Cooling principles

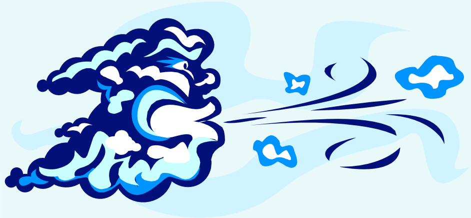
& gas liquefaction

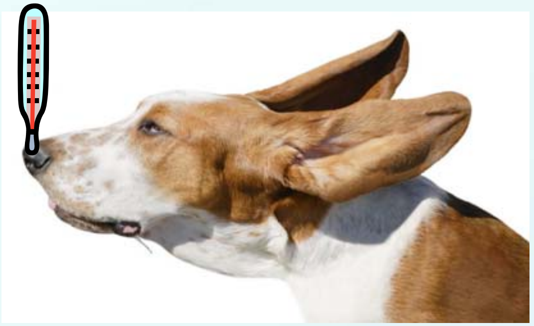
Content

- **Elementary thermodynamics**
- **Cryogases**
- **Industrial usage of cooled gases**
- **Thermometry (1-500K)**
- **Practical refrigerators (domestic and industrial)**
- **Peltier cooler**

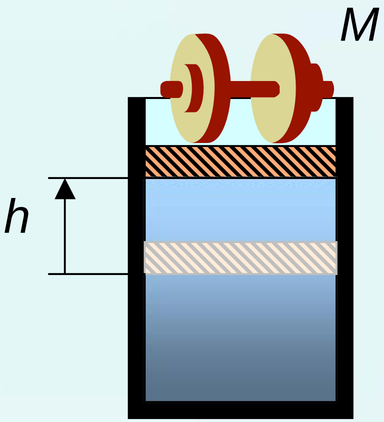
General ways of cooling

- **Remove the most active molecules**





- **Let the gas expand and make a job**



Elementary thermodynamics

First law of thermodynamics:

$$\boxed{Q = \left(U_2 - U_1\right) + A_{12}}$$

work done by
the system

heat

change of internal
energy

For infinitely small or elementary quasi-static process:

$$\boxed{\delta Q = dU + \delta A}$$

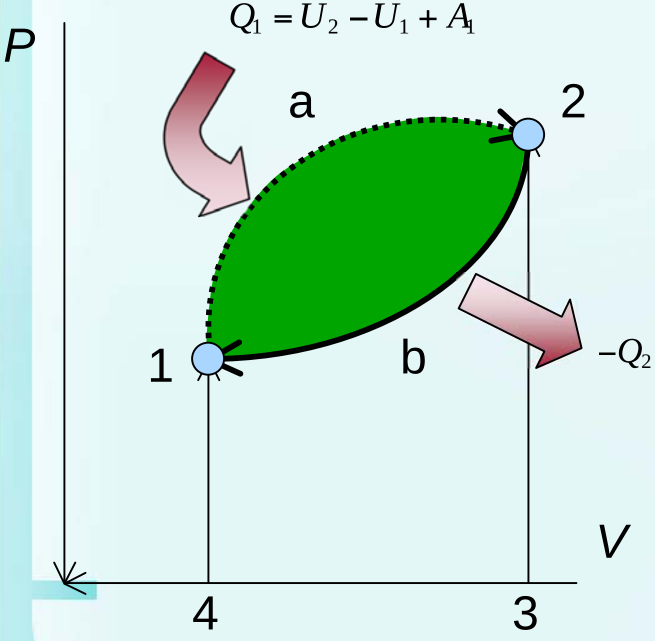
inexact differential

Elementary thermodynamics

Second law of thermodynamics:

“There is no process that, operating in a cycle, produces no other effect than the subtraction of a positive amount of heat from a reservoir and the production of an equal amount of work.**”** (Kelvin-Planck statement; source: Wikipedia)

$Q_1 = U_2 - U_1 + A_1$



$-Q_2 = U_1 - U_2 - A_2$

$$Q_1 - Q_2 = A_1 - A_2$$

For a heat engine:

$$\text{Efficiency} = \frac{\text{work exctracted}}{\text{heat input}}$$

$$\eta = \frac{A_1 - A_2}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$Q_2 \to 0: \quad \eta \to 100\%$$

2nd law: impossible

Elementary thermodynamics

Third law of thermodynamics:

As temperature approaches absolute zero, the entropy of a system approaches a constant.

Allen Ginsberg summarized the three laws of thermodynamics in the following way:

First law: "You can't win."
Second law: "You can't break even."
Third law: "You can't quit."

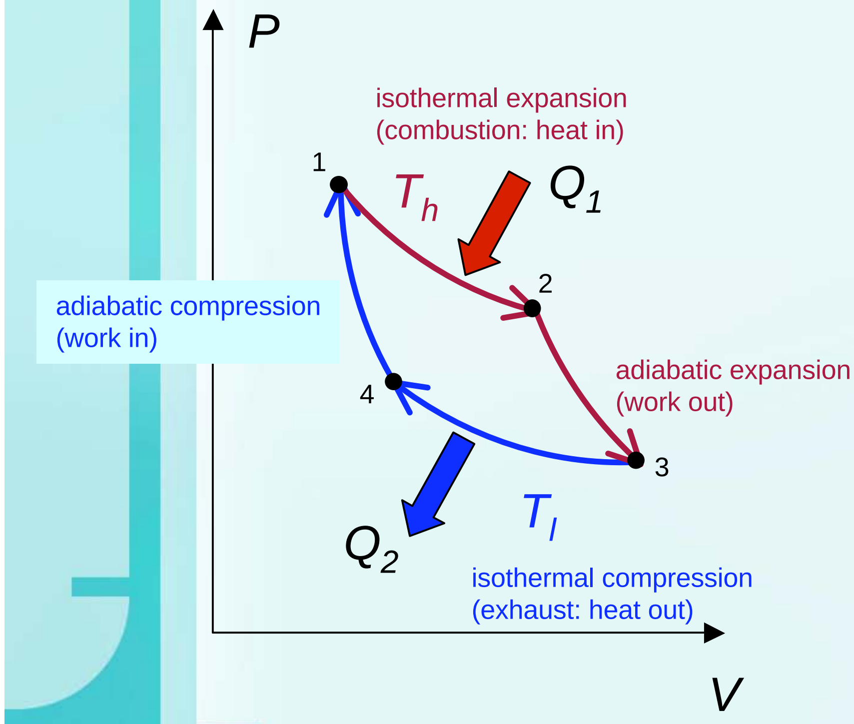
source: Wikipedia

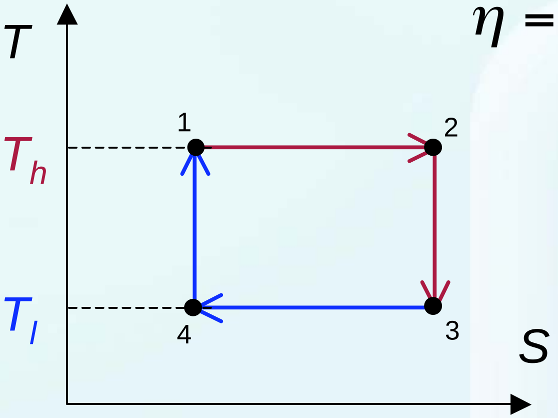
Elementary thermodynamics

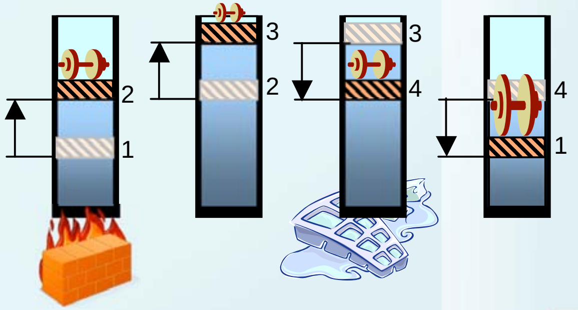
The most efficient ***Carnot cycle*** consists of four *reversible* processes → the cycle as a whole is also *reversible*.

$$\eta = \frac{Q_1 - Q_2}{Q_1} \le \frac{T_h - T_l}{T_l}$$

Carnot theorem







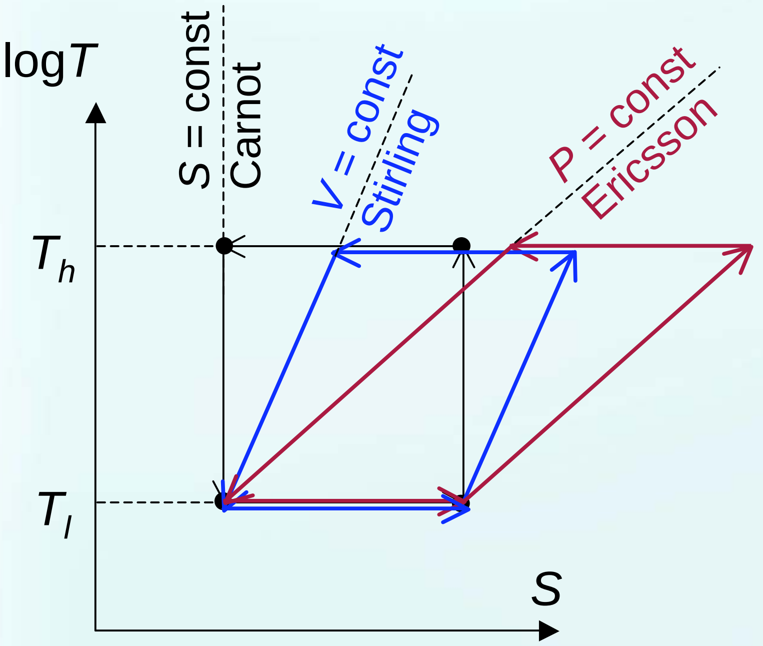
One can extract heat from the cold end by reversing the cycle: refrigeration!

