Cryogenics – why?

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European Cryogenic Course
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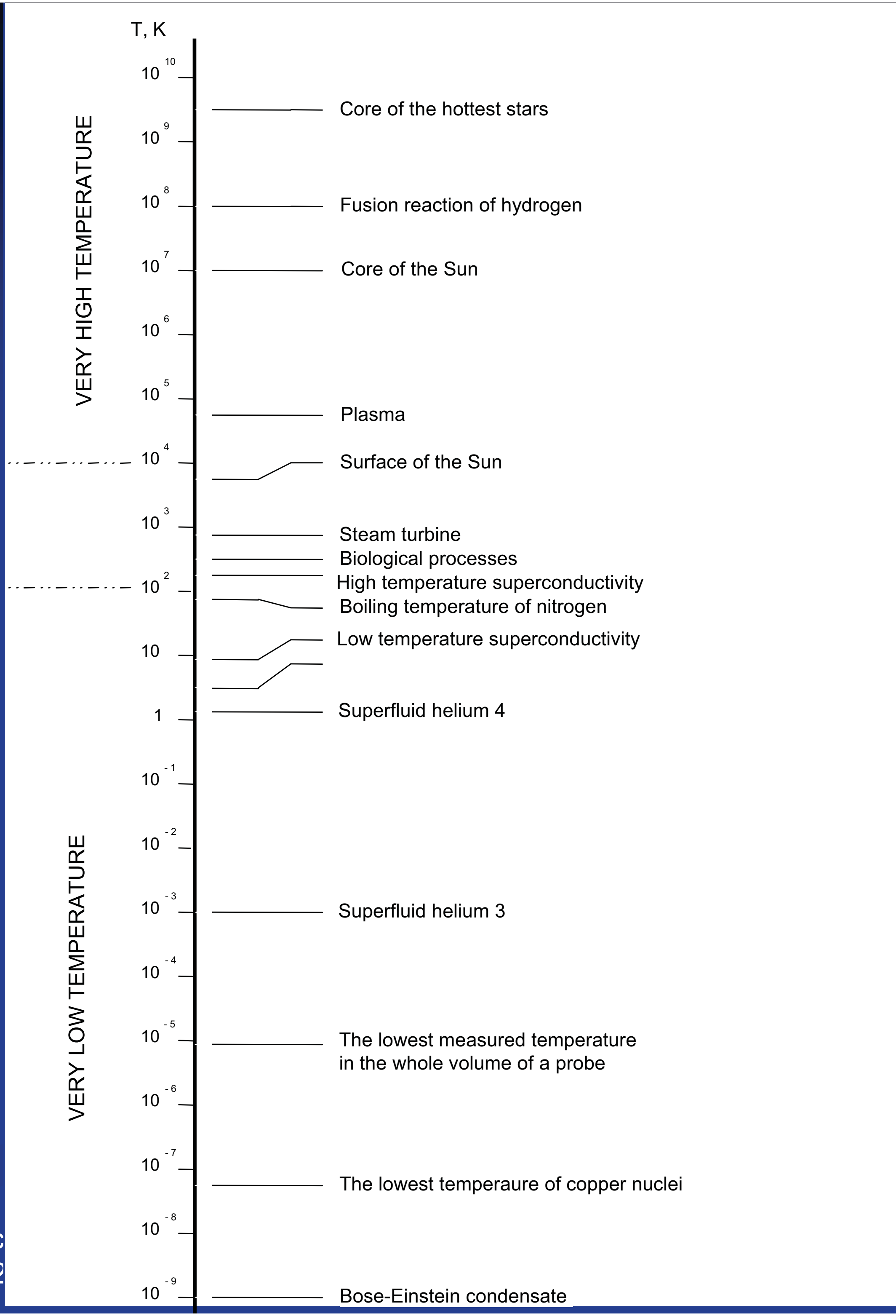
The word cryogenics was introduced by Kamerlingh Onnes and is formed from the Greek:

κρυοζ – cold
γενοζ– generated from

According to the convention adopted at the XIIII Congress of the International Institute of Refrigeration, *cryogenics* treats concepts and technologies connected to reaching and applying temperature below 120 K.
In cryogenic temperatures:

- new physical phenomena are visible (liquefaction of gases, superfluidity, superconductivity);
- all the reactions are slowed down;
- dis-order in the matter is vanishing, noises are avoided (cryo-electronics).



Historical development of cryogenics and related technologies

1883 Karol Olszewski and Zygmunt Wróblewski liquefy air and its components (77 K) – Cracow, Poland

1895 Carl Linde starts LINDE AG

1898 James Dewar invents vacuum insulation and liquefies hydrogen (20,3 K), UK

1902 Georges Claudet starts L'Air Liquide

1908 Kammerlingh Onnes liquefies helium (4,2 K) and discovers superconductivity in mercury in 1911, Leiden, Holand

1950 Collins starts a serial production of helium liquefiers, USA

1986 Bednorz i Mueller discover high temperature superconductivity (the highest Tc is now of 135 K), Zurich, Switzerland

2008 Start of the ITER construction – the biggest concentrated cryogenic system

2009 Start of the LHC superconducting accelerator at CERN, Geneva (over 2000 of superconducting magnets of total length 28 km), 105 tons of He, Geneva, CERN

Karol Olszewski and Zygmunt Wróblewski air, nitrogen, oxygen liquefaction in 1883

1846-1915

Jagiellonian University, Cracow

1845-1888

Technical gases industry has decided abot the metallurgy development – over 100 years of tradition

Carl von Linde – Linde AG founder in 1895

Georges Claudet – co-founder of the L'Air Liquide in 1902

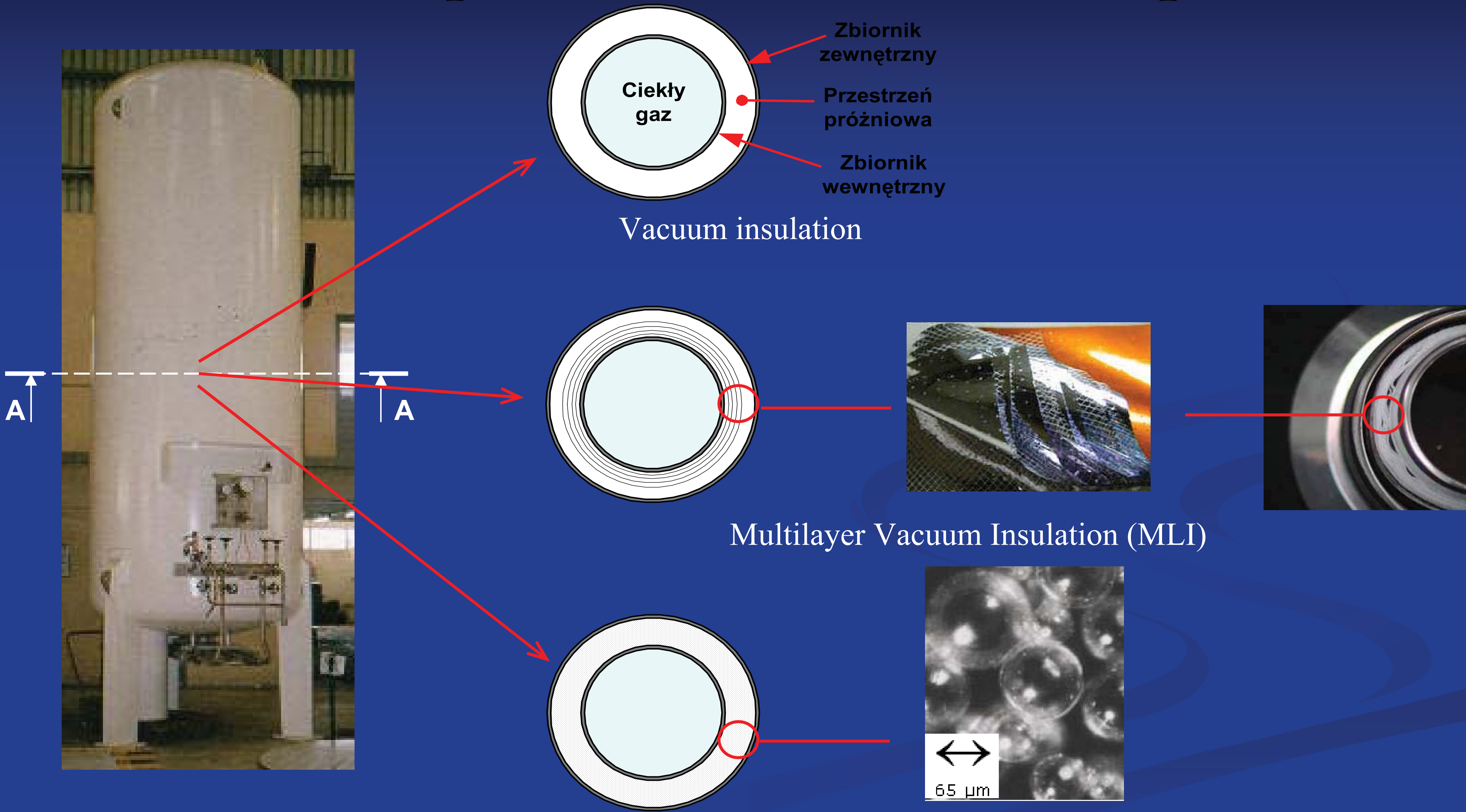
AIR LIQUIDE

Linde Gas Linde

James Dewar and his „vacuum flasks” 1898, vacuum insulation, hydrogen liquefaction

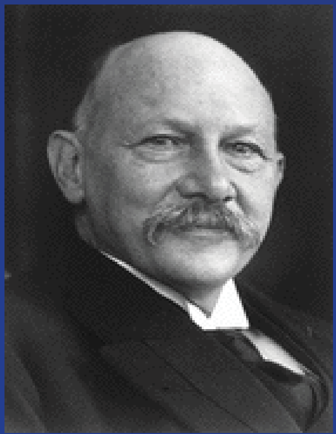
1842-1923

Modern cryogenic insulation systems – development of the Dewar concept

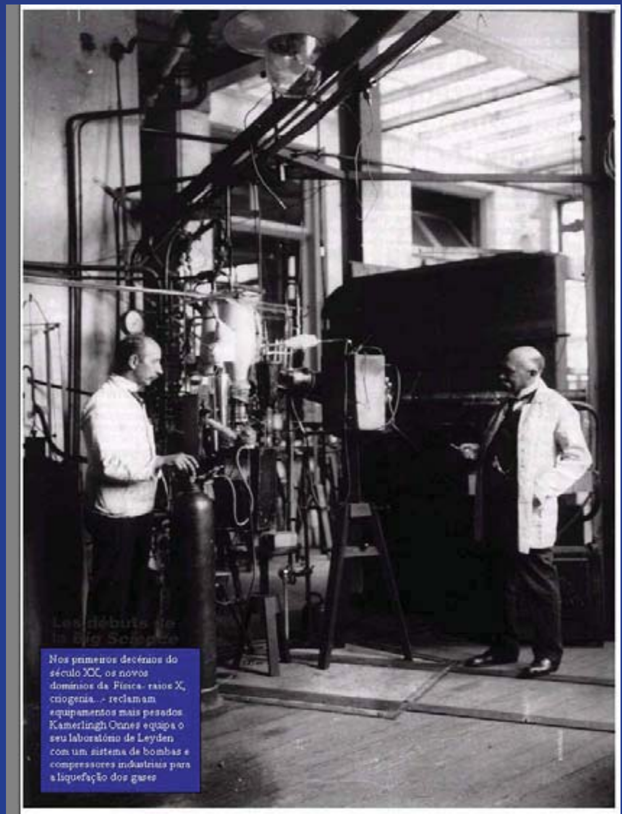


Vacuum Insulation with Glass Spheres

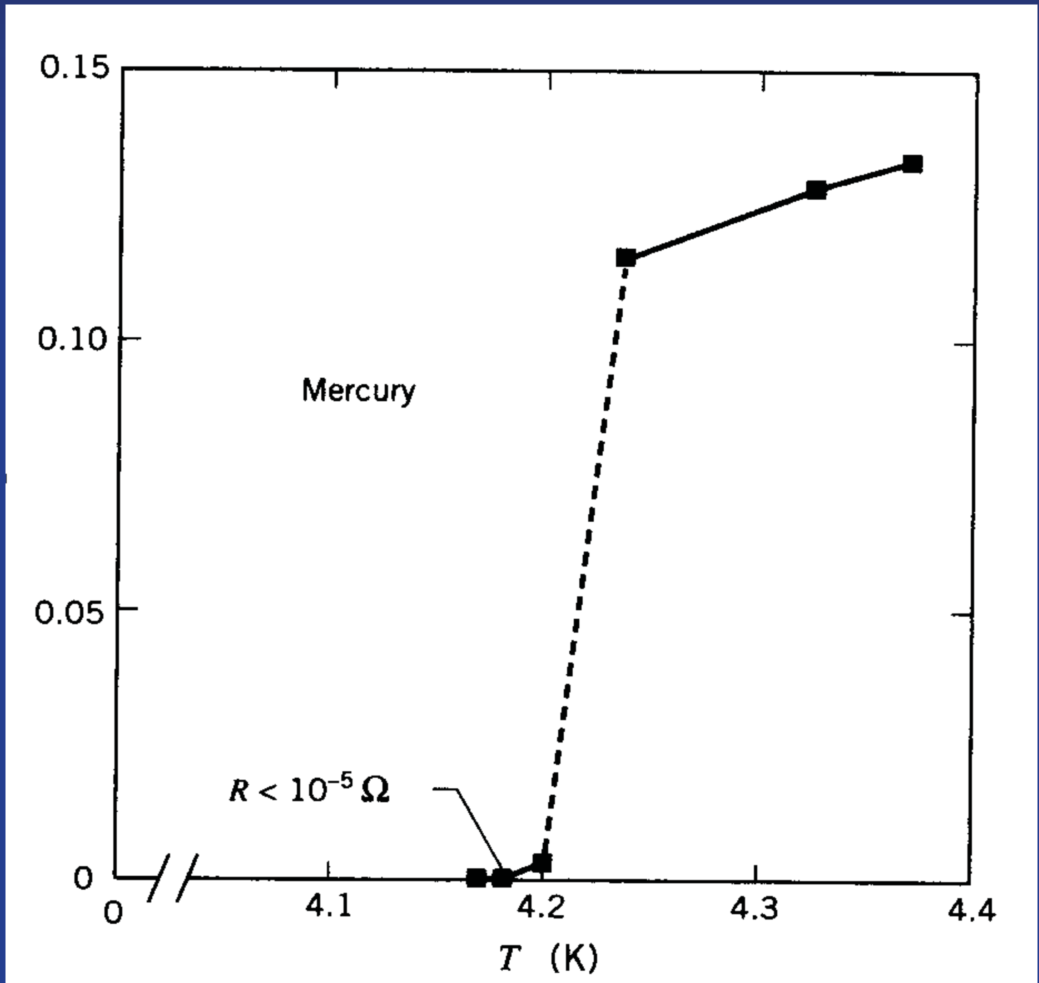
Heike Kamerlingh-Onnes and his „cryo-industry” helium liquefaction 1908

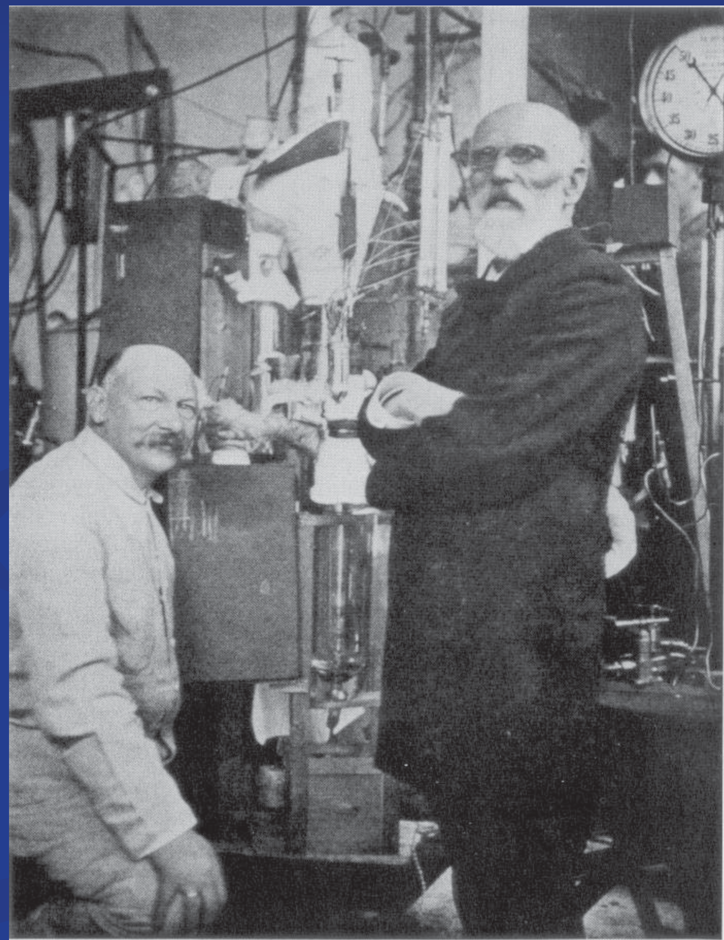


1853-1926



Heike Kamerlingh Onnes
Discovery of superconductivity in mercury 1911 r.



