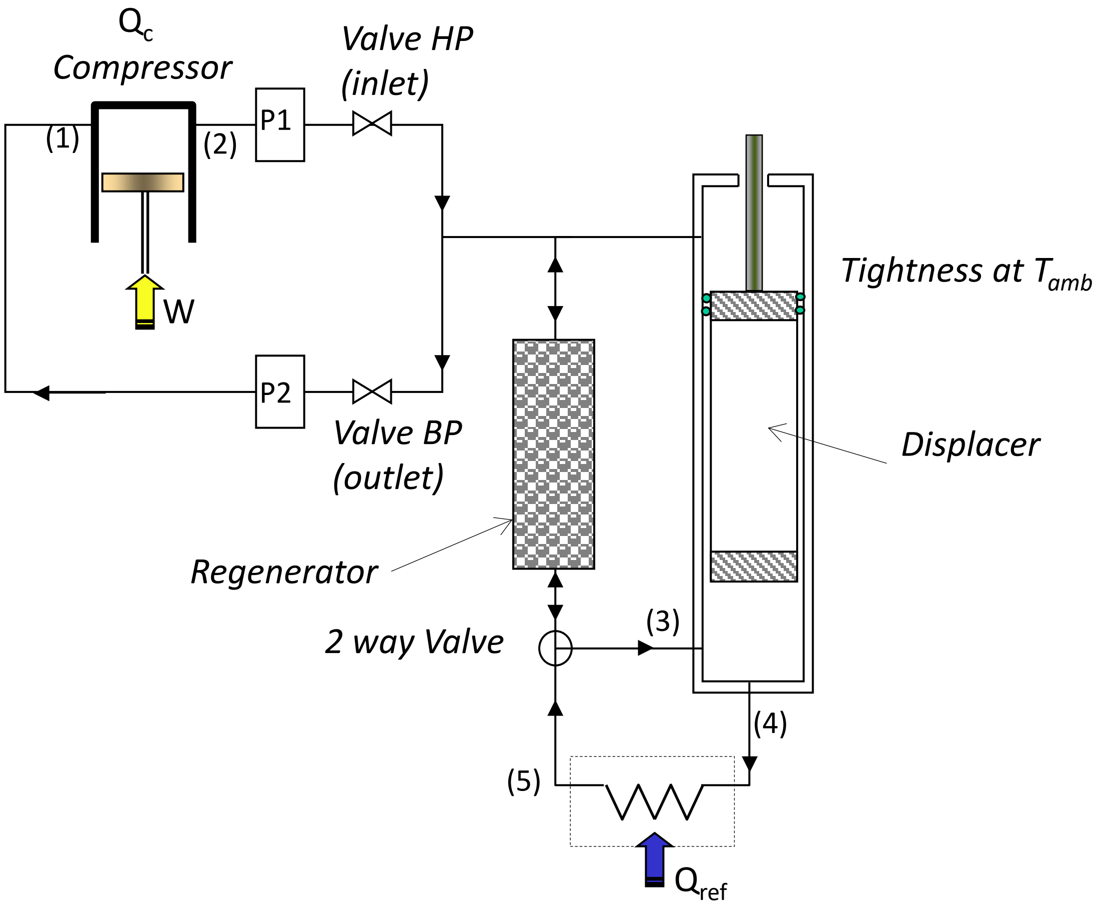
	Without LN_2 precooling	With LN_2 precooling
L70	20 – 35 l/h	40 – 70 l/h
L140	45 – 70 l/h	90 – 140 l/h
L280	100 – 145 l/h	200 – 290 l/h
LR70	100 – 145 Watt	130 – 190 Watt
LR140	210 – 290 Watt	255 – 400 Watt
LR280	445 – 640 Watt	560 – 900 Watt

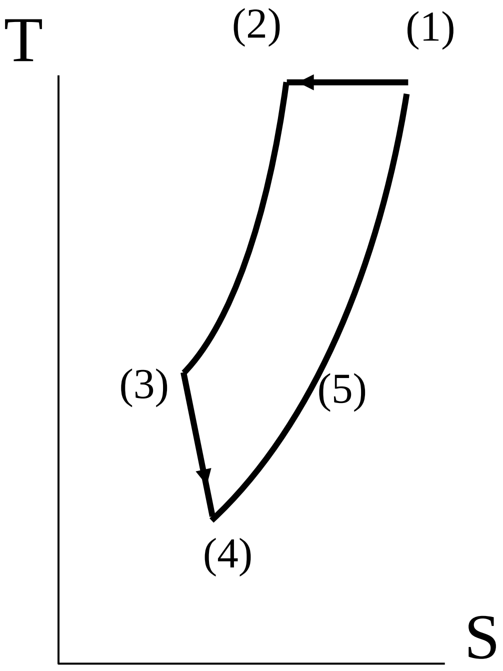
Regenerative cycle



Ericsson cycle: Gifford-Mac Mahon cryocooler

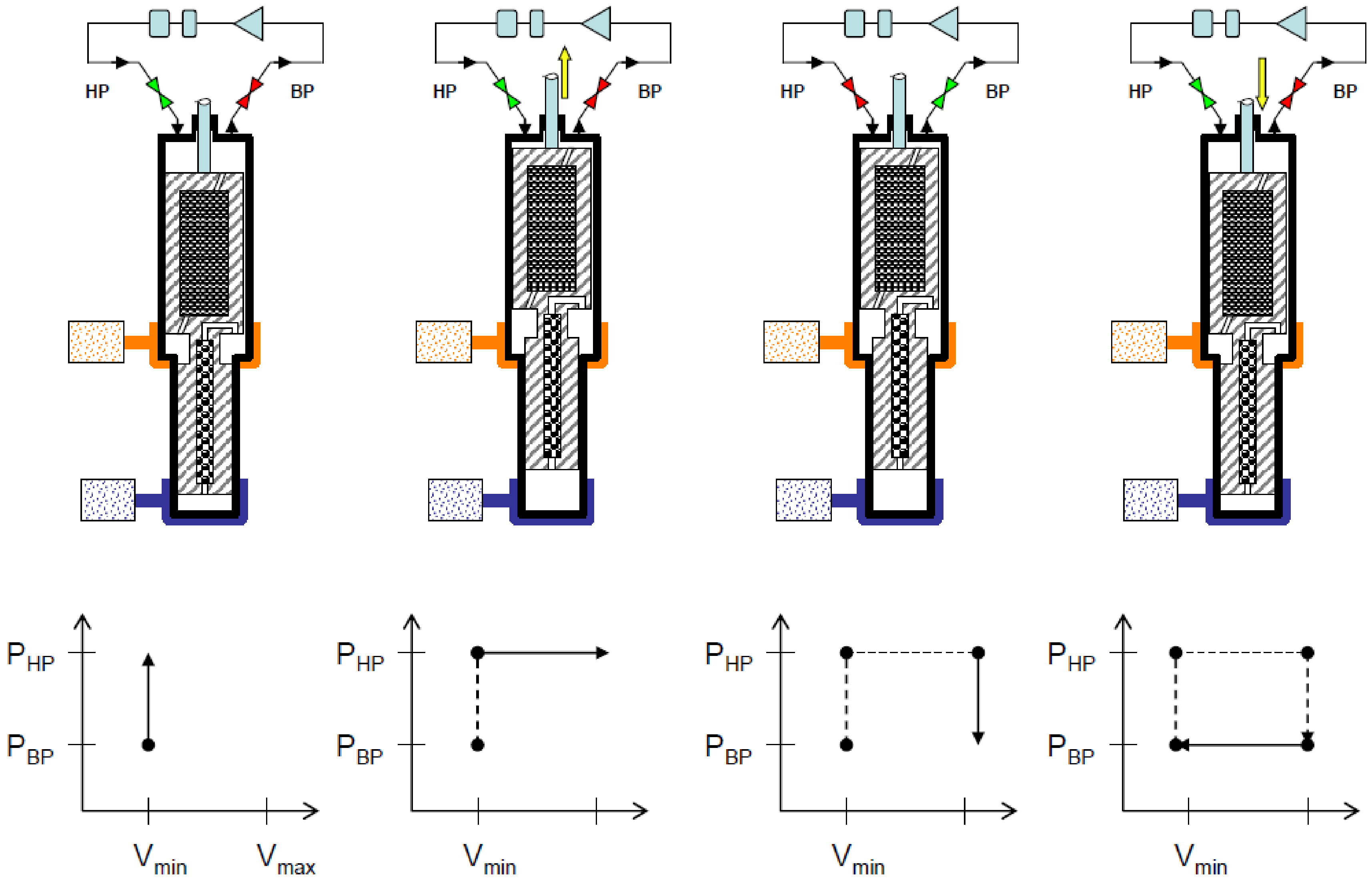
Main components : compressor, displacer, regenerator, valves



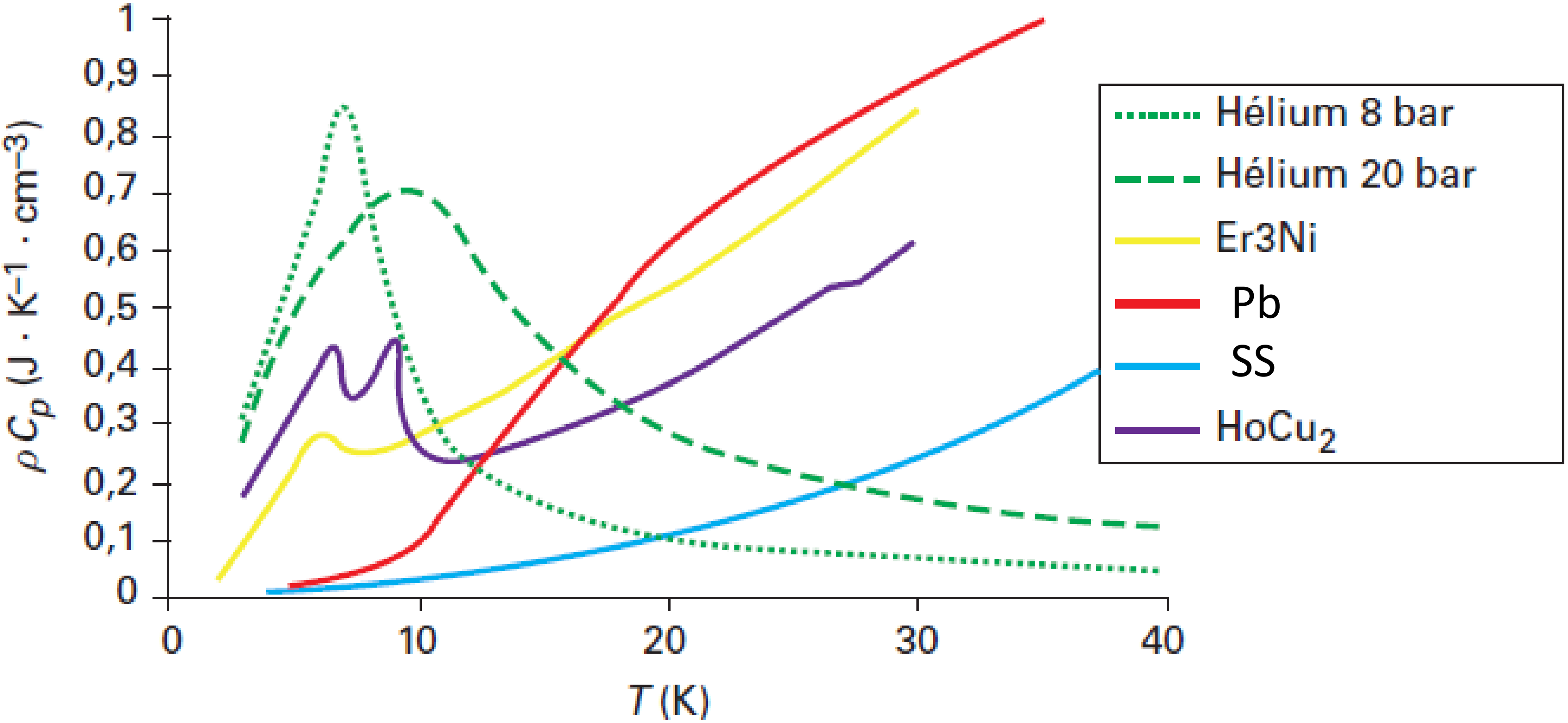


1-2 HP valve open, the HP gas flows into the regenerator. The pressure increases
2-3 The gas is forced through the regenerator by the motion of displacer
3-4 BP valve open, gas expansion
4-5 The displacer forces the cold gas through the regenerator

Ericsson cycle: Gifford-Mac Mahon cryocooler



Regenerator



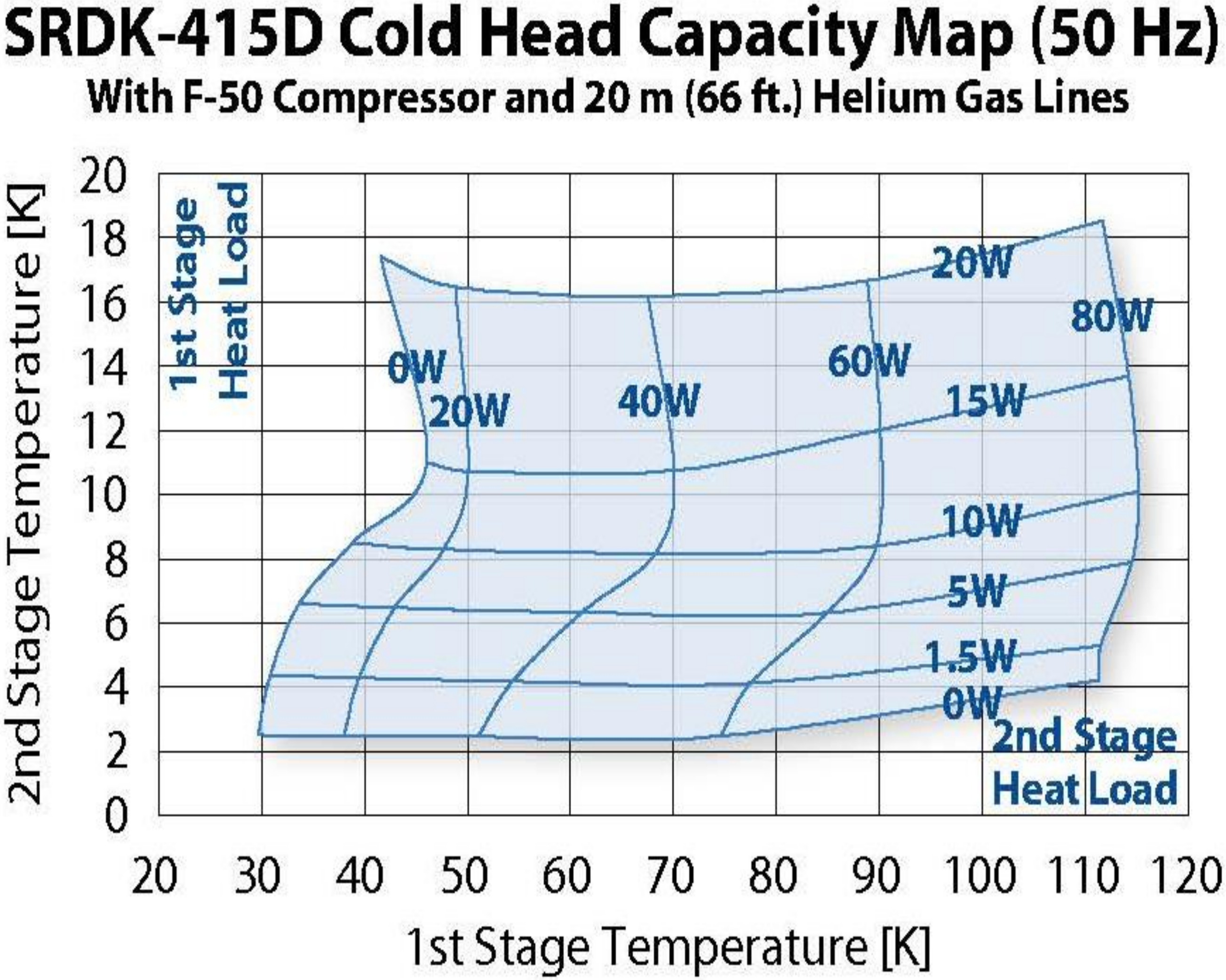
$C_{renegerator} > C_{fluid}$

$\Delta P \approx 0$

Thermal conductivity: low axial, high radial

Gifford-Mac Mahon cryocooler

Cryomech, Sumitomo, CTI,

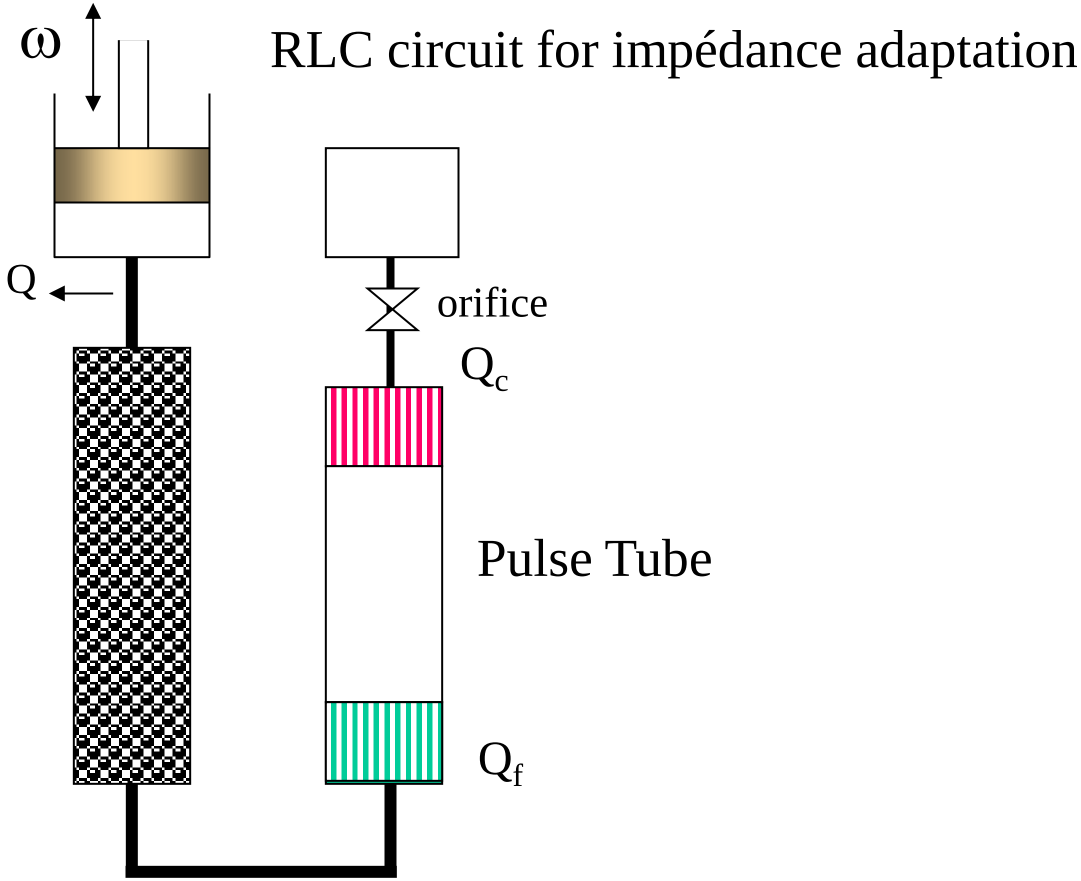


1.5W @ 4.2K

Pulse tube

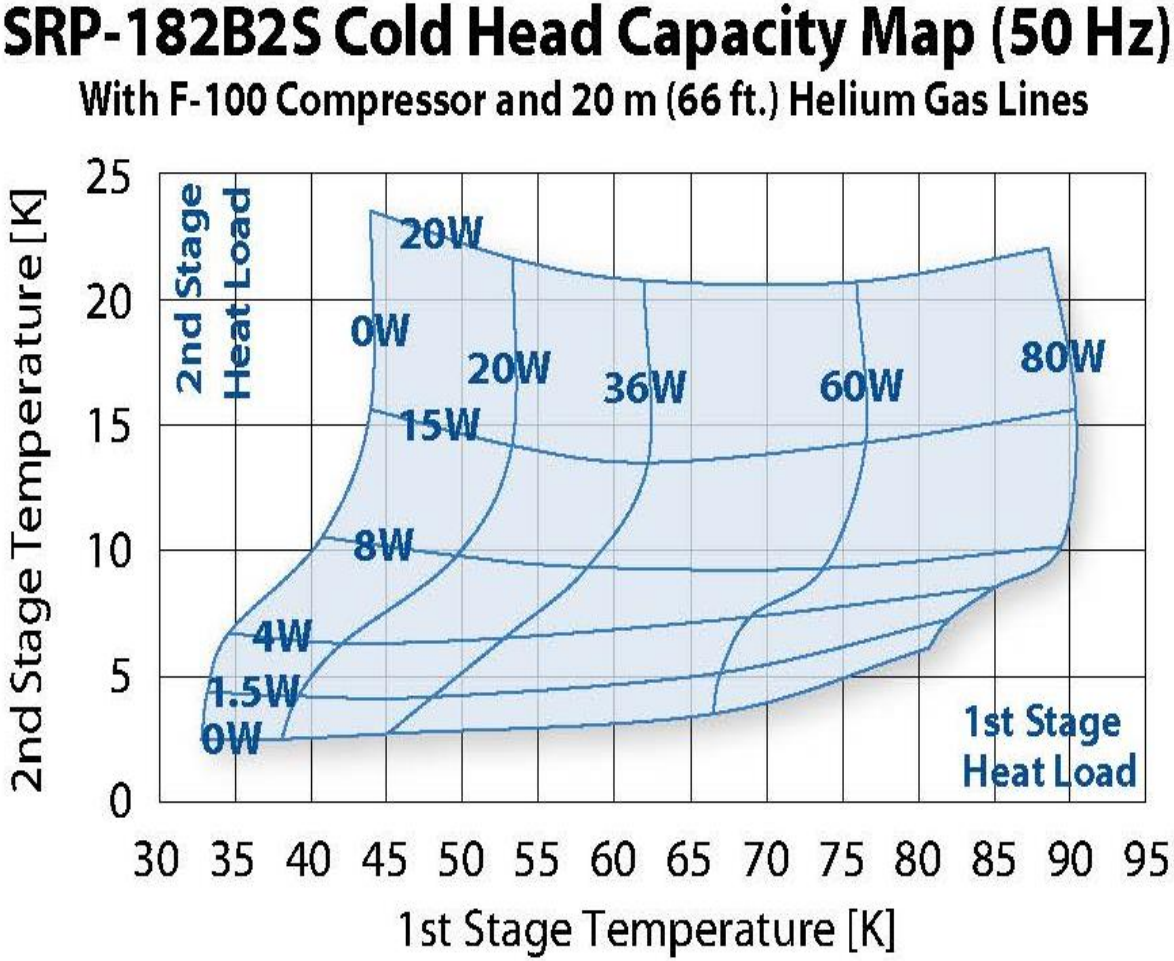
Replacement of the displacer by a fluid piston whose movement in the tube is controlled by inertance (valve sets or orifice on the tank). Based on the phase shift between pressure waves and gas flow, it works in 2 frequency domains:

Low frequency ⇔ Ericsson **high frequency ⇔ Stirling**



Pulse Tube

Cryomech, Sumitomo, CTI,



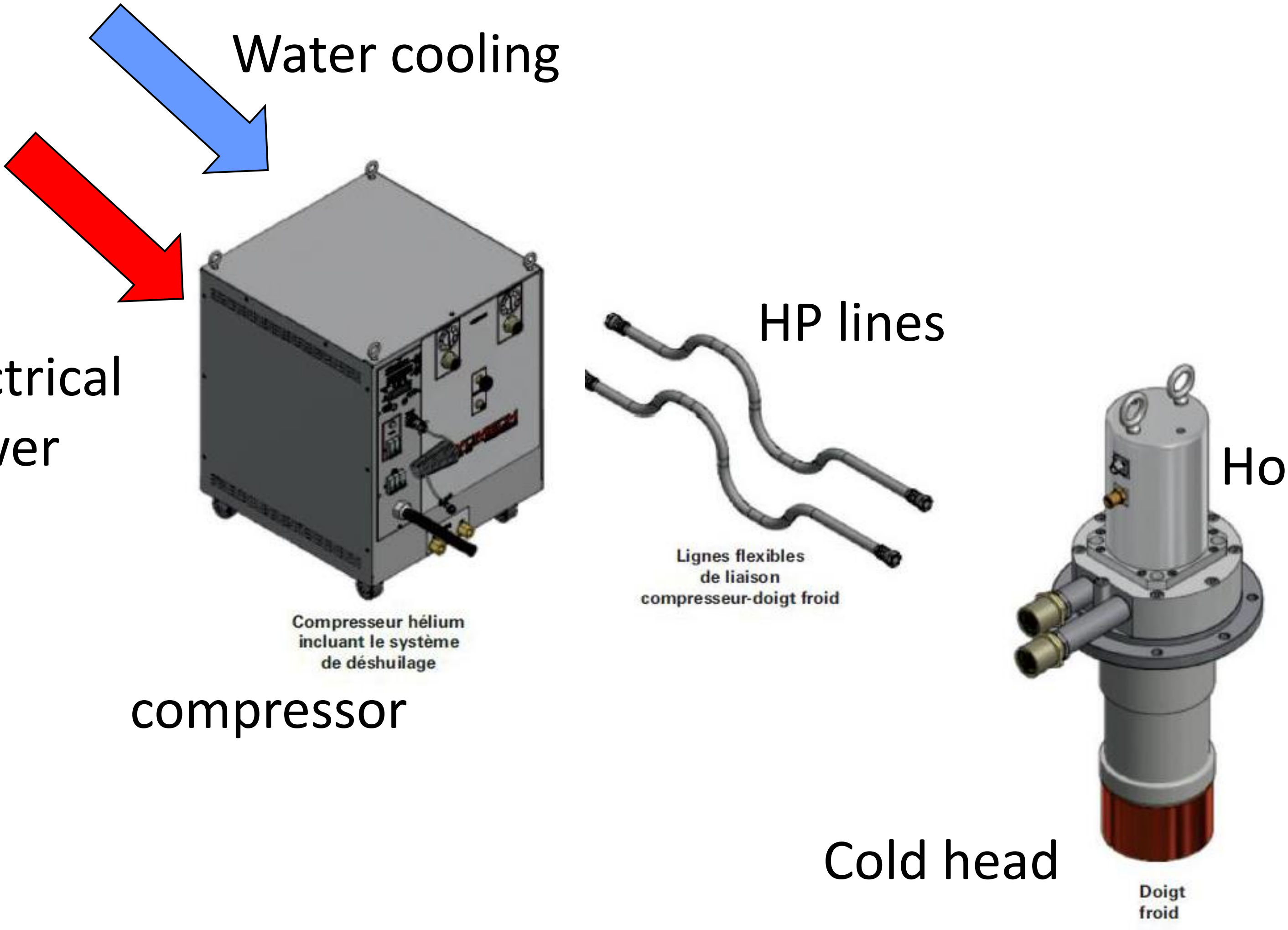
SRP-182B2S Cold Head Capacity Map (50 Hz)