$$\eta = \frac{\text{heat extracted}}{\text{work done}} \le \frac{T_l}{T_h - T_l}$$

Cryo-cooling

Other cycles

Carnot: isothermal-isentropic
Stirling: isothermal-isochoric
Ericsson: isothermal-isobaric



$$\frac{dT}{T} = \frac{dS}{C_P} \quad \text{(isobaric)}$$

$$\frac{dT}{T} = -\frac{dS}{C_V} \quad \text{(isochoric)}$$

The areas (work) of all cycles is the same: efficiency should be close to the ideal one

Cryo-gases

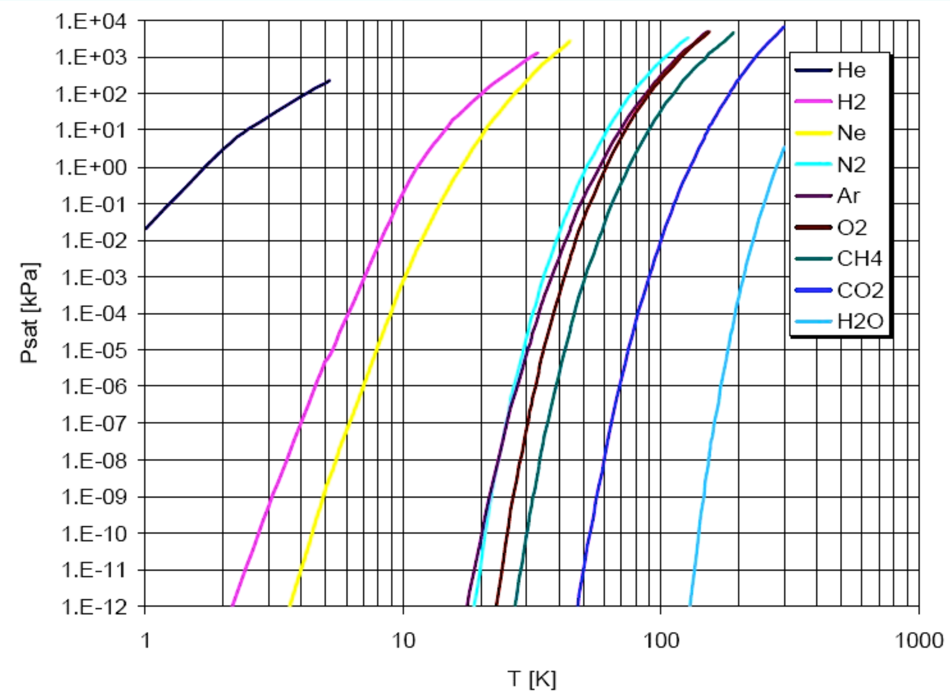
- **Characteristic temperatures (K)**

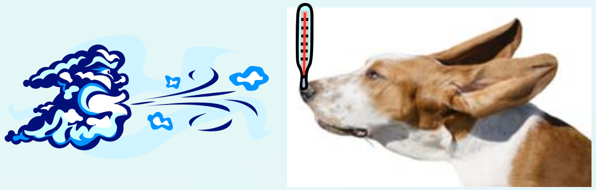
Gas	Triple point	Boiling point	Critical point
He	2.2 (λ)	4.2	5.2
H_2	13.8	20.4	33.2
Ne	24.6	27.1	44.4
N_2	63.1	77.3	126.2
Ar	83.8	87.3	150.9
O_2	54.4	90.2	154.6
CH_4	90.7	111.6	190.5
$CH_3CH_2CH_3$		231.1	

90% of NG

Cryogases

- **Vapor pressures of cryogases**

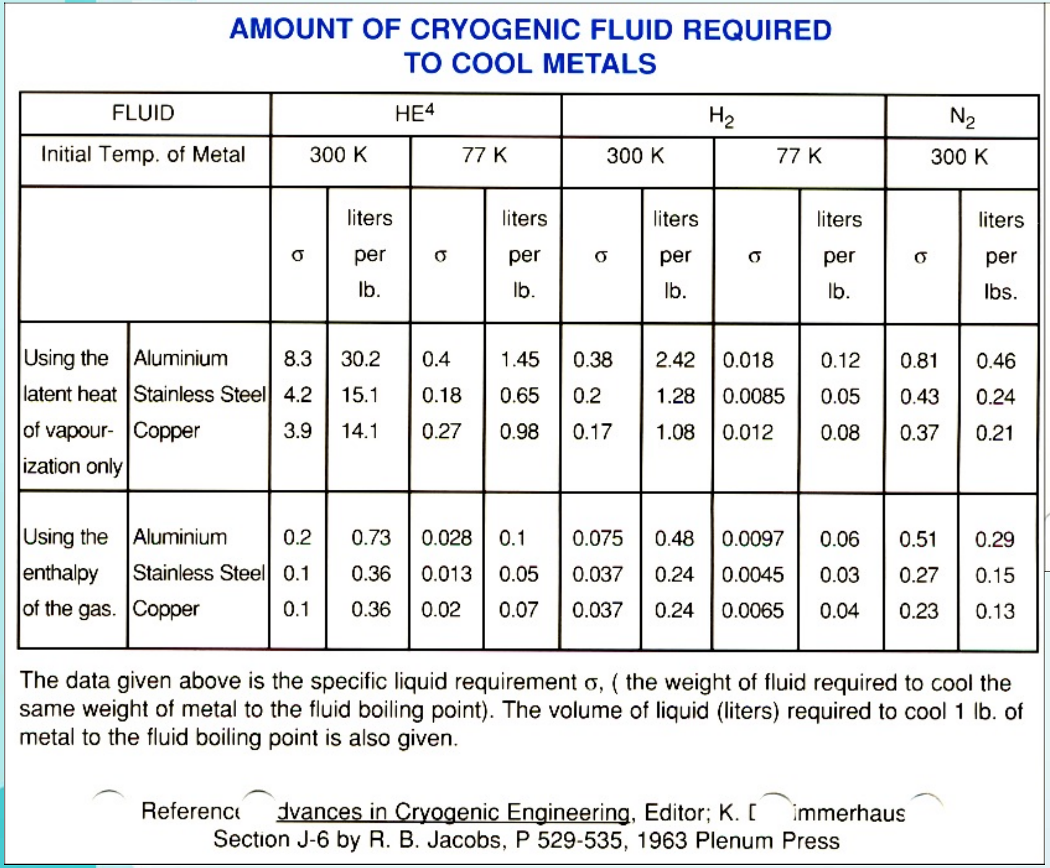




One can further lower T
by pumping cryoliquids

Cooling metals

- **It is quite costly...**

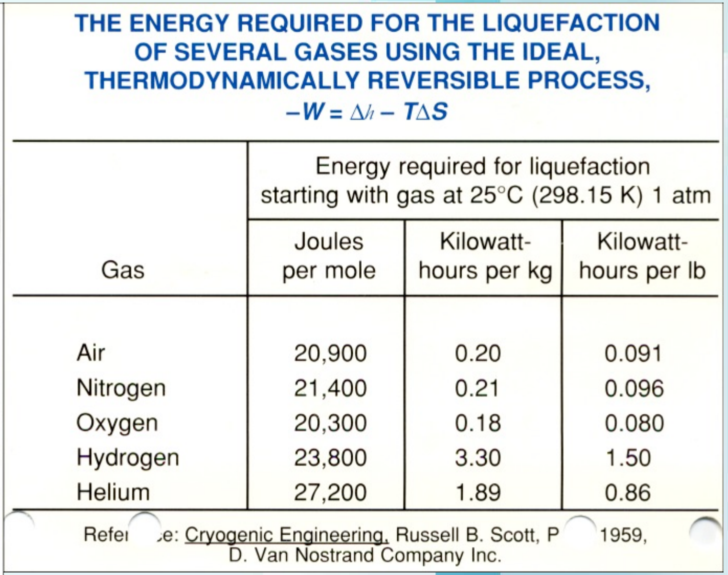


AMOUNT OF CRYOGENIC FLUID REQUIRED TO COOL METALS

FLUID		HE^4				H_2				N_2	
Initial Temp. of Metal		300 K		77 K		300 K		77 K		300 K	
		σ	liters per lb.	σ	liters per lb.	σ	liters per lb.	σ	liters per lb.	σ	liters per lbs.
Using the latent heat of vapourization only	Aluminium	8.3	30.2	0.4	1.45	0.38	2.42	0.018	0.12	0.81	0.46
	Stainless Steel	4.2	15.1	0.18	0.65	0.2	1.28	0.0085	0.05	0.43	0.24
	Copper	3.9	14.1	0.27	0.98	0.17	1.08	0.012	0.08	0.37	0.21
Using the enthalpy of the gas.	Aluminium	0.2	0.73	0.028	0.1	0.075	0.48	0.0097	0.06	0.51	0.29
	Stainless Steel	0.1	0.36	0.013	0.05	0.037	0.24	0.0045	0.03	0.27	0.15
	Copper	0.1	0.36	0.02	0.07	0.037	0.24	0.0065	0.04	0.23	0.13

The data given above is the specific liquid requirement σ, (the weight of fluid required to cool the same weight of metal to the fluid boiling point). The volume of liquid (liters) required to cool 1 lb. of metal to the fluid boiling point is also given.