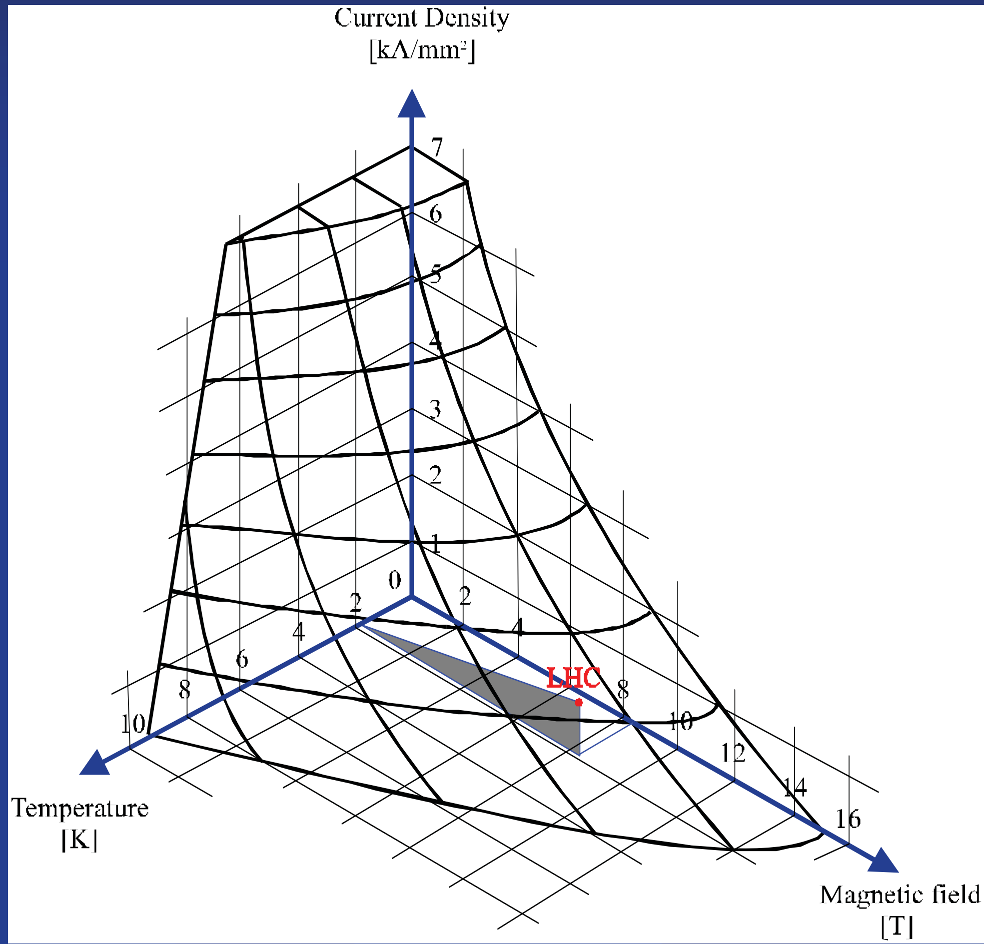


European Cryogenic Course
CERN Geneva 2010

Collins liquefiers – helium available in laboratories from 1950

Capacity of 4 – 8 LHe liter per hour

Comparison of NbTi superconducting wire with copper rods



Phase diagram NbTi

Cryogenics in Large Hadron Collider accelerator, CERN Geneva

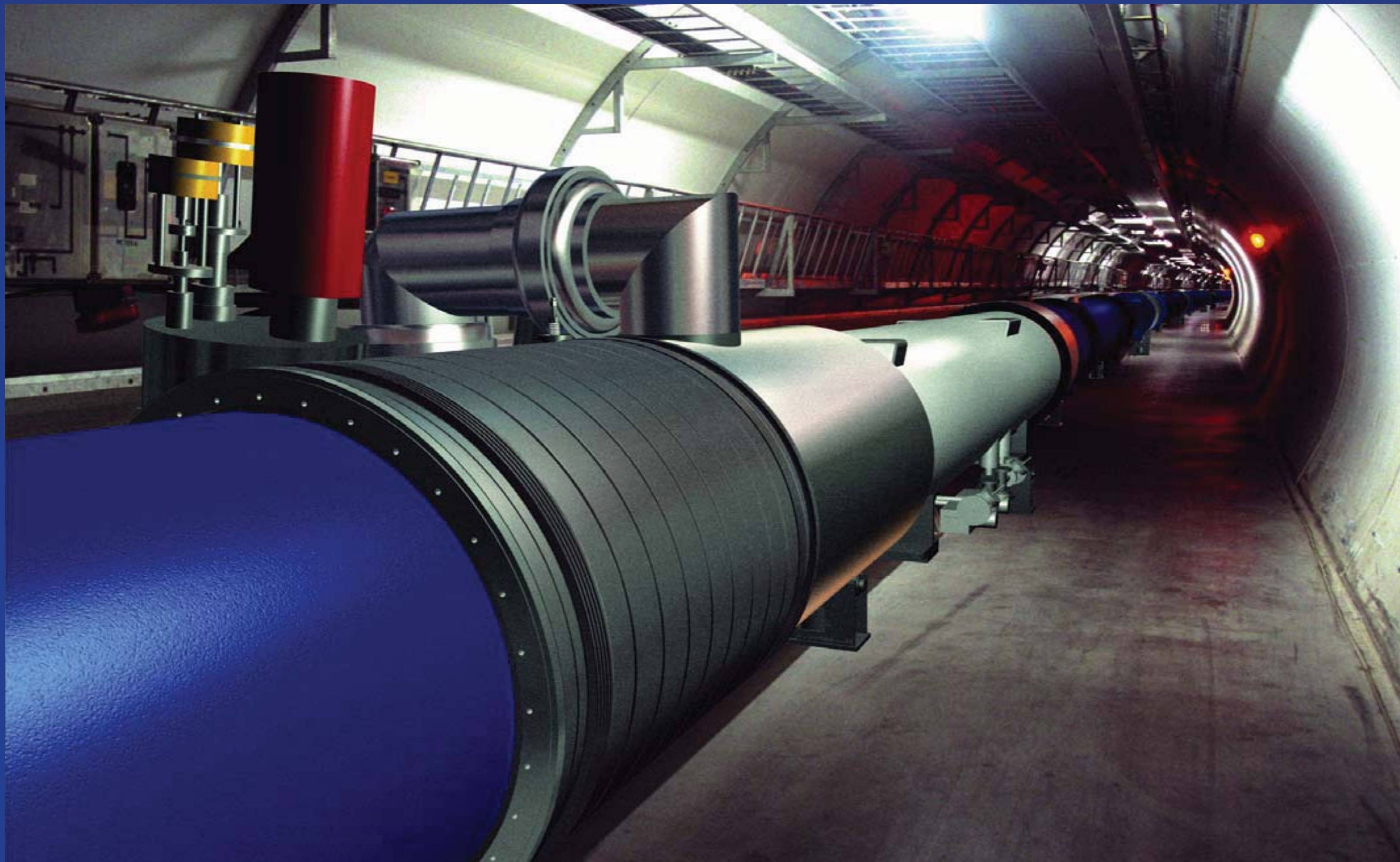
Over 2000 of superconducting magnets of overall length exceeding 27 km

Helium inventory above 100 t

Temperature 1,8 K

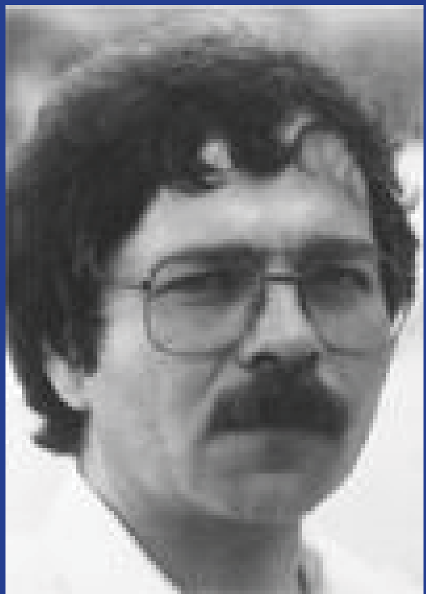
Energy 14 TeV

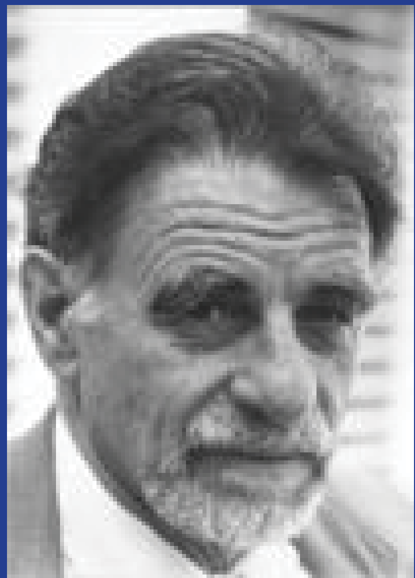
Particles: protons



Bednorz and Mueller high temperature superconductivity discovered in 1986

The Nobel Prize in Physics 1987





IBM Zurich Research Laboratory
Rüschlikon, Switzerland

„It is too early to predict how extensive the technical applications will be, but it is quite evident that the development is being followed with keen interest by representatives of electrical power technology, by microelectronics researchers and by physicists who envisage new applications in measurement technology"

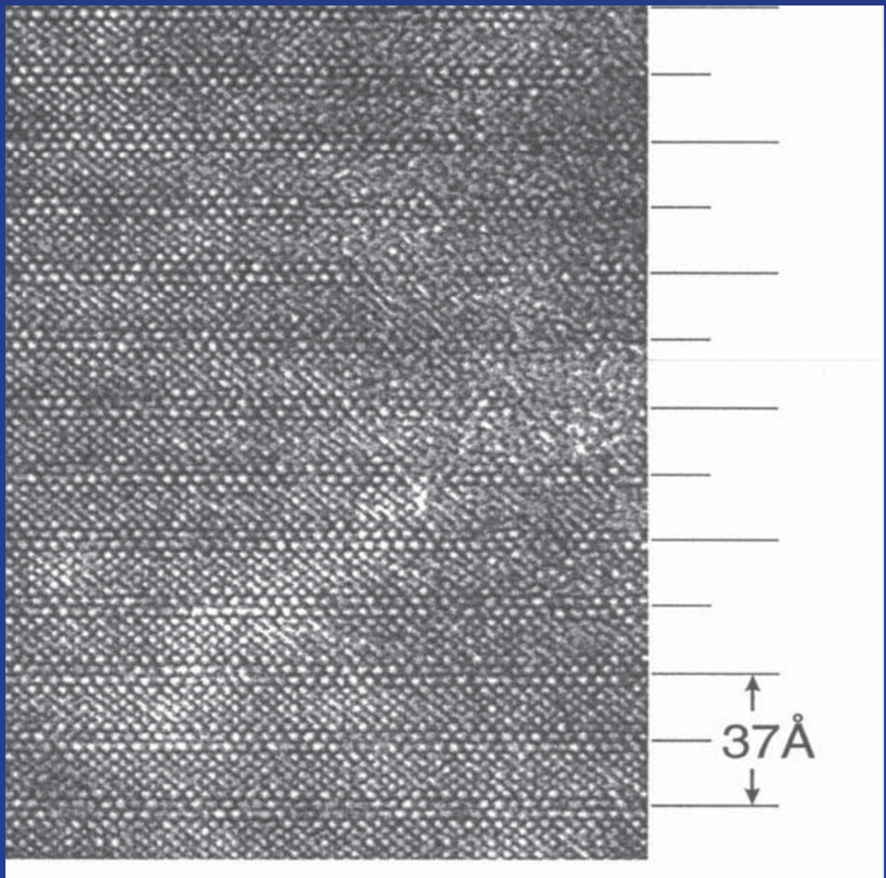
Form the Nobel Prize justification

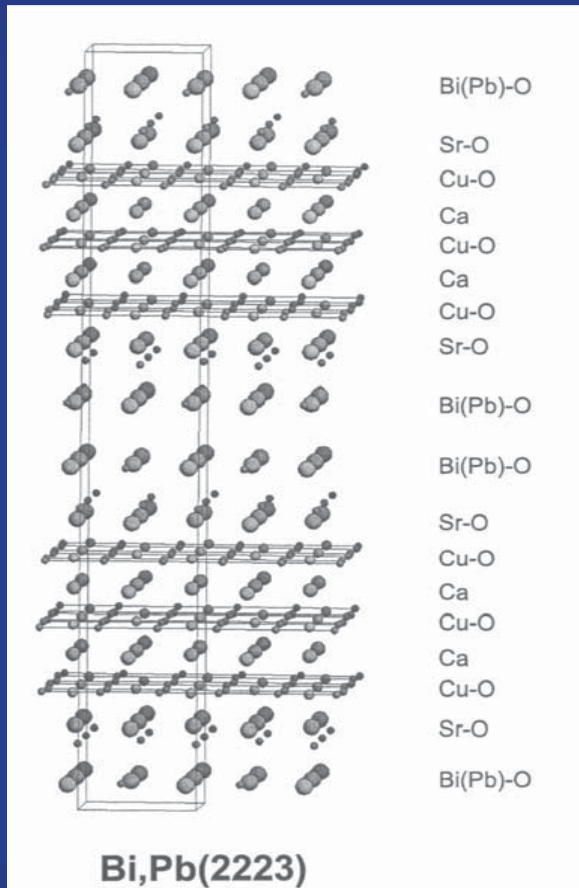
Critical temperatures of HTS superconductors

Group of superconductors	Superconductor	Critical temperature, K
YBCO	$YBa_2Cu_3O_x$ (Y-123)	92
BSCCO	$Bi_2Sr_2CaCu_2Ox$ (Bi-2212) $Bi_2Sr_2Ca_2Cu_3Ox$ (Bi-2223)	85 110
TBCCO	$TlBa_2Ca_2CuO_x$ (Tl-1221) $Tl_2Ba_2Ca_2Cu_3O_x$ (Tl-2223)	122 125
HBCCO	$HgBa_2CuO_x$ (Hg-1201) $HgBa_2CaCu_2O_x$ (Hg-1212) $HgBa_2Ca_2Cu_3O_x$ (Hg-1223)	94 117 135

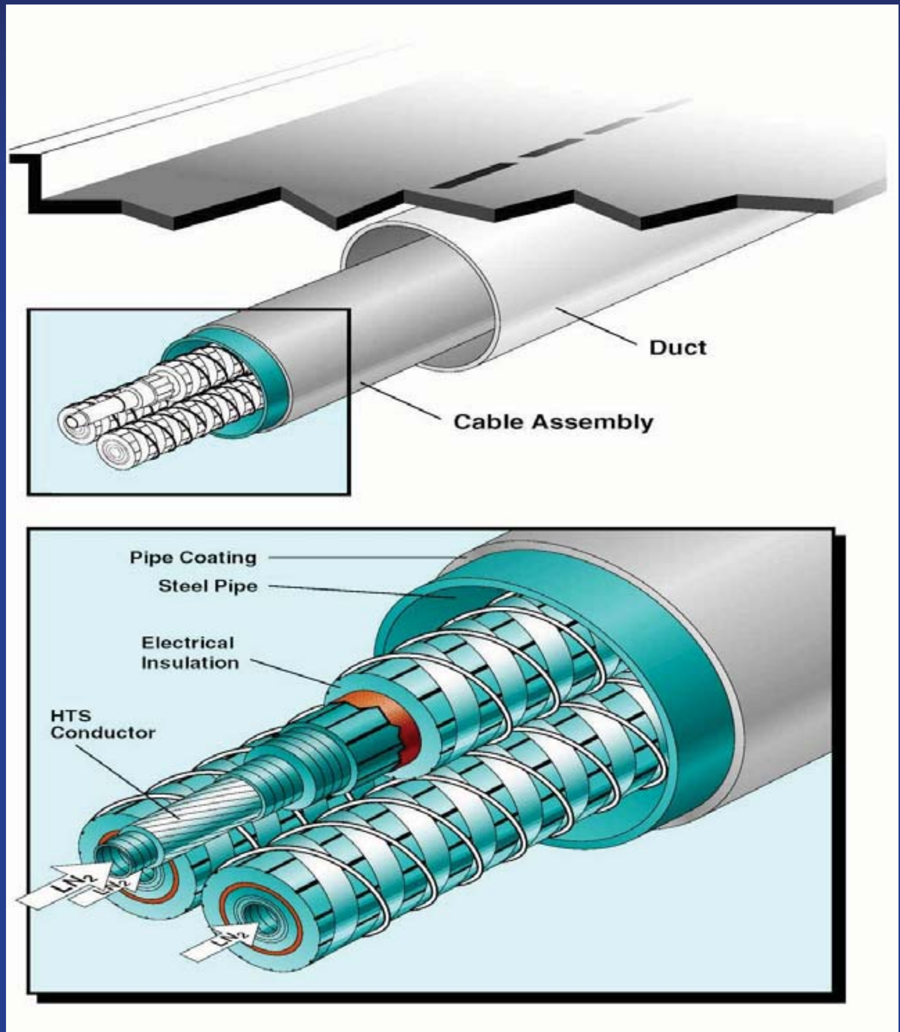
HTS superconductors can be cooled with LN2, cheap and easily available

Structure of B2223 superconductor





HTS prototype cables



Meissner effects, discovered in 1933

The **Meissner effect** (also known as the **Meissner-Ochsenfeld effect**) is the expulsion of a magnetic field from a superconductor. Walther Meissner and Robert Ochsenfeld found that below the superconducting transition temperature the specimens became perfectly diamagnetic, cancelling all flux inside. The experiment demonstrated for the first time that superconductors were more than just perfect conductors and provided a uniquely defining property of the superconducting state.