With F-100 Compressor and 20 m (66 ft.) Helium Gas Lines

1.5W @ 4.2K

Cryocooler

Main components



Water cooling

Electrical power

compressor

HP lines

Hot head

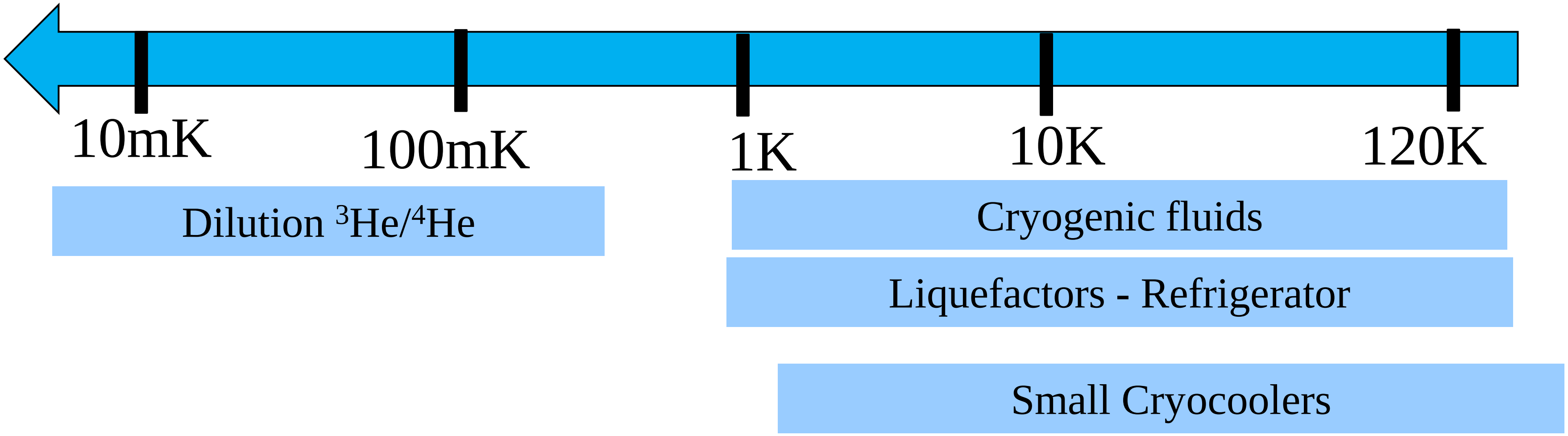
Cold head

Comparison between GM and PT

	Gifford MacMahon (GM)	Pulse Tube (PT)
Principles	Regenerator ⇒ Mouvement at cold temperature	Regenerateur Fixed
Technical parameters	Efficiency higher than PT Not very sensitive to orientation	Lower vibration level Lower temperature limit
Industrial parameters	Lower cost	Lower maintenance

Differents kinds of cooling systems

Continuous cooling


10mK

100mK

1K

10K

120K

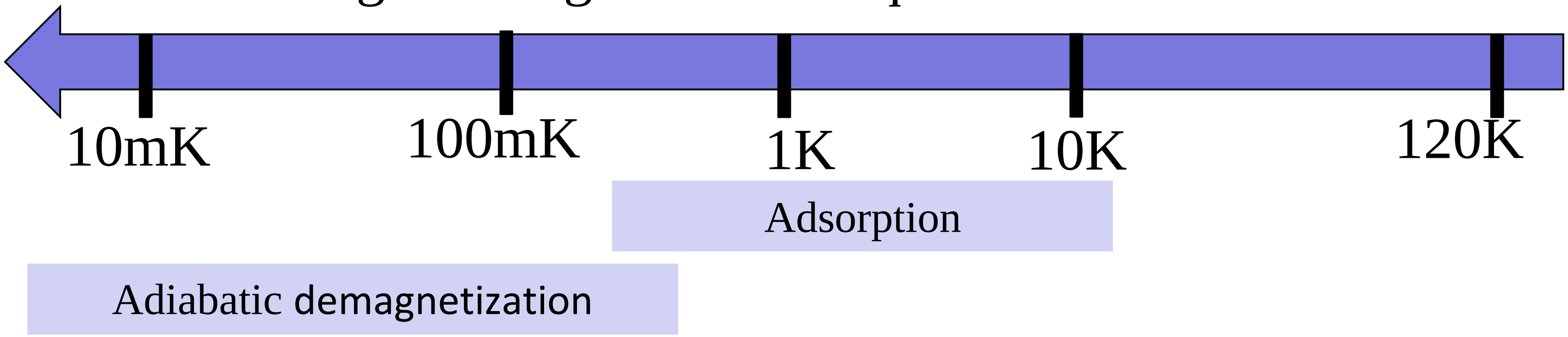
Dilution $^3He/^4He$

Cryogenic fluids

Liquefactors - Refrigerator

Small Cryocoolers

Cooling with regeneration sequence


10mK

100mK

1K

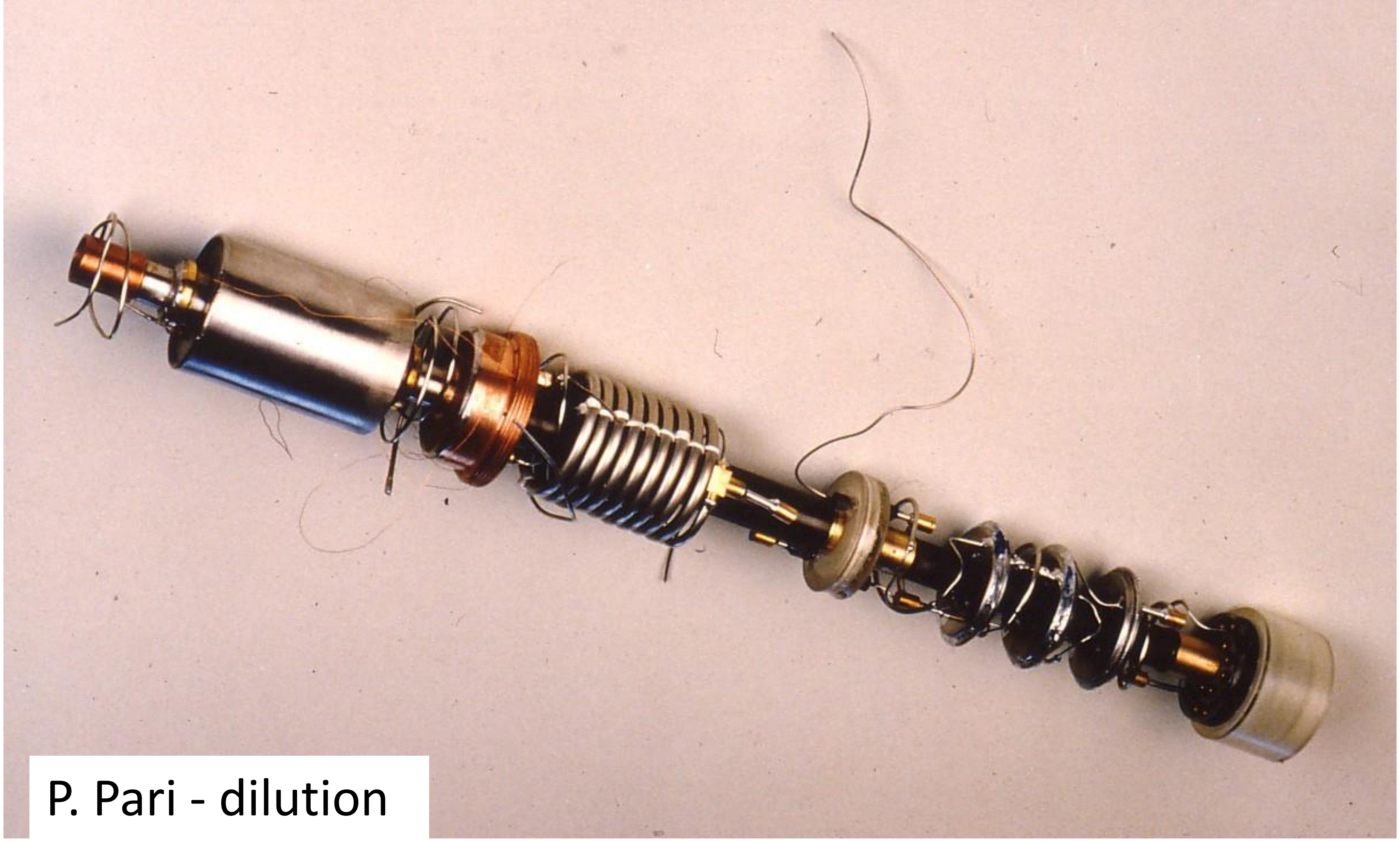
10K

120K

Adsorption

Adiabatic demagnetization

Dilution refrigerator ^{3}He/^{4}He



P. Pari - dilution

1) Introduction

In the past, physicists using dilution were quit often the builder of their apparatus. They were indeed bearing a good knowledge of the physical process running the system and aware of the problems around a bad running apparatus.

Nowadays most of them had the apparatus delivered by a specialized firma and sometime ignoring partially the essential low temp physics and the running principles of theses apparatus.

We will try to give some simple tools to overcome this situation and therefore be more aware how it works and “less lost if any problems appears”.

2) Thermodynamic: Some remindering before explicit formulas applied on dilution process

A few useful thermodynamic functions

Internal energy $U = Q + W$ heat + mechanical work

and for a fluid, gas or liquid

$$dU = dQ - pdV$$

Entropy (disorder of a system) S define as $TdS = dQ$

Enthalpy $H = U + PV$

$$dH = dU + pdV + Vdp = dQ + Vdp$$

Enthalpy is thus **the heat one could releases from a gas or a fluid at constant pressure.**

The heat you could extract from the vapour above the liquid at 1bar up to the room temperature is called sensible heat , to be compared to the latent heat of vaporisation and it is much bigger. It is used to cool all the screens in the cryostat and the incoming gas and/or liquid coming from room temperature.

An other property of the enthalpy is that it is conserved in a Joule Thomson “adiabatic expansion”. It is used in a dilution refrigerator to adiabatically reduce the pressure of the incoming He_3 and in the same time cool it to give liquid instead of gas.

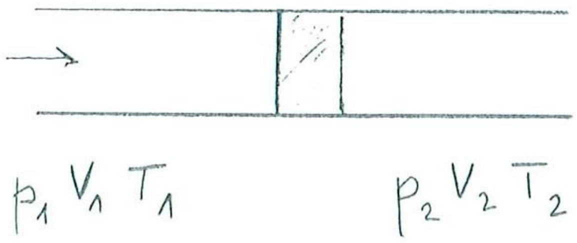
Example of an adiabatic Joule Thomson expansion.

It could be design with a porous plug or a flattened tube isolated in a vaccum

$p_1 > p_2$ $V_1 < V_2$

and T_1 and T_2 depends on the sign of the process

$H_1 = H_2$



3) Generalities : How to produce a low temperature from a very basic point of view?

You take a fluid composed of either molecules or atoms (noble gas) It will be with two phases, a gaseous and a liquid when the temperature is around the binding energy between the atoms or molecules. More precisely we define L as the (molar) latent of evaporation,

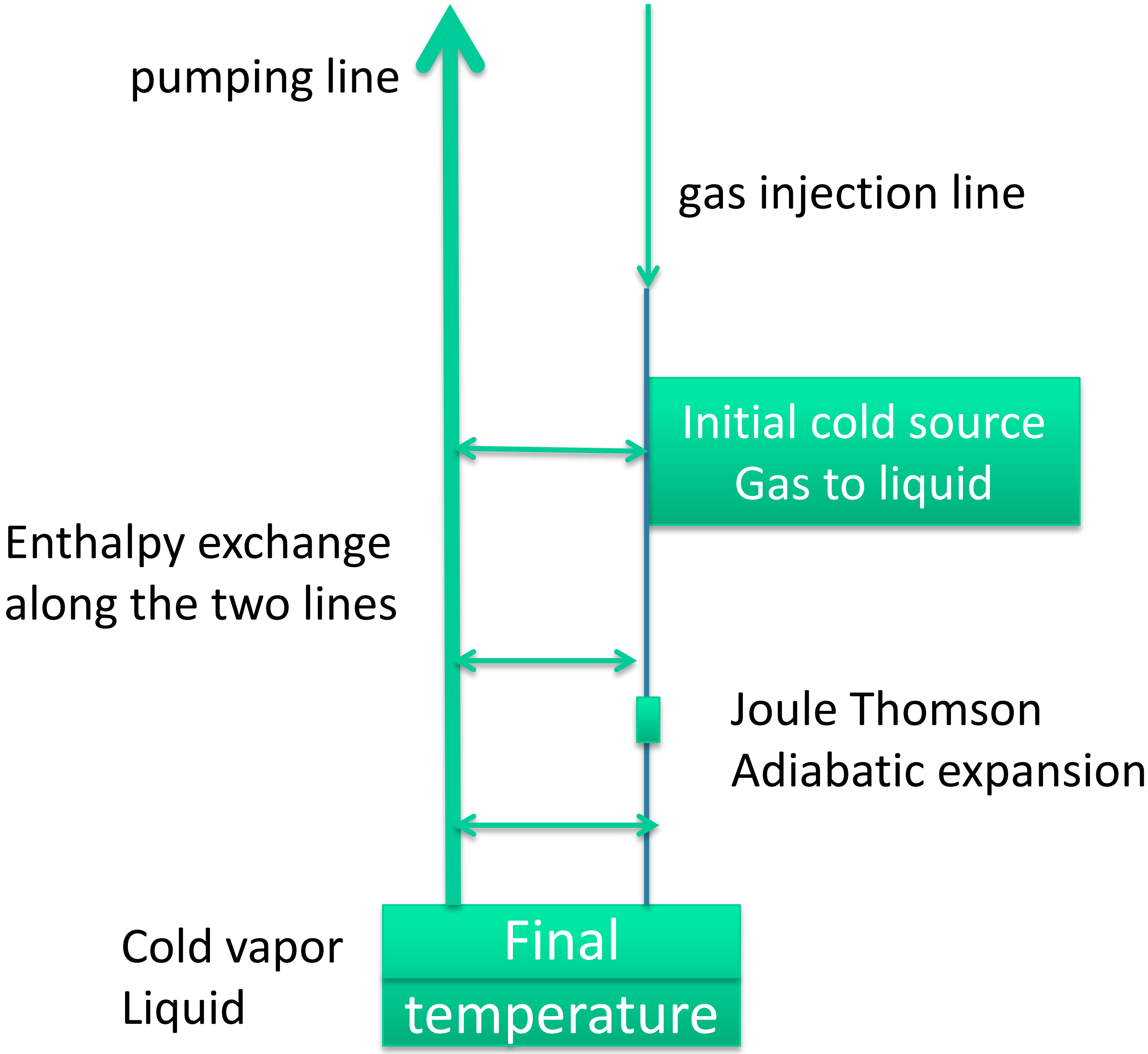
$$\mathbf{RT \approx L}$$

where L is a few time the energy of interaction between two atoms or molecules.

The lower the heat of evaporation, the lower the range of obtainable temperature and consequently nobles gases are the ones to produce very low temperatures. The smaller the atomic number, the smaller the binding energy and the lower the obtainable temperature. The gas in equilibrium with the liquid have at a given temperature a vapour pressure and pumping on the gas will cool the liquid if the system is isolated. The lowest attainable temperature is obtained when the pressure is so low that you are unable to remove a noticeable amount of the fluid (amount = pumping capacity × pressure). If the latent heat of evaporation is L (in joule per mole) the equilibrium pressure will tend to

$$\mathbf{P \;\; \alpha \; exp(-L/RT)}$$

A sketch of a cryogenic apparatus



pumping line

gas injection line

Initial cold source
Gas to liquid

Enthalpy exchange
along the two lines

Joule Thomson
Adiabatic expansion

Cold vapor
Liquid

Final
temperature

4) Let's give the properties and obtainable temperature for a few cryogenic compounds

Nitrogen is liquid at 1bar pressure and 77 K. Its latent heat of evaporation is 5600 J/mole. By pumping on a bath of liquid nitrogen one could obtain 66K, which is the nitrogen solidifying temperature.

Neon is liquid at 1bar and a temperature 27.1 K. The latent heat of vaporisation is 1714 J/mole.

It is a substitute to hydrogen, considered nowadays as too dangerous…

Dewar, in the early 1900 presented experiments with liquid hydrogen to an assembly of scientist at London University!!

Helium 4 with a pressure of 1bar is liquid at a temperature of 4.2K. The latent heat of vaporisation is 82 J/mole (1 liter of liquid He_4 gives 750 liter of gas and hold a power of 0.7 W in the bath during one hour)

Pumping on He decreases easily the temperature to about 1.1 K.

T = 1.5 K P = 4.7 mBar

T = 1.1 K P = 0.38 mBar

But to go much below a constriction

* Limiting the superfluid film is needed. The superfilm creeps along the pumping tube and gives *a heat rate of 1 mW* for a tube with smooth circumference or 1cm !!

* The practical limit is 0.7 K, P = 3×10^{-3} mBar

Helium 3 with a pressure of 1 bar is liquid at 3.25 K

The latent heat of evaporation is 20 J/mole

When pumped it goes easily to low temperature

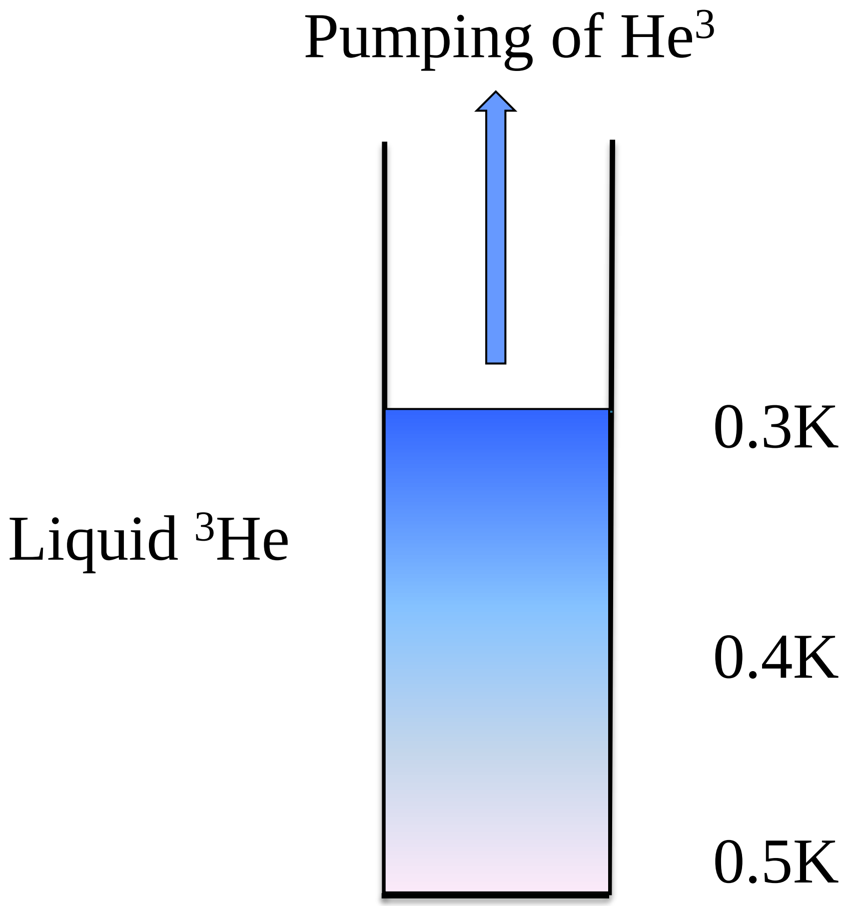
T = 0.4 K P = 2.9×10^{-2} mBar

The limit is around T = 0.2 K with P = 1.6×10^{-5}mBar

* It does not suffer from the presence of superfluidity .

* Notice that He_3 liquid has a very low heat conductivity and no more bubbling below 0.5 K. To homogenize the temperature one needs metallic exchangers between the bottom and surface.

Note that He^3 liquid have a very low heat conductivity and nearly no more bubbling below 0.5K .To homogenize the temperature one needs *metallic exchangers between the bottom and surface* otherwise the situation below will appears with a long time constant.



Pumping of He^3

Liquid ^{3}He

0.3K

0.4K

0.5K

Short note on the origin of the two He isotopes

He_4 is very volatile and do not stay in the atmosphere. But the alpha particle coming from Uranium and Thorium in the earth crust mostly stays and the He gas accumulate within the fossil gas. When the gas is extracted and liquefied, the He_4 is left free and is taken as a by product. In the sixties, it was transported as liquid by plane from for example Texas gas field to Europe.

He_3 is a by product of H bomb. In a H bomb, H_3 is compressed and heated (by an external A bomb) and this produce a (partial) fusion.

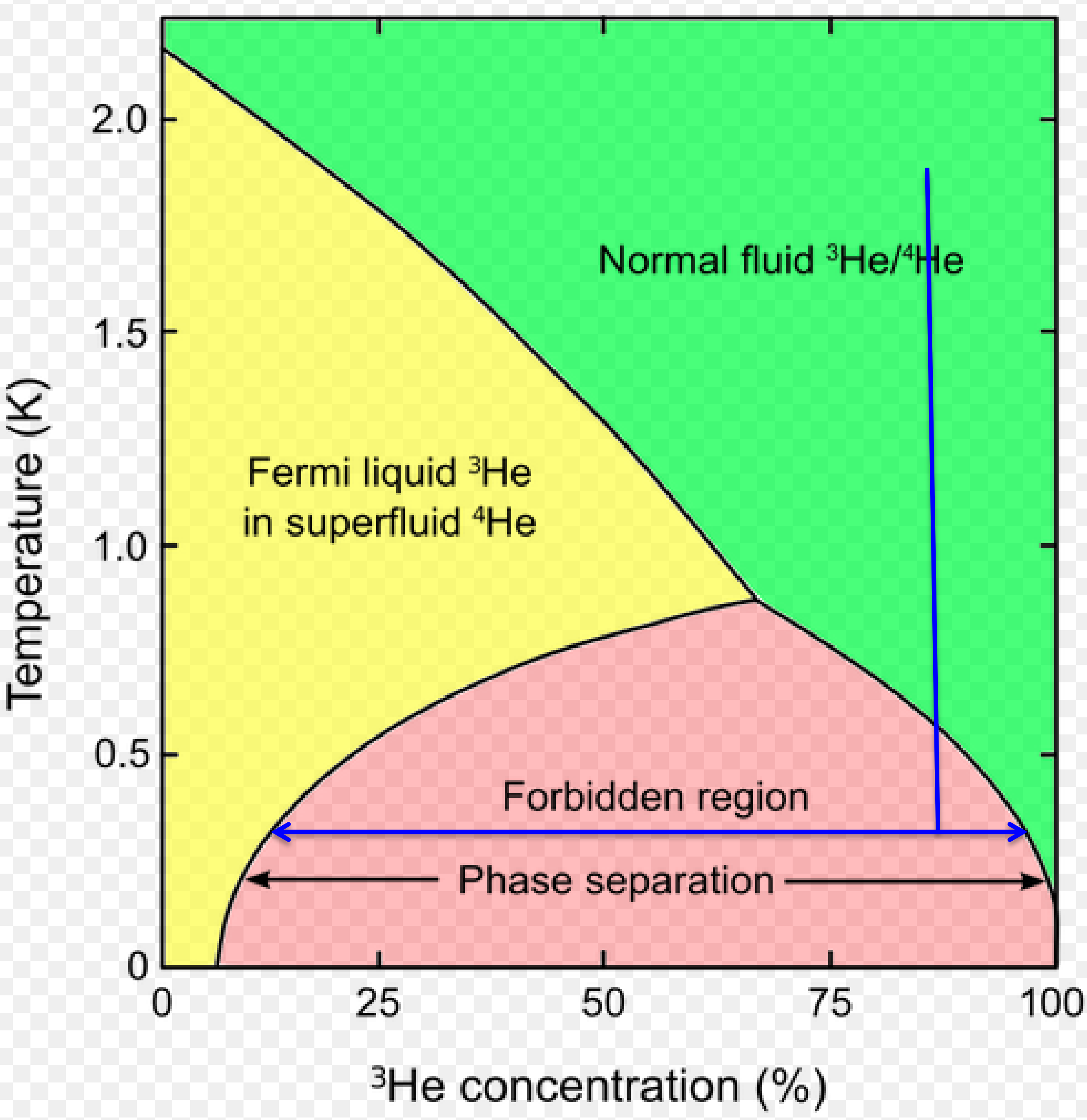
H_3 with a ½ life of 12.3 years decays in He_3. It is why US and Soviet Union where the two first to study He_3 properties.

To be known, the crust of the moon contains He_3 and for future fusion with this isotope the moon could be a competitive source of fuel !