Referenc dvances in Cryogenic Engineering, Editor; K. D immerhaus
Section J-6 by R. B. Jacobs, P 529-535, 1963 Plenum Press



THE ENERGY REQUIRED FOR THE LIQUEFACTION OF SEVERAL GASES USING THE IDEAL, THERMODYNAMICALLY REVERSIBLE PROCESS,
$-W = \Delta h - T\Delta S$

Gas	Energy required for liquefaction starting with gas at 25°C (298.15 K) 1 atm		
	Joules per mole	Kilowatt-hours per kg	Kilowatt-hours per lb
Air	20,900	0.20	0.091
Nitrogen	21,400	0.21	0.096
Oxygen	20,300	0.18	0.080
Hydrogen	23,800	3.30	1.50
Helium	27,200	1.89	0.86

Refer e: Cryogenic Engineering, Russell B. Scott, P 1959,
D. Van Nostrand Company Inc.

1 L of LHe: from 50 to 120 SEK
1 L of LN2: about $2

Usage of cryo gases

- **Liquid Natural Gas (LNG)**

Import of LNG (~110 Mt in total 2002):
Japan: 54 Mton;
South Korea: 17.7 Mton;
Taiwan: 5.3 Mtons.
(totally 70% of the world's LNG demand)

Usage of cryo gases

- **Liquid H_2 and O_2**

LH_2/LO_2 = 100/600 (t)

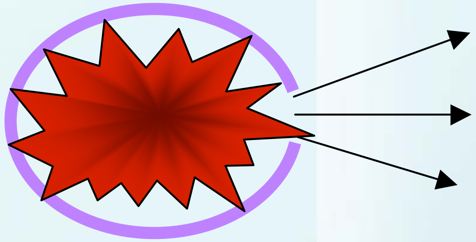
SpaceShuttle

LH_2/LO_2 = 25/130 (t)

Ariane 5

Konstantin Tsiolkovsky's rocket equation (1903):

$$\Delta v = v_e \ln\left(\frac{m_0}{m_1}\right)$$

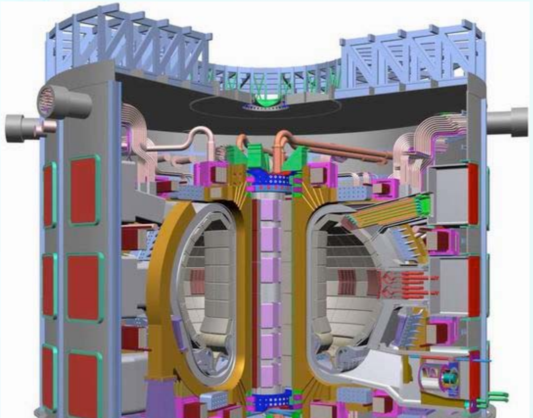


$$v_e^{\max} = \sqrt{\frac{2}{\mu} C_P T}$$

(ideal gas, exaust into vacuum)

Usage of cryo gases

- **Cooling of superconducting devices**



http://www.virtual-formac.com/

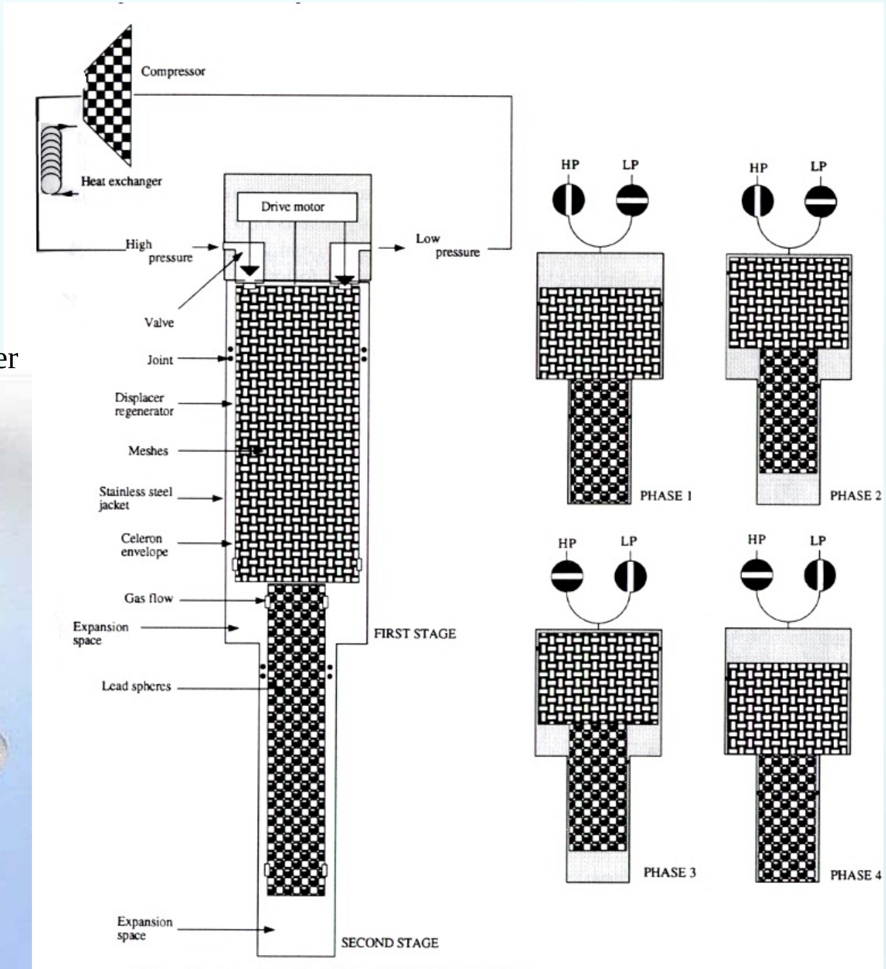
The future Large Hadron Collider (LHC) will use around 1600 superconducting magnets operating at 1.8 K.

21T 900MHz NMR

1.5T High Speed MRI

Practical machines

- **Gifford-McMahon (GM) cooler (Ericsson cycle)**



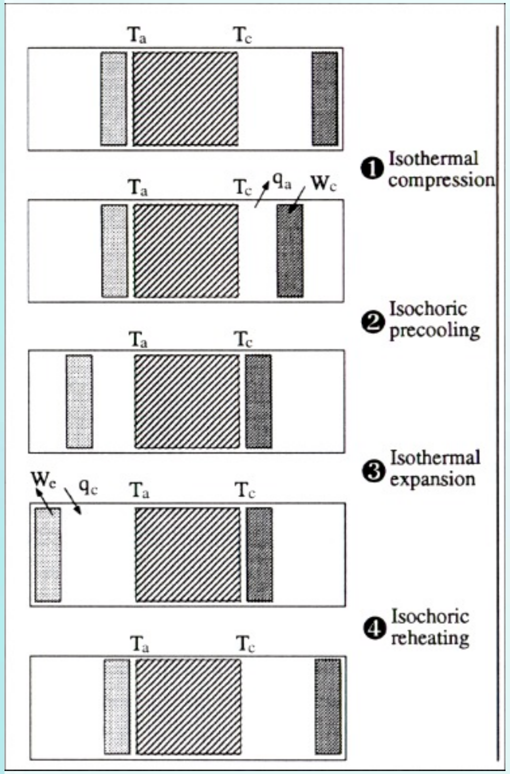
Schematic operation of a Gifford–McMahon cooler.

SHI GM CH210 cooler

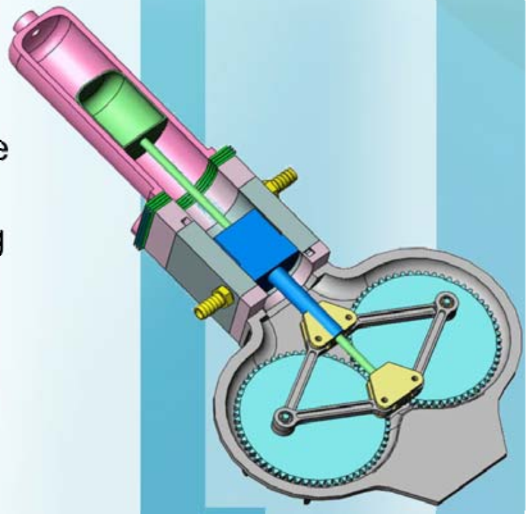
1. High pressure gas fills the regenerator at room temperature
2. The high-pressure gas passes through regenerator and is cooled down isobarically by the matrix
3. The gas undergoes expansion which results in cooling effect.
4. The low-pressure gas passes through regenerator and is warmed up isobarically by the matrix