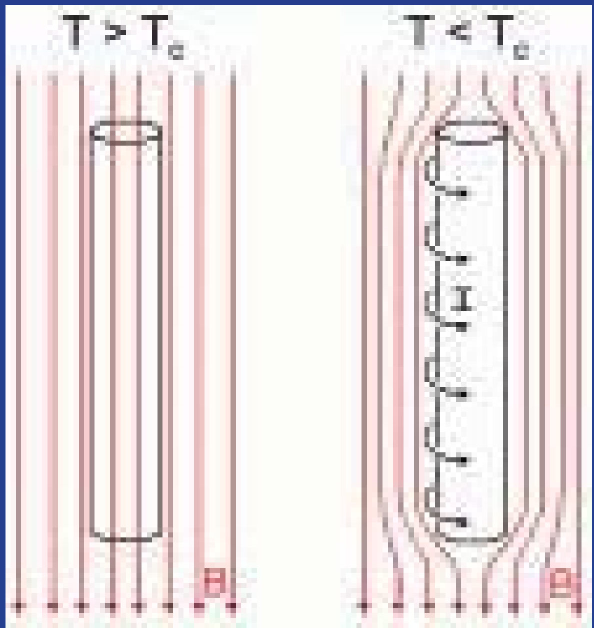
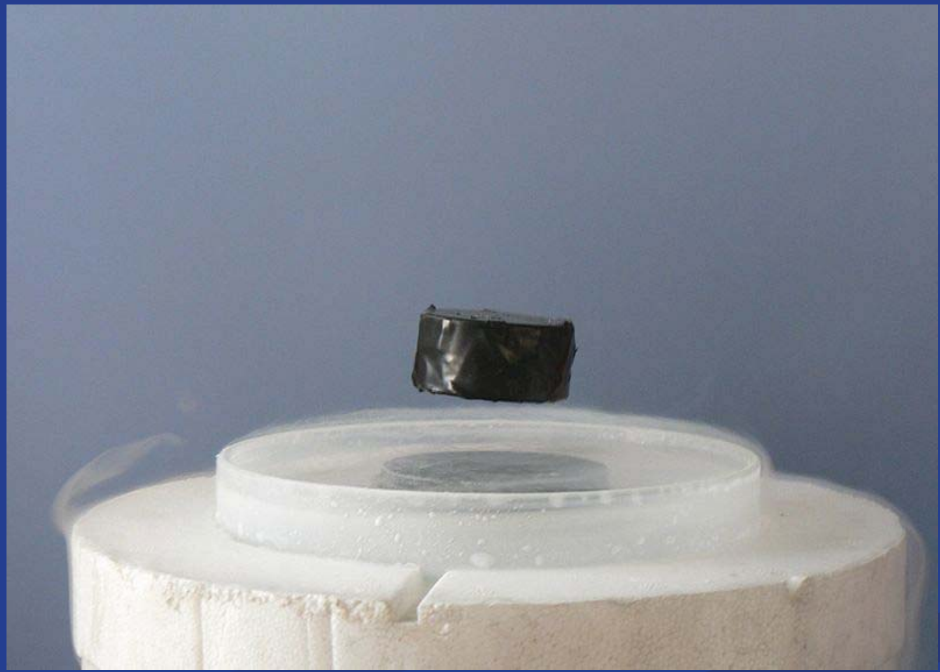


Diagram of the Meissner effect. Magnetic field lines, represented as arrows, are excluded from a superconductor when it is below its critical temperature.



A magnet levitating above a superconductor (cooled by liquid nitrogen).

MAGLEV train Shanghai

Other applications of cryogenics

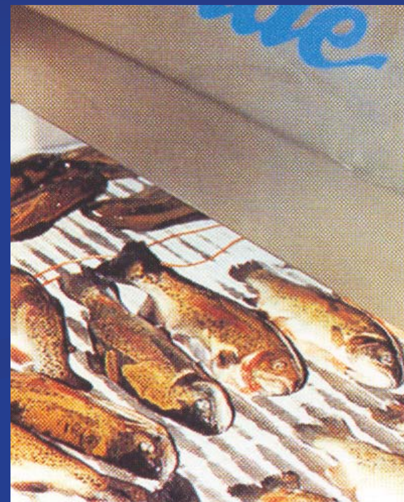
- Technical gases industry (air rectification, liquefaction, transport and storage of gases)
- Food freezing and storage
- Medicine, storage of biological samples
- Rocket industry (LH2)
- Power generation – (LNG), CO2 capture and storage
- Big scientific facilities

Air rectification

Air is a mixture of: nitrogen 78.1%, oxygen 20.9%, argon 0.93%, carbon dioxide 0.03%, neon 1.8E-3%, helium 5.2E-4%, hydrocarbons 3.5E-4%, krypton 1.1E-4%, hydrogen 5.0E-5%, xenon 8.0E-6, ozone 1.0E-6%, radon 6.0E-18%.

The main product of air separtaion are: nitrogen, oxygen, argon, neon, krypton and xenon

Cryogenic food freezing

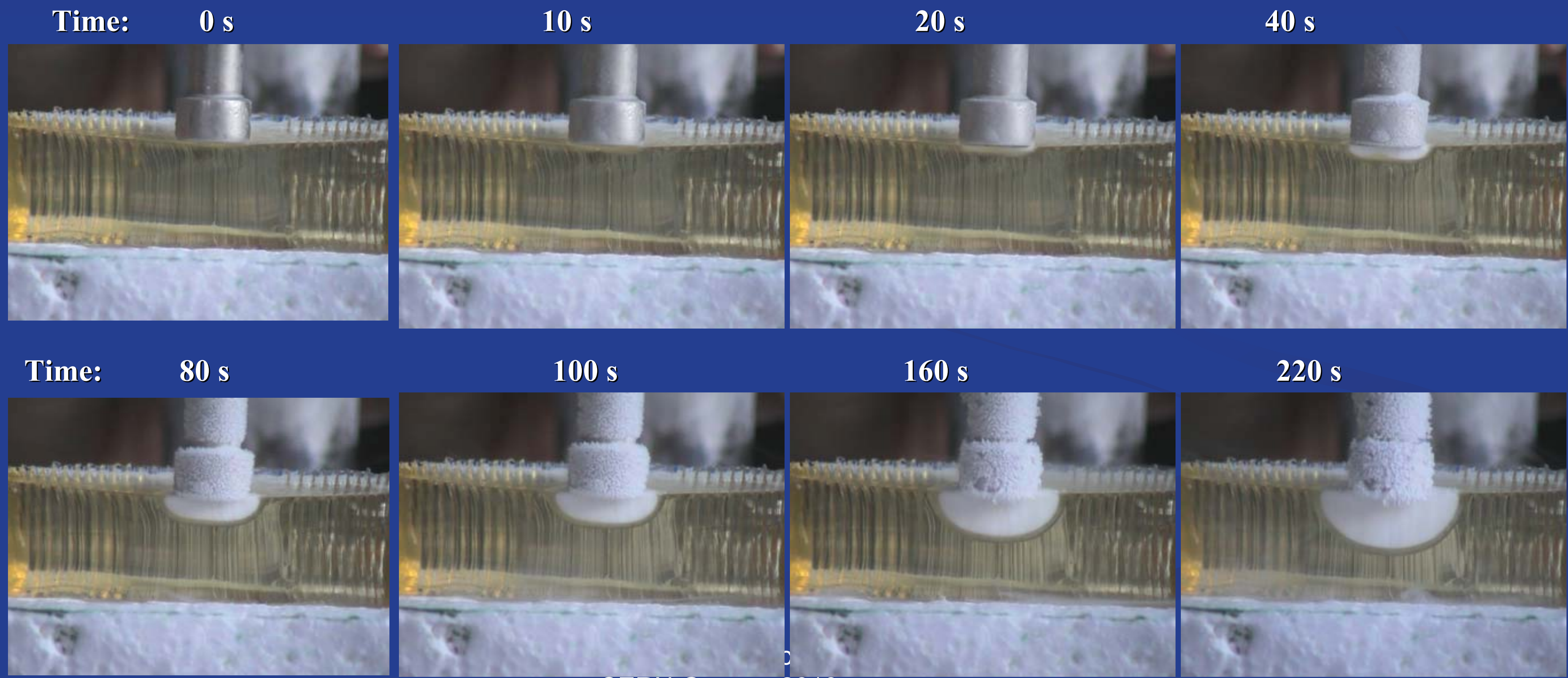


Cryomedicine

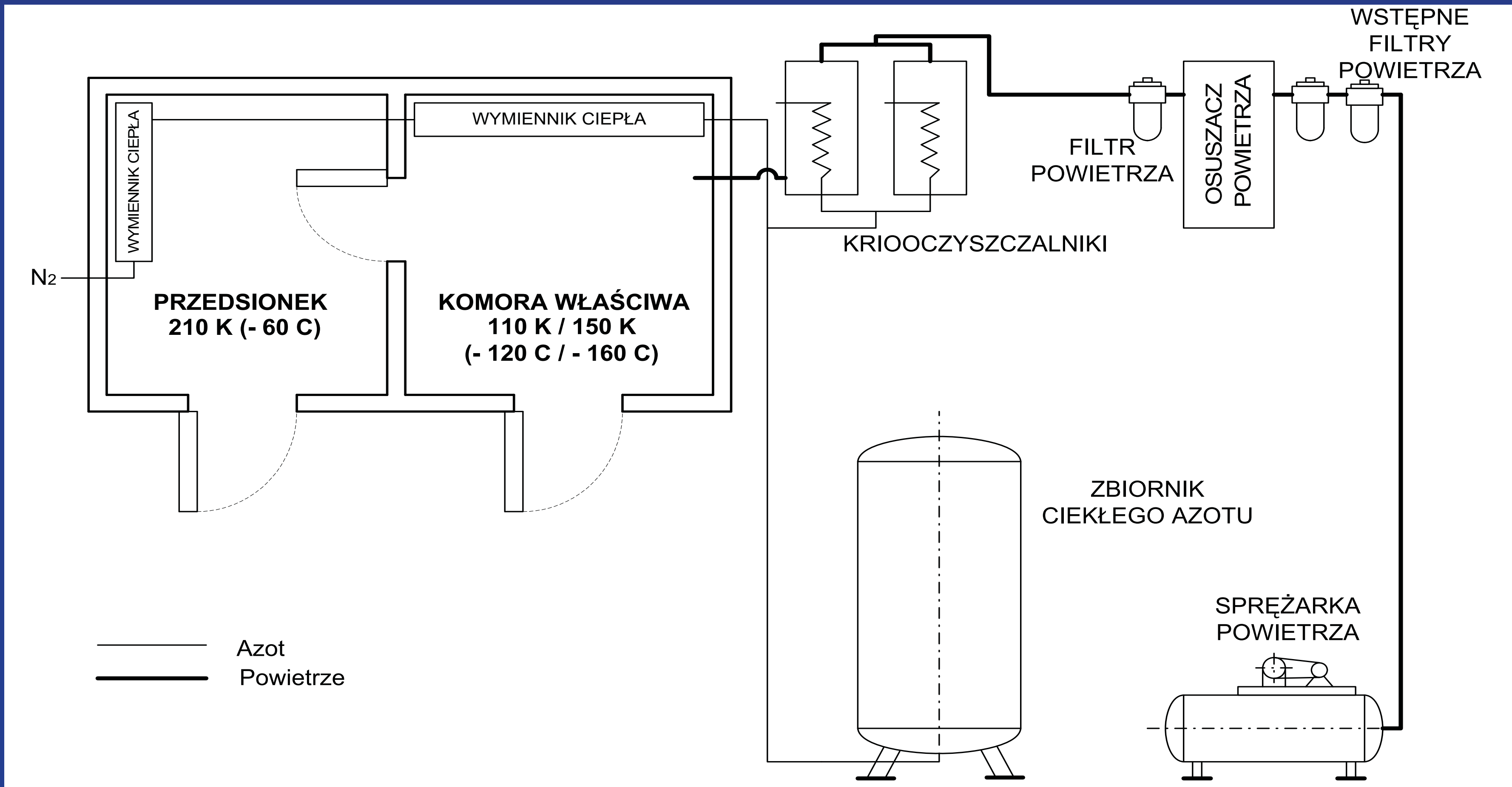
- **CRYOMEDICINE**
  - **CRYOTHERAPY** — CRYOSTIMULATION (to activate defensive reactions)
    - LOCAL
    - WHOLE BODY
  - **CRYOSURGERY** — TISSUE NECROSIS (to destroy pathological cells)
    - SPRAY
    - CONTACT
    - DIRECT EVAPORATING

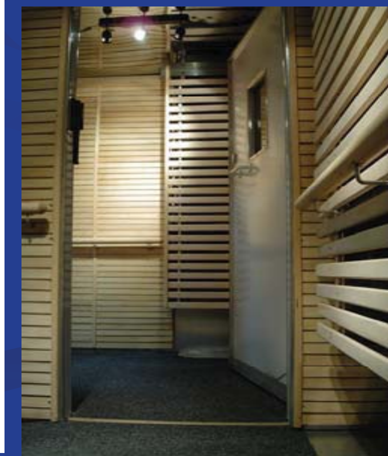
Simulation of cryosurgical treatment

Cryosurgery is aimed at the tissue necrosis, cryosurgical apparatuses are supplied with LN2 or N2O



Cryomedicine - cryochamber

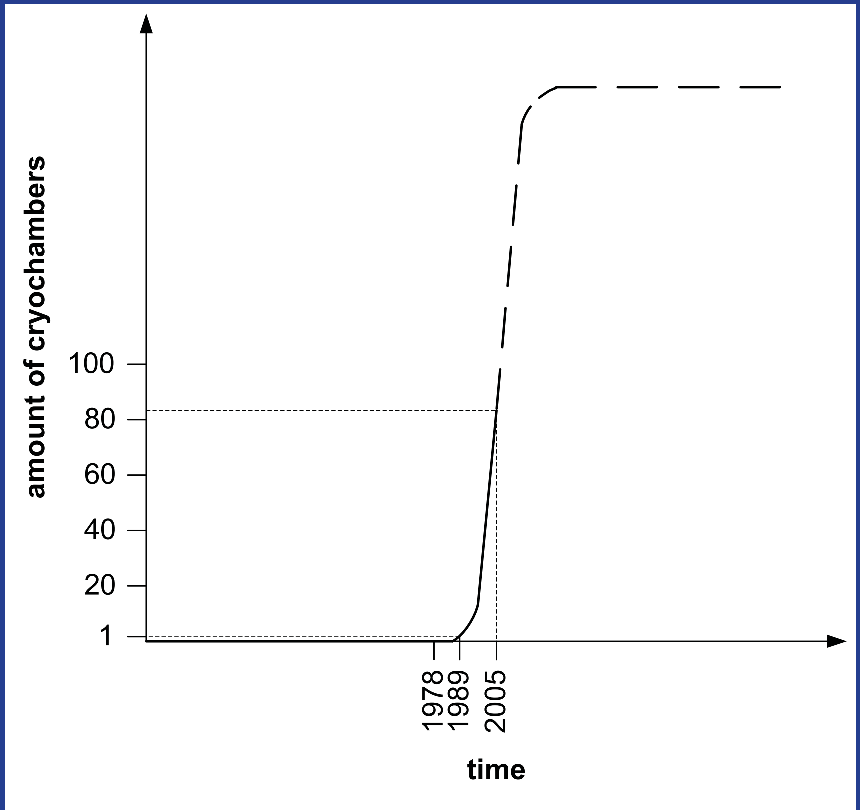




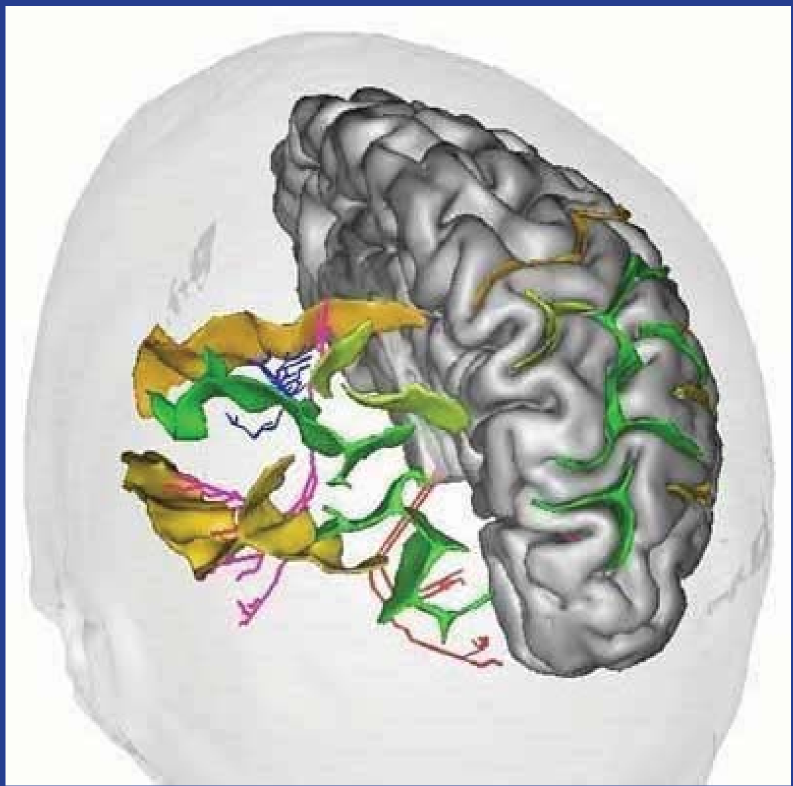
Komora CR-2002 CREATOR Wrocław

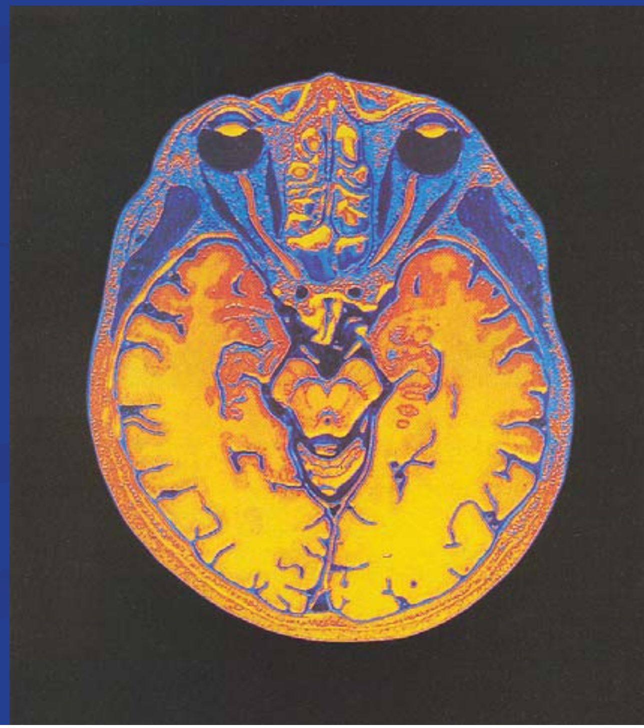
Cryo-chamber entrance

- Cryomedicine in Poland now means over thousand cryogenic installations of different scale and yearly consumption of liquid gases above 5000 Mg.
- A secondary effect is a vast propagation of the use of liquid gases and cryogenic culture in the society.