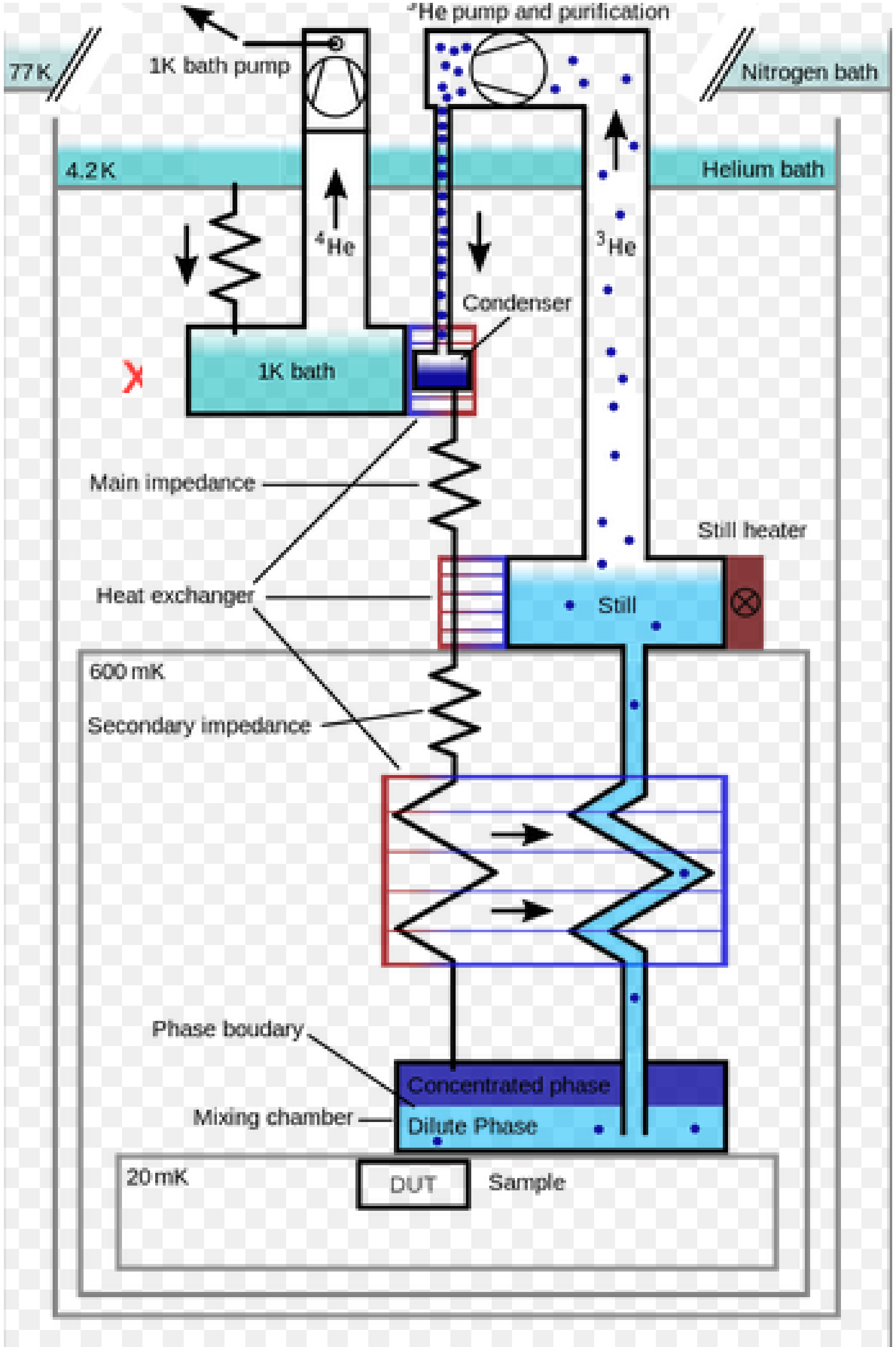
5) Dilution of liquid He_3 in liquid He_4.

The good “newcomer” did come with the study of mixture of liquid He_3 and He_4 at low temperature . Both are liquid and the mixture offers a peculiar behaviour, see the fig below. At very low temperature the mixture separate in 2 phases, one nearly pure He_3, and the other is a dilute phase with 6.3% He_3 in He_4 at 0K. The rich part with a lower density is floating above the dilute one. Before this discovery, it was supposed that the solubility will decrease exponentially, as the pressure for a liquid. But what was found, and later explained was that the solubility at 0K is not decreasing exponentially but tends to a constant .The two liquids are Fermi type with a heat capacity proportional to T which give a heat of dilution decreasing as T^2

See later the exact formulas;


Normal fluid ^{3}He/^{4}He
Fermi liquid ^{3}He
in superfluid ^{4}He
Forbidden region
Phase separation
Temperature (K)
2.0
1.5
1.0
0.5
0
0
25
50
75
100
^{3}He concentration (%)

All theses facts, explainable by the nature of the two fluids has promoted the technic, with systems able to work continuously easily down to 10mK, and with more dedicated exchangers to the record of 2.3mK (G.Frossati, CRTBT Grenoble with 2 mercury secondary pumps *J. Phys. (Paris)* **39 ,** 1578 (1978)) and later to 2mK (Yu.M.Bunkov et al at Lancaster University *J.Low Temp Physics* Vol 83 Nos 5/6 1991) .This was a great change to the previous production of very low temperature, done in one shot by electronic adiabatic demagnetisation processes.



77K

4.2K

1.4K

0.7 - 0.8 K 1%

continuous exchanger ends
T=100mK

Discret heat exchanger

Lowest temperature
6 - 12mK

Let’s now give more details on the processes which happen in a dilution fridge. In a *mixing chamber* at low temperature a rich He_3 phase *is floating* on the dilute phase with 6.3%. (at very low temperature) If He_3 is stirred from the dilute phase a dissolution (*equivalent to an evaporation, but in a media, the superfluid He_4, and not in vacuum*) give a production of cold . Either the phase will cool further, or it will be compensated by the heat coming by external sources and stay at its equilibrium low temperature.

The stirring of He_3 is done at a much higher temperature, in *a still* which is heated around 0.7- 0.8 K. and pumped. The heating of the still , either by the incoming gas or/and by an electrical heating, is **essential**. It give the circulation rate by insuring that the pressure of He_3 is not too low. The pumped gas is essentially He_3 (90-95% of He_3) because at 0.8K the partial pressure of He_4 is still very low and that a constriction limit the amount of He_4 . In the tubing from the mixing chamber to the still the concentration of He_3 decrease from 6.3% to a bout 1% with the still at 0.8K To maintain the equilibrium along the column the stirred He_3 in the still is compensated by the same amount of He3 which is transferred in the dilute phase.

This is equivalent to the pumping of a liquid but with an “evaporation“ pressure not decreasing exponentially.

Along the pumping tubes, because the enthalpy of the dilute He_3 is much bigger than the enthalpy of pure He_3 the incoming He_3 is cooled down and there is still possibility to thermalize for example all measuring cables coming from the hot part (4.2K) of the cryostat down to the lowest temperature. The better the exchange (number and quality of the exchanger), the lower the attainable temperature.

Note that a film of He_4 is present everywhere in the system, both on the concentrated side and in the dilute one. Note also that in the concentrated side bubbles of dilute mixture are produced and may degrade the final temperature.

Note also that being at very low temperature any exchange of heat, inside exchangers or between the experiment and the liquid in the mixing chamber needs very large surfaces and hence surfaces with sintered fine silver powder.

More quantitative

In a dilution chamber the enthalpy of the pure (concentrate, c) He_3 writes

$$Hc = 12T^2 \text{ joule/mole}$$

And for the dilute (d)

$$Hd = 96\ T^2 \text{ joule/mole}$$

If the exchangers are perfects, (could be the case at elevated temperature), the incoming temperature is that of the outcoming fluid

One get then the power of the apparatus as

dQ/dt= $(96 - 12)\ T^2$joule/(mole.s) = **84 T^2joule/(mole.s)**

*Note that **the circulation flux** is only given by the overall power applied to the still, and not on the size of the pump.*

The size of the pump gives the temperature of the still.

How a 1K pot works

It consists of a pumped reservoir connected by an impedance (adjustable or not) to the main bath of He_4.There is some external heat arriving on the pot (He_3 gas, cables anchored on it). If this heat is bigger than the flux of liquid He_4, given by the impedance and a pressure difference of nearly 1bar, the pot is dry and at a temperature normally not suitable to condense He_3.It should not be the case. If on the contrary the heat is less than what the supply gives, then the pot starts to fill until the level in the pumping tube gives a heat coming from 4.2K which exactly compensates the incoming flux. The temperature of the pot is then given by the flux divided by the capacity of the pump.

This temperature is **constant**. At the beginning of the filling of the pot, the temperature is, slightly lower and rises until the equilibrium is obtained. Oxford dilutions have a special way, with two lines and one with a valve which allows a quick filling of a large 1K pot.

NB: The initial design was known to produce vibrating noise du to cavitation of the liquid He entering the pot.The problem was solved by cooling the incoming liquid all along the gradian from 4.2K to the lowest temperature.

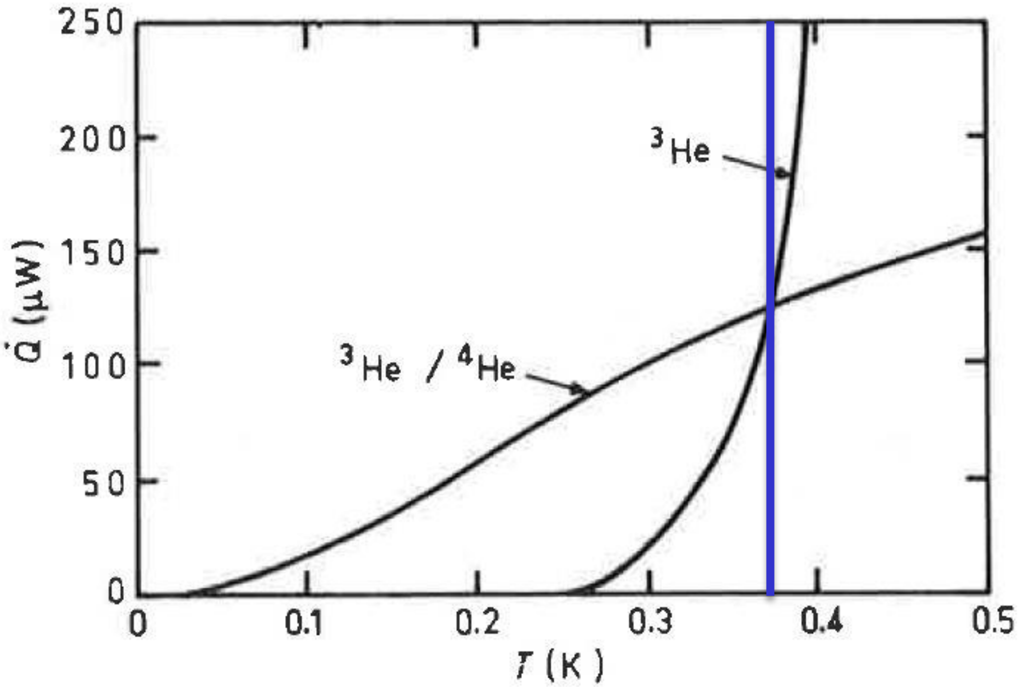
Tricks

A usefull test : the one shot process

Suppose that you are not satisfied by the obtained temperature of you fridge and you believe that you should add more exchangers. Is it usefull? Maybe you do not correctly anchor the cables going down. Do that first, it is by all means valuable to correctly anchor them rather than bying an expensive more powerful machine.

The oneshot essay is done with the same temperature of the still, with a extra heating which replace the one du to the incoming He. Because no more ^{3}He is send to the mixing chamber, the only heat arriving is the cabling, radiating heat and everything coming from the experiment. If it cools down, adding exchanger will help the system. If not, adding exchangers will not reduce the temperature.

Comparison between ^{3}He fridge and dilution ^{3}He-^{4}He refrigerator



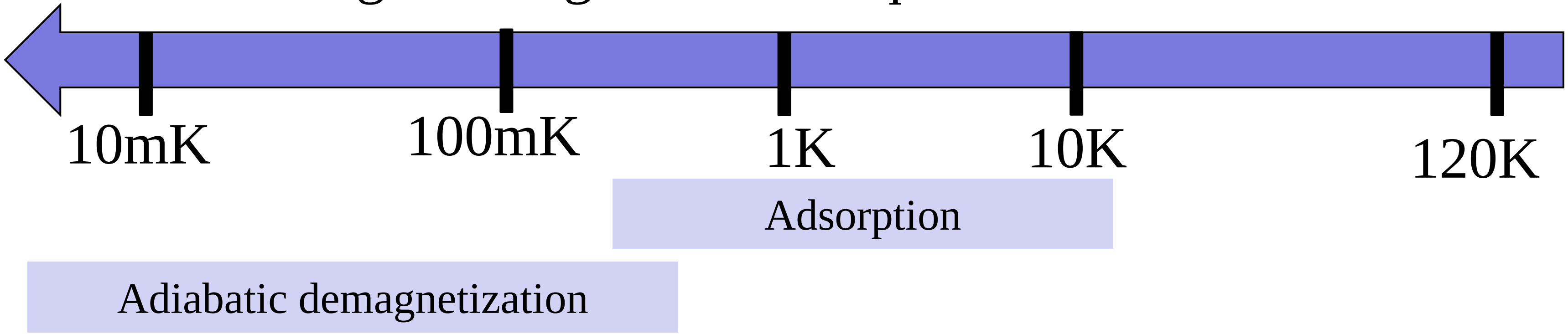
^{3}He fridge ⇒ $P_V \sim \exp[-L_{3(0)} / RT]$ *Clapeyron*

$\dot{Q} = \dot{n}_3 L_{3(0)}$ avec $\dot{n}_3 \sim P_V$

Dilution ^{3}He ^{4}He ⇒ $\dot{Q} \sim \dot{n}_3 T_{BM}^{\ 2}$

$\dot{n}_3$ fixed by the still temperature when the mixing chamber temperature < 100mK

Cooling with regeneration sequence



10mK

100mK

1K

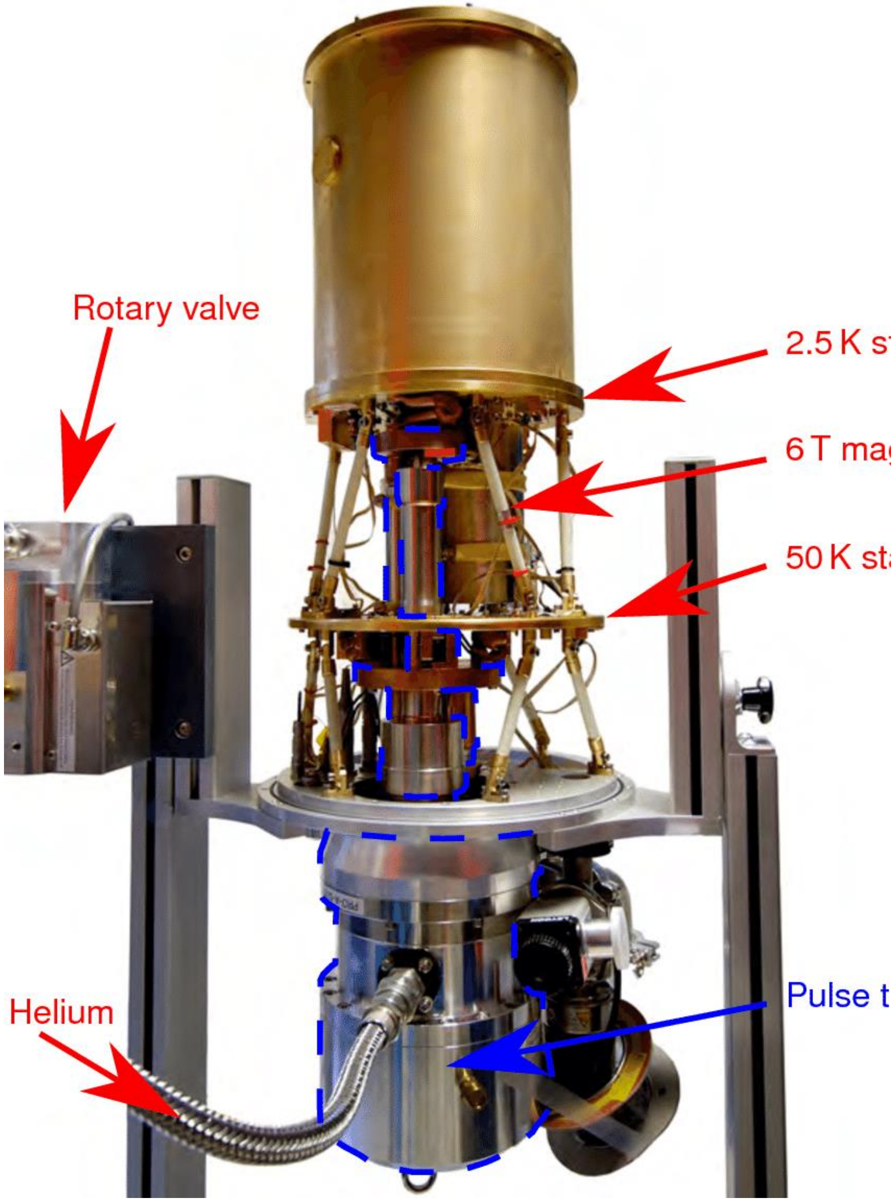
10K

120K

Adsorption

Adiabatic demagnetization

Adiabatic demagnetization and anomalous heat capacities

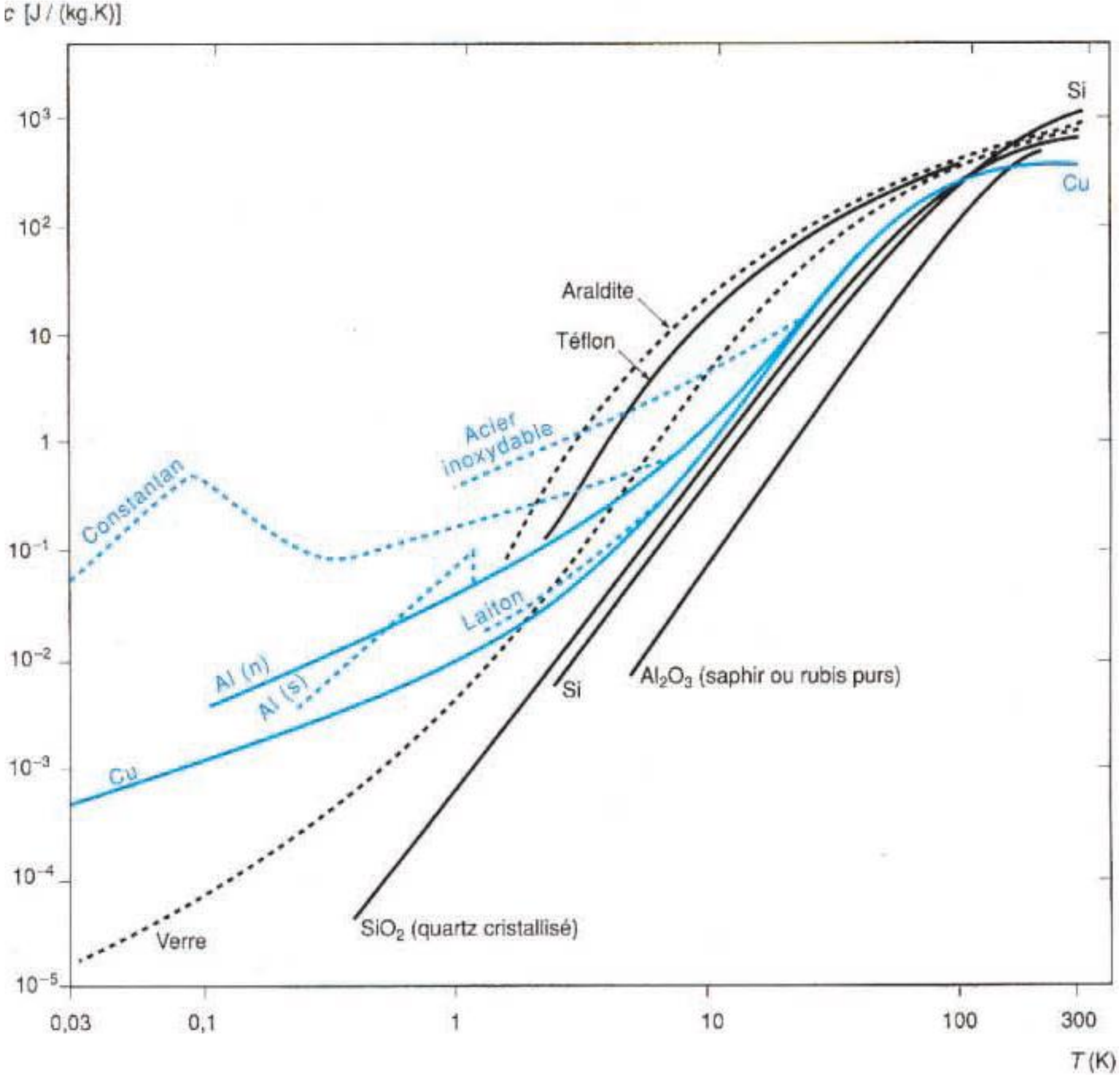


Heat capacities

For T< 100 K, C drops quickly

- For metals $C \propto T$
  electron only
  below 30 K

- For insulators $C \propto T^3$
  phonons only
  much below 100 K



Anomalous heat capacities

“Normal” heat capacities C at low temperature as presented by Jean-Pierre and Manuel are:

First phonons, elastics vibrations existing everywhere.

The associated heat capacity is

$$C_{ph} \alpha T^3$$

Fermi fluids (normal metals, liquid He_3, concentrated or dilute)

$$C_F \alpha T$$

And for a superconducting metal, C_F a exp(-2D/T) because the part of normal component (upper level) decreases exponentially.

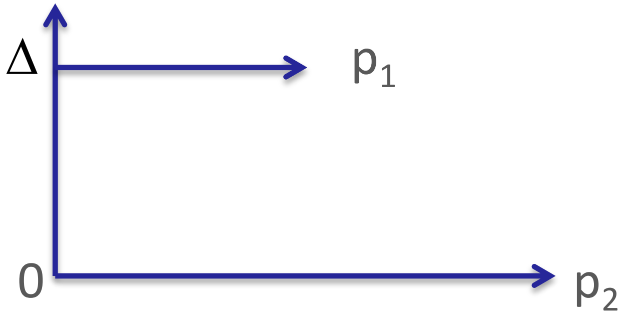
Amorphous Material $C_A \alpha T^2$

and then tend to $C_A \alpha T$

Schottky heat capacity

Suppose that you deal with a system with two level separated by Δ.

The ratio of the upper (p_1) level population to the lower (p_2) is given by the Boltzmann exponential

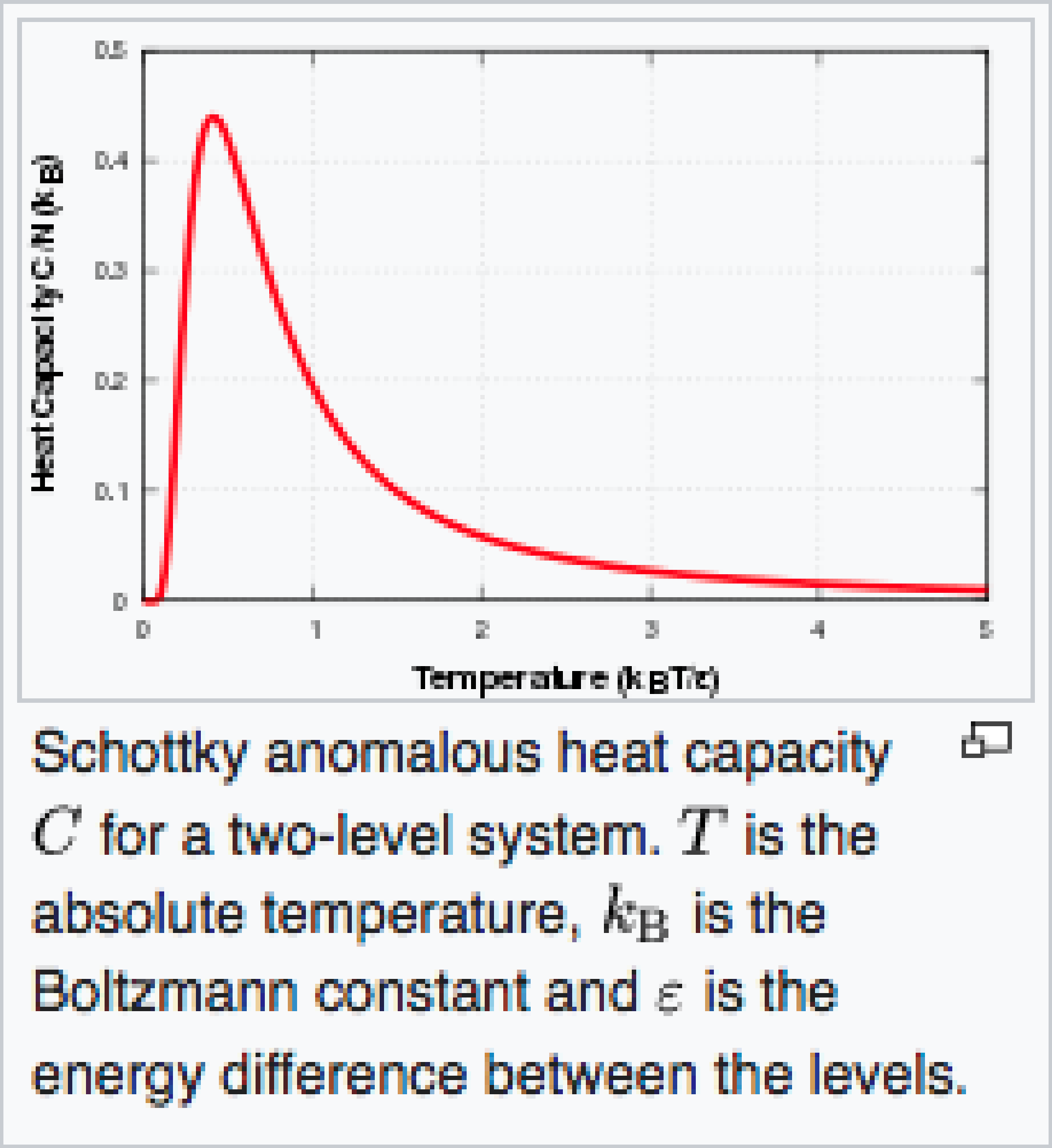


$$\frac{p_1}{p_2} = e^{\left(-\frac{\Delta}{kT}\right)}$$

The energy U of the system is 0 + $p_1 * \Delta$. The specific heat is dU/dT. With a simple calculation one get:

$$\boxed{C_{\text{Schottky}} = R\left(\frac{\Delta}{T}\right)^2 \frac{e^{\Delta/T}}{[1+e^{\Delta/T}]^2}}$$

Schottky heat capacity



Schottky anomalous heat capacity C for a two-level system. T is the absolute temperature, k_{B} is the Boltzmann constant and ε is the energy difference between the levels.