Practical machines

- **Stirling-type cooler**

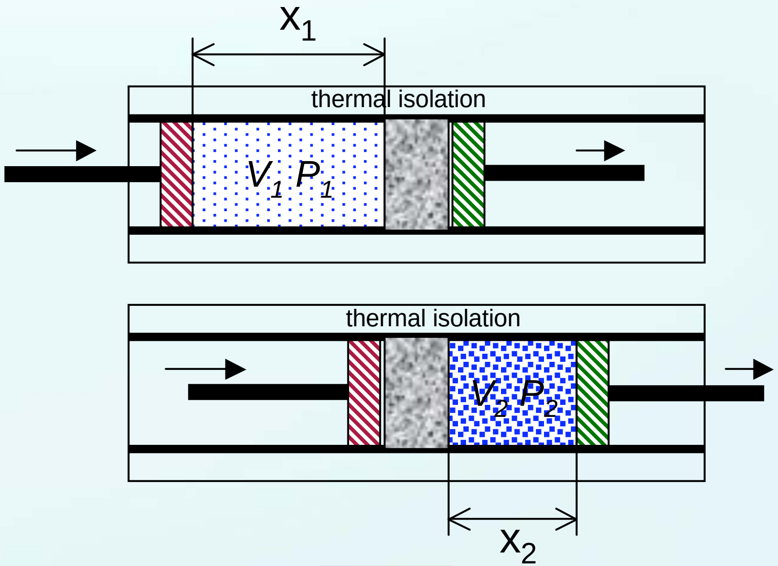


1. The compression piston isothermally compresses the gas. A work is transmitted to the gas and the heat is rejected at ambient T.
2. Both pistons are moved simultaneously (constant volume); the gas is pressed through the regenerator and is cooled transferring heat to the regenerator.
3. The expansion piston is moved to expand the gas; the work is extracted and the heat is absorbed.
4. Both pistons are moved simultaneously. The gas is heated up to the room temperature.



Practical machines

- **Joule-Thomson-Expansion cooler**



$$\boxed{\Delta T\ ?}$$

$$A = P_2\, x_2 s - P_1\, x_1 s = P_2 V_2 - P_1 V_1$$

thermal isolation → $Q \equiv (U_2\text{-}U_1)+A = 0$

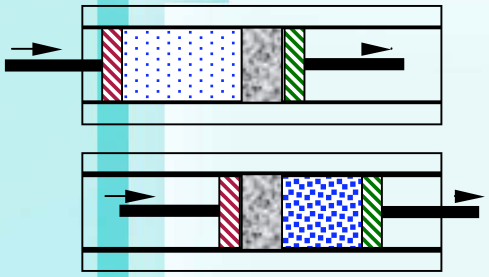
$$U_2 + P_2 V_2 = U_1 + P_1 V_1$$

$$H_2 = H_1$$

(isenthalpic process)

Practical machines

- **Joule-Thomson-Expansion cooler (contd.)**



$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_P \Delta T + \left(\frac{\partial H}{\partial P}\right)_T \Delta P = 0;$$

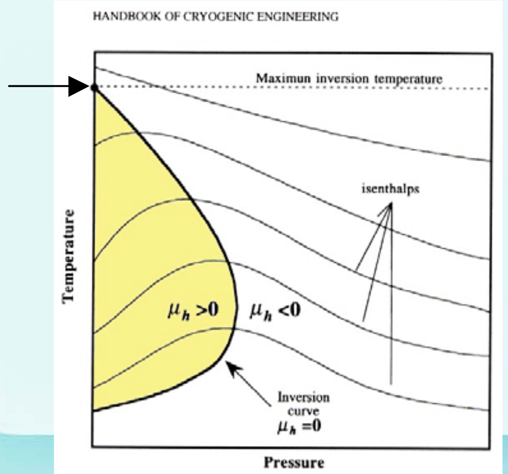
$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\boxed{\left(\frac{\Delta T}{\Delta P}\right)_H = \frac{T\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P}}$$

for an ideal gas: $PV = RT$ and $T\left(\frac{\partial V}{\partial T}\right)_P = V$, i.e. $\left(\frac{\Delta T}{\Delta P}\right)_H = 0$ NB!

for real gases, van der Waals equation can be used: $\left(P + \frac{a}{V^2}\right)(V - b) = RT$



Joule–Thomson expansion inversion curve.

$$\boxed{\left(\frac{\Delta T}{\Delta P}\right)_H = \frac{\frac{2a}{RT} - b}{C_P}}$$

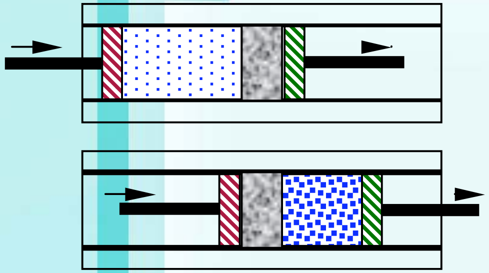
Inversion temperature
$T_i = 2a/Rb$

Maximum Joule-Thomson inversion temperatures (K)

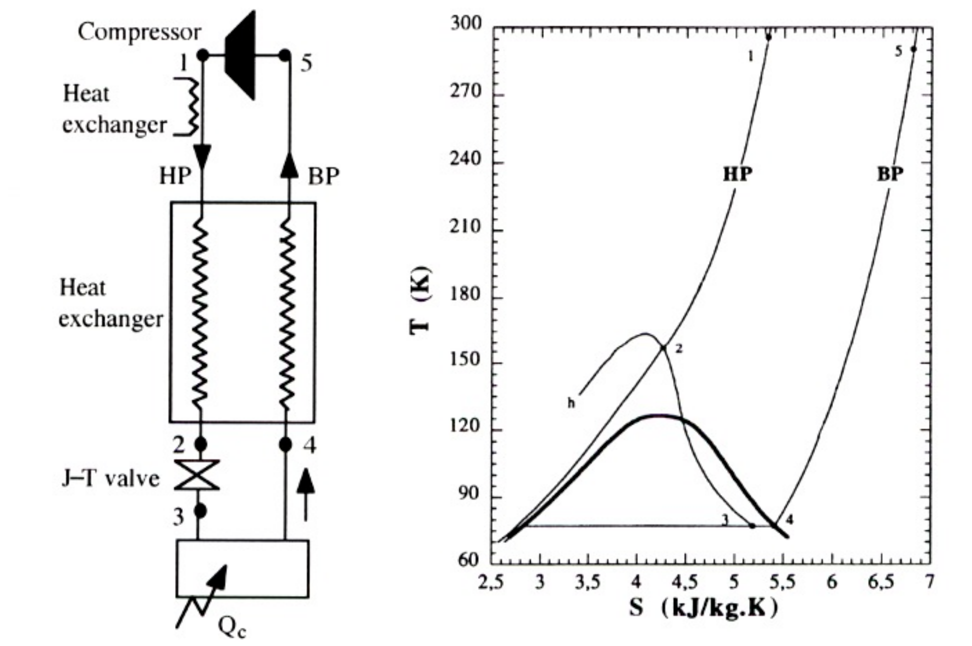
O_2	Ar	N_2	Air	Ne	H_2	He
761	794	621	603	250	205	40

Practical machines

- **Joule-Thomson-Expansion cooler (contd.)**



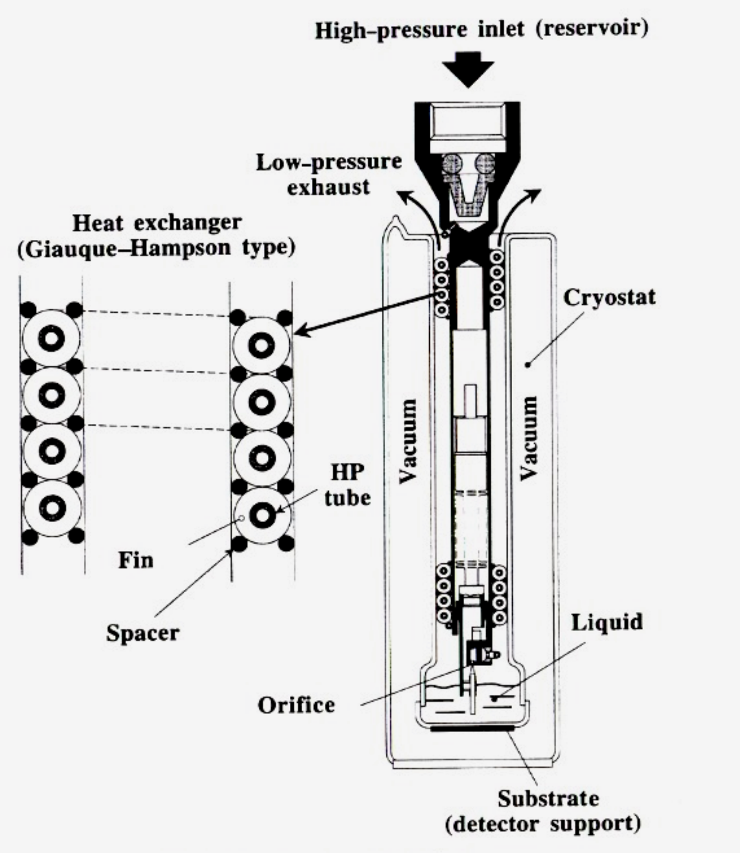
1. The high-P gas is precooled (1-2) by the low-P (4-5) in a heat exchanger.
2. The isenthalpic expansion of the HP gas leads to a 2-phase mixture of liquid and vapor (3) at LP
3. The heat load is removed at T=const by evaporation of the liquid fraction of the mixture (3-4)



Joule–Thomson cycle (*T*–*S* diagram).

Practical machines

- **Joule-Thomson-Expansion cooler (contd.)**



Schematic of a Joule–Thomson cooler.