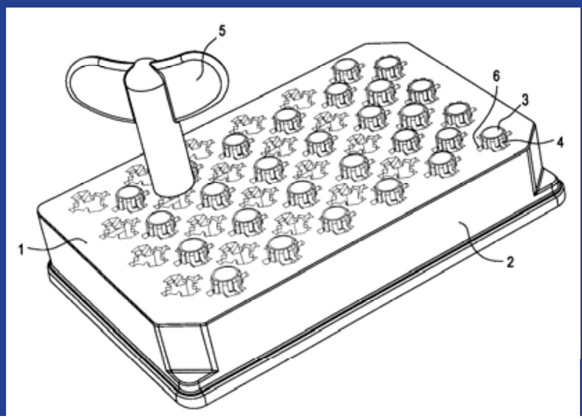


Seprconducting magnet cooling and diagnostics - NMR





Biological samples storage:



Rocket industry – liquid hydrogen

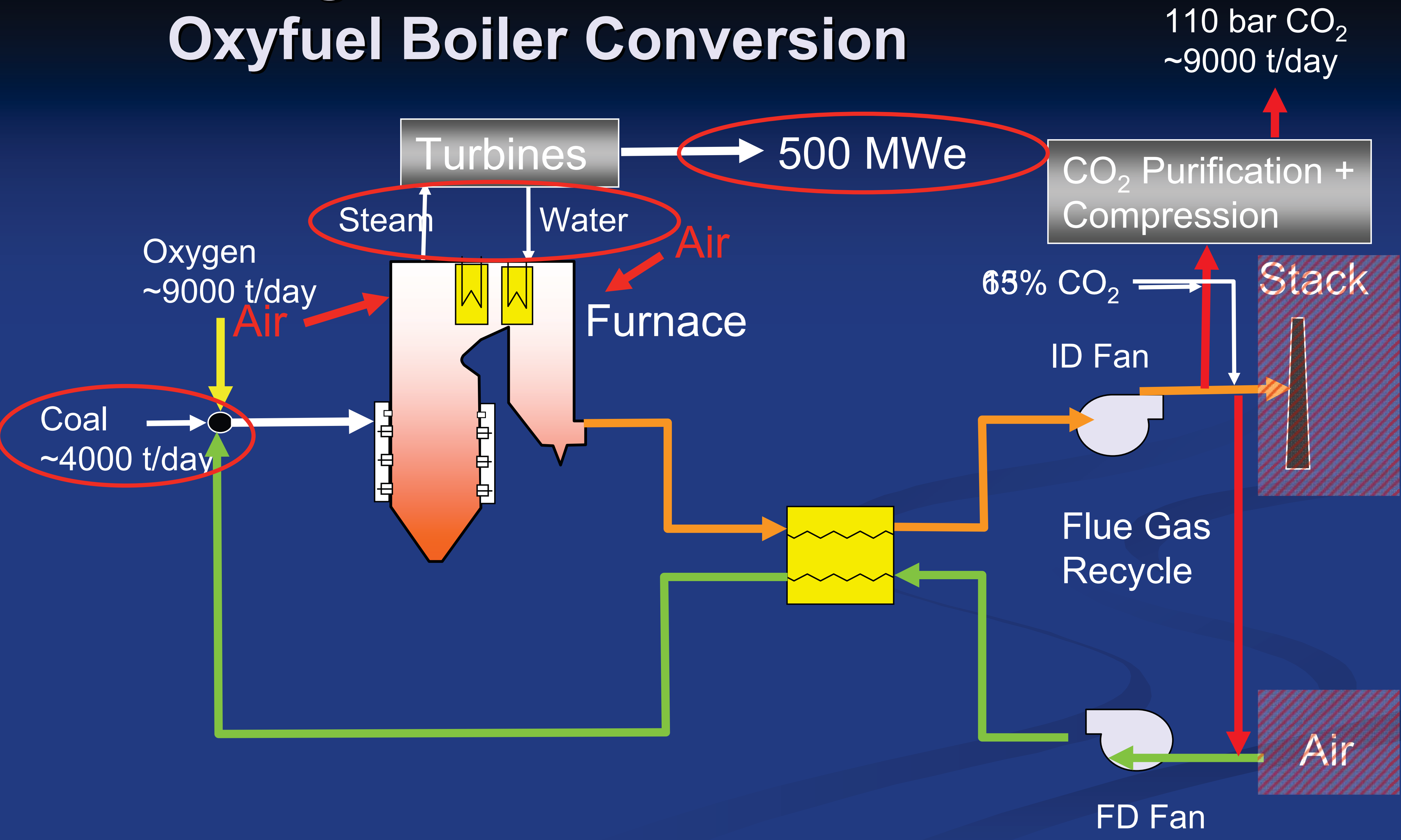
- There are three hydrogen isotopes: protonium H, deuterium D, and tritium T.
- Boiling temp.: H2: 20.28 K (HD: 20.13 K)
- Melting temp.: 13.96 K
- ρ_{vap} = 1.34 kg/m3
- ρ_{liq} = 70.8 kg/m3
- ρ_{solid} = 86.7 kg/m3
- Heat of evap.: 85.7 kJ/kg
- Heat of melting: 16.6 kJ/kg

- Hydrogen is used as rocket fuel

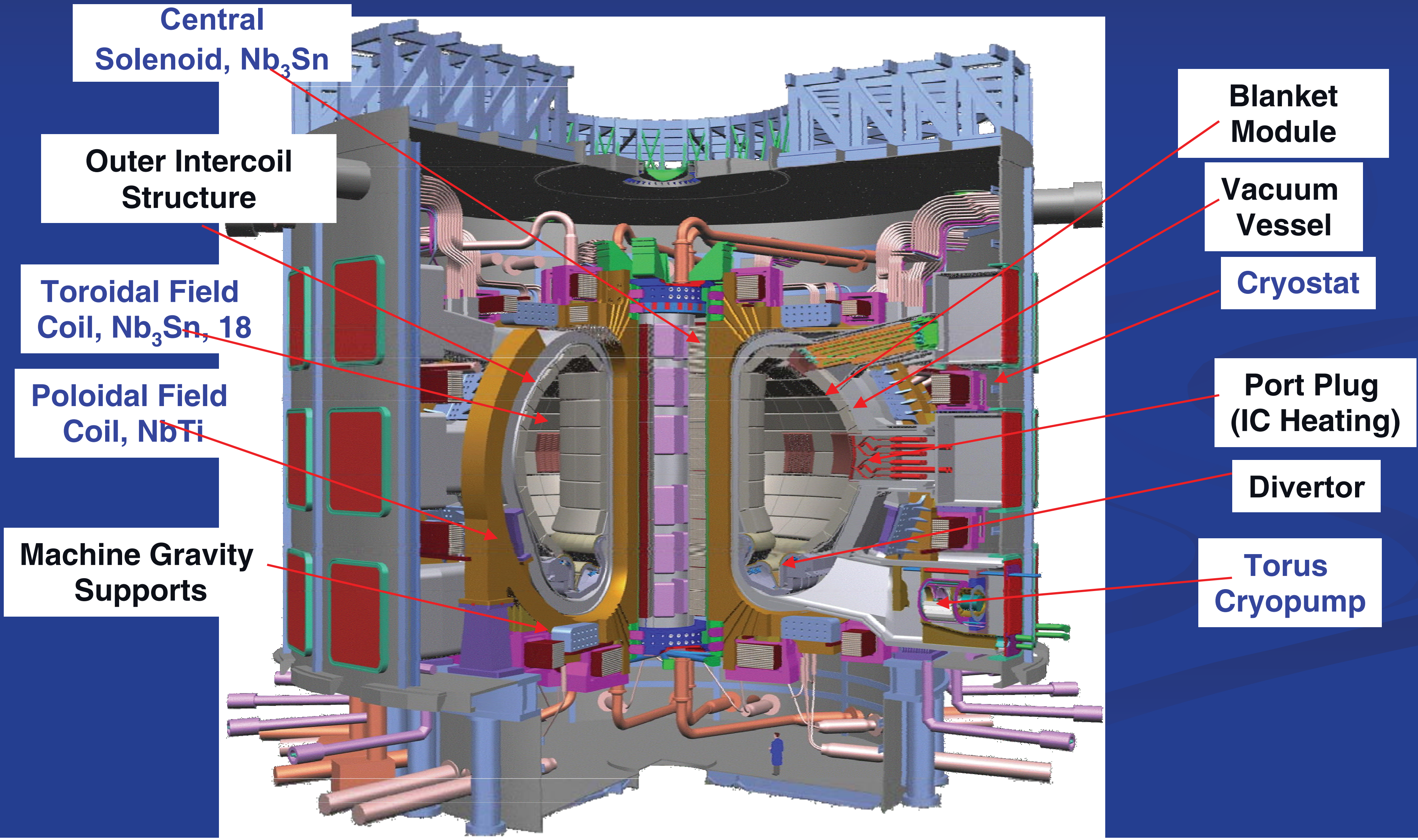
Power generation - terminal LNG

Natural gas transport without cryogenics ?

Power generation - Coal-Fired Oxyfuel Boiler Conversion



ITER cryogenics – the biggest concentrated cryogenic system in the world



ITER site, March 2008

Cryogenics – how?

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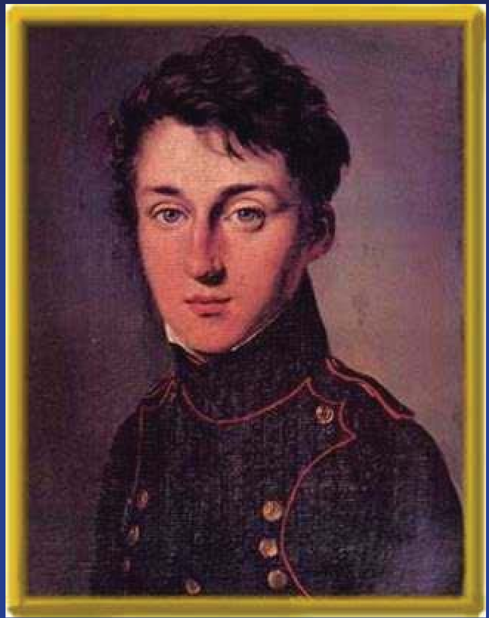
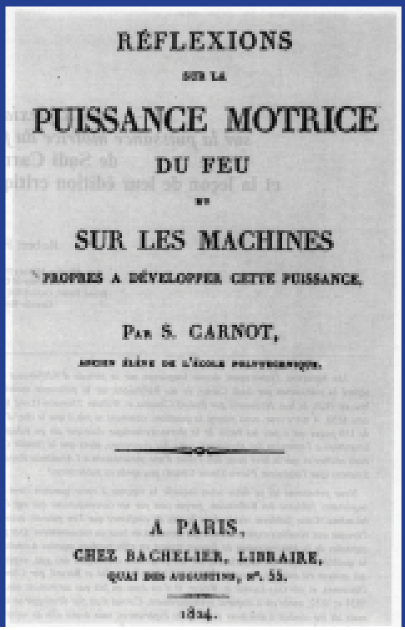
European Cryogenic Course
CERN, Geneval, 2010

Sadi Carnot and his waterwheel analogy





RÉFLEXIONS

SUR LA

PUISSANCE MOTRICE

DU FEU

ET

SUR LES MACHINES

PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,

ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

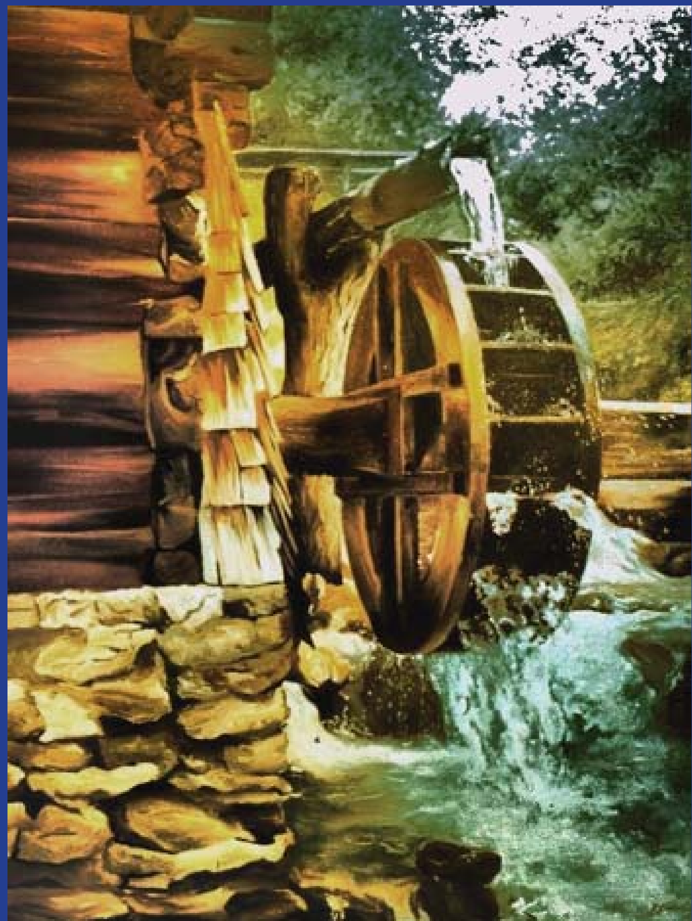
A PARIS,

CHEZ BACHELIER, LIBRAIRE,

QUAI DES AUGUSTINS, N°. 55.

1824.

Water (Heat) will not flow spontaneously from a low level (cold object) to a high level (hot object).



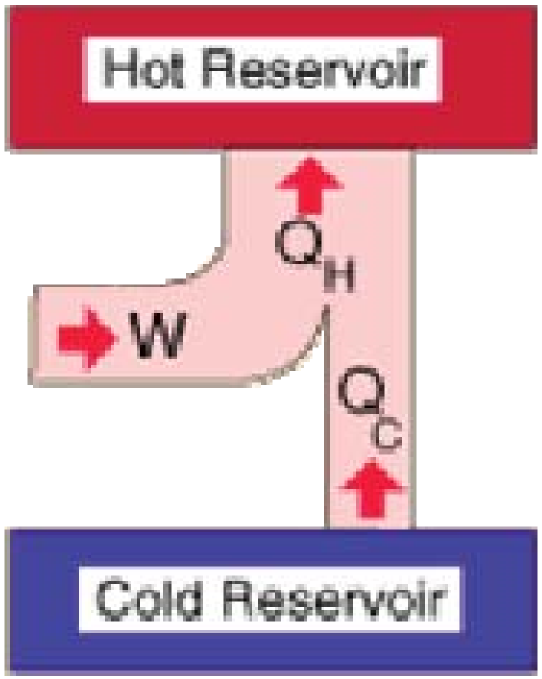
High level (temperature)

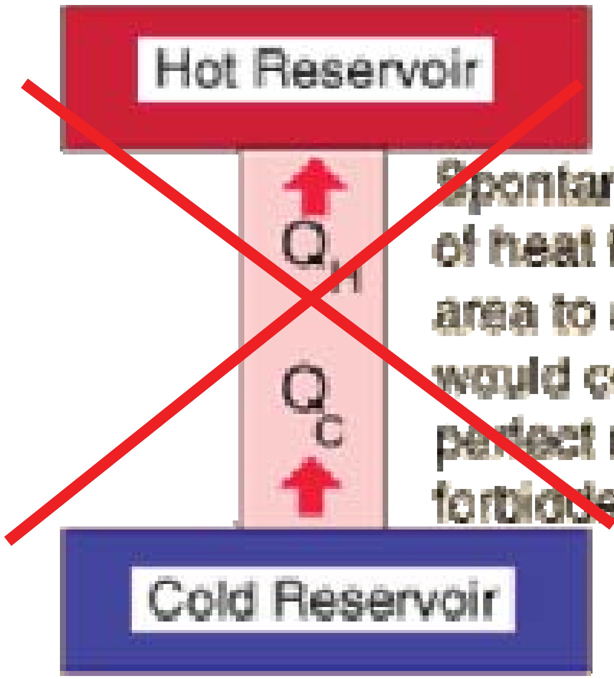
Low level (temperature)

Second Law of Thermodynamics

- It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow.