Schottky heat capacity

Cmax @ $kT \approx 0.417\Delta$

and if $kT \gg \Delta$ $C = k(\Delta/kT)^2$

Order of magnitude $1\text{MHz} = 4.79 \times 10^{-5}\text{K}$

$1\text{K} = 20\text{GHz}$

Unless the others heat capacities, this is bigger the lower the temperature.

This type of situation arose:

- If there are nuclear quadrupole interaction in the sample
- If nuclear spins like copper (or silver) are in a magnetic field.

Quadrupole interaction

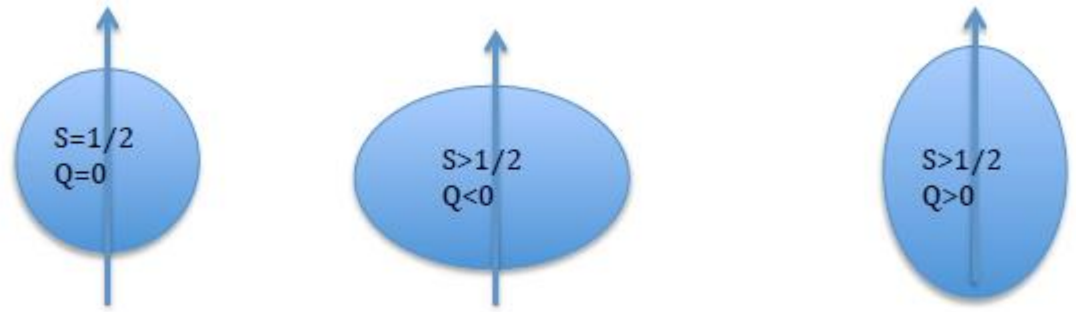
Mixture of Z proton and A neutron, they are bounded by the strong force. The proton and the neutron have both a spin ½. They will combine in such a way that the total spin is much less than (Z+A)*1/2.

A few examples (see Varian table with the refrences)

Al^{27} S = 5/2 Q = 0,149

Bi^{209} S = 9/2 Q = -0,4

Beside a spin the nucleus have a quadrupolar electric moment Q. This is due to the fact that except for a spin 1/2 the distribution of the electric charge is not spherical.



The arrow is the quantized axis along with the quadrupole is aligned. It will play a great role in the spectrum of energy of nuclei in solid and sometime as possible spurious heat capacity.

Quadrupole interaction

This moment feels the derivative of the electric field produced by the surrounding ions and if it is not cubic environment it develops energy levels specific to the quadrupolar moment and the derivative of the electric field at the nucleus position.

The effect of theses growing heat capacities depends on the coupling between the nuclei and the lattice. Three main situations

1) the coupling is strong and will prevent the use of the sample as bolometer,

2) the coupling is very weak and the anomalous heat will not be seen,

3) intermediate situation, in which the long decay will appears together with a smaller signal.

Some examples are shown below.

The first is Al nuclei in sapphire

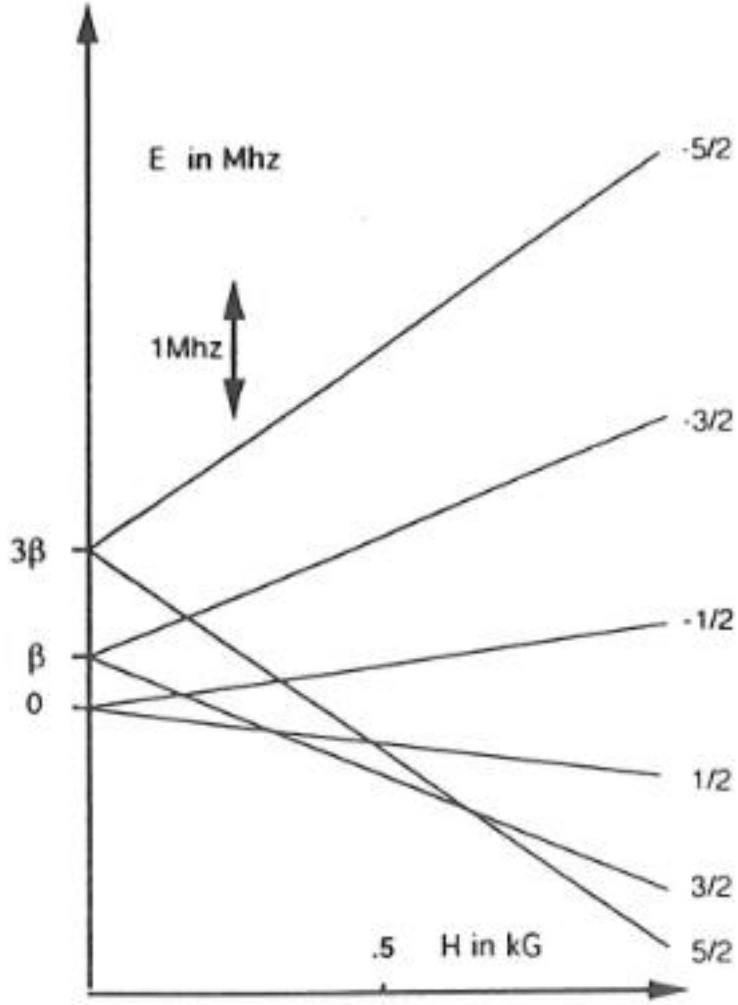


Fig. 1. Energy levels of Al nuclei in a magnetic field along the *c*-axis.

Quadrupole interaction

With the above example the phonon heat capacity cross the quadrupolar one at 250mK and the ratio decrease with a ratio T^5. It have been observed with sapphire at 100mK (C. Enss and al)

We present possible couplings between the nuclei and the lattice depending on the magnetic field applied on the cristal.

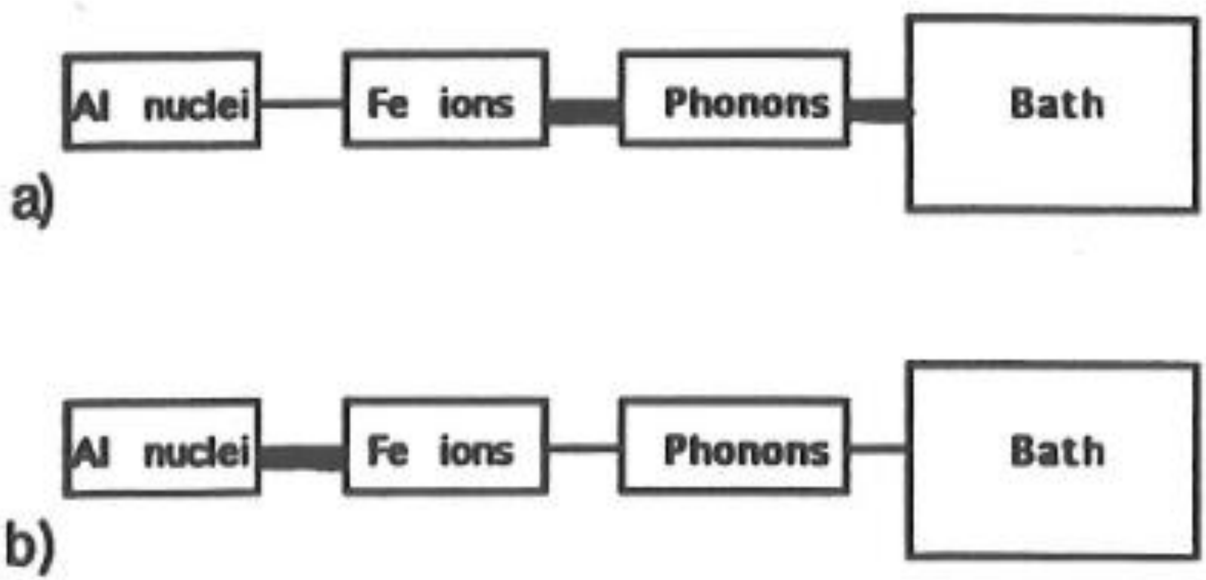
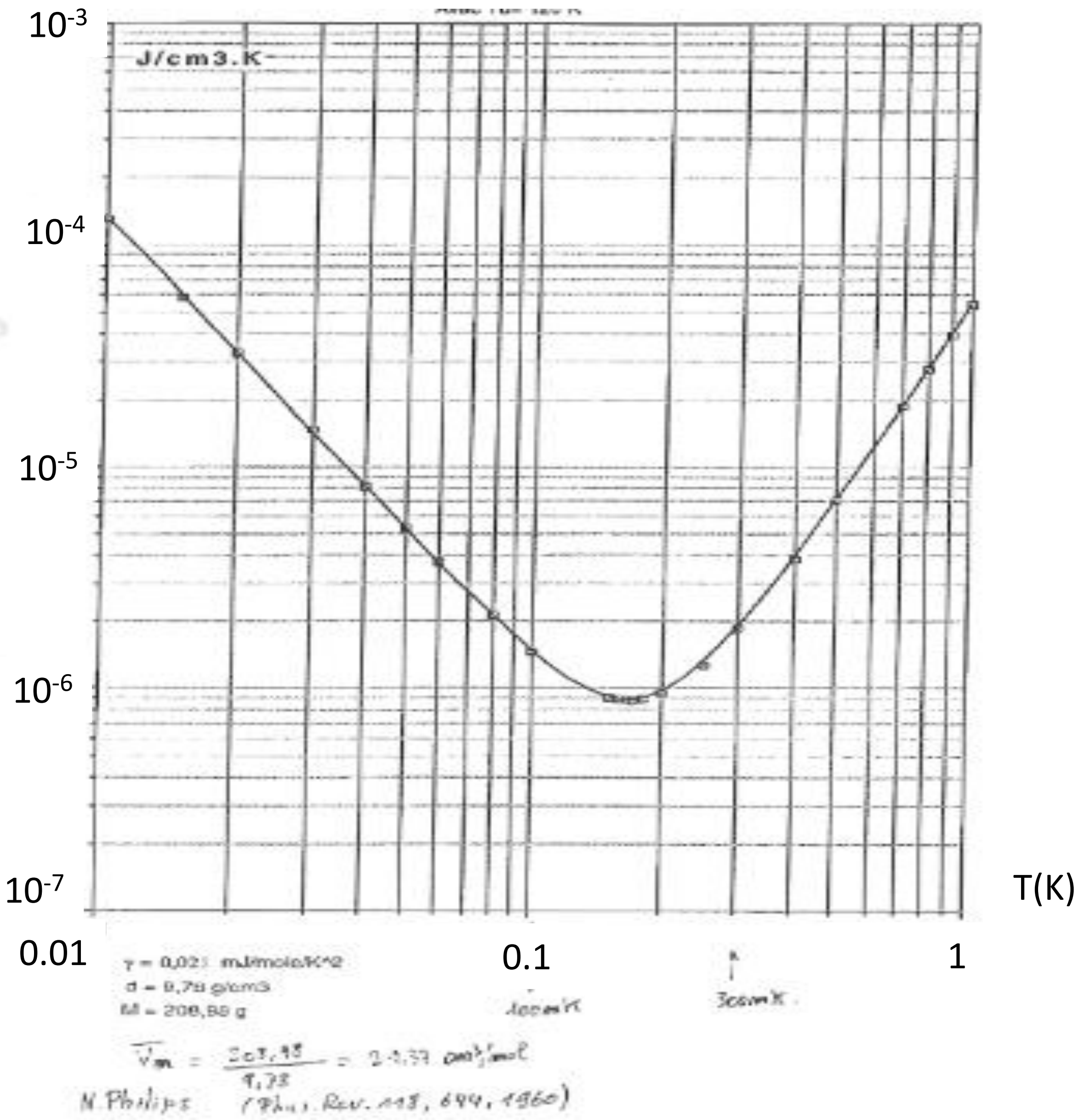


Fig. 2. Coupling between Al nuclei, Fe ions, phonons of the crystal and the main bath. (a) Applied magnetic field, (b) zero field. The strength of the coupling is visualized by the thickness of the line.

An other example is shown below with metallic bismuth, used as target in some light bolometers



γ = 0,021 mJ/mole/K^2
d = 9,78 g/cm3
M = 208,98 g

$\overline{V_m} = \frac{208{,}98}{9{,}78} = 21{,}37$ cm³/mol

N. Philips (Phys. Rev. 118, 644, 1960)

Hydrogen ortho para state

The hydrogen case. Ortho para situation

The molecule H2 contains two hydrogens, that is two proton nucleus with a spin ½. There are two states, one with the spins parallele (named ortho, but in fact paramagnetic!) the other with the spin antiparallele, name para (non magnetic).

Because they are fermions, the quantum mechanic (which apply even at room temperature in this case !!) make them with different rotation state J the ortho having J = 1 and the para J = 0

The situation is then **the ortho is in a quantum state 174K above the para state**. At room temperature there is 3 times more ortho than para and lowering the temperature the ortho should relaxe to the para state! The danger is if it does not disappears, it left an enormous latent heat which could eventually vaporized the liquid. When the process of liquefying is done it is essential to insure that the conversion is done. Some catalyst is needed as iron oxyde. The high magnetic field breaks the undisability of the two proton.

For cryogenist the problem arose if some hydrogen is embedded in a metal like copper. The relaxation is slow and may prevent for a long time the copper to be at the low temperature. It is the essential to choose copper with as low as possible hydrogen…

For your knowledge, the water have also the same situation….

Hydrogen ortho para state

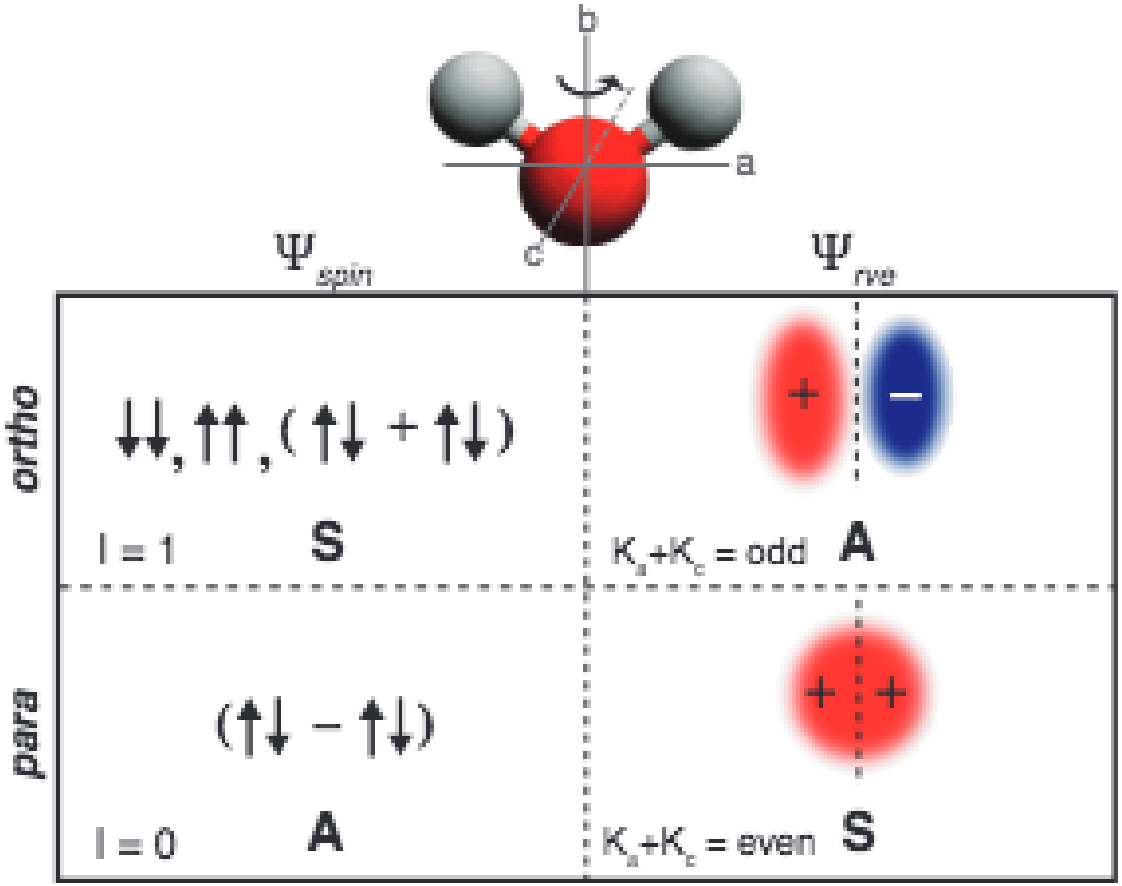
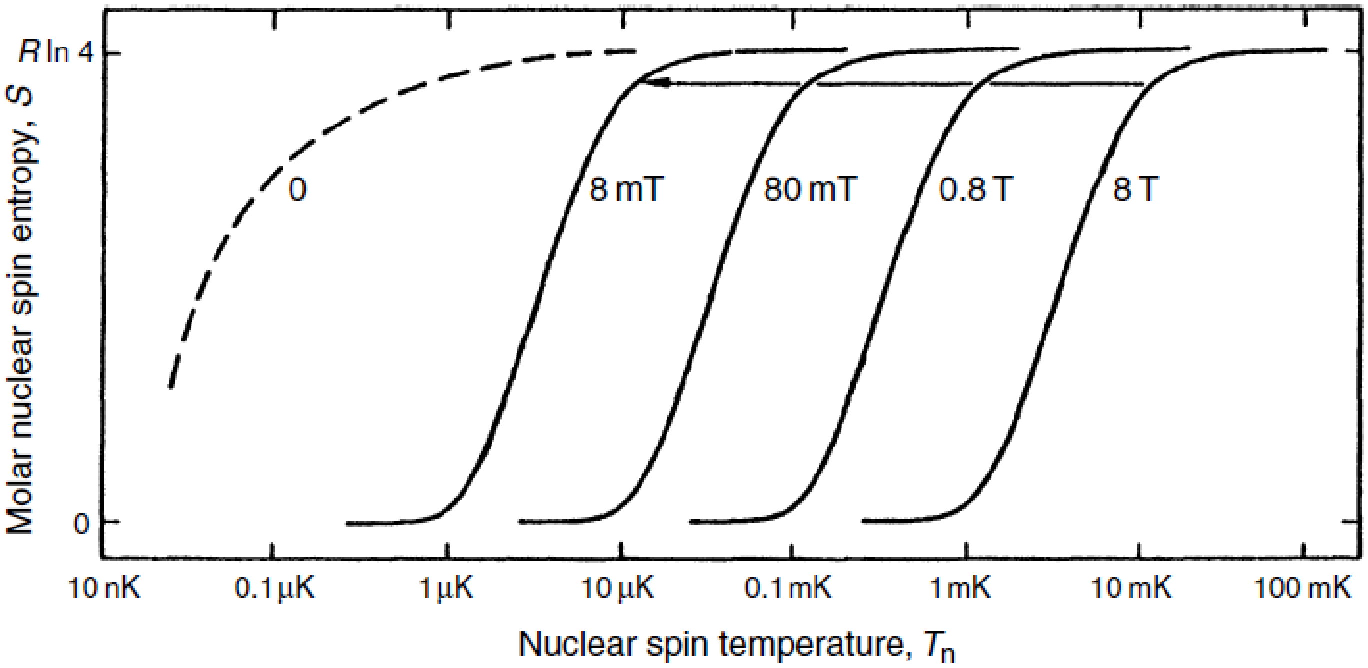


Figure 1: Water spin isomers. The necessity for an overall antisymmetric wavefunction requires that the symmetric (S) spin combinations Ψ_{spin} of *ortho* water combine with an antisymmetric (A) rovibronic eigenstate Ψ_{rve}, and *vice versa* for *para* water.

Copper at low temperature and high magnetic field



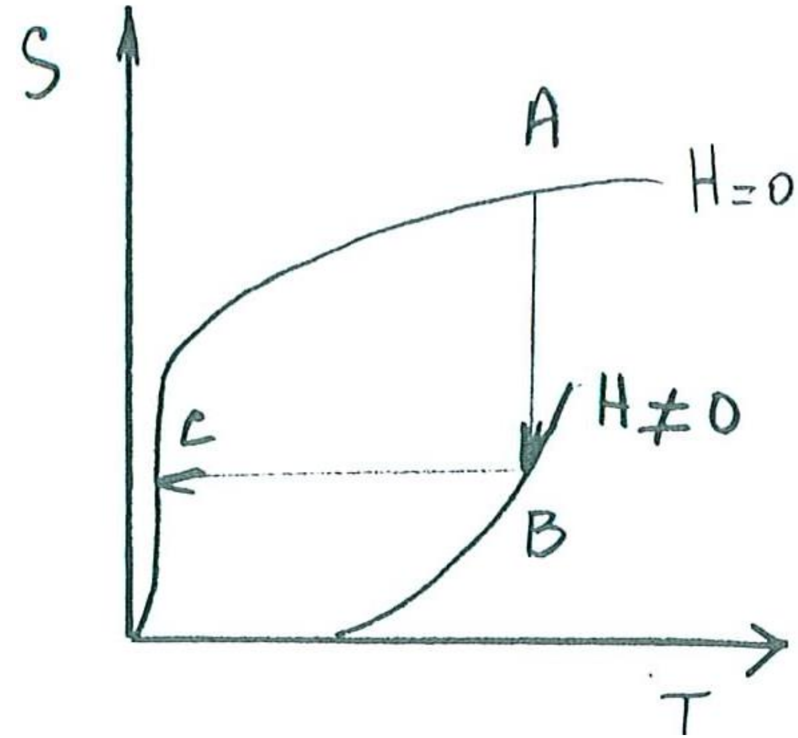
The copper has two isotopes Cu^{63} (69%) and Cu^{65} (31%) their NMR frequencies for 1T are respectively 11.28 MHz and 12.09 MHz, consequently the entropy of 1 mol of copper in 8 T and 10 mK is shown in the above figure.

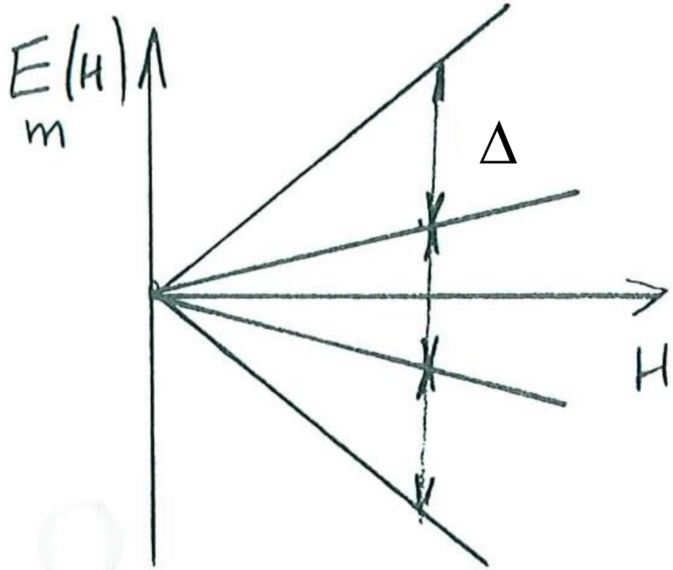
From this, you can deduce that the heat releases from below 0.5 K to 10 mK is 0.91 J/mol !!! That means a long cooling time for only 63 g of copper.

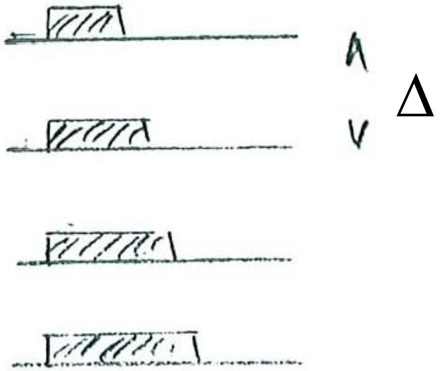
To overcome this situation a simple solution is to replace the copper by silver which has two isotopes Ag^{107} (51%) and Ag^{109} (49%), their NMR frequencies for 1T are 1.72 MHz and 1.98 MHz.

Since the heat capacities vary has the square of the frequency, the replacement of copper by **silver will reduce the heat release roughly by a factor 100**!

Adiabatic demagnetization







Adiabatic demagnetization

When a magnetic field is applied on a system with electronic magnetic moment the orientation of the moment reduces the entropy. $A \rightarrow B$

If the system is isolated, the temperature from B to C by reducing the magnetic field.

One could give more detail to explain the limitation. The electronic moment from spin I placed the magnetic field H gives 2I+1 level separated by $\boldsymbol{\Delta = g.\beta.H}$

g : gyromagnetic moment

β : nuclear magnetic moment

At equilibrium temperature T, the ratio of adjacent population is given by the Boltzmann ratio $\boldsymbol{\rho = \exp(-\Delta/kT)}$**.**

If we reduce H on the isolated system, the population of the sub-level is constant.