Practical machines

- **Pulsed Tube cooler**

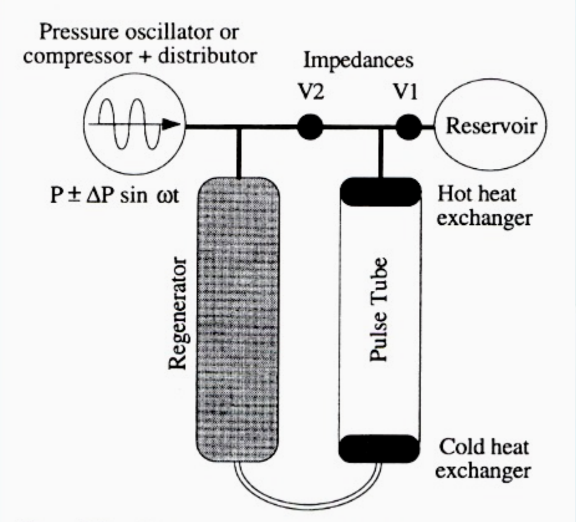


Figure 7-21 Schematic of a pulse-tube cooler.

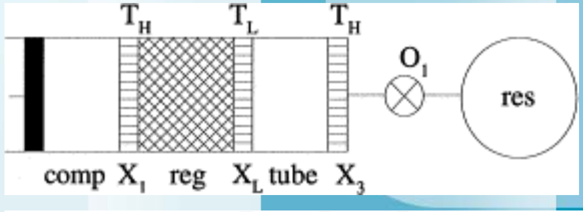
Two Stage Pulse Tube Cryocooler
from Janis and Sumitomo (SHI)

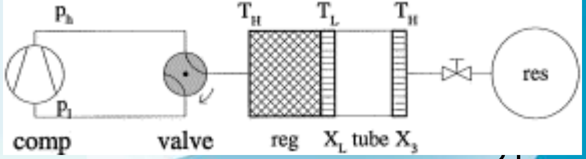
$$<\dot{Q}_c> + <\dot{Q}_{\mathrm{loss}}> = <\dot{H}> = <\dot{Q}_{\mathrm{a}}>$$

$$<\dot{H}> = \frac{C_P}{\tau}\int_0^{\tau} \dot{m}\, T\, dt; \quad \dot{m} = \rho s u = \frac{P}{RT} s u;$$

$$<\dot{H}> = \frac{C_P\, s}{RT}\int_0^{\tau} u\, P\, dt; \quad P = \overline{P} + \Delta P \sin \omega t; \, u = u_0 \sin(\omega t - \varphi);$$

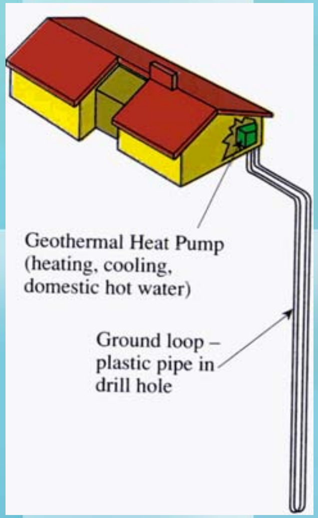
$$<\dot{H}> = \frac{C_P\, s}{2R} u_0\, \Delta P \cos \varphi$$

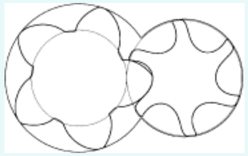


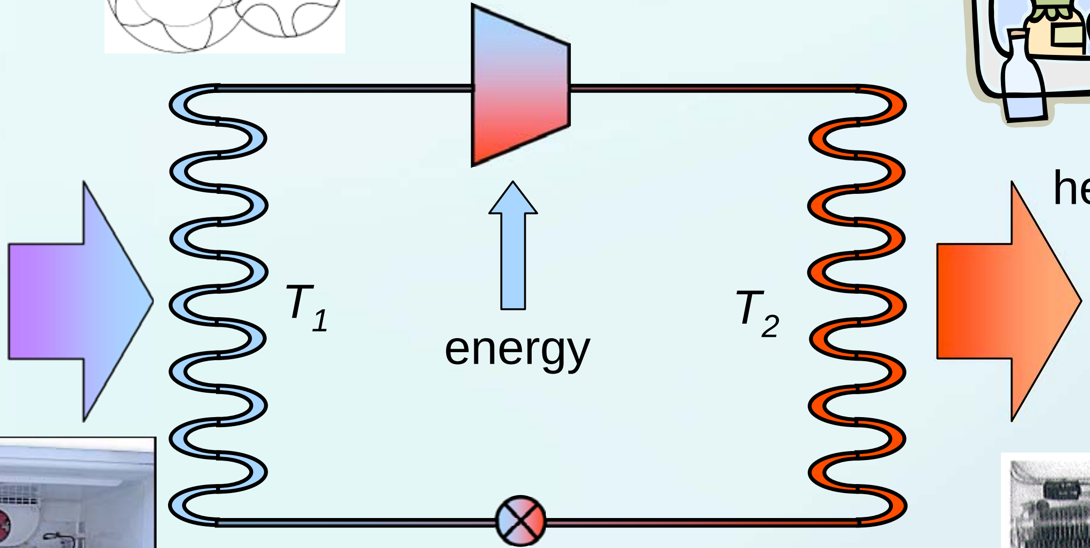


Thermodynamics at work

- **Domestic refrigerators & heat pumps**

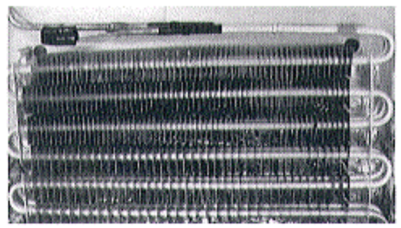






expansion valve (aperture)

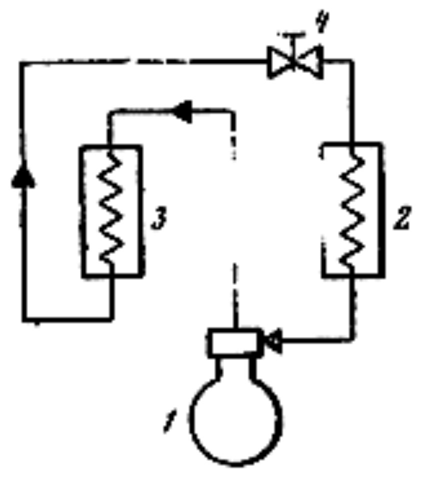
evaporator



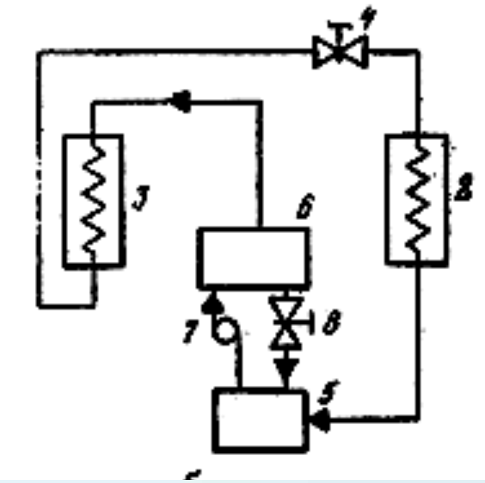
condenser

Absorption refrigerator

- **1922: the two Swedish students, Carl Munters and Baltzar von Platen invented absorption technology. A patent is granted on March 8, 1923.**
- **1925: Electrolux acquires the von Platen-Munters patent and introduces the world's first absorption refrigerator for households. A patent is granted in the U.S. in 1926.**



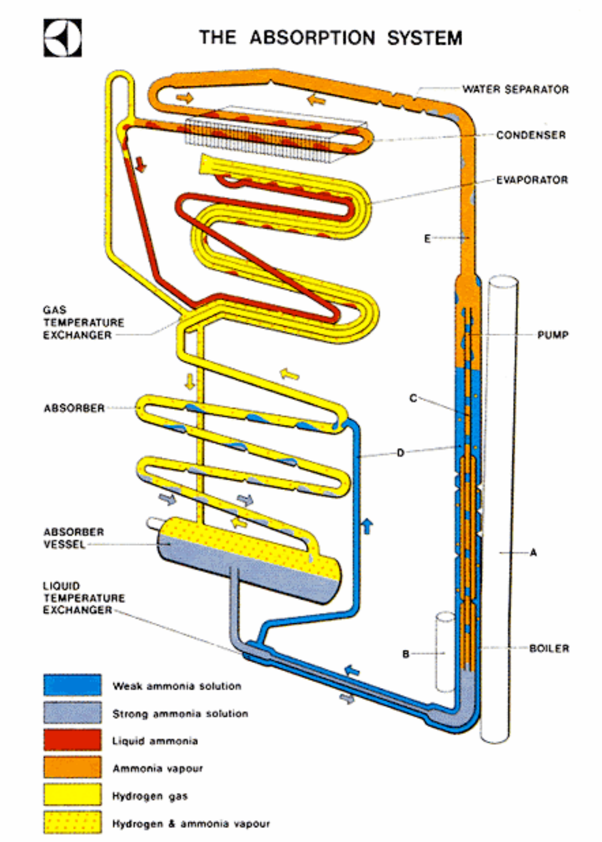
Conventional technique (compressor)