All real refrigerators require work to get heat to flow from a cold area to a warmer area.





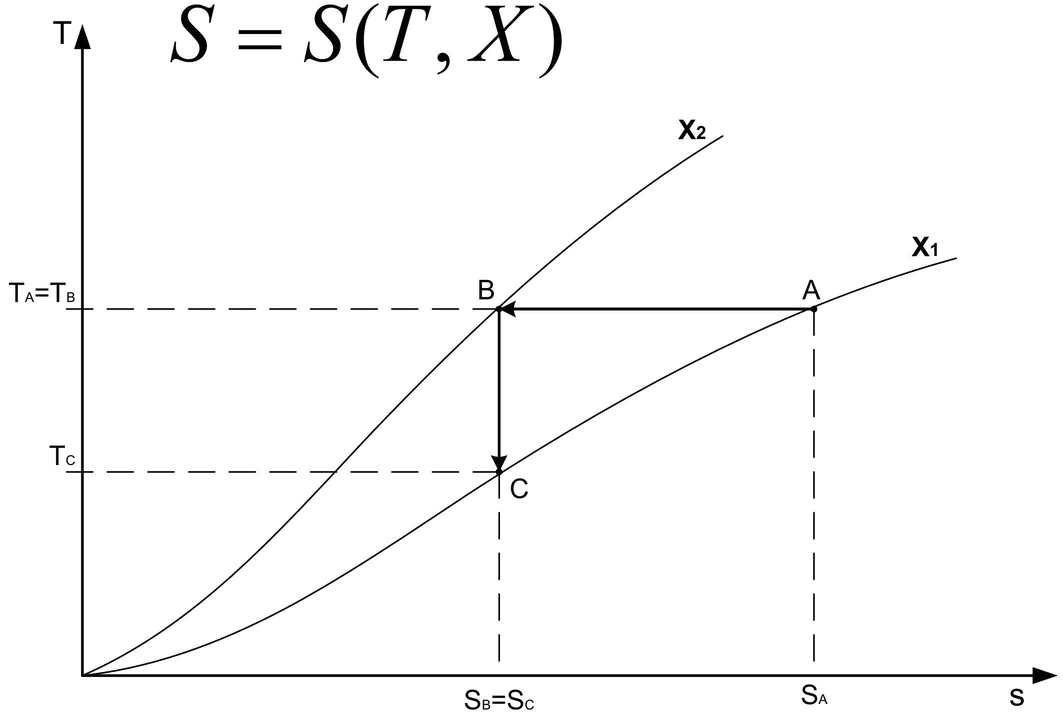
Spontaneous flow of heat from a cold area to a hot area would constitute a perfect refrigerator, forbidden by the second law.

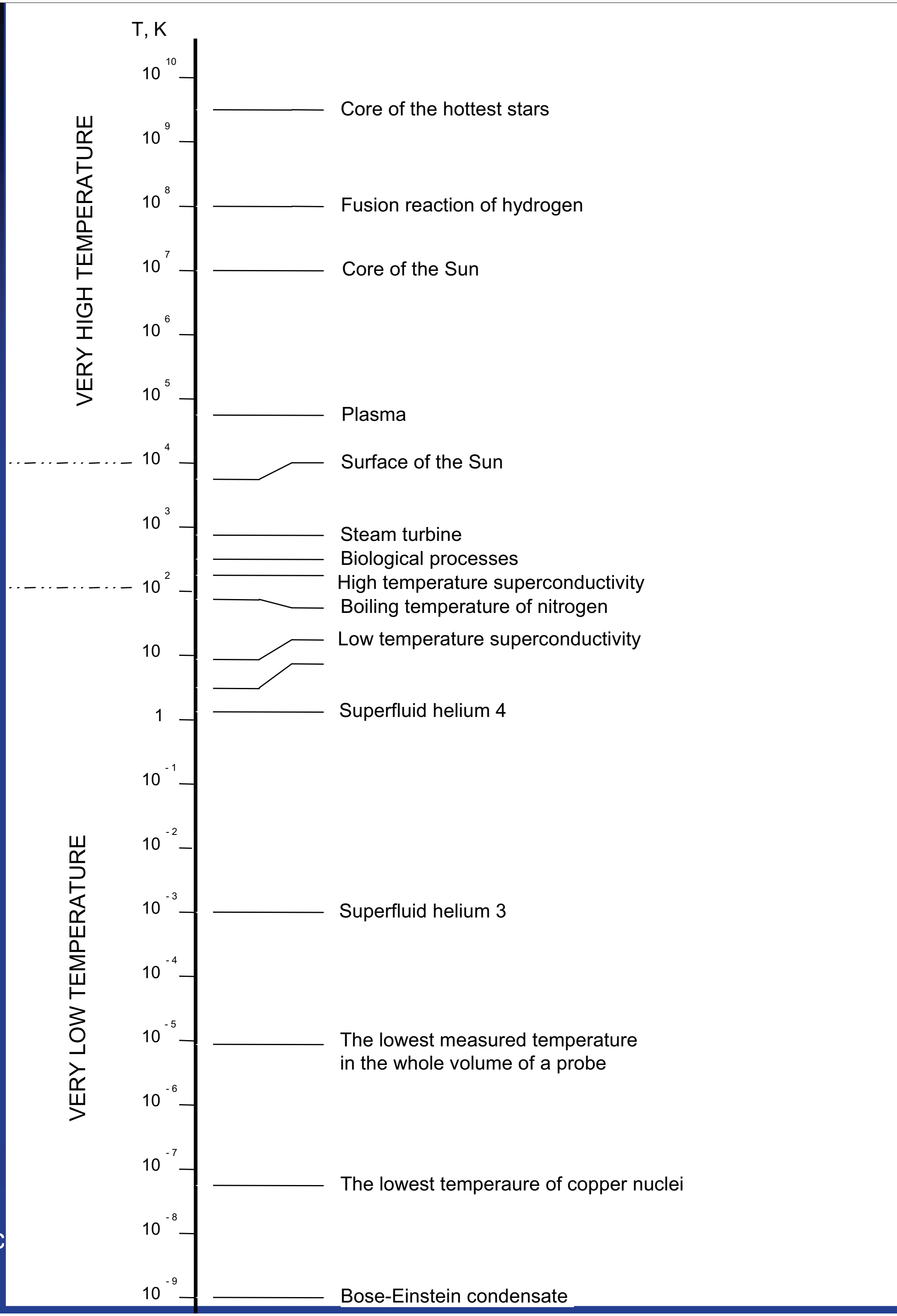
Third Law of Thermodynamics:

The entropy of all systems and of all states of a system is zero at absolute zero

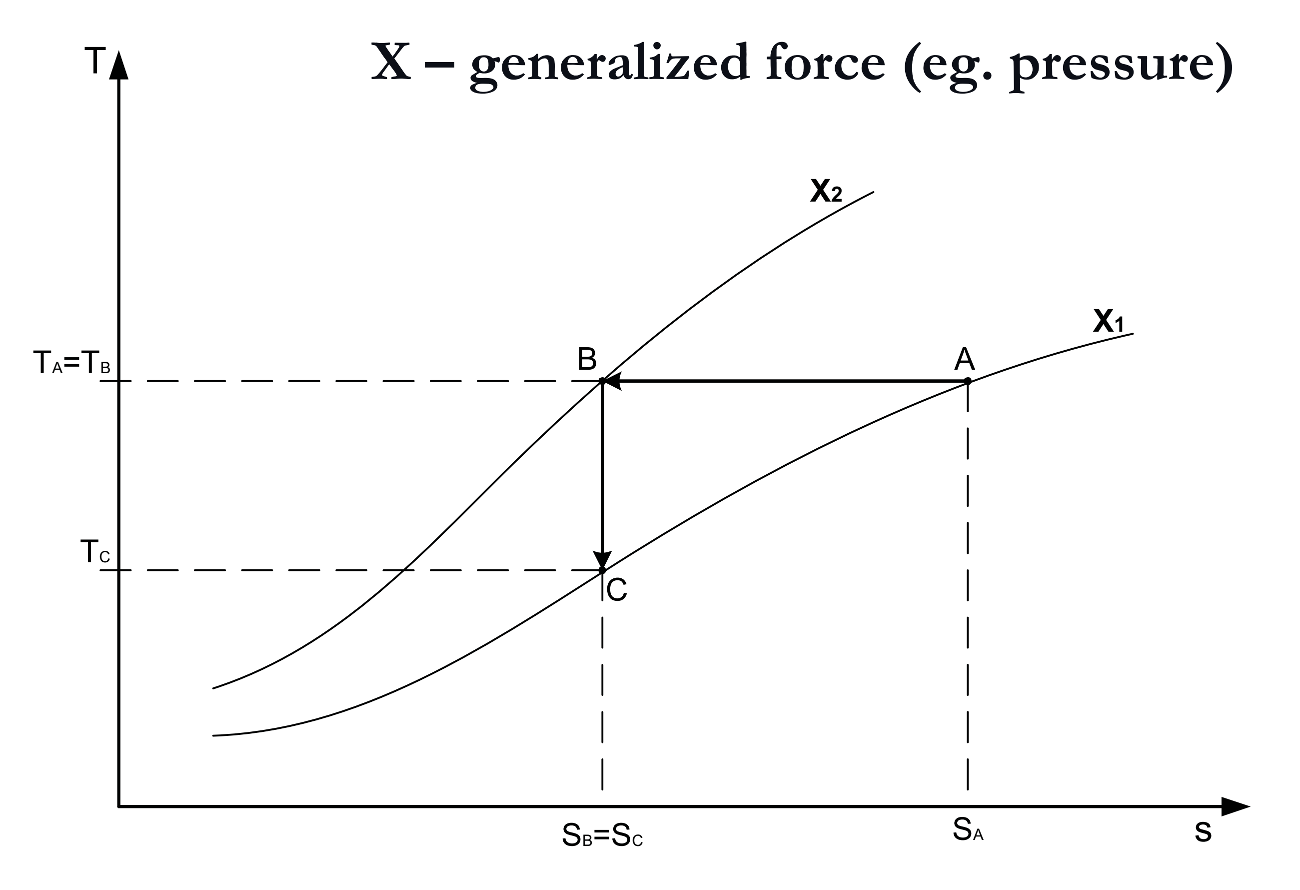
It is impossible to reach the absolute zero of temperature by any finite number of processes

$$S = S(T, X)$$





Generalized cooling process



Heat taken over in A-B transformation:

$$Q = T_A\left(s_A - s_B\right)$$

Temperature drop (T_A-T_C) appears when generalized force x goes adiabaticaly to its initial value:

$X_2 \longrightarrow X_1$

x - generalized force of conjugate variables: **force - displacement**

Example: for conjugate variables p-V: **pressure p is generalized force**

volume V is generalized displacement

Substance	Force X (Conjugate	Displacement Y Variables)	Process of entropy decreasing (ordering)	Process of temperature lowering
Gas	pressure, p [Pa]	Volume V , [m3]	Isothermal compression	Isentropic expantion
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Paramagne tic substance	Magnetic flux denisity, H [A/m]	Magneric dipol moment $\mu_o M$, [Wb m]	Isothermal magnetization	Adiabatic demagnetization
Dielectric substance	Magnetic flux denisity E, [V/m]	Electric dipol moment P, [Cm]	Isothermal electrization	Adiabatic de-electrisation
Electron gas	Electrical potential ε, [V]	Electic charge Z, [C]	Electron compacting	Electron dilution
Salt	Chemical potential μ[J/mol]	Mole number n	Drying	Dissolving
Rod	Mechanical force F	Length l	Compression	Stress relaxation
Polymer	Mechanical force F	Length l	Tension (fiber elongation)	Tention relaxation

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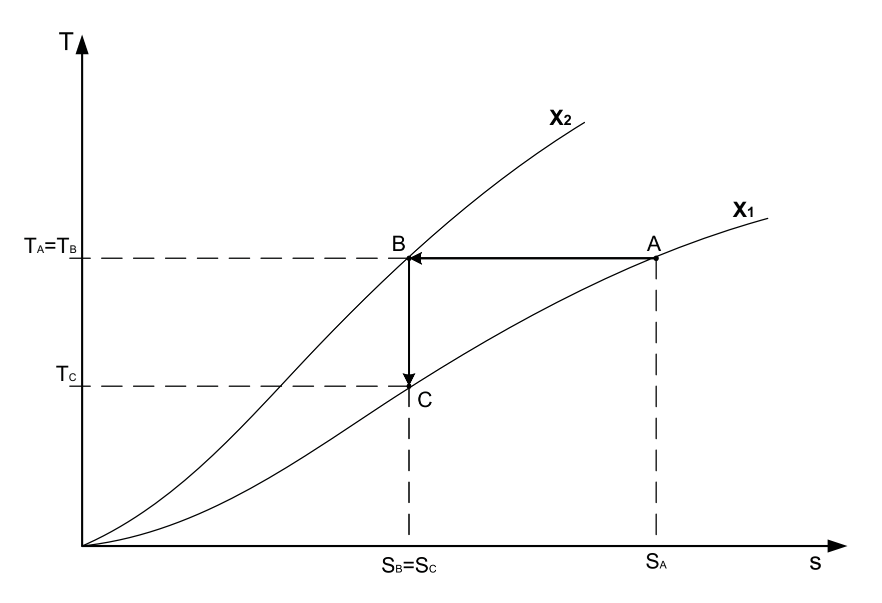
Temperature drop by isentropic change of X parameter



$$S = S(T, X)$$

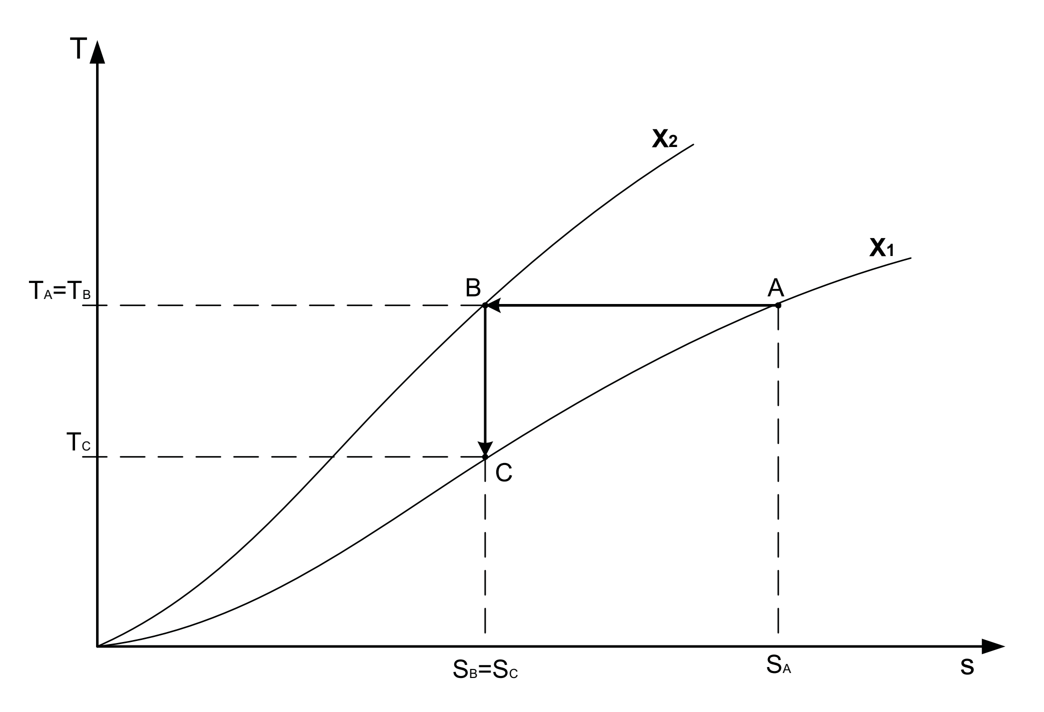
$$dS = \left(\frac{\partial S}{\partial T}\right)_X dT + \left(\frac{\partial S}{\partial X}\right)_T dX = 0$$

$$\mu_s = \left(\frac{dT}{dX}\right)_s = -\frac{\left(\frac{\partial S}{\partial X}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_X}$$