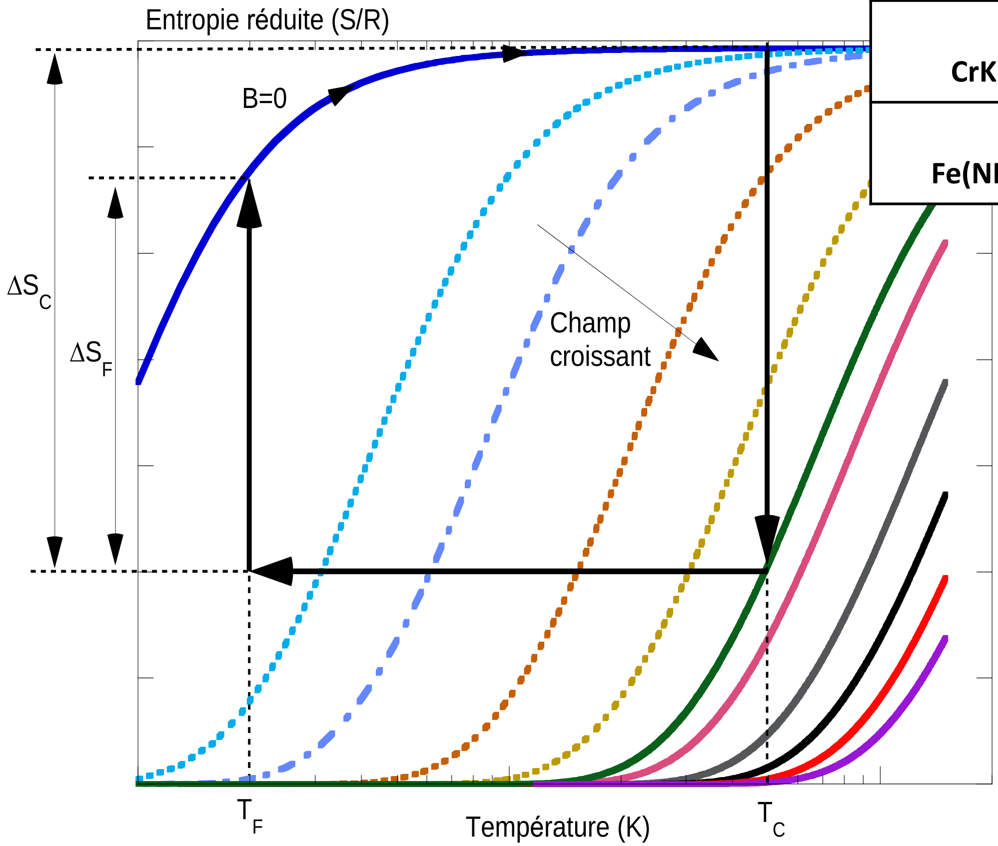
The result is $H/T = cst$ which gives impression that the system will reach low temperature.

This is of course wrong because each spin sees additional average field H_{loc} produces by the over spins. H_{loc} depends of the concentration of the paramagnetic ions and their interactions in the solid.

The smaller H_{loc}, the lower the temperature limit will be of the order of $\boldsymbol{kT_{limit} = g.\beta.H_{loc}}$

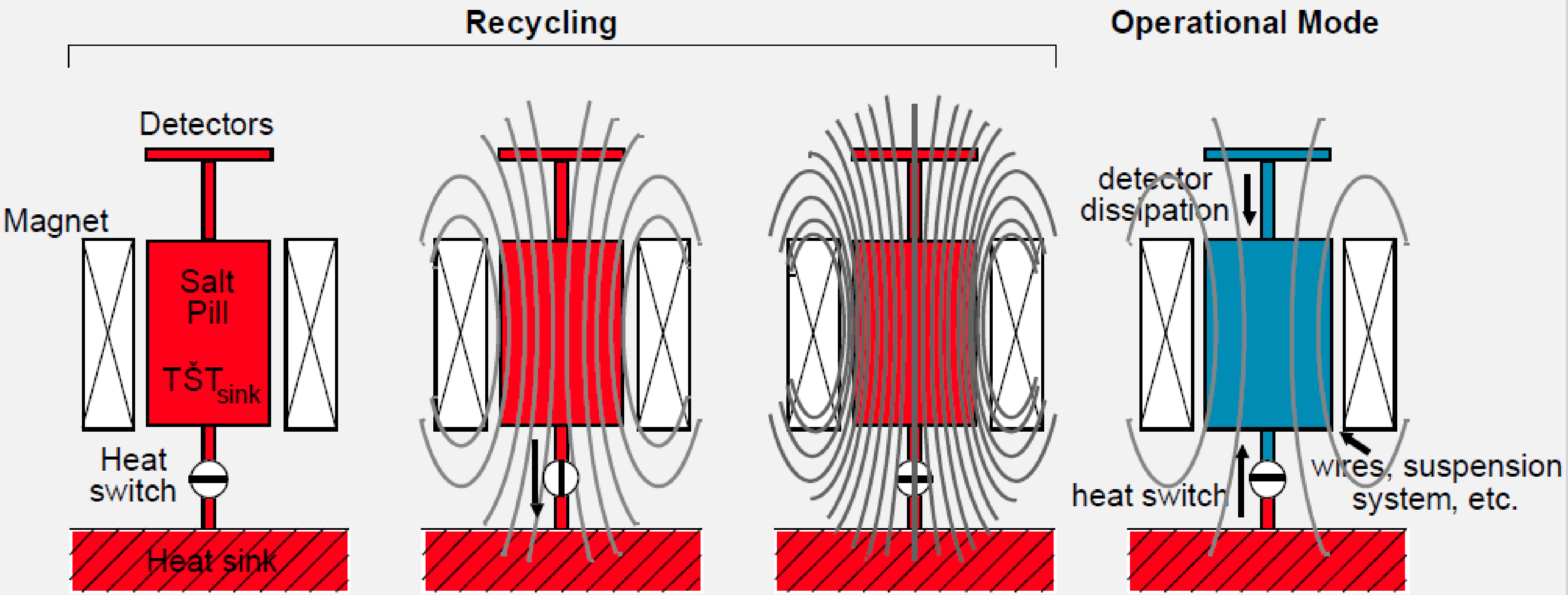
Adiabatic demagnetization

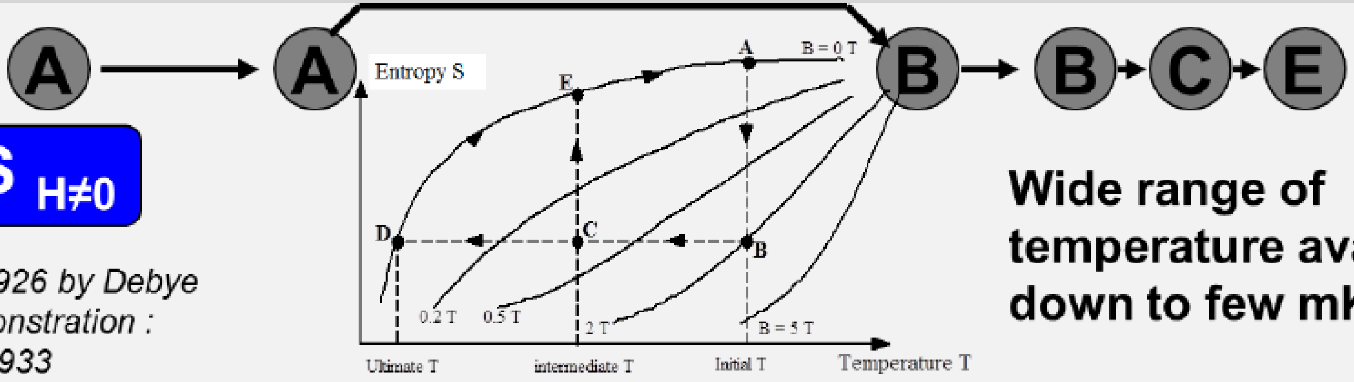
Sel	J	$T_{Néel}$ (mK)	T_{Max} (°C)	M (g/mole)	Densité ($g.cm^{-3}$)
CCA $CsCr(SO_4)_2, 12H_2O$	1.5	10	116	593	2.06
CMN $Ce_2Mg_3(NO_3)_{12}, 24\ H_2O$	0.5	1.5		1530	2.1
CPA $CrK(SO_4)_2, 12H_2O$	1.5	17	89	499	1.83
FAA $Fe(NH_4)(SO_4)_2, 6H_2O$	2.5	26	39	482	1.71



T.I. fascicule

Adiabatic demagnetization





$S_{H=0} > S_{H \neq 0}$

First proposed in 1926 by Debye
First practical demonstration :
(De Haas et al.) : 1933

Wide range of temperature available down to few mK

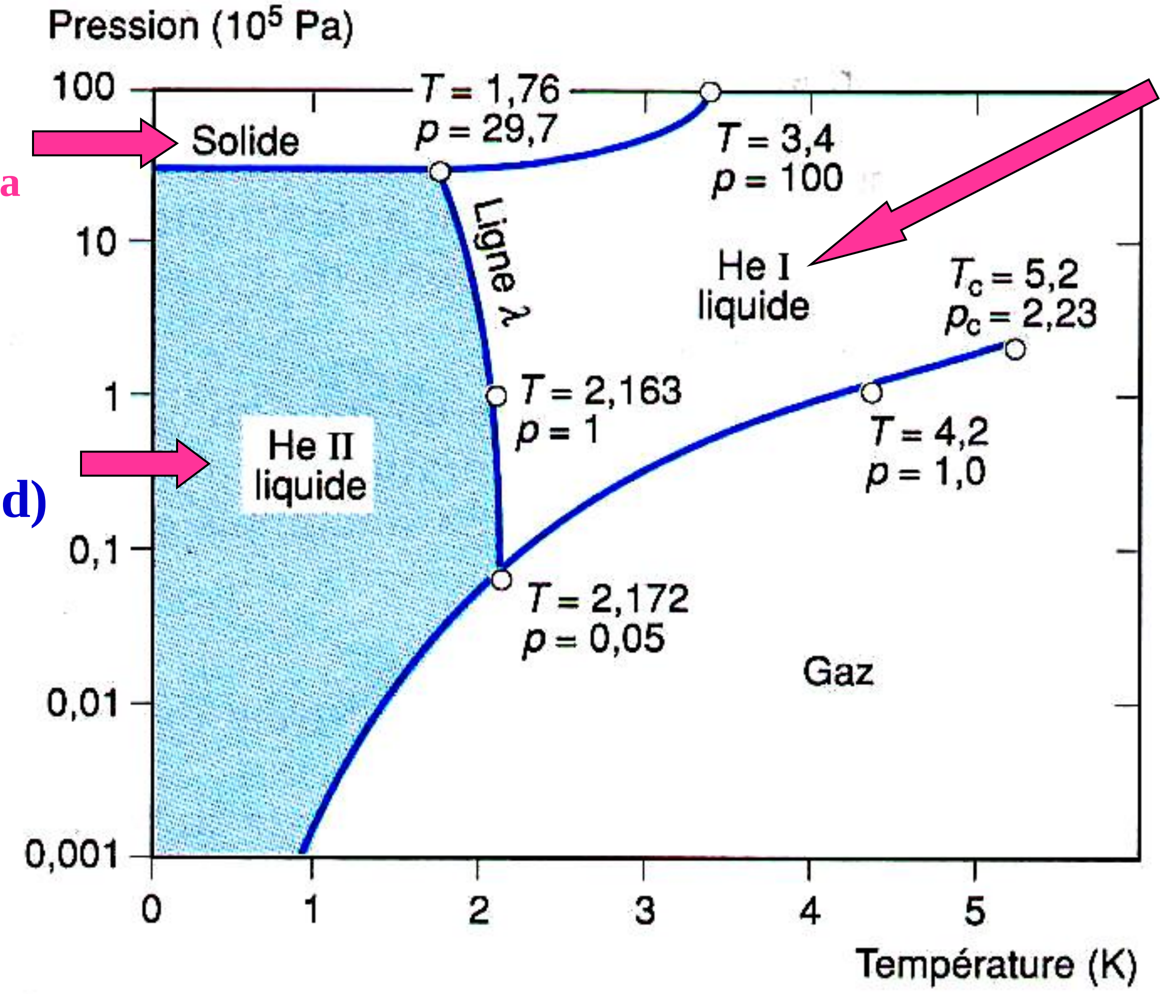
Adsorption He coolers

Chase Research Cryogenics

^{4}He fridge

Gas Gap Thermal Switch

Helium - ^{4}He



Solid

p>2,9 MPa

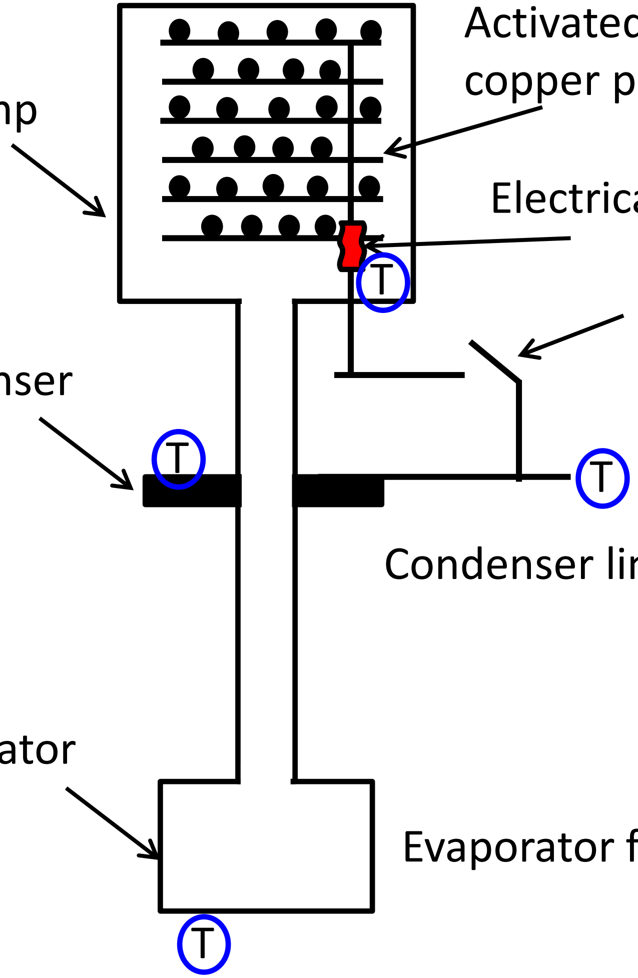
He II (superfluid)

He I (normal)

Adsorption He cooler

Filling pressure at room temperature p_m : a few dozen bars

1000 à 1500 m^2/gr



Cryopump

Activated carbon glued on copper plates

Electrical heater

Thermal swith to connect/disconnect the cryopump to the cryocoller cold head

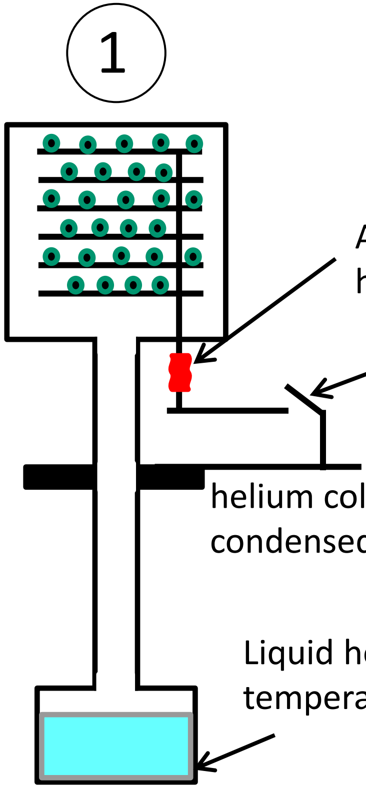
Condenser

Condenser linked to the cold head à $T_f \leq 4K$

Evaporator

Evaporator filling with liquid helium

Adsorption He coolers
Cycling

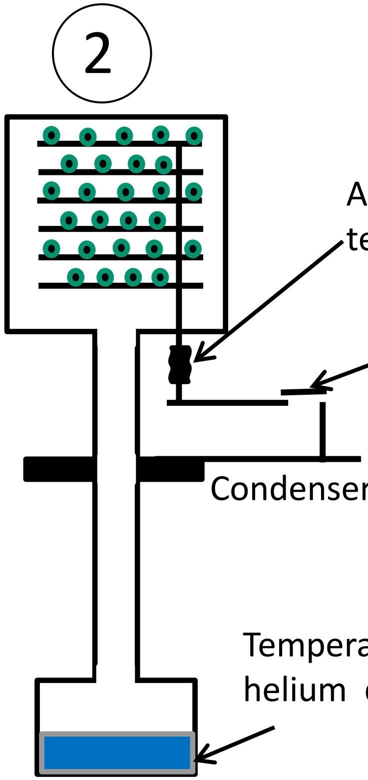


Activated carbon heating at $T_c \geq 20K$

Heat switch open

helium cold vapors are condensed at T_f (2.5K à 4K)

Liquid helium at T_L : temperature close to T_f

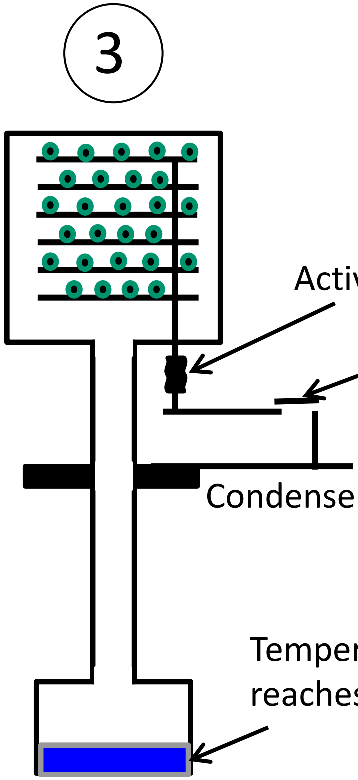


Activated carbon temperature decreases

Heat switch closed

Condenser at T_f (2.5K à 4K)

Temperature of liquid helium decreases



Activated carbon temperature close to T_f

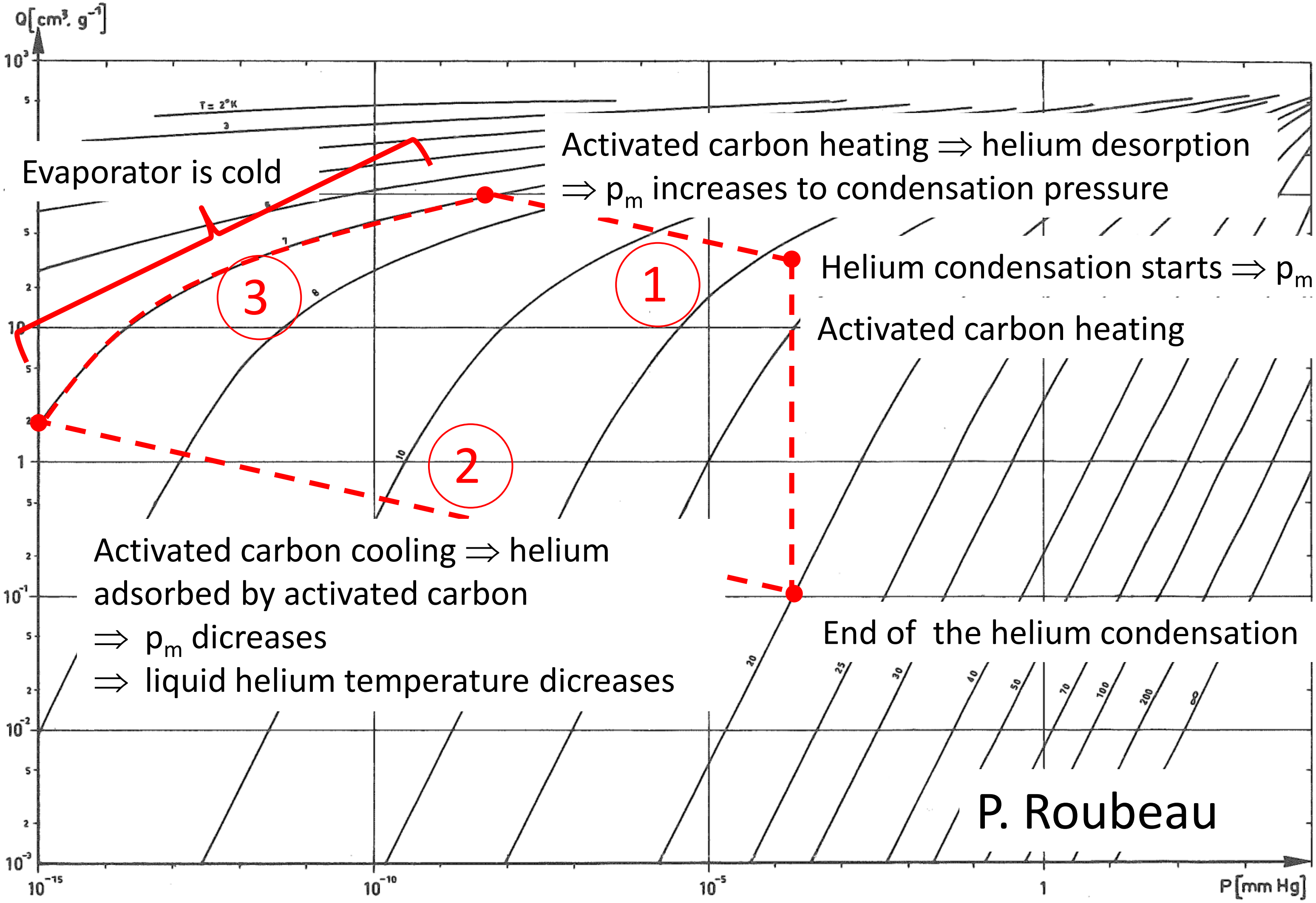
Heat switch closed

Condenser at T_f (2.5K à 4K)