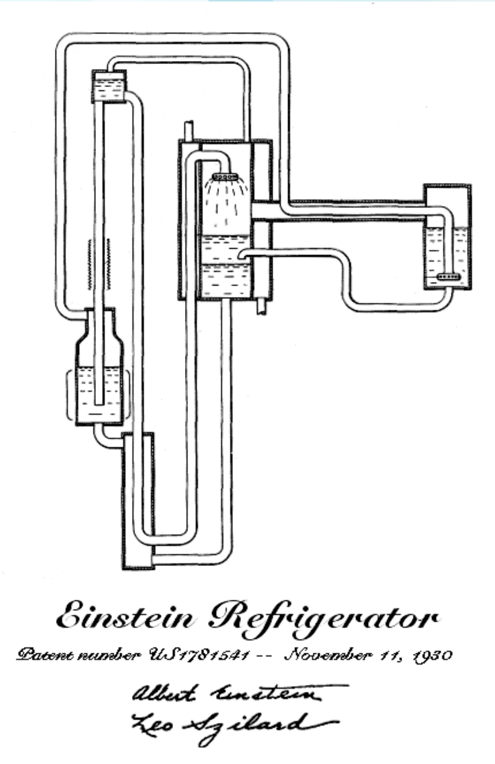
Absorption technique (no compressor)

Absorption refrigerator

- **Neat idea: no expansion valve by adding H_2 gas**
- **All depends on *partial* pressures**



http://www.gas-refrigerators.com



Refrigerants

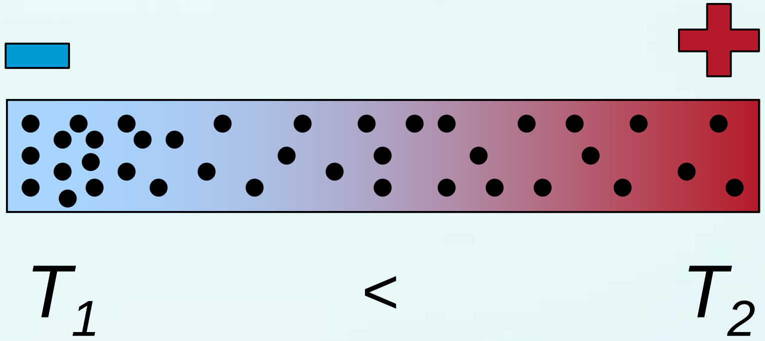
are R-numbered and can be dangerous

Refrigerant	R number	Boiling toC	Toxic group
$CFCl_3$	R11	24	5
CF_2Cl_2	R12	-30	6
CF_3Cl	R13	-82	6
CF_4	R14	-128	6
$CHFCl_2$	R21	9	4
CHF_2Cl	R22	-40	5
CHF_3	R23	-84	5
$CFCl_2$ CF_2Cl	R113	-47	4
$CFCl_2$ CF_3	R114A	3	6
CF_2Cl_2 CF_3Cl	R114	3	6
CF_2Cl_2 CF_3	R115	-39	n/a
CO_2	R744	-78	
NH_3	R717	-33	2

Toxic group 1: death after breathing for ~5 min

Other ways…

- **Thermoelectric effects**

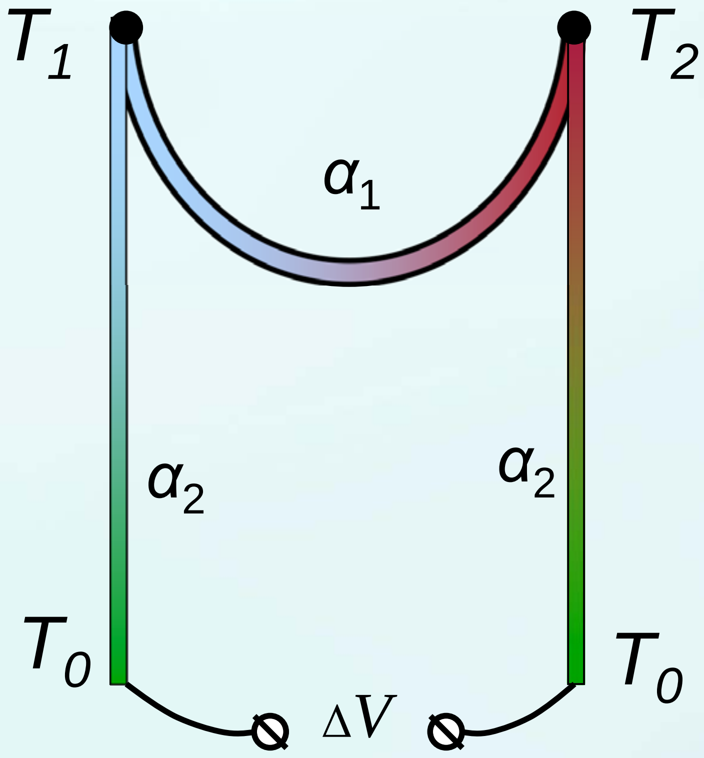


$$\begin{cases} \boldsymbol{E} = \rho\, \boldsymbol{j} + \alpha \nabla \boldsymbol{T} \\ \boldsymbol{q} = \pi\, \boldsymbol{j} - \kappa \nabla \boldsymbol{T} \\ \pi = \alpha T \end{cases}$$

- ρ – resistivity [Ω m]
- α – Seebeck coefficient [V/K]
- π – Peltier coefficient [V]
- κ – thermal conductivity [W/(m K)]
- $\boldsymbol{E}$ – electrical field [V/m]
- $\boldsymbol{q}$ – heat flow density [W/m^2]
- $\boldsymbol{j}$ – electrical current density [A/m^2]
- ∇T – temperature gradient [K/m]

Other ways…

- **Thermocouple**

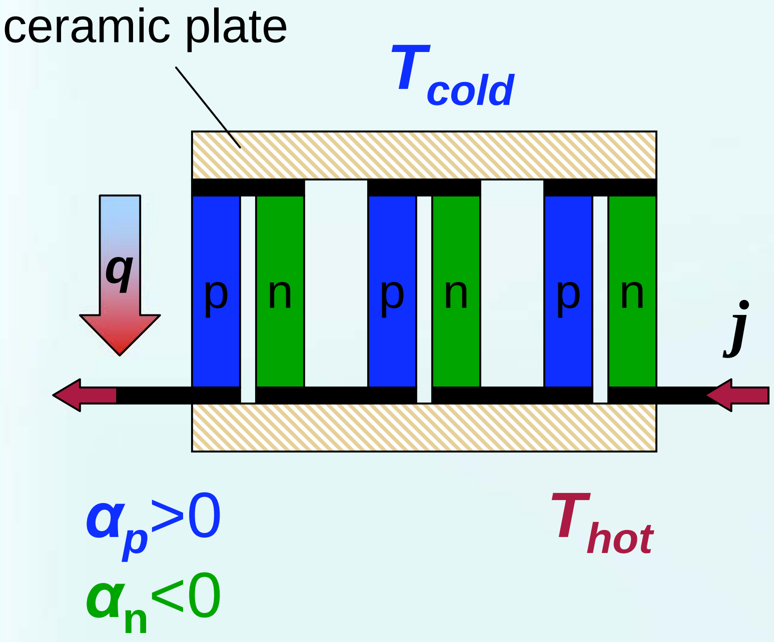


Material	EMF (mV) (0-100C) vs. Pt
Cu	0.76
Au	0.78
Ni	-1.48
Pd	-0.57
W	1.12
Al	0.42
Fe	1.89
Alumel	-1.29
Chromel	2.81
Constantan	-3.51
90%Pt-10%Rh	0.643
Bi_2Te_3	~24
UO_2	~75

$$\Delta V = \alpha_2(T_1 - T_0) + \alpha_1(T_2 - T_1) + \alpha_2(T_0 - T_2) = (\alpha_1 - \alpha_2)(T_2 - T_1)$$

Other ways…

- **Peltier cooler**



All solid-state heat pump

Dimensionless figure of merit:

$$ZT = \frac{\alpha^2 T}{\kappa \rho}$$

(the larger the better)

