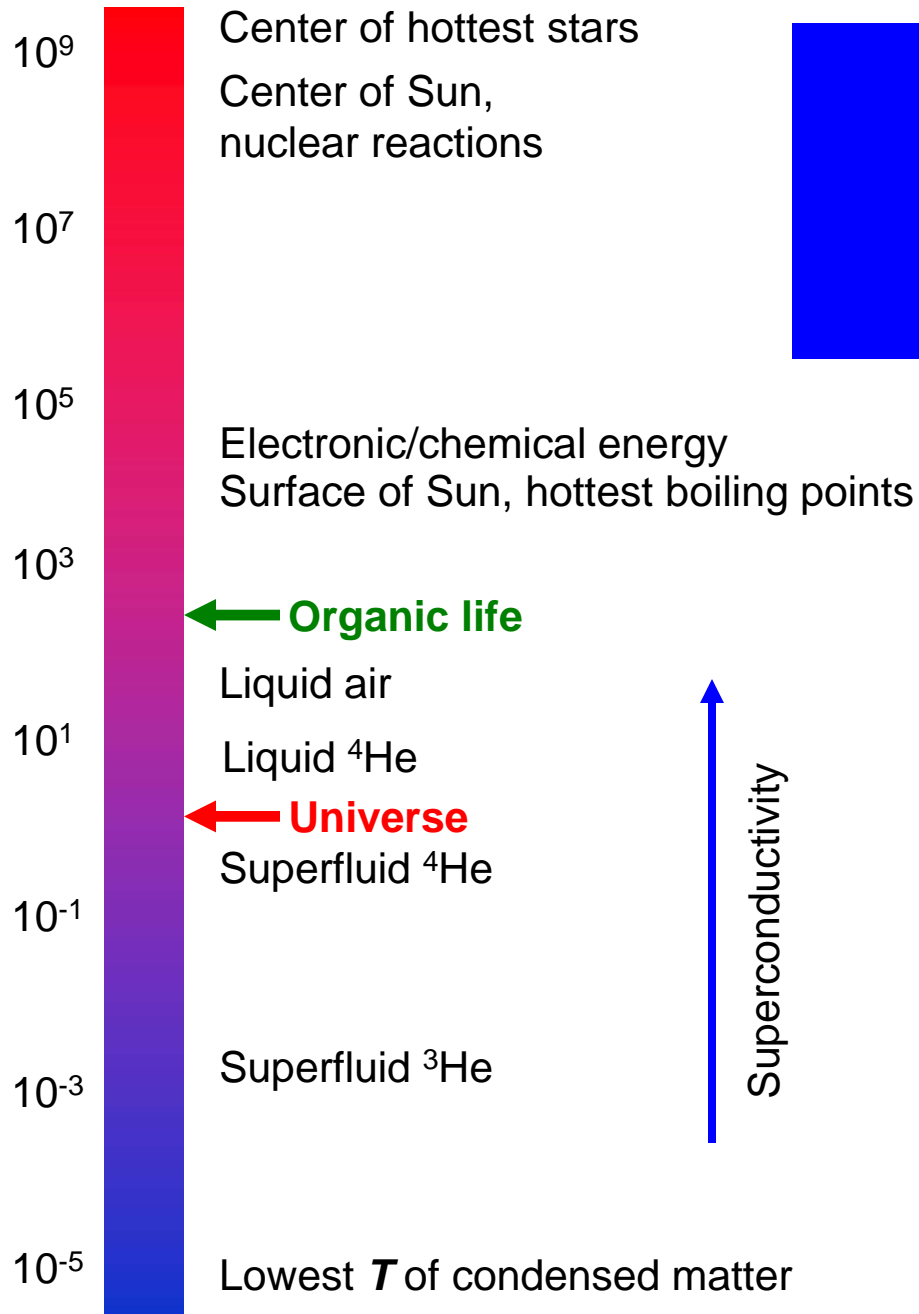


# Lecture 12. Refrigerators. Toward Absolute Zero (Ch. 4)

Temperature, K



Superconductivity

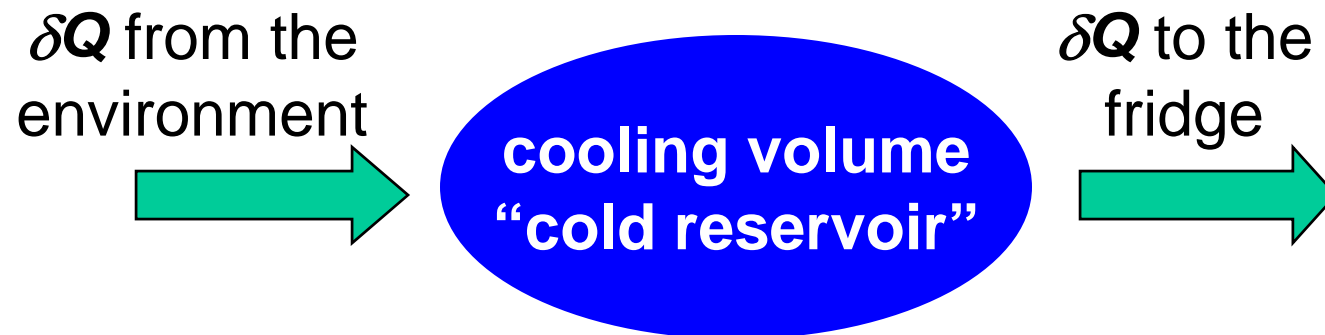
Electronic magnetism

Nuclear magnetism



# How Low Temperatures Are Produced

Although the efficiency of an “ideal” refrigerator does not depend on the working substance, in practice ***the choice of working substance is very important*** because



At the lowest  $T$ , these two flows of thermal energy compensate each other.