Temperature of liquid helium reaches the temperature limit

Adsorption He cooler

Adsorption He cooler sequences



Evaporator is cold

Activated carbon heating ⇒ helium desorption

⇒ p_m increases to condensation pressure

Helium condensation starts ⇒ $p_m \approx$ cste

Activated carbon heating

End of the helium condensation

Activated carbon cooling ⇒ helium adsorbed by activated carbon

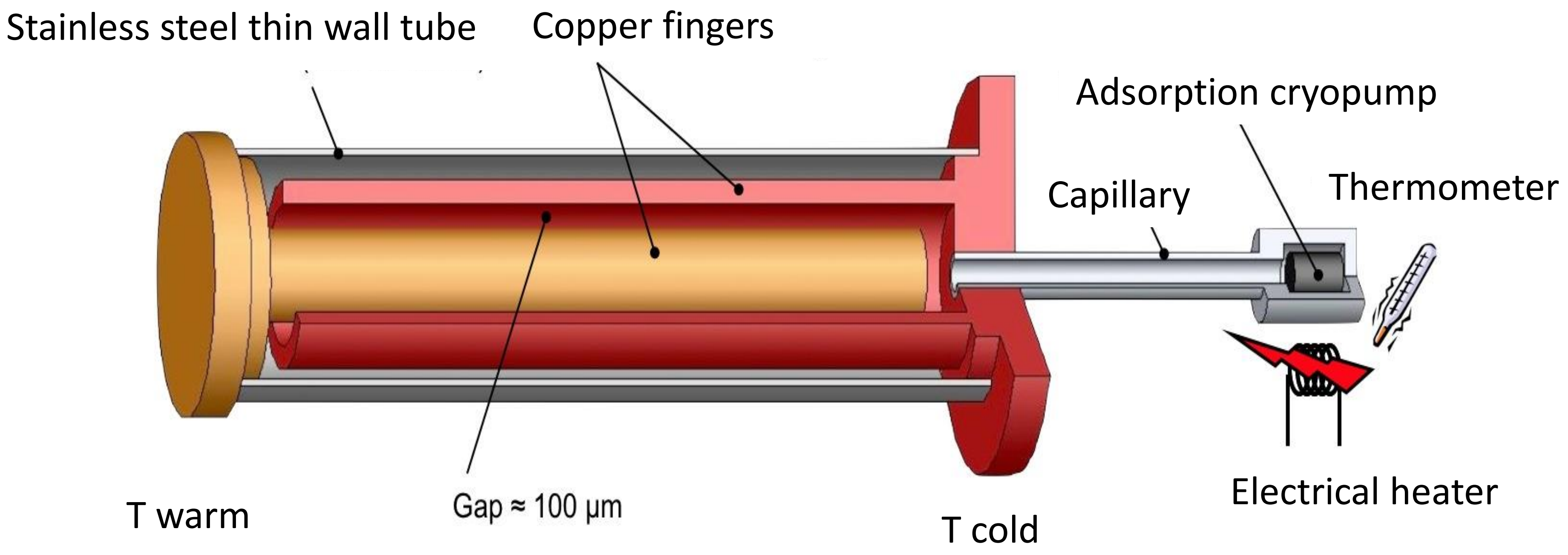
⇒ p_m dicreases

⇒ liquid helium temperature dicreases

P. Roubeau

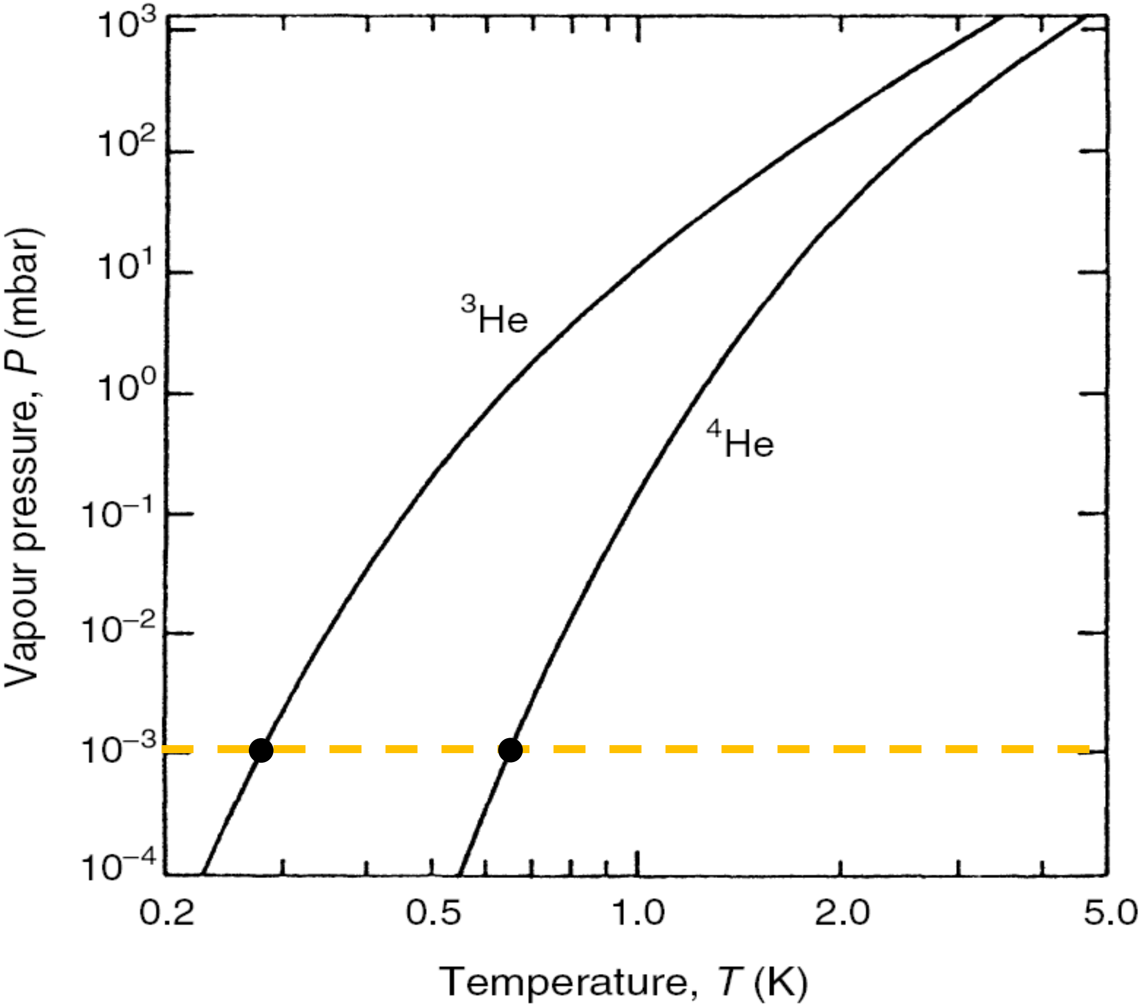
Adsorption He cooler

Gas Gap Thermal Switch



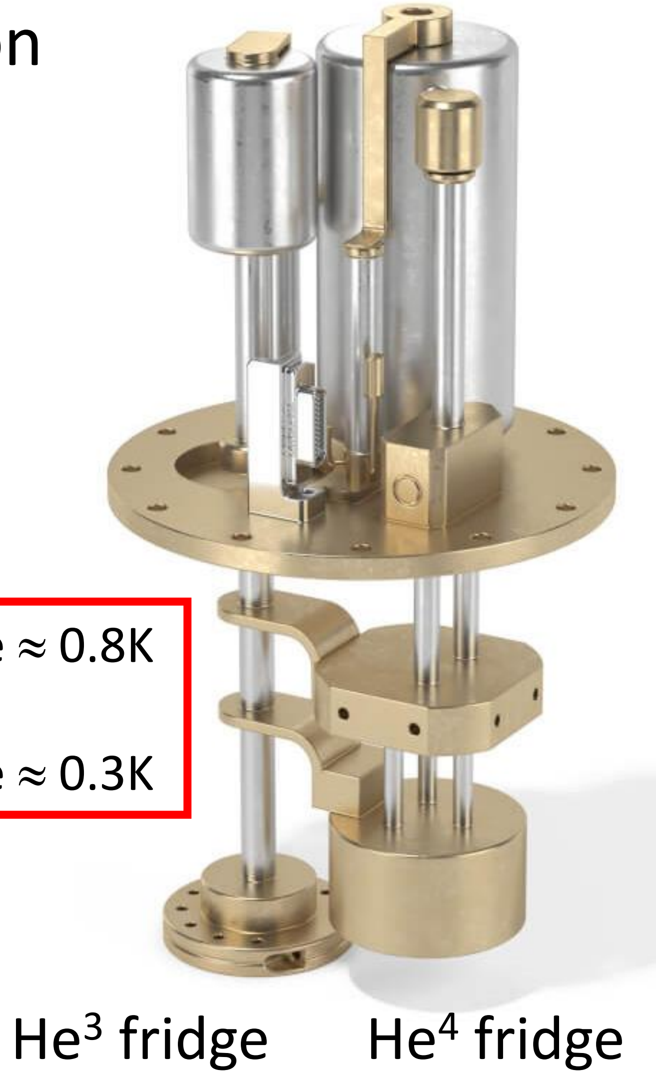
Adsorption He cooler

Lower temperature for operation



^{4}He ≈ 0.8K

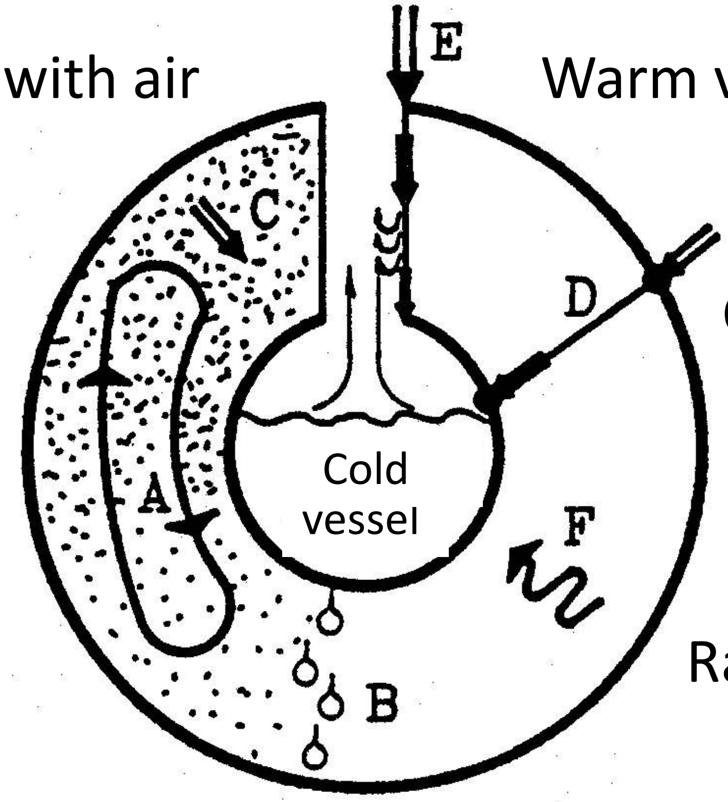
^{3}He ≈ 0.3K



Heat transfer

Different kinds of heat transfer inside a cryogenic equipment

Heat transfer from the warm vessel (at room temperature) to the cold vessel (at cryogenic temperature)



Warm vessel with air

Warm vessel under vacuum

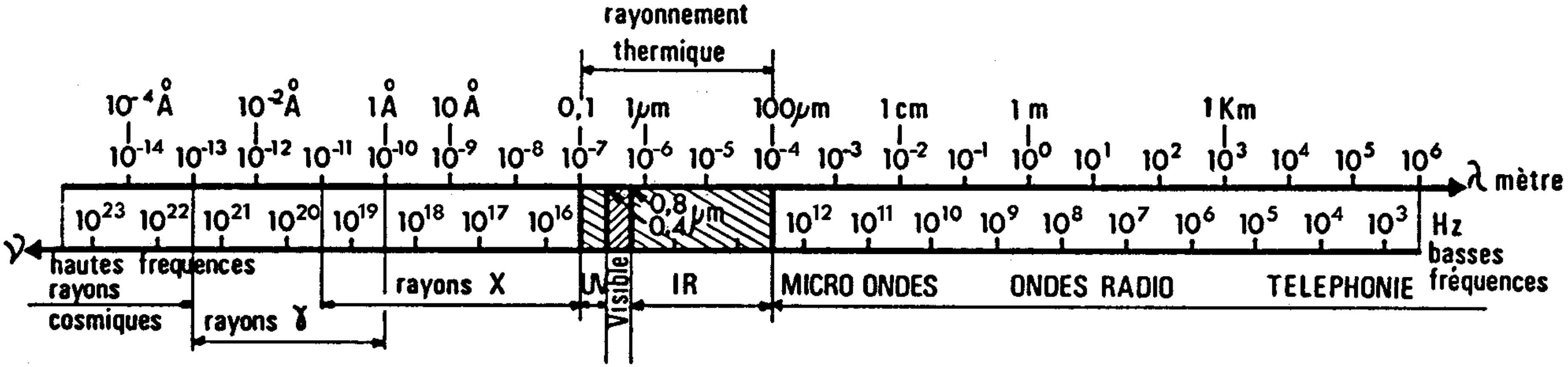
Conduction

Cold vessel

Radiation

Warm vessel

Thermal radiation



$$\boxed{\Phi = \varepsilon \sigma A T^{4}}$$

Stefan–Boltzmann law

Φ : thermal power [W]

ε : surface emissivity ($\varepsilon < 1$)

σ : Stefan-Boltzmann constant = 5,67 10^{-8} [W.m^{-2}.K^{-4}]

A : surface [m^2]

T : surface temperature [K]

Thermal radiation

$$Emissivity\ \varepsilon = \frac{thermal\ radiation\ from\ a\ surface}{thermal\ radiation\ from\ an\ ideal\ black\ surface}$$

Emissivities of materials at cold temperature

	300 K	**78 K**	**4,2 K**
Silver	0,02	0,01	0,005
Aluminium	0,20	0,10	0,06
Copper	0,10	0,06	0,02
Stainless steel	0,20	0,12	0,10
Glass	0,8		
Water	0,9		

T↓ ⇒ ε↓

Oxyded surfaces ⇒ ε↑

Thermal radiation

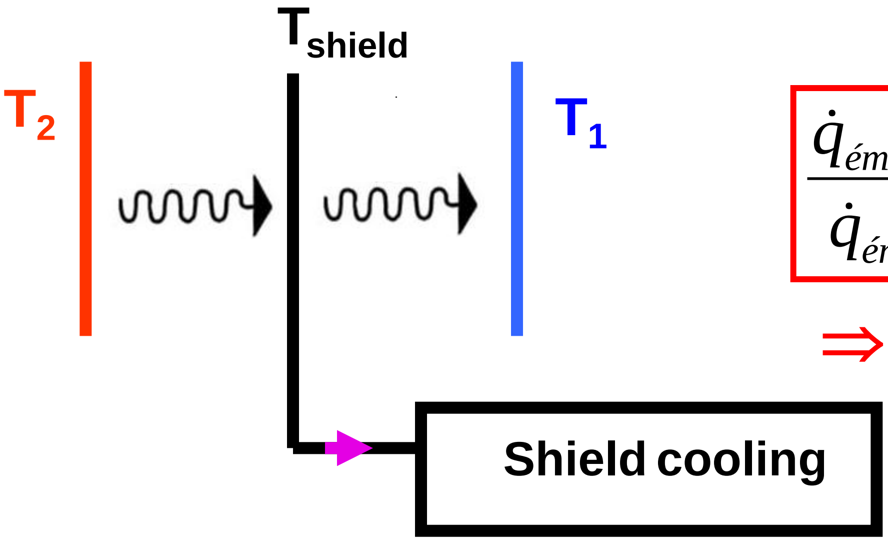
The black body completely absorbs the radiation it receives

$$(\mathrm{W.m^{-2}})\quad \boxed{\dot{q}_{\acute{e}mis} = \sigma . T^4}\quad (\mathrm{K})$$

$\sigma = 5{,}67.10^{-8}\ \mathrm{W.m^{-2}.K^{-4}}$

Stefan-Boltzmann constant

T(K)	300	80	40	20	10	4	2	1	0.4	0.1
W/m²	459	2.32	0.145	9.1×10^{-3}	5.7×10^{-4}	1.45×10^{-5}	9.1×10^{-7}	5.7×10^{-8}	1.45×10^{-9}	5.7×10^{-12}



$$\boxed{\frac{\dot{q}_{\acute{e}mis}(300\ \mathrm{K})}{\dot{q}_{\acute{e}mis}(80\ \mathrm{K})} = 200}$$

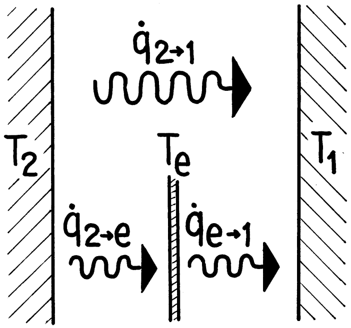
⚠

⇒ Use of cooled thermal shield

Thermal radiation

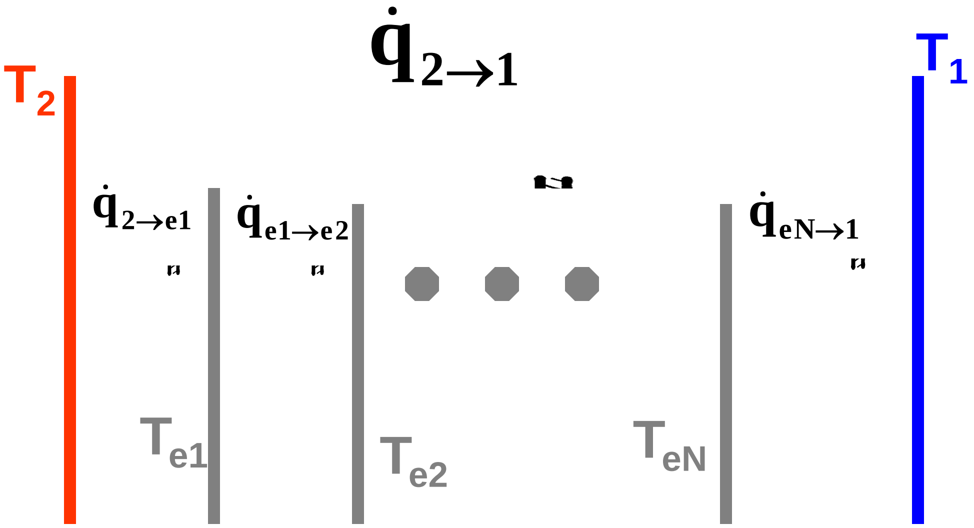
- Reduction of radiation heat flow rate

Isolated thermal shield : One isolated shield installed between two surfaces at different tempertaure



$$\dot{q}_{2\to e} = \dot{q}_{e\to 1} = \frac{\dot{q}_{2\to 1}}{2}$$

$$T_e = \sqrt[4]{\frac{T_2^{\,4} + T_1^{\,4}}{2}}$$



N isolated shields :

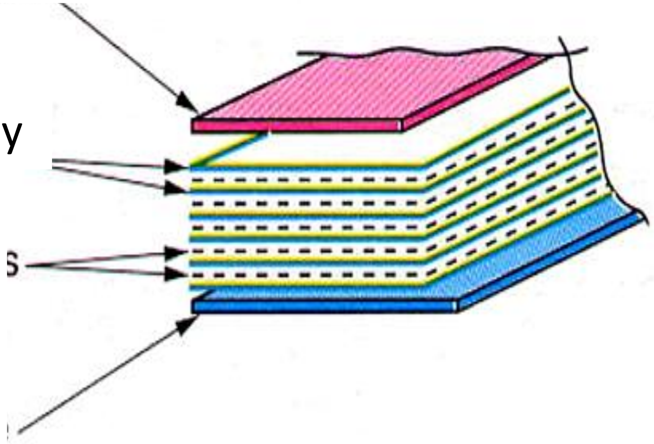
$$\dot{q}_{2\to e1} = \dot{q}_{e1\to e2} = \ldots = \dot{q}_{eN\to 1}$$

$$\dot{q}_N = \frac{\dot{q}_0}{N+1}$$

Thermal radiation

Multi-layer insulation (MLI) is thermal insulation composed of multiple layers of thin sheets. Generally, the layers are held apart by a thin cloth mesh.

With N layers $$\dot{q}_N = \frac{\dot{q}_0}{N+1}$$

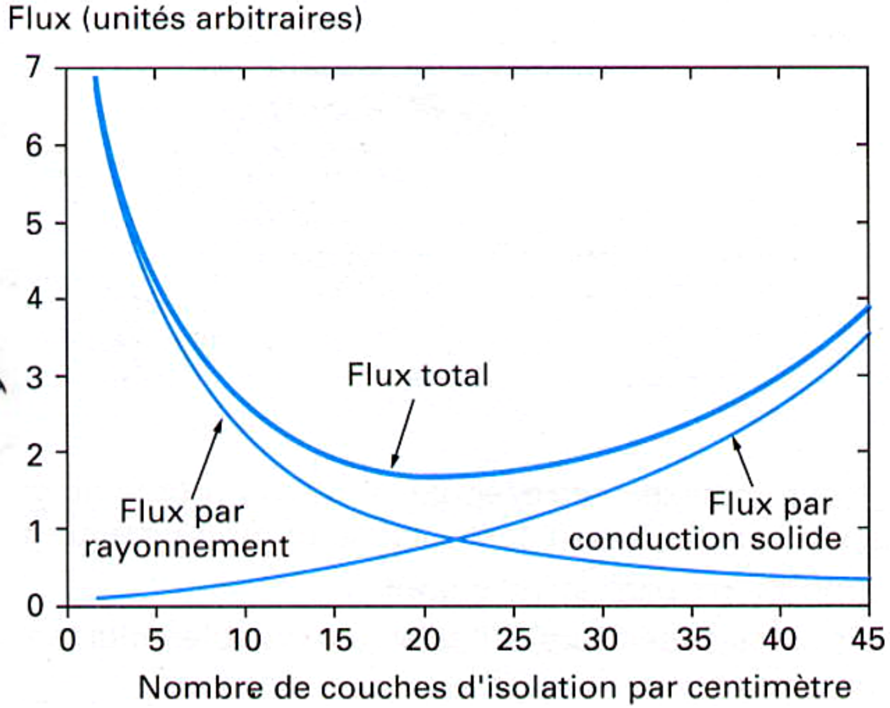


warm wall

Sheet with low emissivity

Insulating Spacers

cold wall



Thermal conductivity

- Non-metallic solids

main mechanism: transfer of energy by vibration of the network (phonons)

  - *k* ~ *T*^{3} (Crystallized insulators)
  - At low temperatures their conductivity decreases more quickly

- Metal
  - at low temperatures, heat conduction is mainly due to free electrons
  - strong variation of k with temperature

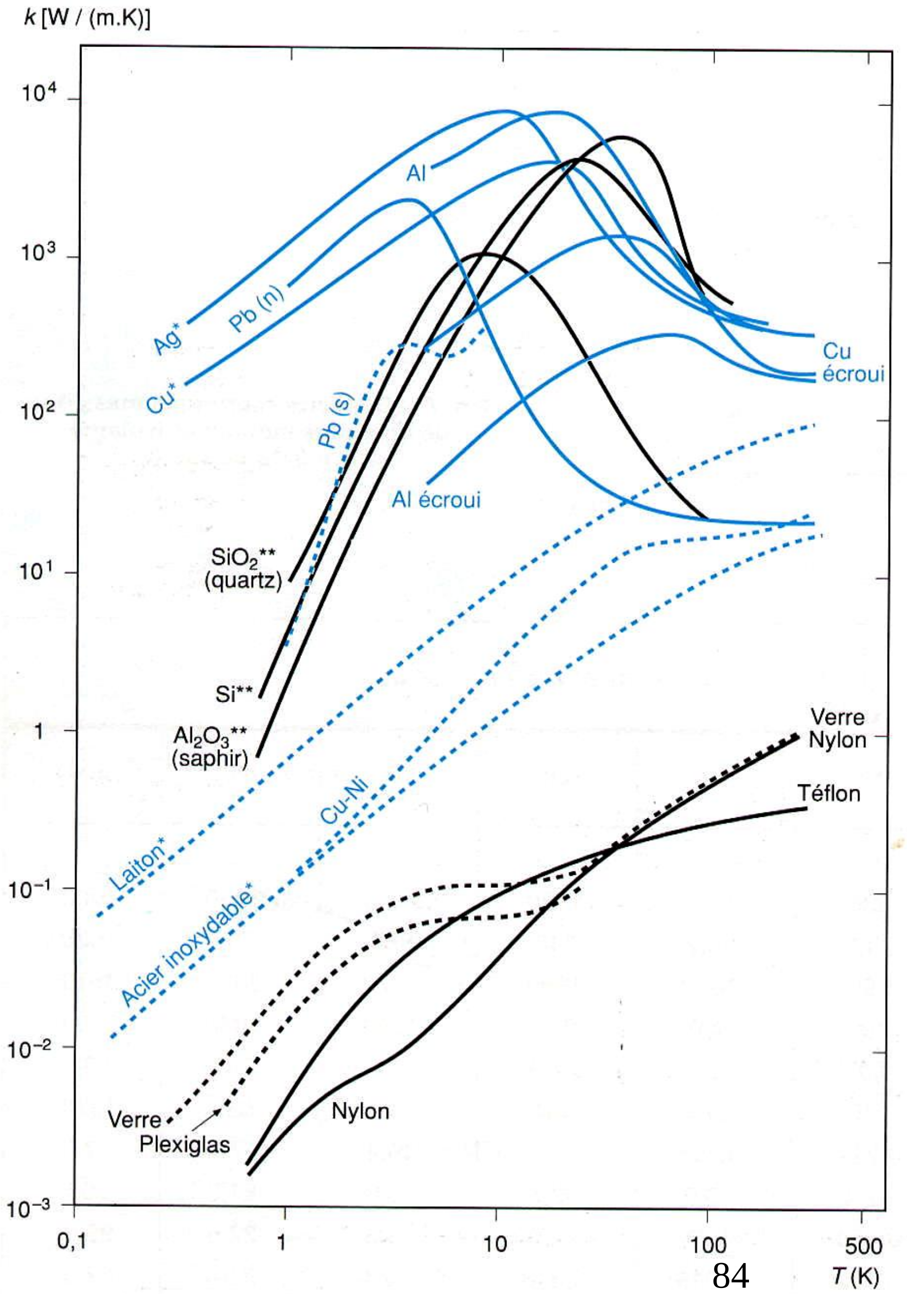
Wiedermann-Franz law:

$$k \cdot \rho_{élec} = L_0 T$$

$\rho_{élec}$: electrical resistivity (Ω/m)

L_0 : Lorentz number
= 2,45 10^{-8} V^2/K^2

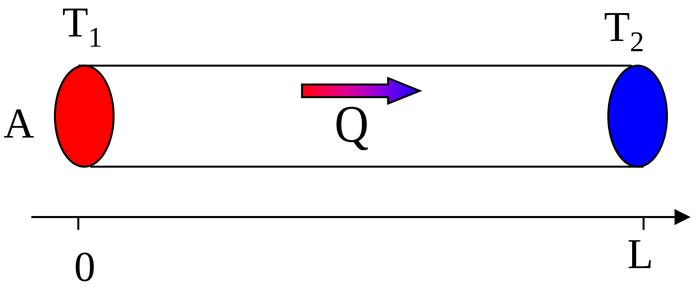
$\Rightarrow k \sim T$, pour T < 10 K



Thermal conduction

- Cas 1D (x direction)

adiabatic conduction through the bar – calculation of the thermal flow rate



A [m^2] : conduction surface

L [m] : distance between T_1 and T_2

$\dot{Q}$ [W] : heat flux through the surface A

$$\dot{q}_x = \dot{q} = -k \cdot \frac{dT}{dx} \qquad \dot{Q} = A \cdot \dot{q} = -A \cdot k \cdot \frac{dT}{dx}$$

$$\dot{Q} \cdot dx = -A \cdot k \cdot dT$$

First principle $\Rightarrow$ $\dot{Q} = \text{constante}$

$$\int_{L_1}^{L_2} \dot{Q}.\, dx = -A \int_{T_1}^{T_2} k(T).\, dT$$

$$\dot{Q}.\,(L_2 - L_1) = \dot{Q}.\,L = -A \int_{T_1}^{T_2} k(T).\, dT$$

Thermal conduction

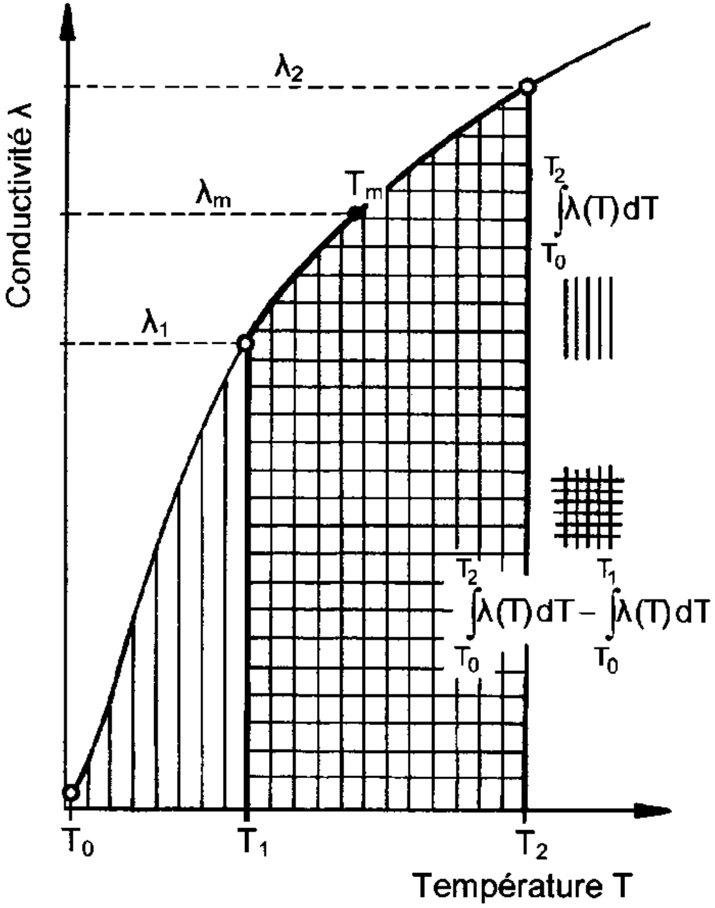
Cryogenic environment

The thermal conductivity *k* varies with the temperature

$$\dot{Q} = -\frac{A}{L}\int_{T_1}^{T_2} k(T)\cdot dT$$

Using material properties data, the integral between two distinct temperatures is found using:

$$\int_{T_1}^{T_2} k(T)\cdot dT = \int_{T_0=4K}^{T_2} k(T)\cdot dT - \int_{T_0=4K}^{T_1} k(T)\cdot dT$$