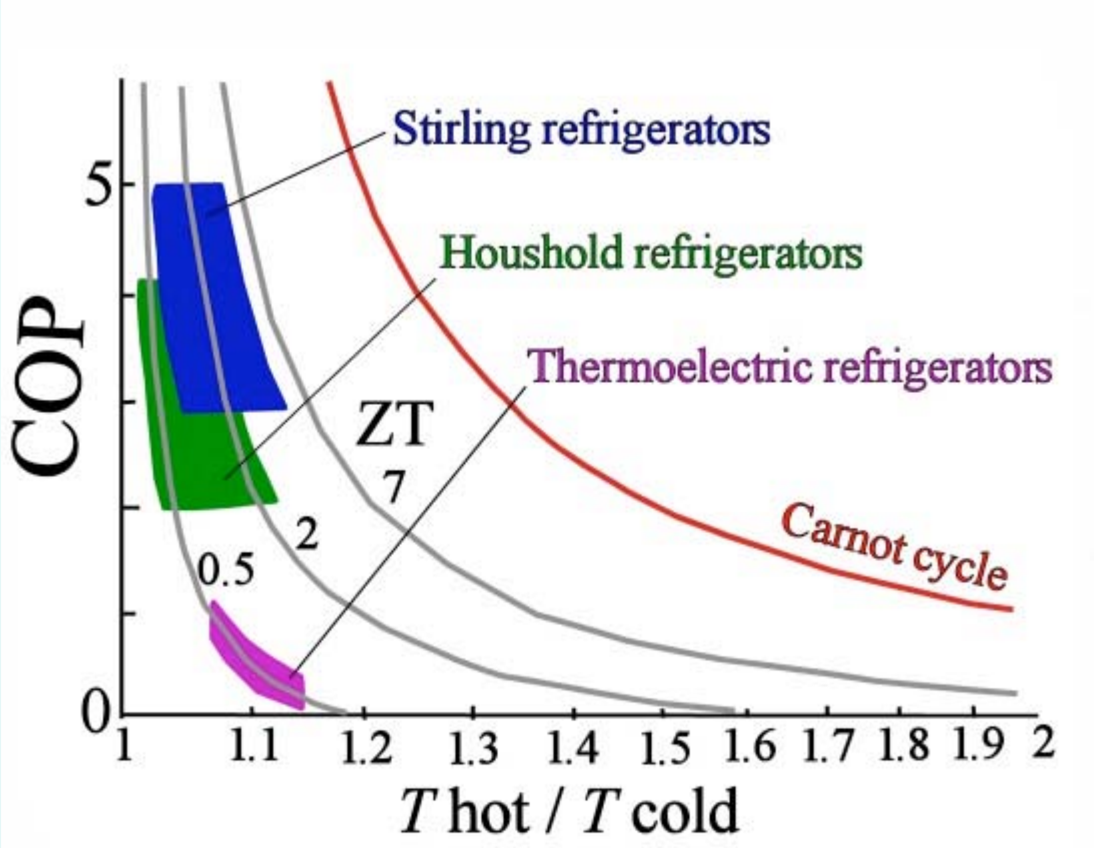
The best materials are small band gap semiconductors; Bi_2Te_3 has α = 220 μV/K and $ZT = 1$ at room temperature. However, ZT greater than 3 is needed to compete with other cooling techniques.

http://www.rmtltd.ru

Efficiency of Peltier cooler

- ***ZT* is not sufficiently large**

=



Primary thermometers

- **Ideal-gas thermometer**

$$PV = \frac{m}{\mu} RT$$

Problems:

- volume is not constant (can be compensated for)
- non-ideality of gas which condenses at low temperature (He best)

Primary thermometers

- **Acoustic thermometer**

$c = \sqrt{\frac{dP}{d\rho}}$ sound velocity in a gas

Newton: sound is an isothermal process (P/ρ=const)

$$c_N = \sqrt{\left(\frac{dP}{d\rho}\right)_T} = \sqrt{\frac{RT}{\mu}}$$

Laplace: sound is an adiabatic process $\gamma PdV + VdP = 0; \quad \gamma = C_P / C_V$

$$c_L = \sqrt{\gamma \frac{P}{\rho}} = \sqrt{\gamma}\, c_N$$

Water triple point = 273.16 K *exactly*

Then, $\boxed{\frac{T}{273.16} = \lim_{P \to 0} \left(\frac{c(P,T)}{c(P,T_{\text{triple}})} \right)}$

Primary thermometers

- **Noise thermometer**

Nyquist derived the following equation from thermodynamic calculations valid for frequencies *f* << *k T/h*,

$$< U^2 > = 4 k_B T \Delta f$$

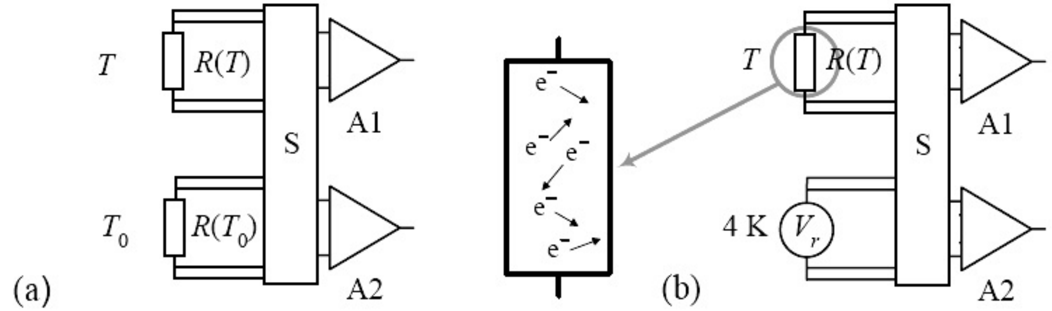


Figure 2: (a) Block diagram for the conventional relative method with switched-input noise correlator, S: switching, A1, A2: amplification and digitisation. (b) Block diagram for the new absolute method.

http://emtech.boulder.nist.gov/

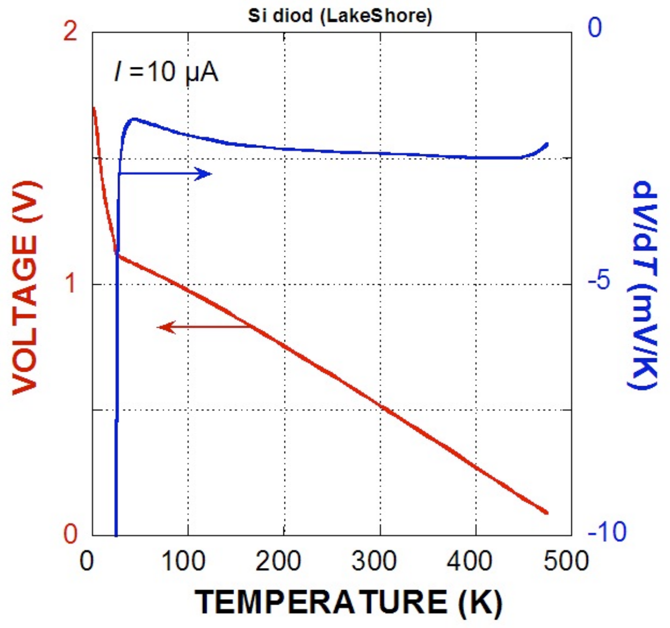
Problem:
- long measurement time (10^{-5} accuracy requires 8 weeks)

Secondary temperature sensors

- **Si diodes**

2 mm

http://www.lakeshore.com/



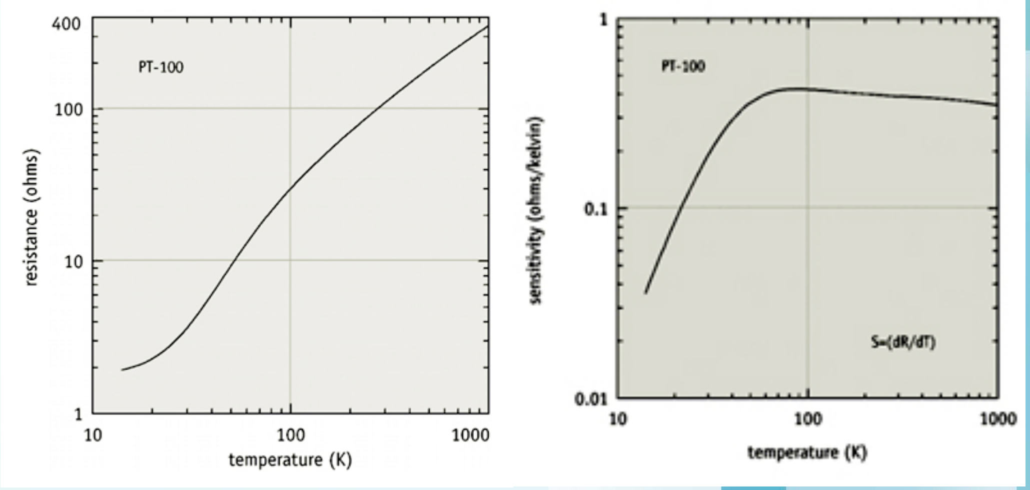
$200 - $300 & not calibrated
add $140 for calibration (B=0)

Compare to 1N4001 from ELFA
for 1:- SEK which can equally well be used
for temperature measurements !

Secondary temperature sensors

- **Pt thermometers**

http://www.lakeshore.com/

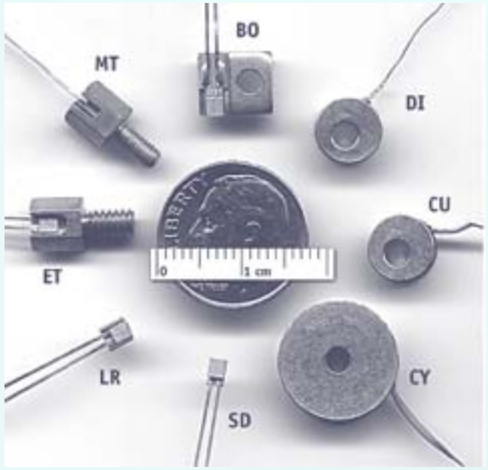


$80 - $140 & standard curve; add $100-800 for exact calibration in μ$H \neq 0$

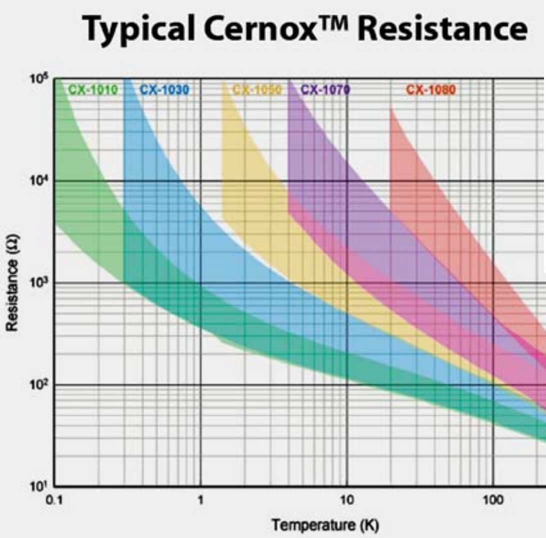
Compare to Pt100/Pt1000 from ELFA
for ~150:- SEK which can equally well be used
for temperature measurements !