$$\left(\frac{\partial S}{\partial T}\right)_X = ?$$

$$\left(\frac{\partial S}{\partial X}\right)_T = ?$$

Temperature drop by isentropic change of X parameter



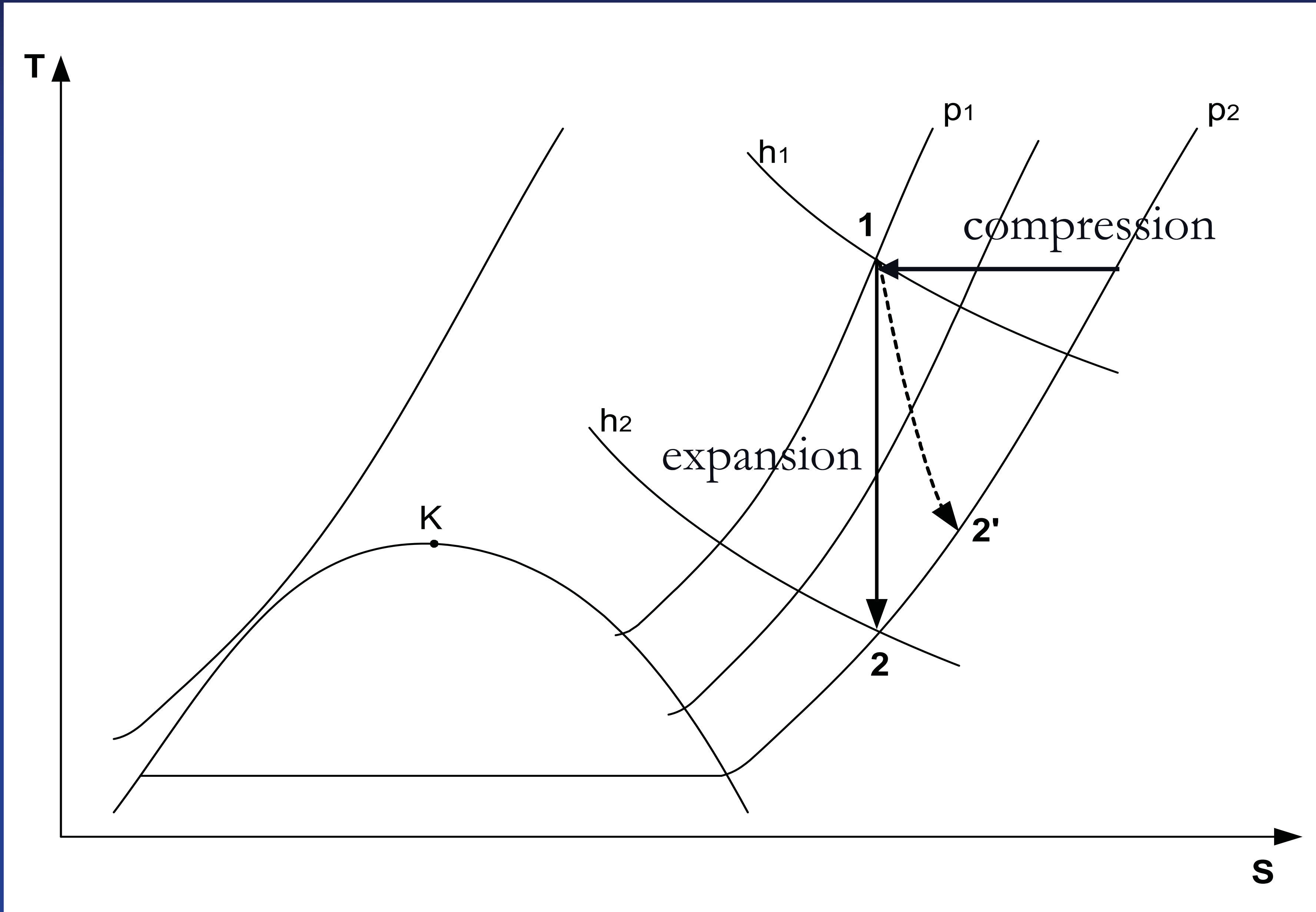
$$\mu_s = \left(\frac{dT}{dX}\right)_s = -\frac{\left(\frac{\partial S}{\partial X}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_X}$$

$$c_X dT = T ds \longrightarrow \left(\frac{\partial S}{\partial T}\right)_X = \frac{c_X}{T} \longrightarrow \mu_s = \left(\frac{dT}{dX}\right)_s = -\frac{T\left(\frac{\partial S}{\partial X}\right)_T}{c_X}$$

From Maxwell relations: $$\left(\frac{\partial S}{\partial X}\right)_T = -\left(\frac{\partial Y}{\partial T}\right)_X$$

$$\mu_s = \left(\frac{dT}{dX}\right)_s = \frac{T\left(\frac{\partial Y}{\partial T}\right)_X}{c_X}$$

Isentropic expansion with external work



Isentropic expansion with external work

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = 0 \longrightarrow \mu_s = \left(\frac{dT}{dp}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{cp}{T}$$

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

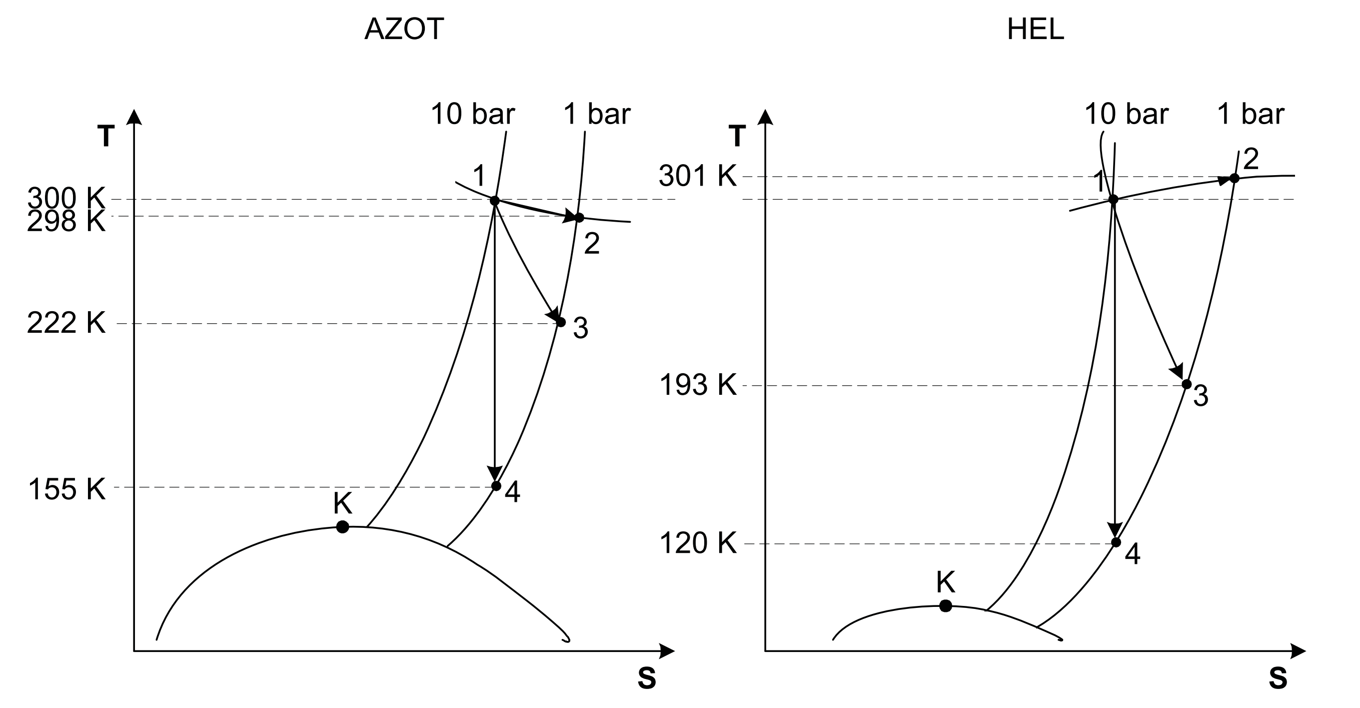
$$\mu_s = \left(\frac{dT}{dp}\right)_S = \frac{T\left(\frac{\partial v}{\partial T}\right)_p}{cp} = \frac{Tv\beta}{cp}$$

Isentropic expansion with external work

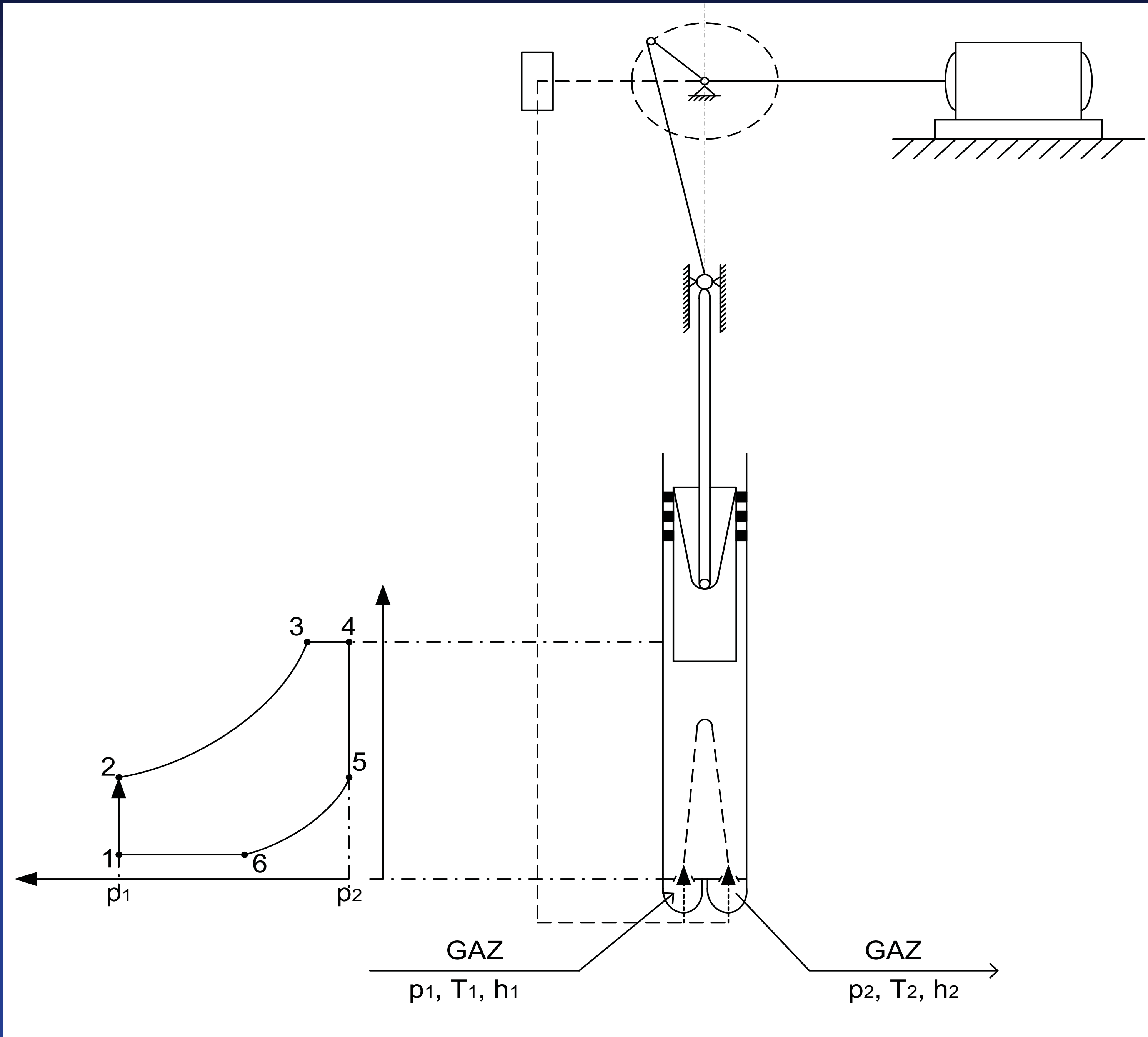
$$Pv = RT \longrightarrow \mu_s = \left(\frac{dT}{dp}\right)_S = \frac{T\left(\frac{\partial v}{\partial T}\right)_p}{cp} = \frac{Tv\beta}{cp}$$

We get: $$\mu_s = \frac{\kappa - 1}{\kappa}\frac{T}{p}$$

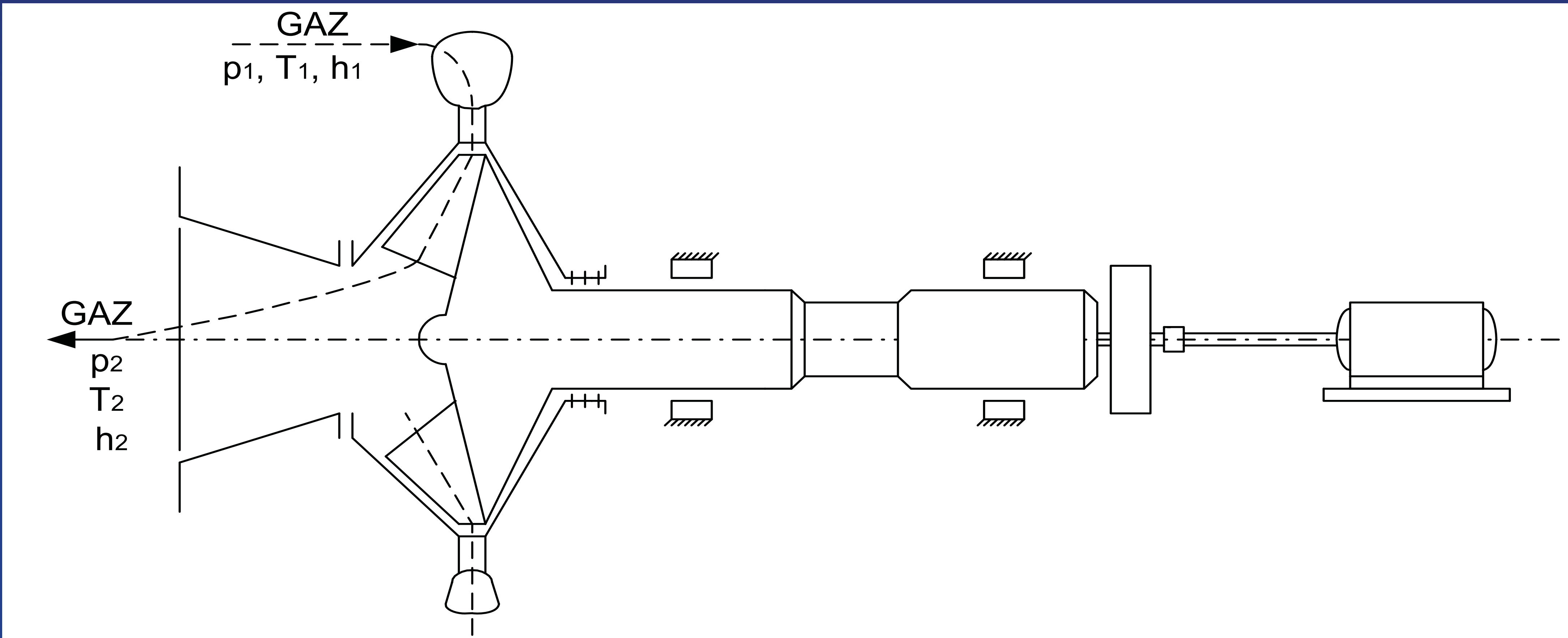
After integration $$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\kappa-1}{\kappa}}$$