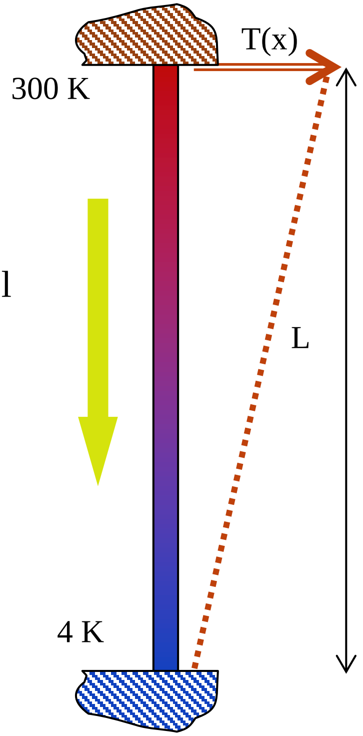


See T.I. fascicule, BE9 811, p. 11 - 13

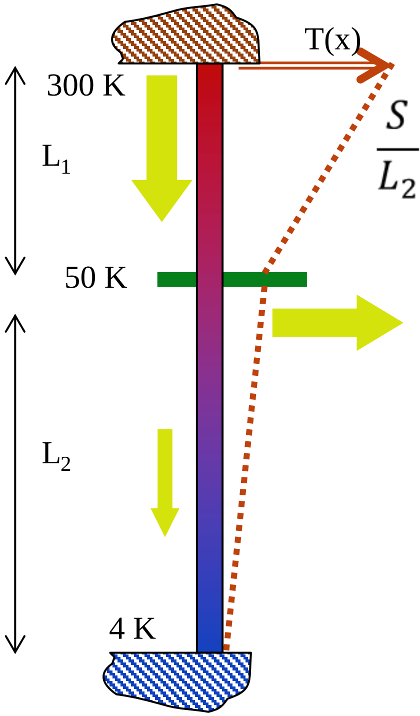
Thermal conduction

- Thermalisation at intermediate temperature: example of stainless steel rod

Stainless steel
L = 20 cm
S= 1cm²



L$_1$ = 7 cm
L$_2$ = 13 cm



$$\underbrace{\frac{S}{L_2}\int_{50K}^{300K} k(T)dT}_{30.8\ -\ 1.36\ \mathrm{W/cm}} = \frac{1}{7}\times 29.4 = 4.2\ W$$

$$Q_{50K} = 4.2\ - 0.105 = 4.1\ W$$

$$Q_{4K} = \underbrace{\frac{S}{L}\int_{4K}^{300K} k(T)dT}_{30.8\ \mathrm{W/cm}} = \frac{1}{20}\times 30.8 = 1.54\ W$$

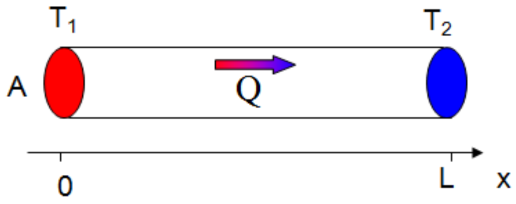
$$Q^*_{4K} = \underbrace{\frac{S}{L_2}\int_{4K}^{50K} k(T)dT}_{1.36\ \mathrm{W/cm}} = \frac{1}{13}\times 1.36 = 0.105\ W$$

$$Q_{4K} = 1.54\ W\ > Q^*_{4K} = 0.105\ \mathrm{W}$$

Heat flux at 4K is greatly reduced

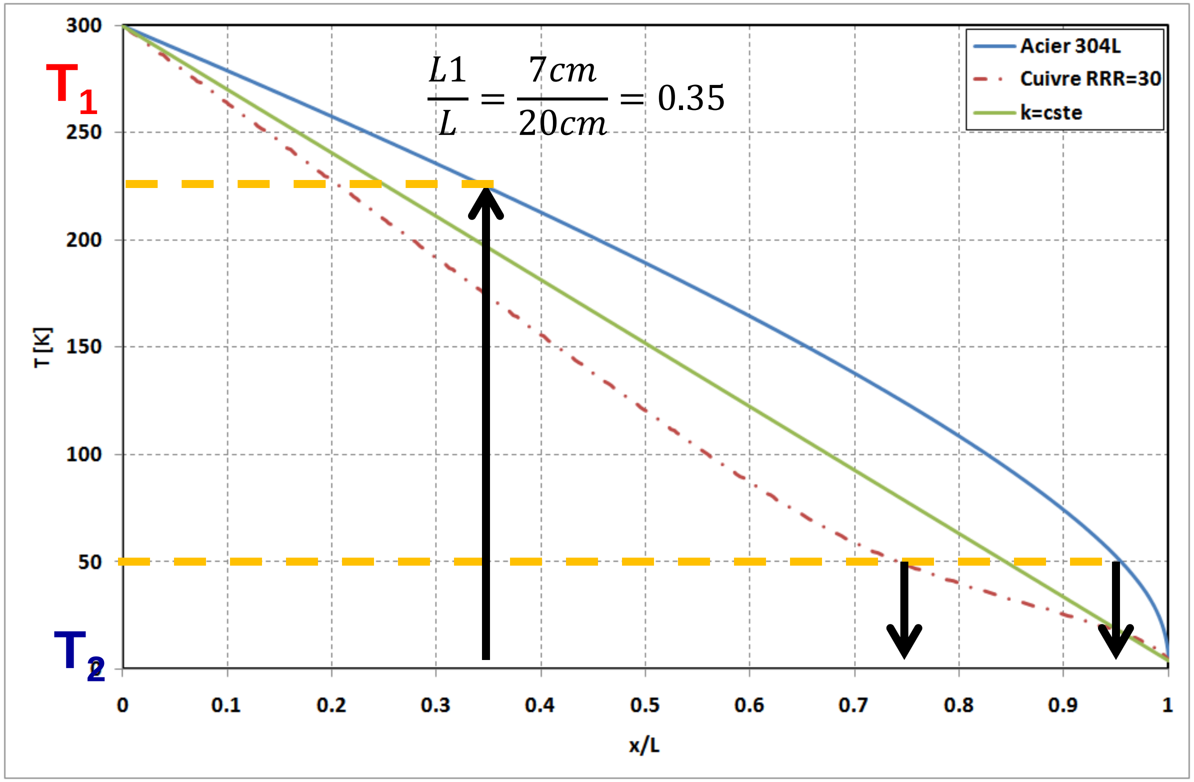
Thermal conduction

Evolution of the temperature along the rod



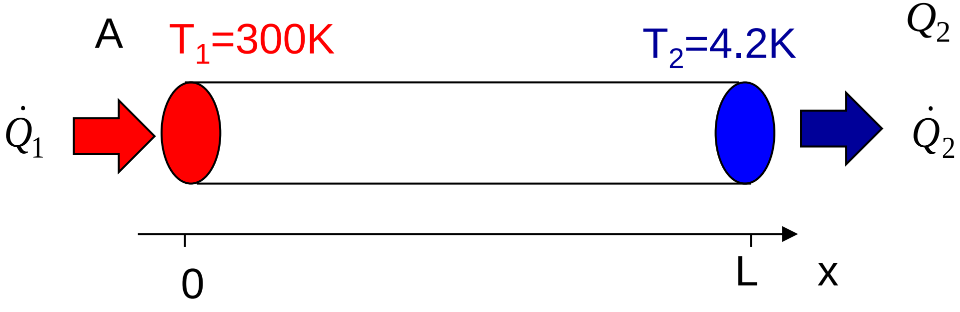
$$\dot{Q} = -\frac{A}{x}\int_{T_1}^{T} k(T)\cdot dT = -\frac{A}{L}\int_{T_1}^{T_2} k(T)\cdot dT = \text{constante}$$

$$\frac{x}{L} = \frac{\int_{T_1}^{T} k(T)\cdot dT}{\int_{T_1}^{T_2} k(T)\cdot dT}$$



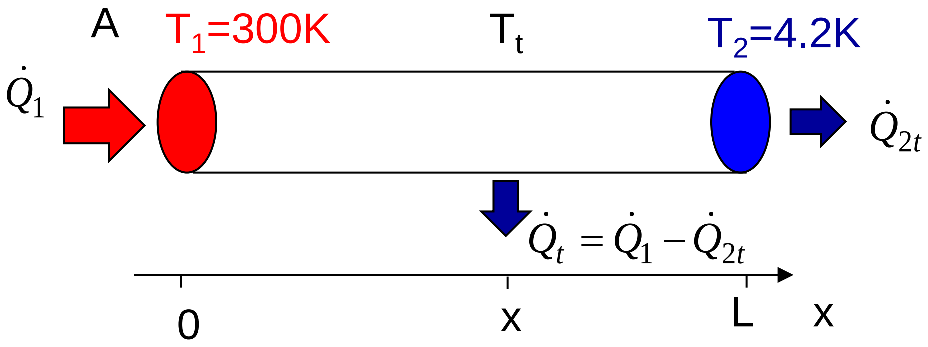
Thermal conduction

Energy efficiency



$$\dot{Q}_2 = -\frac{A}{L}\int_{T_2}^{T_1} k(T)\cdot dT = 1.54\text{W} \quad\Rightarrow\quad \dot{W} = \dot{Q}_2 \frac{T_1 - T_2}{T_2}$$

$$\dot{W} = \frac{300 - 4.2}{4.2} \times 1.54 = 108\ W$$



$$\dot{Q}_{2t} = -\frac{A}{L - x}\int_{T_2}^{T_t} k(T)\cdot dT = 0.105\text{ W}$$

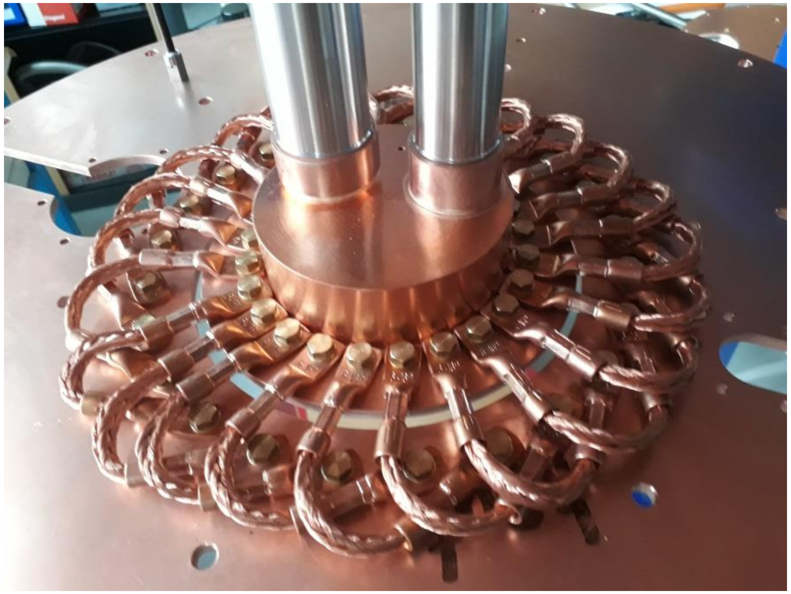
$$Q_t = 4.2 - 0.105 = 4.1\ W$$

$$\dot{W} = \frac{300 - 4.2}{4.2} \times 0.105 + \frac{300 - 50}{50} \times 4.1 = 27.9\ W$$

Thermal anchorage

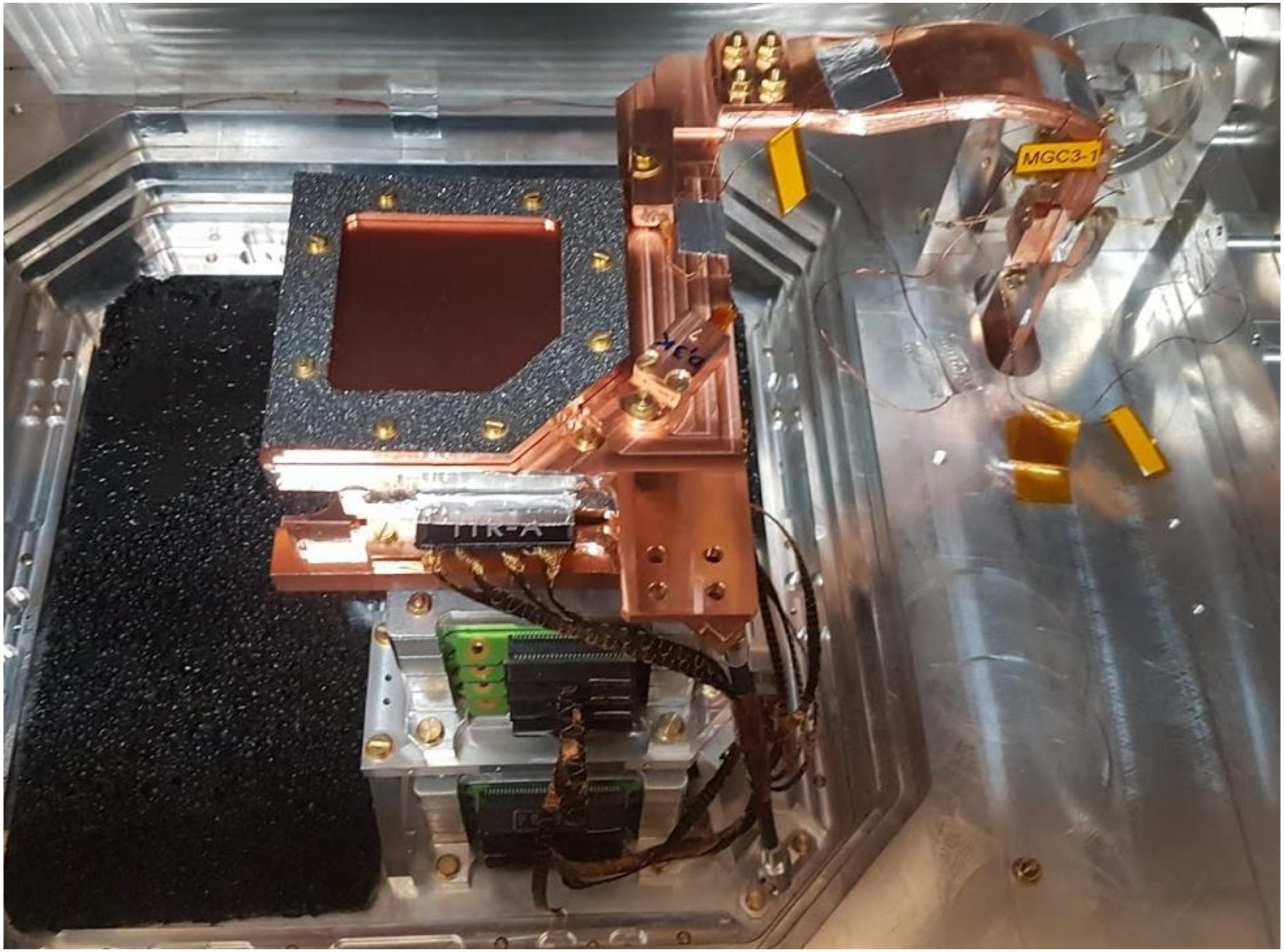
Heat transfer by solid conduction with a high value thermal conductivity metal (copper, aluminum, etc.)

- Braids
- foil
- Rigid plate



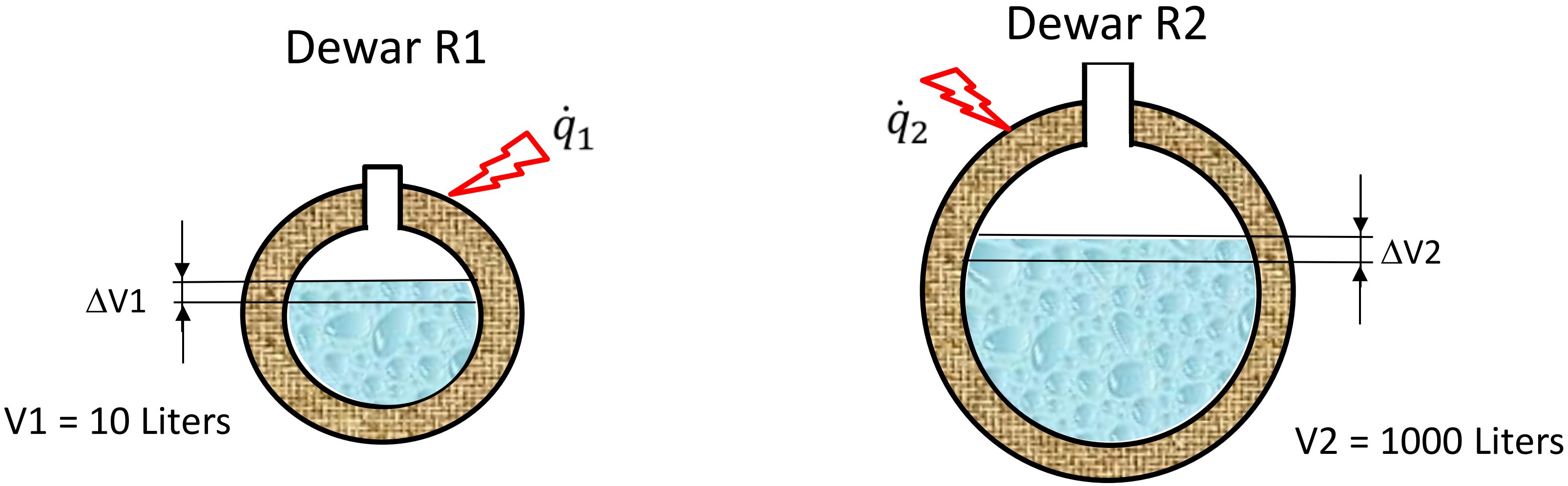
Heat transfer by heat pipe using cryogenic fluid : helium, nitrogen, …

Thermal anchorage



Energy efficiency

Identical insulation for the both Dewar $\dot{q}_1 = \dot{q}_2 \quad (\frac{W}{m^2})$



Relative losses by evaporation by day the Dewar R1 : $\Delta V_1/V_1 = 10\%$

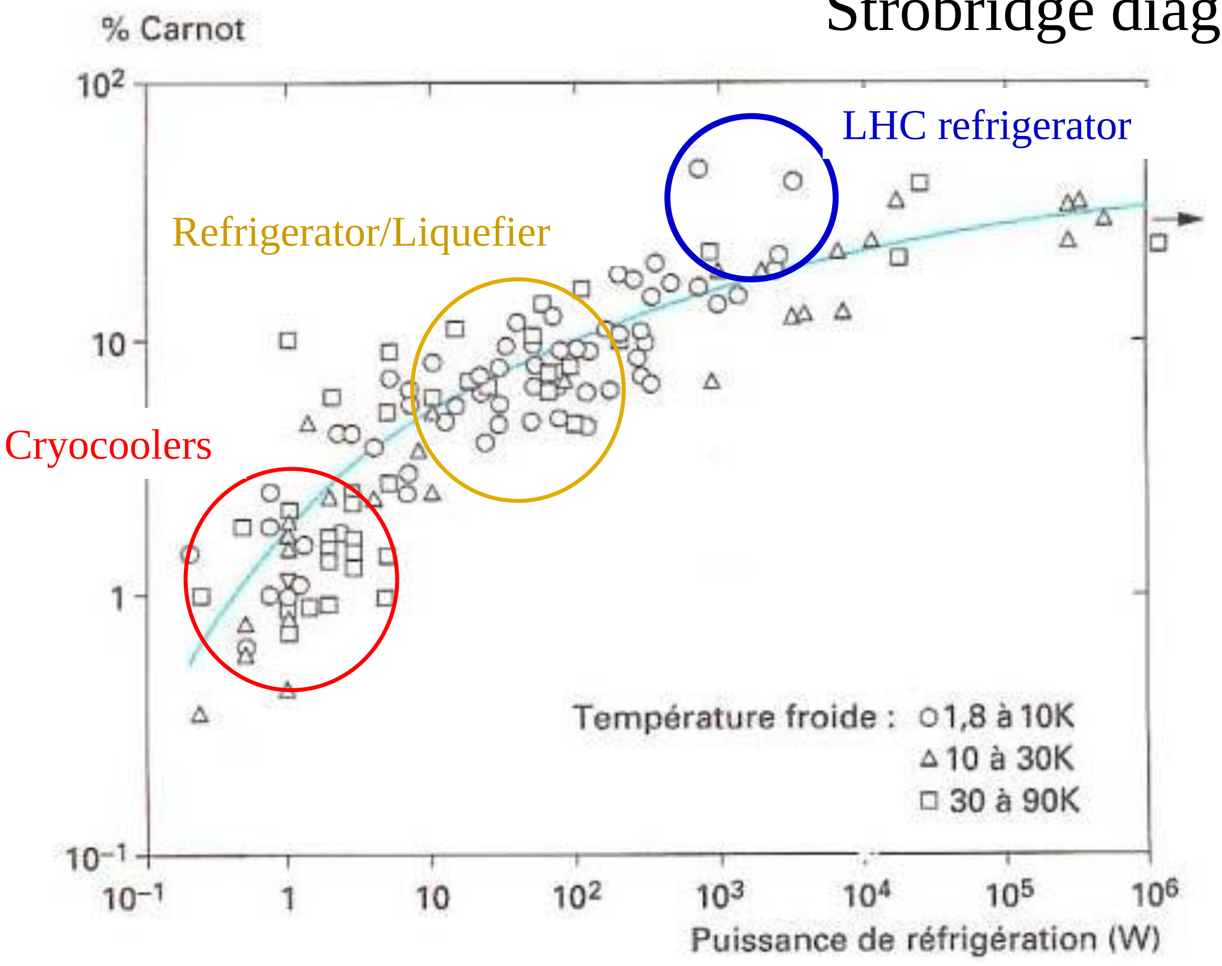
What are the relative losses by evaporation of the Dewar R2 ?

$$\frac{\Delta V_2}{V_2} = \frac{\Delta V_1}{V_1}\frac{D_1}{D_2} = \frac{\Delta V_1}{V_1}\sqrt[3]{\frac{V_1}{V_2}} = 2.1\%$$

Energy efficiency

- Efficiency of refrigerators evolves with their dimensions, the cold power produced
- The operating temperature of refrigerators has little impact on efficiencies.

Strobridge diagram



Formations en cryogénie

ANF IN2P3 : Vide et Cryogénie

Ecoles AFF-CCS : Cryogénie et supraconductivité

CNRS Formation : Cryogénie
Niveau ingénieur
GRENOBLE
du lundi 18/03/2024 au vendredi 22/03/2024
Niveau technicien
GRENOBLE
du lundi 24/06/2024 au vendredi 28/06/2024

SFV/UPC/IJCLab : Cryogénie
Tronc Commun
PARIS
Du mardi 14 mai au jeudi 16 mai 2024
Parcours différencié Technicien et Ingénieur
ORSAY
Du mardi 11 juin au jeudi 13 juin 2024

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Experimental Principles and Methods Below 1K - O.V. Lounasmaa, Academic Press – 1997

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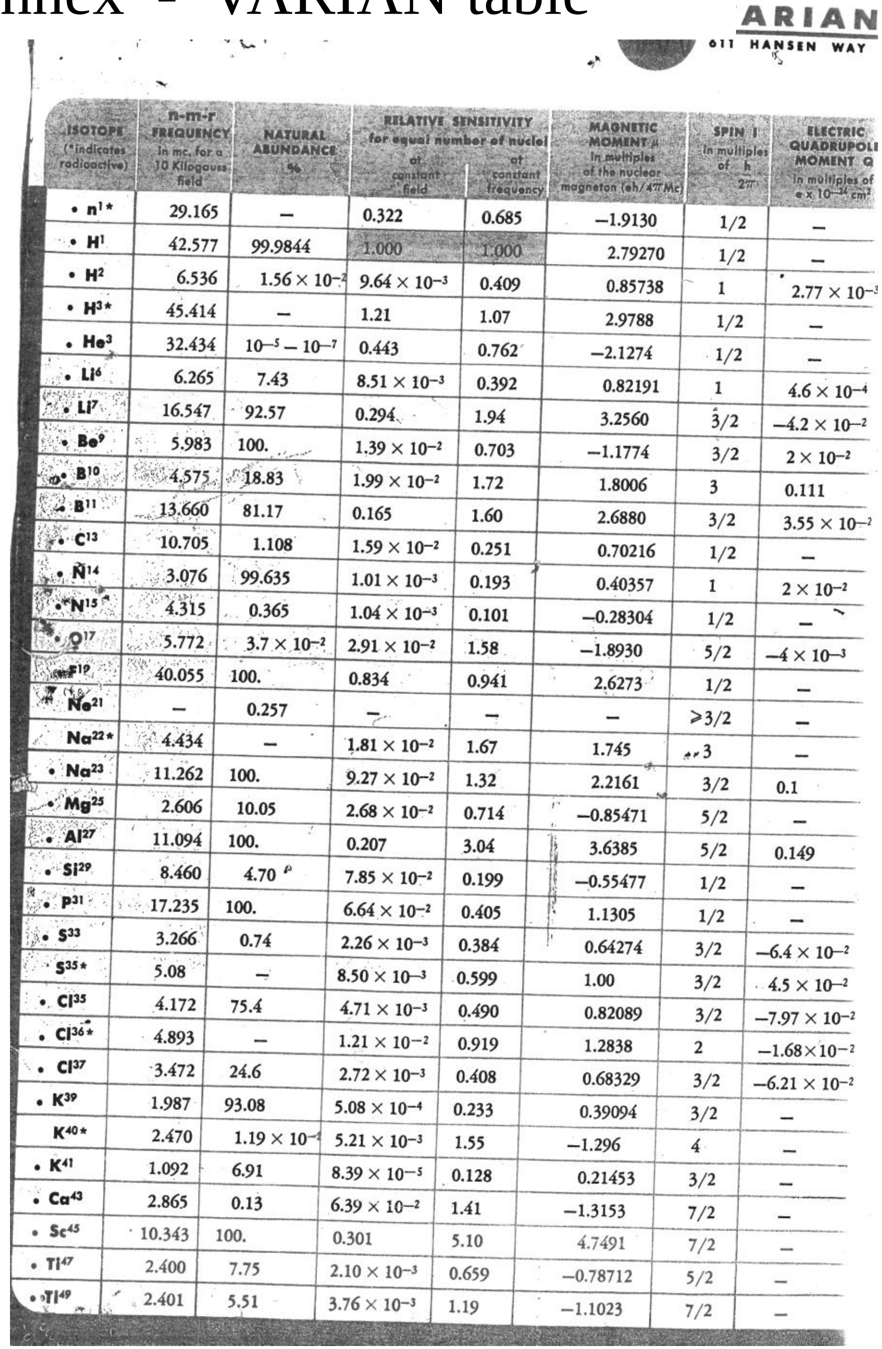
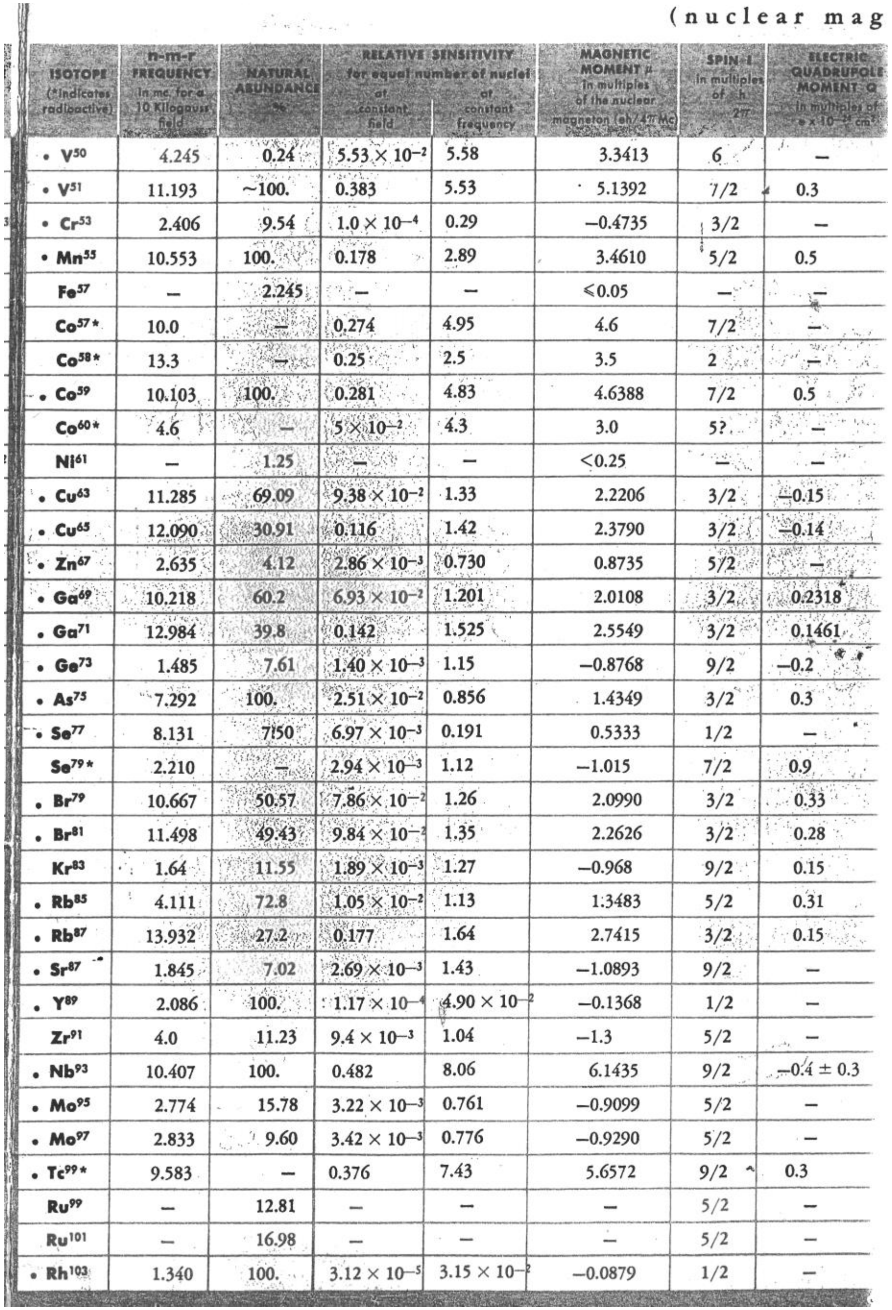
Annex - VARIAN table