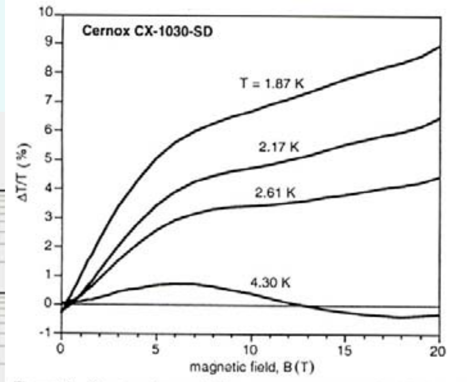
Secondary temperature sensors

- **Cernox thermometers**



http://www.lakeshore.com/





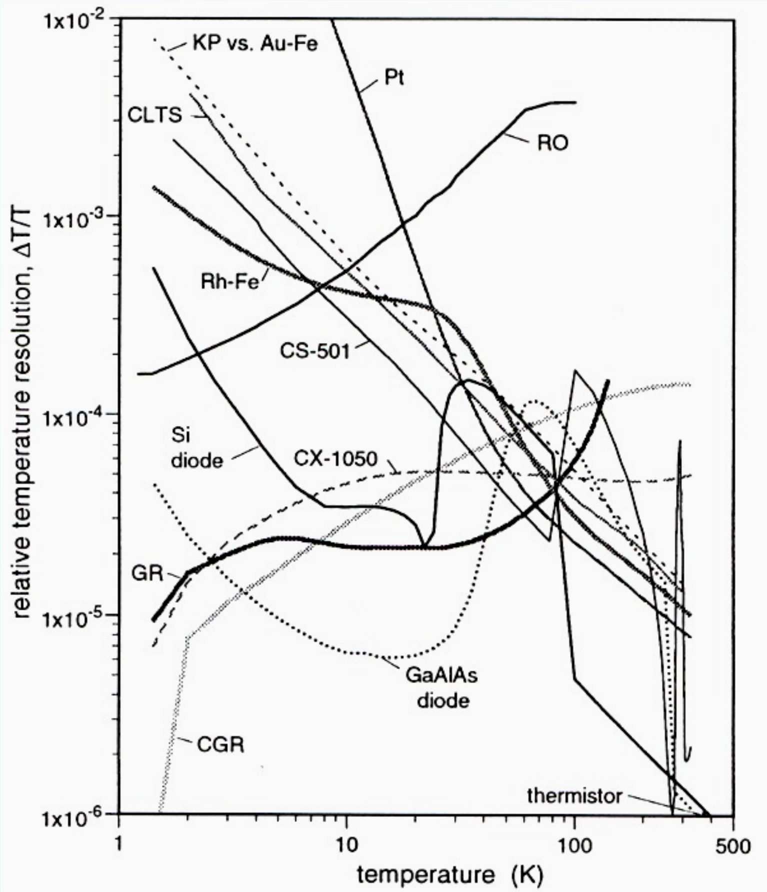
\$150 - \$240 & uncalibrated; add \$100-800 for exact calibration in µ*H* ≠ 0

Very good in high magnetic fields !!!

No equivalent from ELFA (carbon resistors, may be)

Secondary temperature sensors

- **Sensitivity summary**

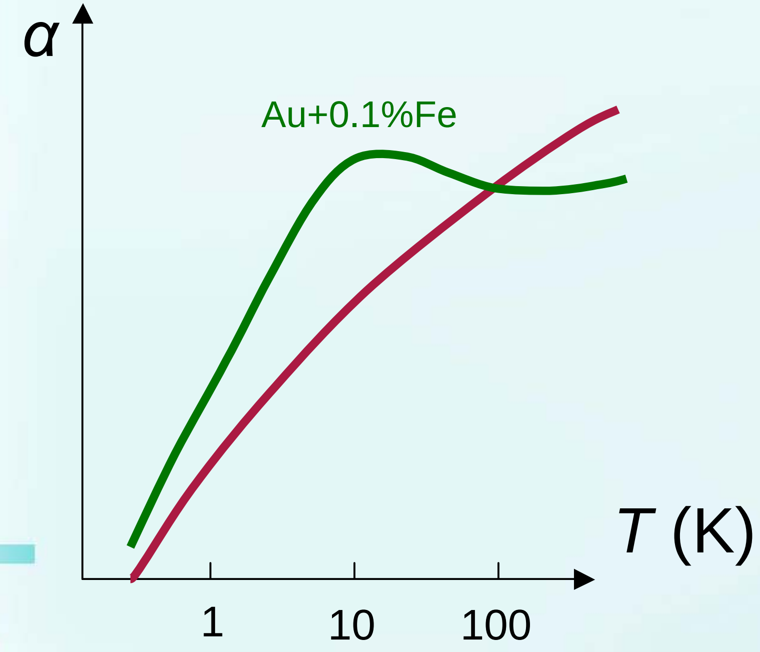


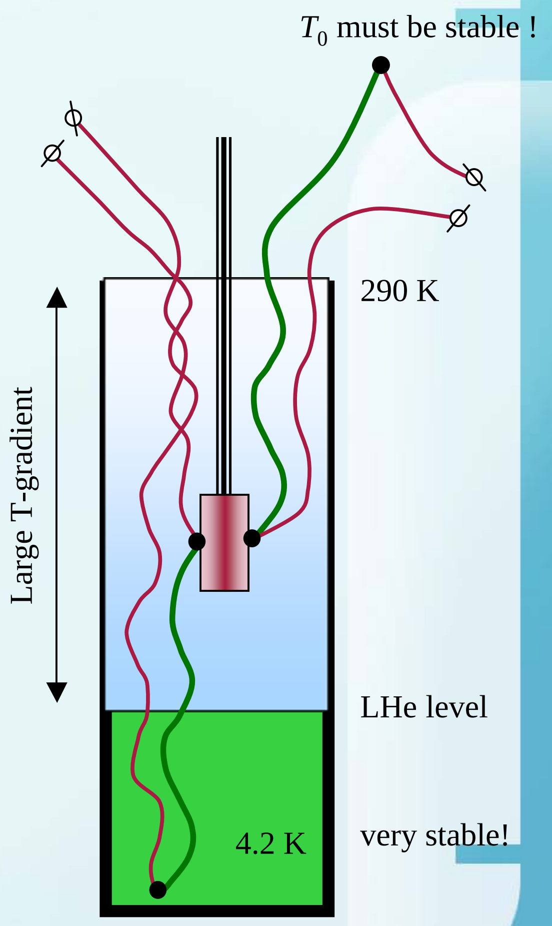
Thermocouple

- **Thermocouple**

Problems:

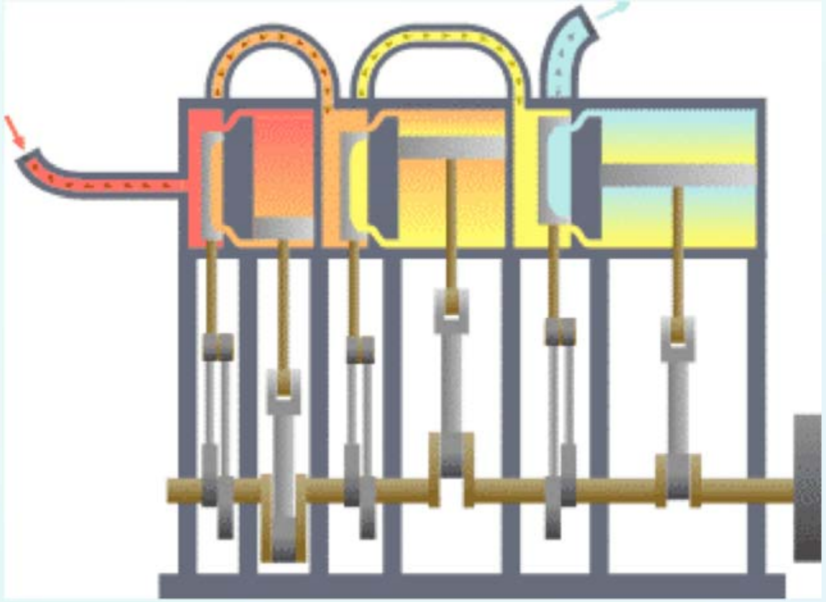
- $\alpha \to 0$ as $T \to 0$: small voltages
- stability of T for reference jncn.
- homogeneous wires





Material	EMF vs. Pt
Cu	0.76
Au	0.78
Ni	-1.48
Pd	-0.57
W	1.12
Al	0.42
Fe	1.89
Alumel	-1.29
Chromel	2.81
Constantan	-3.51
90%Pt-10%Rh	0.643
Bi_2Te_3	~24
UO_2	~75

Triple stage expansion machine



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