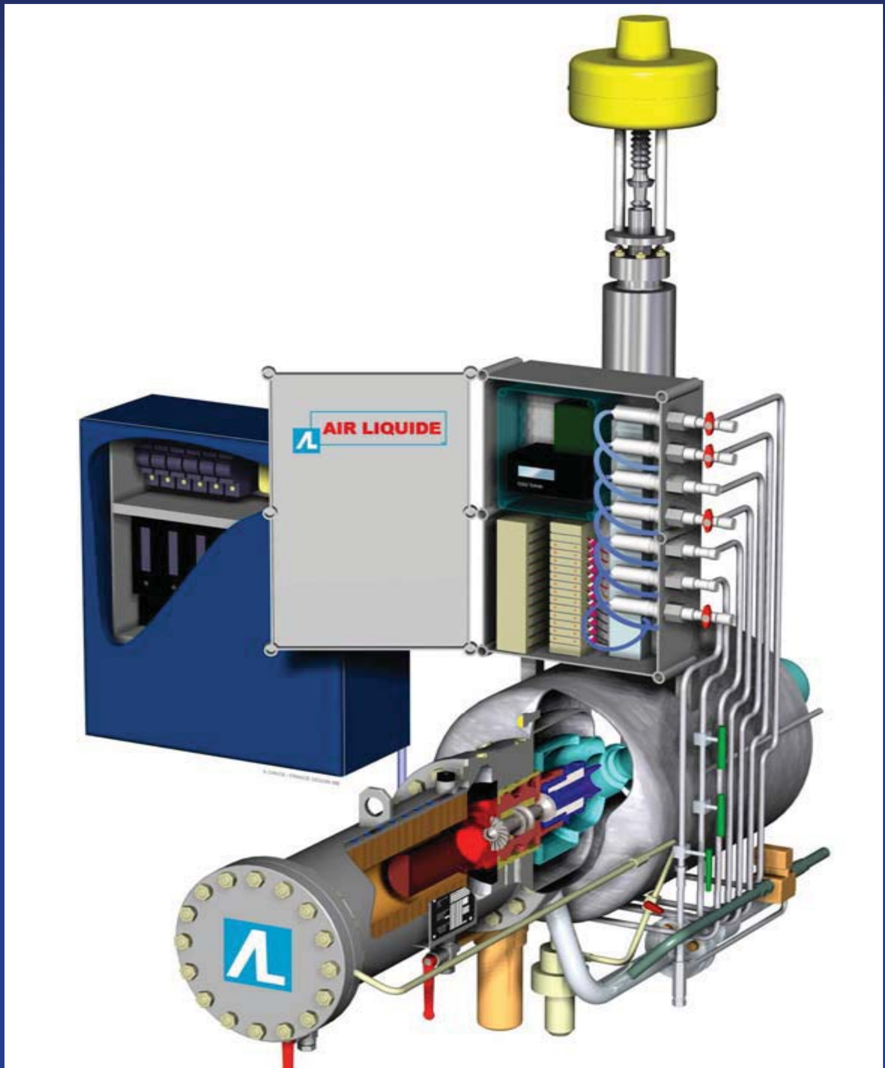
Piston expander

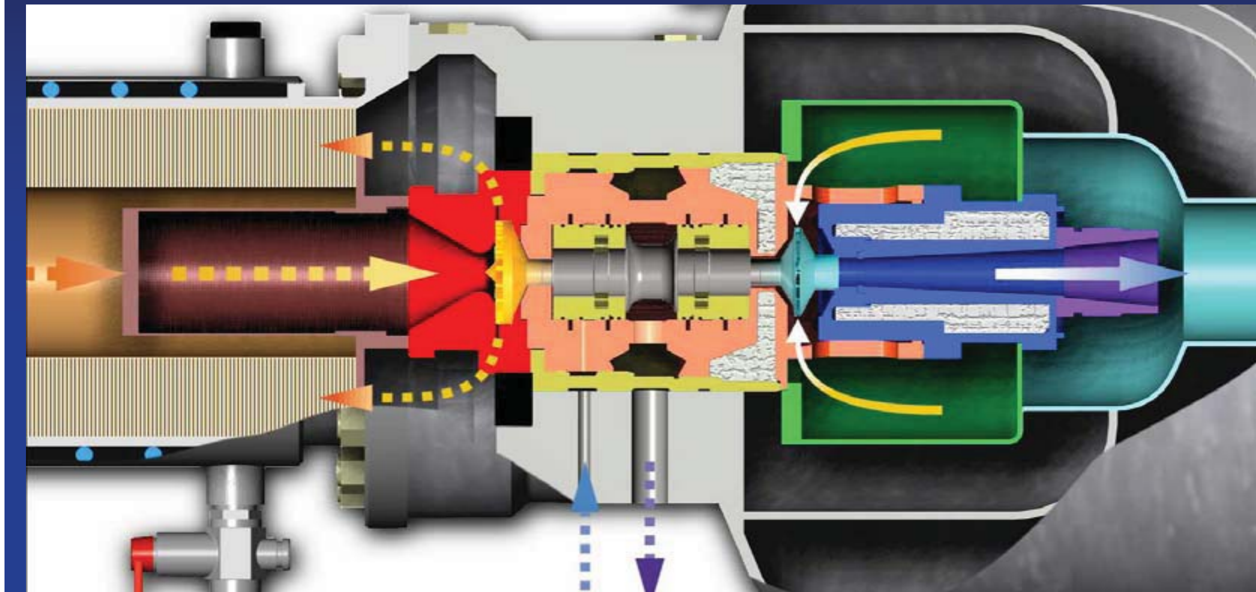


Turbine expander



Turbine expander





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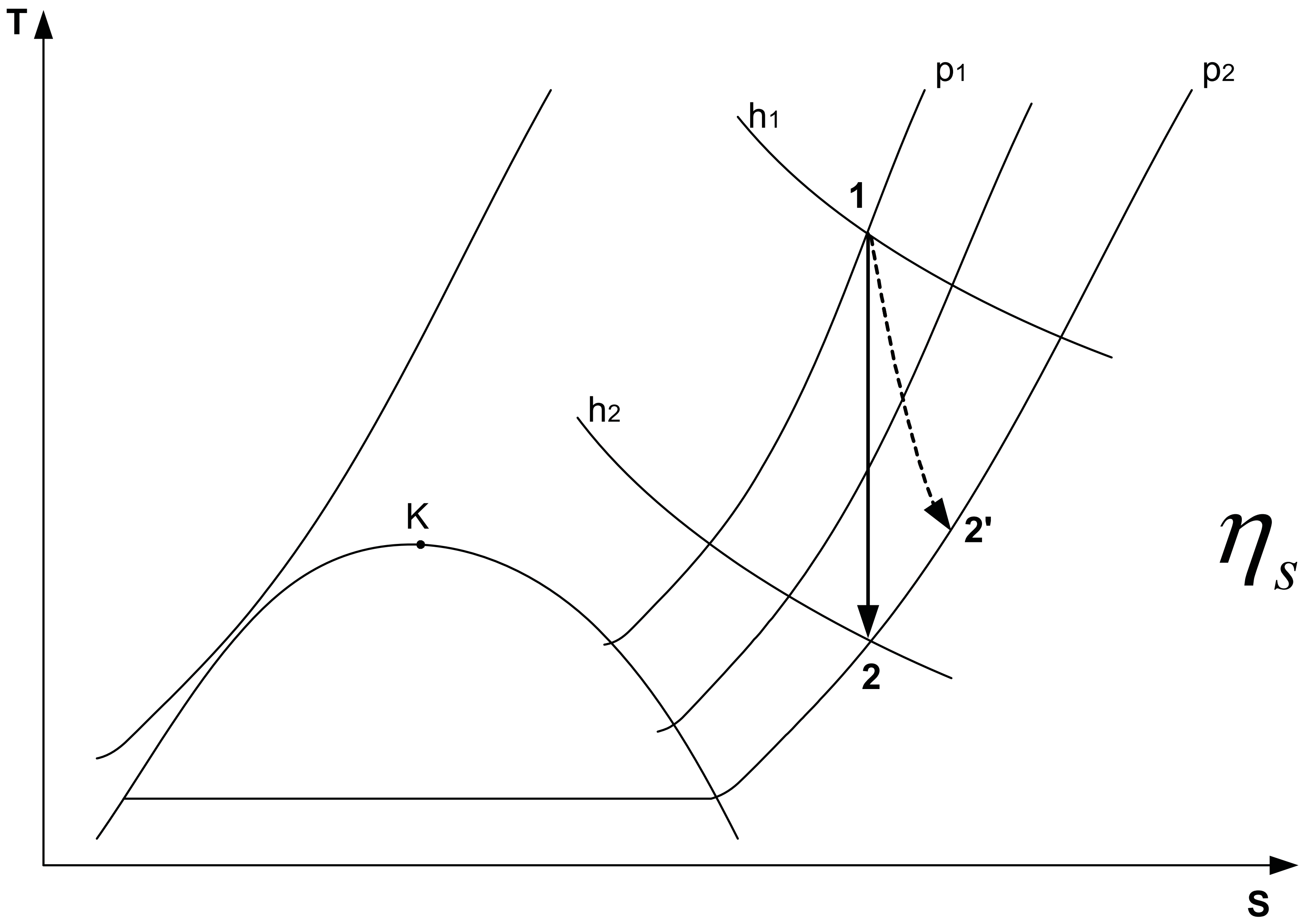
Cryogenic helium turbo-expander:

1 – gas turbine,

2 – gas bearing,

3 – gas work extractor

Isentropic expansion with external work – isentropic efficiency of the expander

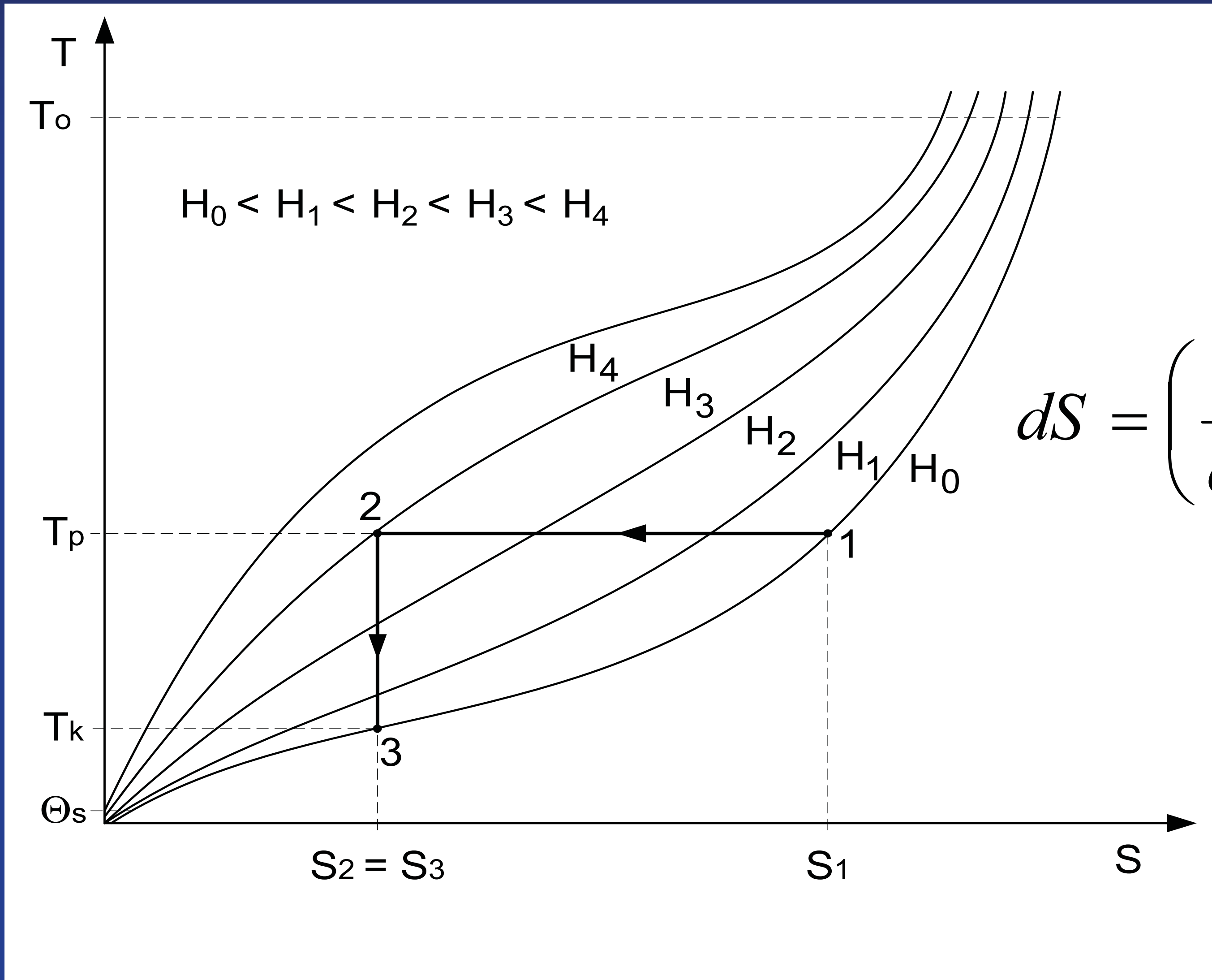


$$\eta_s = \frac{h_1 - h_{2'}}{h_1 - h_2}$$

Adiabatic demagnetization

Substance	Force X (Conjugate	Displacement Y Variables)	Process of entropy decreasing (ordering)	Process of temperature lowering
Gas	pressure, p [Pa]	Volume V , [m3]	Isothermal compression	Isentropic expantion
Gas	pressure, p [Pa]	Volume V , [m3]	Isothermal compression	Isenthalpic expantion
Paramagnetic substance	Magnetic flux denisity, H [A/m]	Magneric dipol moment $\mu_o M$, [Wb m]	Isothermal magnetization	Adiabatic demagnetization
Dielectric substance	Magnetic flux denisity E, [V/m]	Electric dipol moment P, [Cm]	Isothermal electrization	Adiabatic de-electrisation
Electron gas	Electrical potential ε, [V]	Electic charge Z, [C]	Electron compacting	Electron dilution
Salt	Chemical potential μ[J/mol]	Mole number n	Drying	Dissolving
Rod	Mechanical force F	Length l	Compression	Stress relaxation
Polymer	Mechanical force F	Length l	Tension (fiber elongation)	Tention relaxation

Adiabatic demagnetization of paramagnetic substances



$$S = S(T, H)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_X dT + \left(\frac{\partial S}{\partial H}\right)_T dH = 0$$

$$\mu_s = \left(\frac{dT}{dH}\right)_s = -\frac{\left(\frac{\partial S}{\partial H}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_X}$$

Adiabatic demagnetization of paramagnetic substances

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Adiabatic demagnetization of paramagnetic substances

$$Tds = c_H dT \longrightarrow \left(\frac{\partial S}{\partial T}\right)_H = \frac{c_H}{T}$$

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_o \left(\frac{\partial M}{\partial T}\right)_H$$

and

$$M = \chi H$$

Equivalent to the equatio of state for gases

How do we get the formulas?

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_o \left(\frac{\partial M}{\partial T}\right)_H$$

$$M = \chi H$$

$$dU = dQ - pdV + \mu_o H dM$$

→

$$dU = TdS + \mu_o H dM$$

Potencjał Gibbsa:

$$G = U - \mu_o HM - TS$$

$$\frac{\partial^2 G}{\partial T \partial H} = \frac{\partial^2 G}{\partial H \partial T}$$

→

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_o \left(\frac{\partial M}{\partial T}\right)_H$$

General equation to calculate the magnetocaloric coefficient if the relation governing the *M,H* and *T* is known:

$$\mu_s = \left(\frac{dT}{dH}\right)_s = -\frac{T\left(\frac{\partial S}{\partial H}\right)_T}{c_H} = -\frac{\mu_o T\left(\frac{\partial M}{\partial T}\right)_H}{c_H}$$

$$M = \chi H$$

Curie law (valid for not very high magnetic fields): → $\chi = \frac{C}{T}$

Final temperature afetr demagnetization:

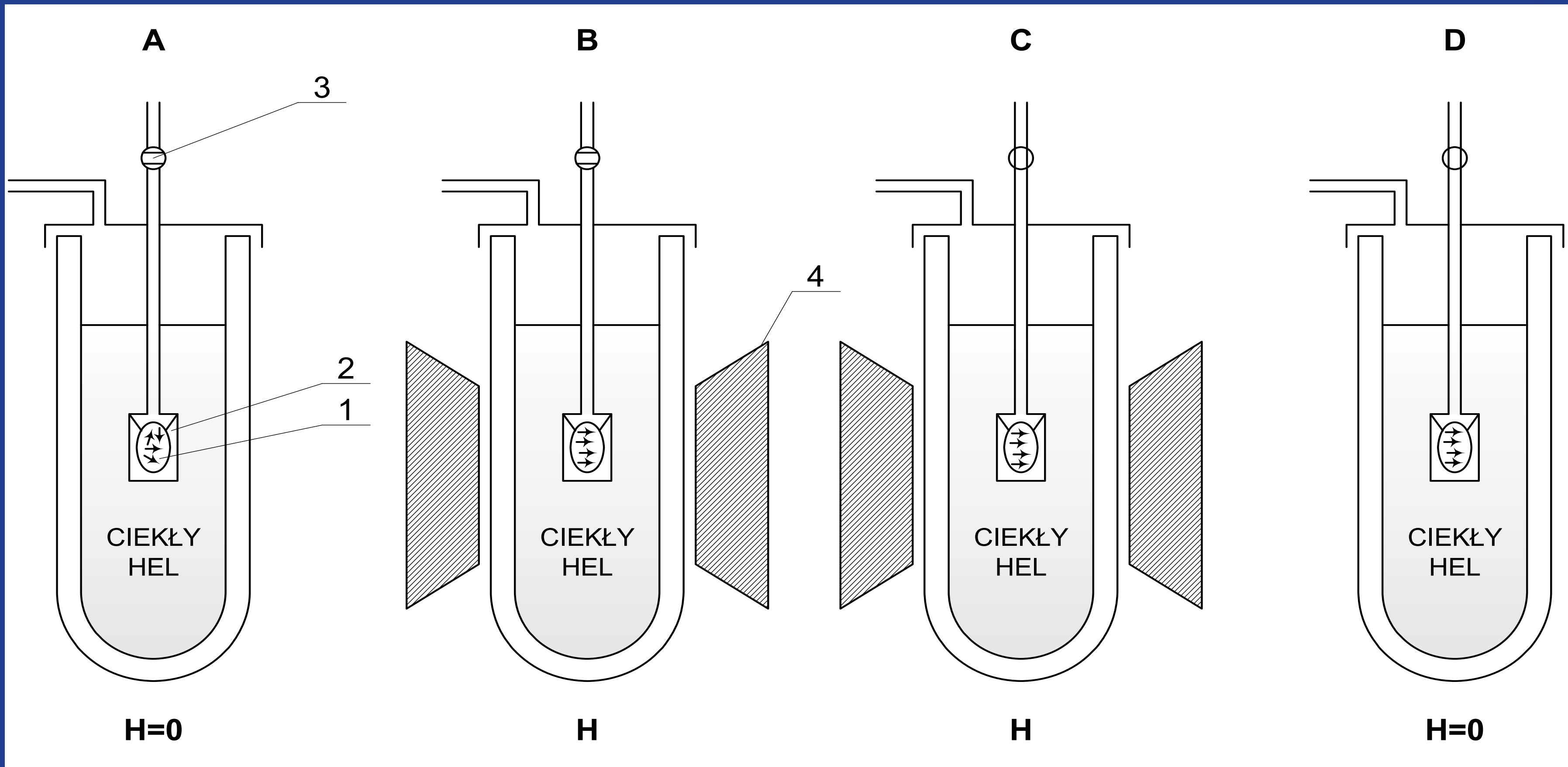
$$\mu_s = \left(\frac{dT}{dH}\right)_s = \frac{\mu_0 CH}{c_H T}$$