ARIAN
611 HANSEN WAY

ISOTOPE (*indicates radioactive)	n-m-r FREQUENCY in mc. for a 10 Kilogauss field	NATURAL ABUNDANCE %	RELATIVE SENSITIVITY for equal number of nuclei at constant field	at constant frequency	MAGNETIC MOMENT μ in multiples of the nuclear magneton ($eh/4\pi Mc$)	SPIN I in multiples of $\frac{h}{2\pi}$	ELECTRIC QUADRUPOLE MOMENT Q in multiples of $e \times 10^{-24}$ cm²
• n^{1*}	29.165	—	0.322	0.685	−1.9130	1/2	—
• H^1	42.577	99.9844	1.000	1.000	2.79270	1/2	—
• H^2	6.536	1.56×10^{-2}	9.64×10^{-3}	0.409	0.85738	1	2.77×10^{-3}
• H^{3*}	45.414	—	1.21	1.07	2.9788	1/2	—
• He^3	32.434	$10^{-5} - 10^{-7}$	0.443	0.762	−2.1274	1/2	—
• Li^6	6.265	7.43	8.51×10^{-3}	0.392	0.82191	1	4.6×10^{-4}
• Li^7	16.547	92.57	0.294	1.94	3.2560	3/2	-4.2×10^{-2}
• Be^9	5.983	100.	1.39×10^{-2}	0.703	−1.1774	3/2	2×10^{-2}
• B^{10}	4.575	18.83	1.99×10^{-2}	1.72	1.8006	3	0.111
• B^{11}	13.660	81.17	0.165	1.60	2.6880	3/2	3.55×10^{-2}
• C^{13}	10.705	1.108	1.59×10^{-2}	0.251	0.70216	1/2	—
• N^{14}	3.076	99.635	1.01×10^{-3}	0.193	0.40357	1	2×10^{-2}
• N^{15}	4.315	0.365	1.04×10^{-3}	0.101	−0.28304	1/2	—
• O^{17}	5.772	3.7×10^{-2}	2.91×10^{-2}	1.58	−1.8930	5/2	-4×10^{-3}
• F^{19}	40.055	100.	0.834	0.941	2.6273	1/2	—
Ne^{21}	—	0.257	—	—	—	≥3/2	—
Na^{22*}	4.434	—	1.81×10^{-2}	1.67	1.745	3	—
• Na^{23}	11.262	100.	9.27×10^{-2}	1.32	2.2161	3/2	0.1
• Mg^{25}	2.606	10.05	2.68×10^{-2}	0.714	−0.85471	5/2	—
• Al^{27}	11.094	100.	0.207	3.04	3.6385	5/2	0.149
• Si^{29}	8.460	4.70	7.85×10^{-2}	0.199	−0.55477	1/2	—
• P^{31}	17.235	100.	6.64×10^{-2}	0.405	1.1305	1/2	—
• S^{33}	3.266	0.74	2.26×10^{-3}	0.384	0.64274	3/2	-6.4×10^{-2}
• S^{35*}	5.08	—	8.50×10^{-3}	0.599	1.00	3/2	4.5×10^{-2}
• Cl^{35}	4.172	75.4	4.71×10^{-3}	0.490	0.82089	3/2	-7.97×10^{-2}
• Cl^{36*}	4.893	—	1.21×10^{-2}	0.919	1.2838	2	-1.68×10^{-2}
• Cl^{37}	3.472	24.6	2.72×10^{-3}	0.408	0.68329	3/2	-6.21×10^{-2}
• K^{39}	1.987	93.08	5.08×10^{-4}	0.233	0.39094	3/2	—
K^{40*}	2.470	1.19×10^{-2}	5.21×10^{-3}	1.55	−1.296	4	—
• K^{41}	1.092	6.91	8.39×10^{-5}	0.128	0.21453	3/2	—
• Ca^{43}	2.865	0.13	6.39×10^{-2}	1.41	−1.3153	7/2	—
• Sc^{45}	10.343	100.	0.301	5.10	4.7491	7/2	—
• Ti^{47}	2.400	7.75	2.10×10^{-3}	0.659	−0.78712	5/2	—
• Ti^{49}	2.401	5.51	3.76×10^{-3}	1.19	−1.1023	7/2	—

Annex - VARIAN table

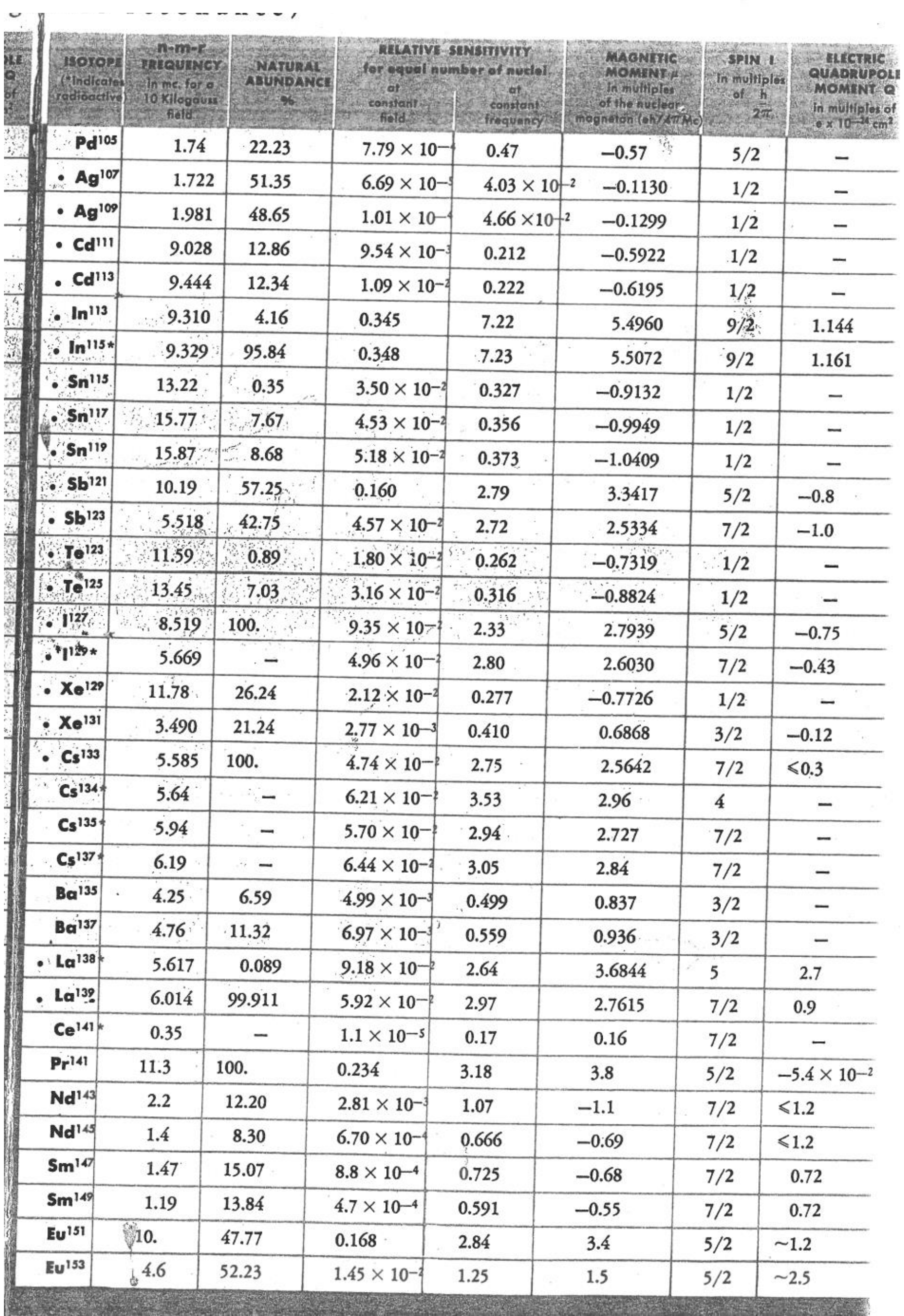


NMR

(nuclear mag

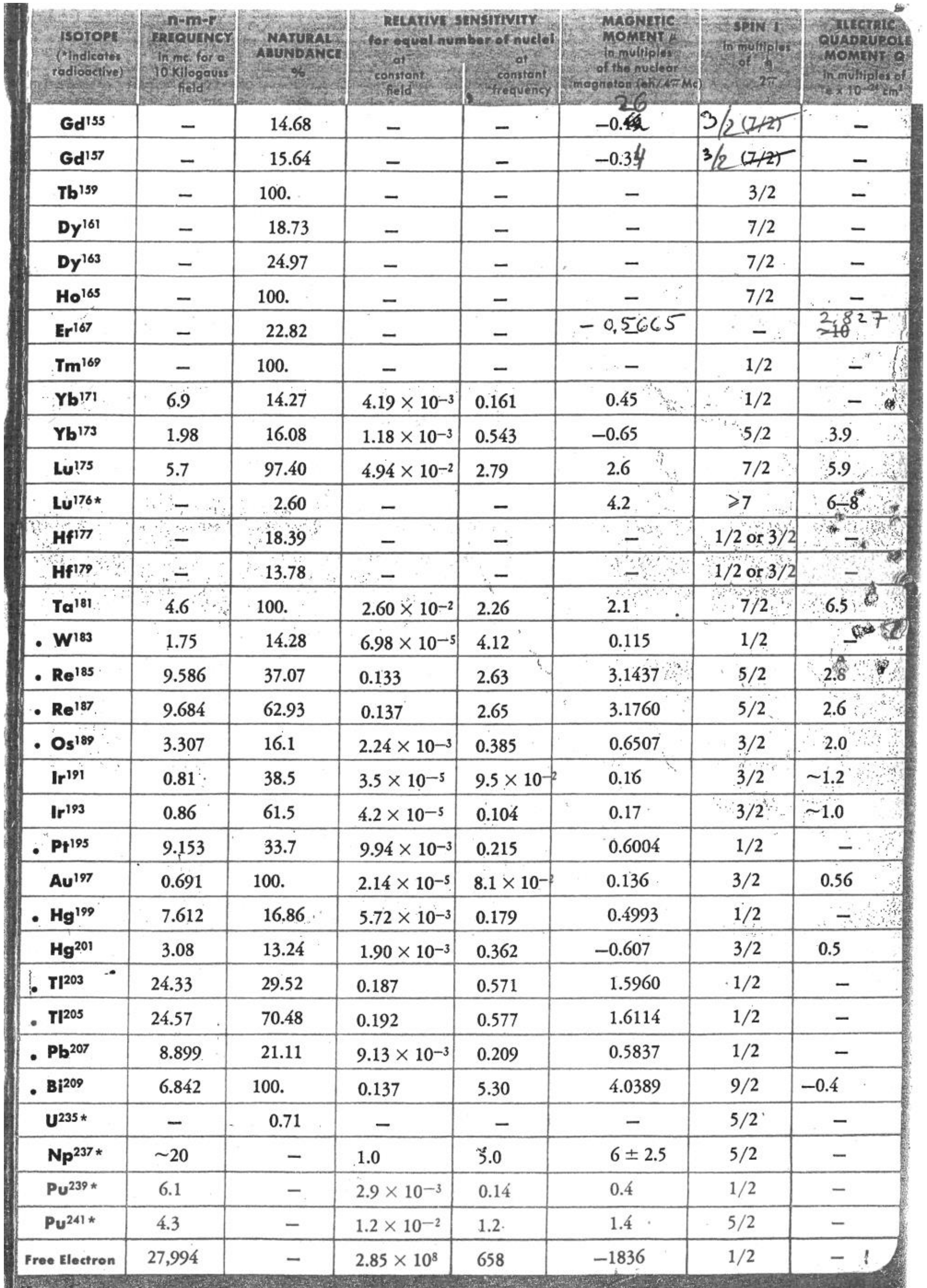
ISOTOPE (*indicates radioactive)	n-m-r FREQUENCY in mc. for a 10 Kilogauss field	NATURAL ABUNDANCE %	RELATIVE SENSITIVITY for equal number of nuclei at constant field	at constant frequency	MAGNETIC MOMENT μ in multiples of the nuclear magneton (eh/4πMc)	SPIN I in multiples of $\frac{h}{2\pi}$	ELECTRIC QUADRUPOLE MOMENT Q in multiples of $e \times 10^{-24}$ cm^2
• V^{50}	4.245	0.24	5.53×10^{-2}	5.58	3.3413	6	—
• V^{51}	11.193	~100.	0.383	5.53	5.1392	7/2	0.3
• Cr^{53}	2.406	9.54	1.0×10^{-4}	0.29	−0.4735	3/2	—
• Mn^{55}	10.553	100.	0.178	2.89	3.4610	5/2	0.5
Fe^{57}	—	2.245	—	—	≤0.05	—	—
Co^{57*}	10.0	—	0.274	4.95	4.6	7/2	—
Co^{58*}	13.3	—	0.25	2.5	3.5	2	—
• Co^{59}	10.103	100.	0.281	4.83	4.6388	7/2	0.5
Co^{60*}	4.6	—	5×10^{-2}	4.3	3.0	5?	—
Ni^{61}	—	1.25	—	—	<0.25	—	—
• Cu^{63}	11.285	69.09	9.38×10^{-2}	1.33	2.2206	3/2	−0.15
• Cu^{65}	12.090	30.91	0.116	1.42	2.3790	3/2	−0.14
• Zn^{67}	2.635	4.12	2.86×10^{-3}	0.730	0.8735	5/2	—
• Ga^{69}	10.218	60.2	6.93×10^{-2}	1.201	2.0108	3/2	0.2318
• Ga^{71}	12.984	39.8	0.142	1.525	2.5549	3/2	0.1461
• Ge^{73}	1.485	7.61	1.40×10^{-3}	1.15	−0.8768	9/2	−0.2
• As^{75}	7.292	100.	2.51×10^{-2}	0.856	1.4349	3/2	0.3
• Se^{77}	8.131	7.50	6.97×10^{-3}	0.191	0.5333	1/2	—
Se^{79*}	2.210	—	2.94×10^{-3}	1.12	−1.015	7/2	0.9
• Br^{79}	10.667	50.57	7.86×10^{-2}	1.26	2.0990	3/2	0.33
• Br^{81}	11.498	49.43	9.84×10^{-2}	1.35	2.2626	3/2	0.28
Kr^{83}	1.64	11.55	1.89×10^{-3}	1.27	−0.968	9/2	0.15
• Rb^{85}	4.111	72.8	1.05×10^{-2}	1.13	1.3483	5/2	0.31
• Rb^{87}	13.932	27.2	0.177	1.64	2.7415	3/2	0.15
• Sr^{87}	1.845	7.02	2.69×10^{-3}	1.43	−1.0893	9/2	—
• Y^{89}	2.086	100.	1.17×10^{-4}	4.90×10^{-2}	−0.1368	1/2	—
Zr^{91}	4.0	11.23	9.4×10^{-3}	1.04	−1.3	5/2	—
• Nb^{93}	10.407	100.	0.482	8.06	6.1435	9/2	−0.4 ± 0.3
• Mo^{95}	2.774	15.78	3.22×10^{-3}	0.761	−0.9099	5/2	—
• Mo^{97}	2.833	9.60	3.42×10^{-3}	0.776	−0.9290	5/2	—
• Tc^{99*}	9.583	—	0.376	7.43	5.6572	9/2	0.3
Ru^{99}	—	12.81	—	—	—	5/2	—
Ru^{101}	—	16.98	—	—	—	5/2	—
• Rh^{103}	1.340	100.	3.12×10^{-5}	3.15×10^{-2}	−0.0879	1/2	—

Annex - VARIAN table



ISOTOPE (*indicates radioactive)	n-m-r FREQUENCY in mc. for a 10 Kilogauss field	NATURAL ABUNDANCE %	RELATIVE SENSITIVITY for equal number of nuclei		MAGNETIC MOMENT μ in multiples of the nuclear magneton (eh/4πMc)	SPIN I in multiples of $\frac{h}{2\pi}$	ELECTRIC QUADRUPOLE MOMENT Q in multiples of $e \times 10^{-24}$ cm^2
			at constant field	at constant frequency			
Pd^{105}	1.74	22.23	7.79×10^{-4}	0.47	−0.57	5/2	—
• Ag^{107}	1.722	51.35	6.69×10^{-5}	4.03×10^{-2}	−0.1130	1/2	—
• Ag^{109}	1.981	48.65	1.01×10^{-4}	4.66×10^{-2}	−0.1299	1/2	—
• Cd^{111}	9.028	12.86	9.54×10^{-3}	0.212	−0.5922	1/2	—
• Cd^{113}	9.444	12.34	1.09×10^{-2}	0.222	−0.6195	1/2	—
• In^{113}	9.310	4.16	0.345	7.22	5.4960	9/2	1.144
• In^{115*}	9.329	95.84	0.348	7.23	5.5072	9/2	1.161
• Sn^{115}	13.22	0.35	3.50×10^{-2}	0.327	−0.9132	1/2	—
• Sn^{117}	15.77	7.67	4.53×10^{-2}	0.356	−0.9949	1/2	—
• Sn^{119}	15.87	8.68	5.18×10^{-2}	0.373	−1.0409	1/2	—
• Sb^{121}	10.19	57.25	0.160	2.79	3.3417	5/2	−0.8
• Sb^{123}	5.518	42.75	4.57×10^{-2}	2.72	2.5334	7/2	−1.0
• Te^{123}	11.59	0.89	1.80×10^{-2}	0.262	−0.7319	1/2	—
• Te^{125}	13.45	7.03	3.16×10^{-2}	0.316	−0.8824	1/2	—
• I^{127}	8.519	100.	9.35×10^{-2}	2.33	2.7939	5/2	−0.75
• I^{129*}	5.669	—	4.96×10^{-2}	2.80	2.6030	7/2	−0.43
• Xe^{129}	11.78	26.24	2.12×10^{-2}	0.277	−0.7726	1/2	—
• Xe^{131}	3.490	21.24	2.77×10^{-3}	0.410	0.6868	3/2	−0.12
• Cs^{133}	5.585	100.	4.74×10^{-2}	2.75	2.5642	7/2	⩽0.3
Cs^{134*}	5.64	—	6.21×10^{-2}	3.53	2.96	4	—
Cs^{135*}	5.94	—	5.70×10^{-2}	2.94	2.727	7/2	—
Cs^{137*}	6.19	—	6.44×10^{-2}	3.05	2.84	7/2	—
Ba^{135}	4.25	6.59	4.99×10^{-3}	0.499	0.837	3/2	—
Ba^{137}	4.76	11.32	6.97×10^{-3}	0.559	0.936	3/2	—
• La^{138*}	5.617	0.089	9.18×10^{-2}	2.64	3.6844	5	2.7
• La^{139}	6.014	99.911	5.92×10^{-2}	2.97	2.7615	7/2	0.9
Ce^{141*}	0.35	—	1.1×10^{-5}	0.17	0.16	7/2	—
Pr^{141}	11.3	100.	0.234	3.18	3.8	5/2	-5.4×10^{-2}
Nd^{143}	2.2	12.20	2.81×10^{-3}	1.07	−1.1	7/2	⩽1.2
Nd^{145}	1.4	8.30	6.70×10^{-4}	0.666	−0.69	7/2	⩽1.2
Sm^{147}	1.47	15.07	8.8×10^{-4}	0.725	−0.68	7/2	0.72
Sm^{149}	1.19	13.84	4.7×10^{-4}	0.591	−0.55	7/2	0.72
Eu^{151}	10.	47.77	0.168	2.84	3.4	5/2	~1.2
Eu^{153}	4.6	52.23	1.45×10^{-2}	1.25	1.5	5/2	~2.5

Annex - VARIAN table



ISOTOPE (*indicates radioactive)	n-m-r FREQUENCY in mc. for a 10 Kilogauss field	NATURAL ABUNDANCE %	RELATIVE SENSITIVITY for equal number of nuclei		MAGNETIC MOMENT μ in multiples of the nuclear magneton ($e h / 4\pi M c$)	SPIN I in multiples of $\frac{h}{2\pi}$	ELECTRIC QUADRUPOLE MOMENT Q in multiples of $e \times 10^{-24}$ cm²
			at constant field	at constant frequency			
Gd^{155}	—	14.68	—	—	−0.~~44~~ 26	3/2 ~~(7/2)~~	—
Gd^{157}	—	15.64	—	—	−0.34	3/2 ~~(7/2)~~	—
Tb^{159}	—	100.	—	—	—	3/2	—
Dy^{161}	—	18.73	—	—	—	7/2	—
Dy^{163}	—	24.97	—	—	—	7/2	—
Ho^{165}	—	100.	—	—	—	7/2	—
Er^{167}	—	22.82	—	—	− 0,5665	—	~~>10~~ 2,827
Tm^{169}	—	100.	—	—	—	1/2	—
Yb^{171}	6.9	14.27	4.19×10^{-3}	0.161	0.45	1/2	—
Yb^{173}	1.98	16.08	1.18×10^{-3}	0.543	−0.65	5/2	3.9
Lu^{175}	5.7	97.40	4.94×10^{-2}	2.79	2.6	7/2	5.9
Lu^{176*}	—	2.60	—	—	4.2	≥7	6–8
Hf^{177}	—	18.39	—	—	—	1/2 or 3/2	—
Hf^{179}	—	13.78	—	—	—	1/2 or 3/2	—
Ta^{181}	4.6	100.	2.60×10^{-2}	2.26	2.1	7/2	6.5
• W^{183}	1.75	14.28	6.98×10^{-5}	4.12	0.115	1/2	—
• Re^{185}	9.586	37.07	0.133	2.63	3.1437	5/2	2.8
• Re^{187}	9.684	62.93	0.137	2.65	3.1760	5/2	2.6
• Os^{189}	3.307	16.1	2.24×10^{-3}	0.385	0.6507	3/2	2.0
Ir^{191}	0.81	38.5	3.5×10^{-5}	9.5×10^{-2}	0.16	3/2	~1.2
Ir^{193}	0.86	61.5	4.2×10^{-5}	0.104	0.17	3/2	~1.0
• Pt^{195}	9.153	33.7	9.94×10^{-3}	0.215	0.6004	1/2	—
Au^{197}	0.691	100.	2.14×10^{-5}	8.1×10^{-2}	0.136	3/2	0.56
• Hg^{199}	7.612	16.86	5.72×10^{-3}	0.179	0.4993	1/2	—
Hg^{201}	3.08	13.24	1.90×10^{-3}	0.362	−0.607	3/2	0.5
• Tl^{203}	24.33	29.52	0.187	0.571	1.5960	1/2	—
• Tl^{205}	24.57	70.48	0.192	0.577	1.6114	1/2	—
• Pb^{207}	8.899	21.11	9.13×10^{-3}	0.209	0.5837	1/2	—
• Bi^{209}	6.842	100.	0.137	5.30	4.0389	9/2	−0.4
U^{235*}	—	0.71	—	—	—	5/2	—
Np^{237*}	~20	—	1.0	3.0	6 ± 2.5	5/2	—
Pu^{239*}	6.1	—	2.9×10^{-3}	0.14	0.4	1/2	—
Pu^{241*}	4.3	—	1.2×10^{-2}	1.2	1.4	5/2	—
Free Electron	27,994	—	2.85×10^{8}	658	−1836	1/2	— !

Nous vous remercions pour votre attention