$$T_k = T_o \sqrt{1 - \frac{\mu_o CH_o^{\;2}}{c_H T_o^{\;2}}}$$

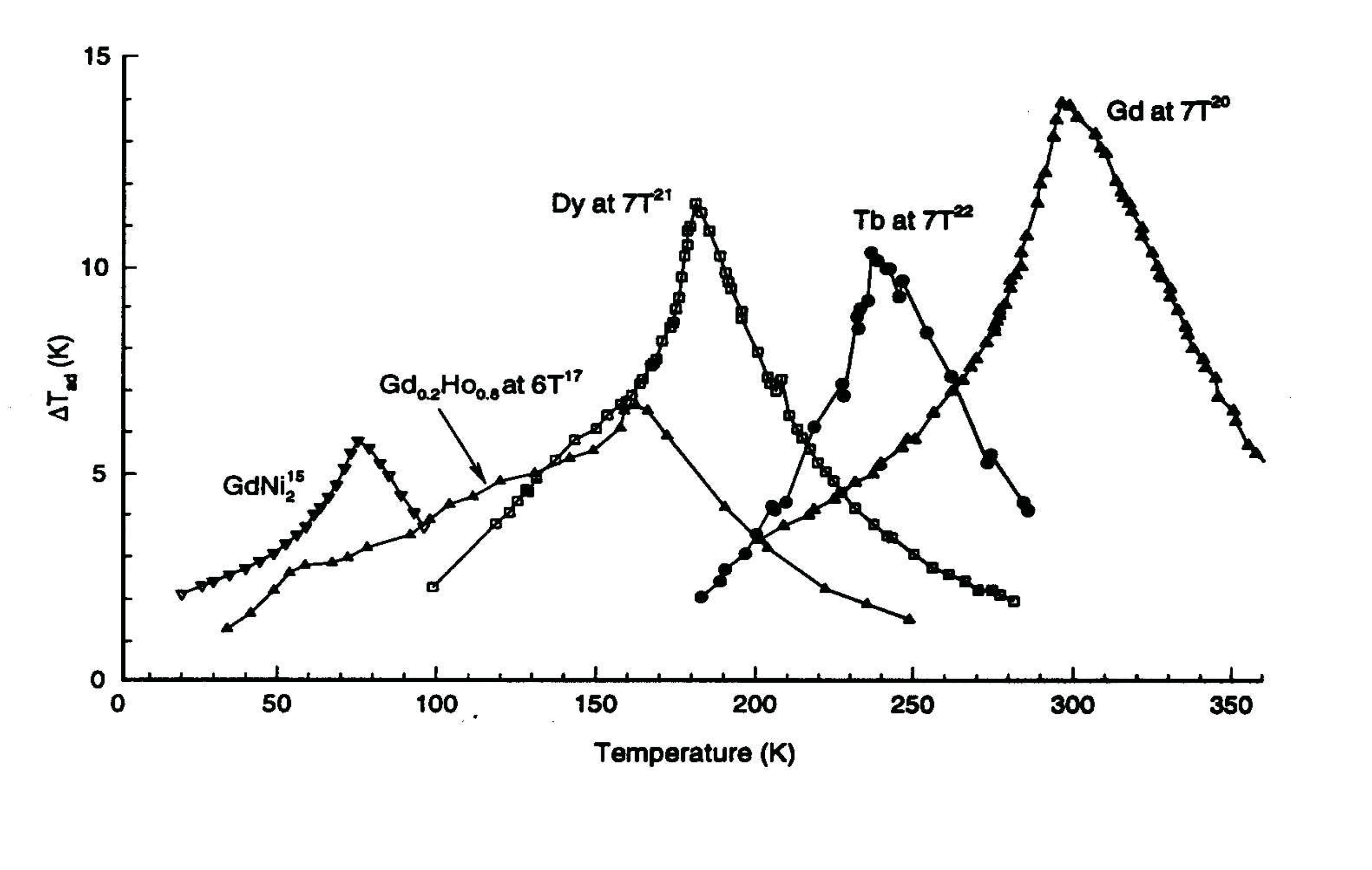
Cooling capacity:

$$Q = T \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH = -\frac{\mu_o CH^2}{2T}$$

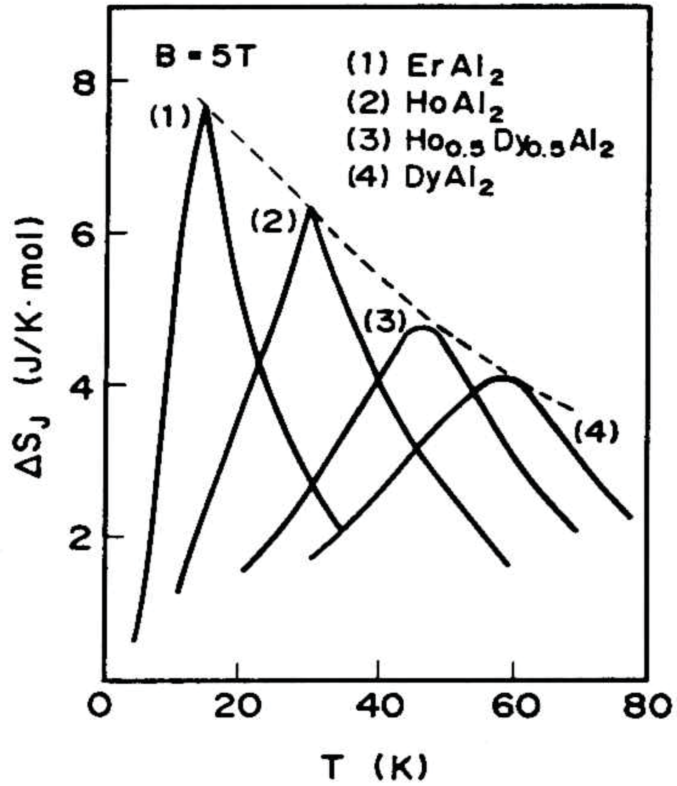
Magnetic refrigerator – principle of operation, A – initial cooling of the sample, B – isothermal magnetization, C – removal of the heat exchange gas, D – adiabatic demagnetization; 1 – paramagnetic substance, 2 – sample chamber, 3 – valve, 4 – magnet

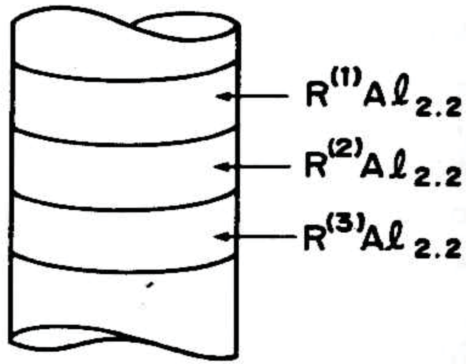


Examples of paramagnetic substances

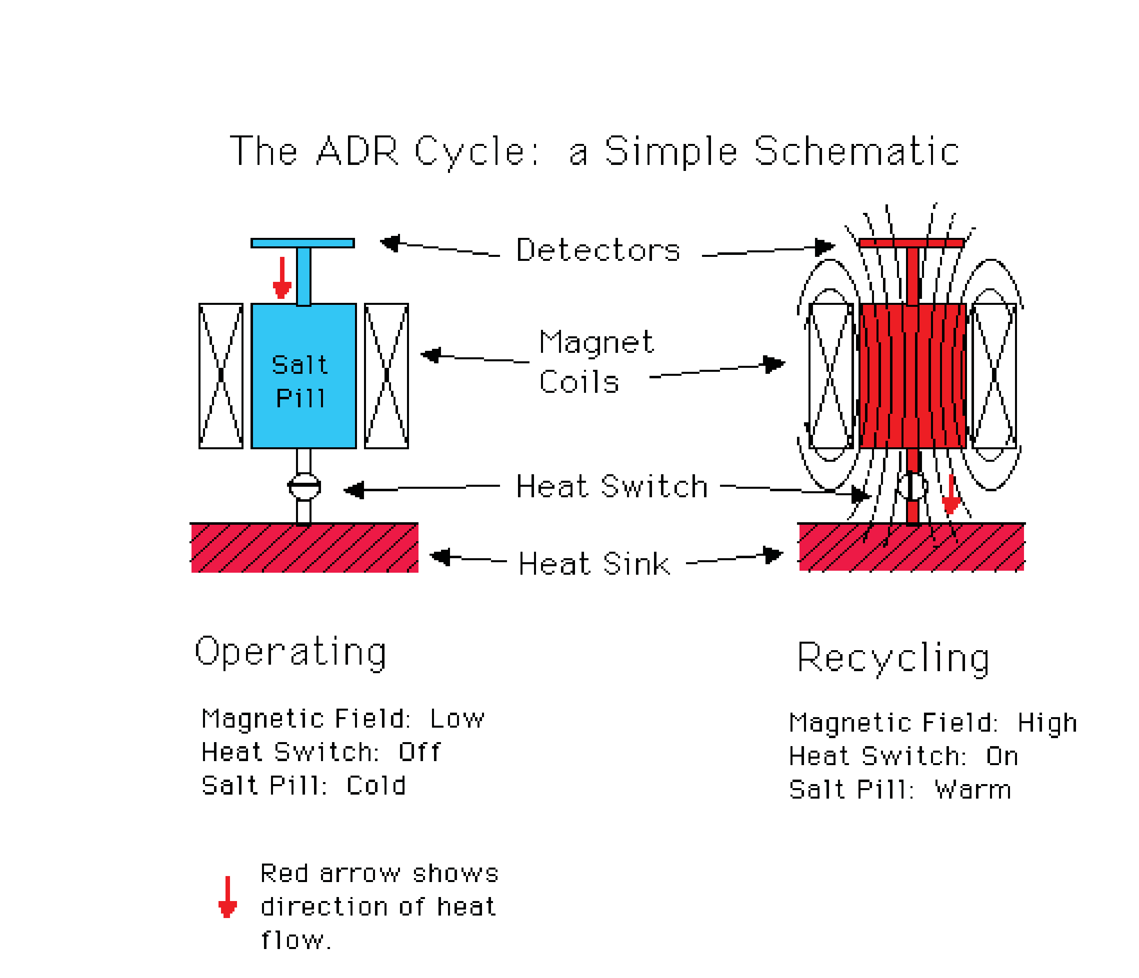


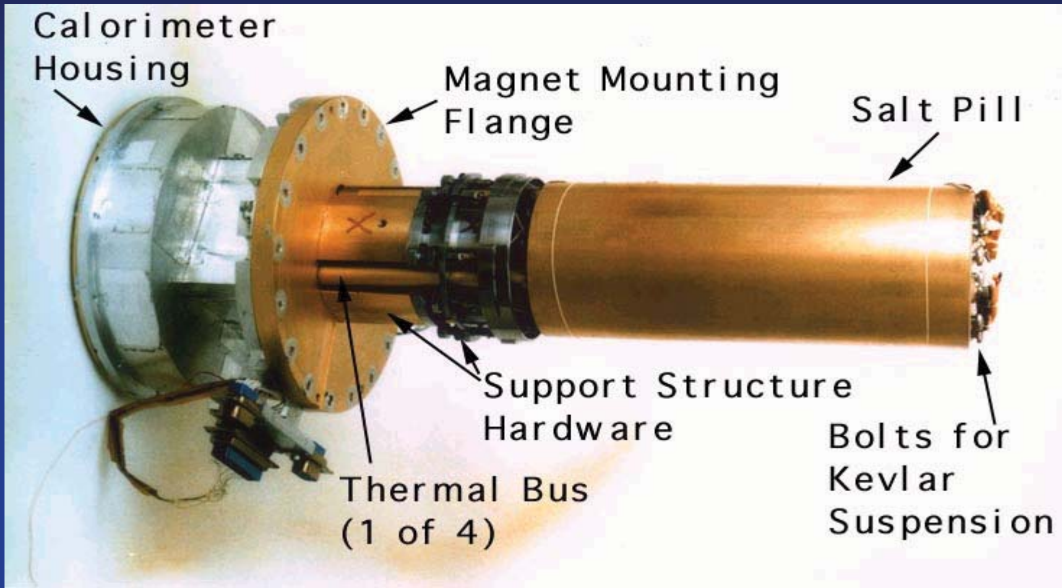
Magnetic stack - example,

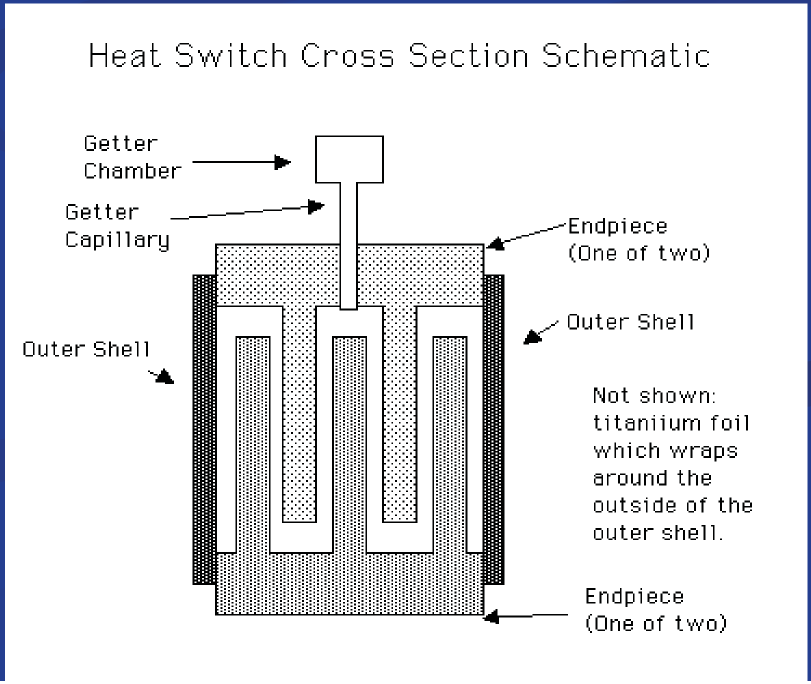




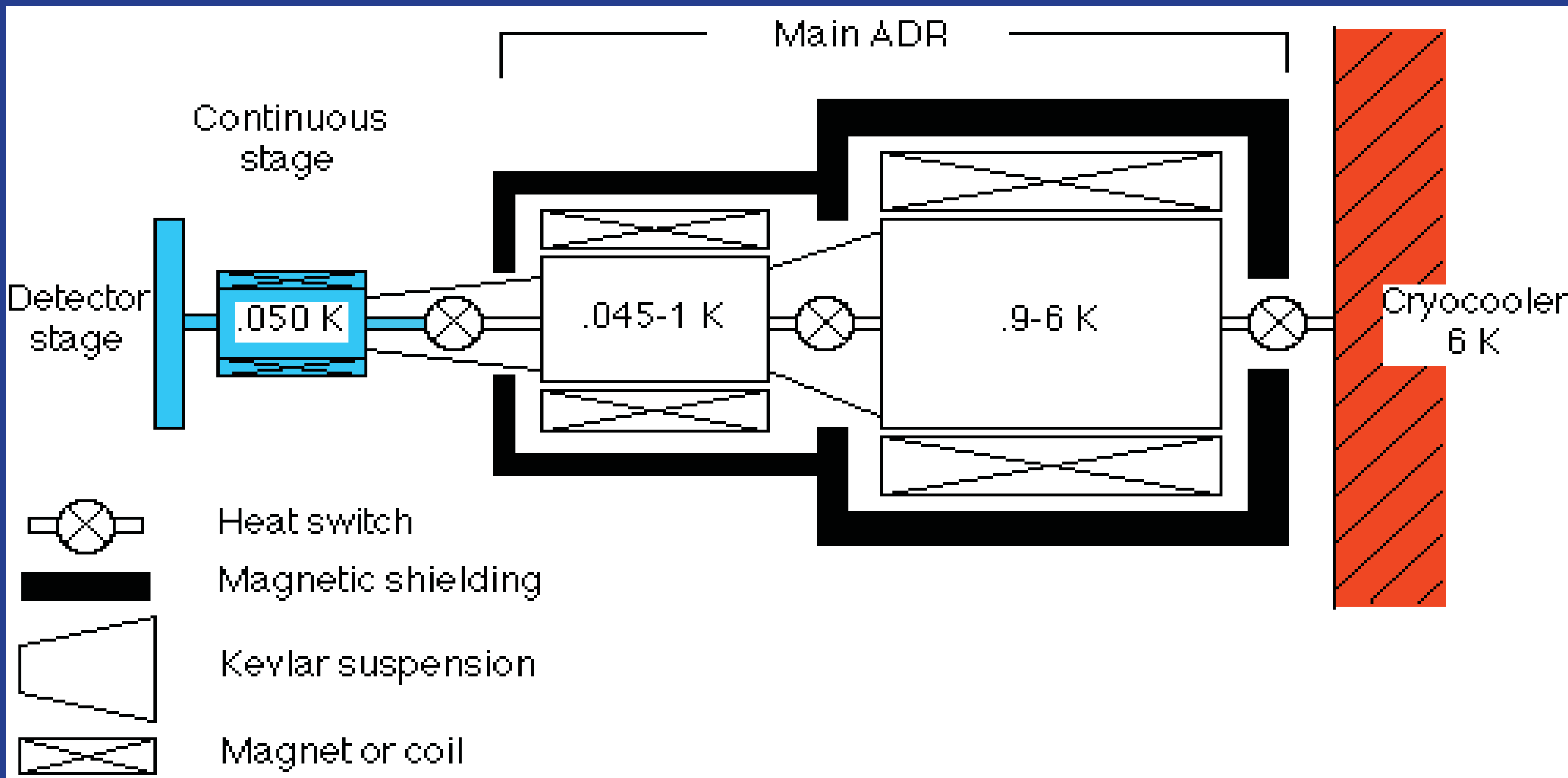
Magnetic refrigerator







Multistage magnetic refrigerator



General way to lower the temperature

A. The entropy must be a function of two parameters: temperature T and X, where X is a generalized force (gas pressure, magnetic field). At the room temperature the entropy must be high enough.

B. The entropy can be lowered by external work done on the body (gas compression, paramagnetic magnetization) in isothermal process.

C. By isentropic process the temperature of the body will go down.