## More on Enthalpy

$$H = U(T) + PV = \int_0^T C_P dT$$

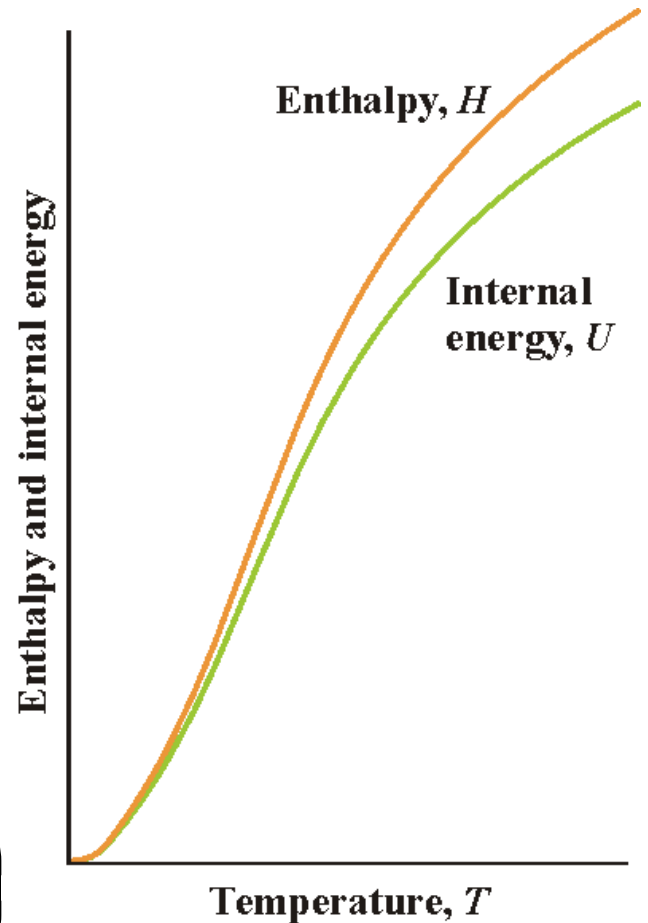
Recall:  $\Delta U + P\Delta V = \Delta H$

$$\left( \begin{array}{l} dH = dU + PdV + VdP \quad P = \text{const} \\ \Rightarrow dH = dU + PdV \end{array} \right)$$

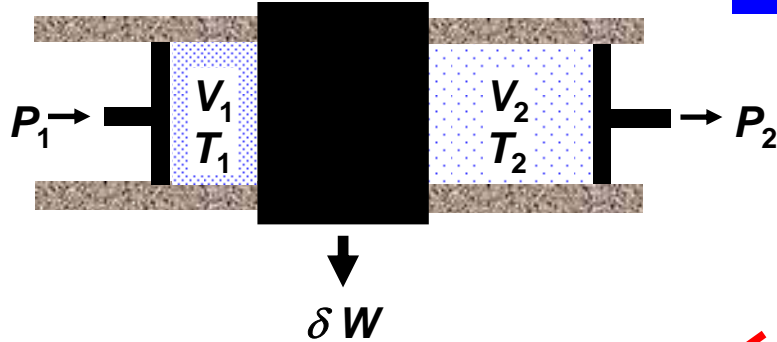
**The latent heat  $L$**  of phase transformation at  $P = \text{const}$ :

$$(H_1 - H_2)_P = L$$

$$\left( \begin{array}{l} dH = dU + PdV + VdP = TdS + VdP \\ dS = \frac{L}{T} \end{array} \right)$$



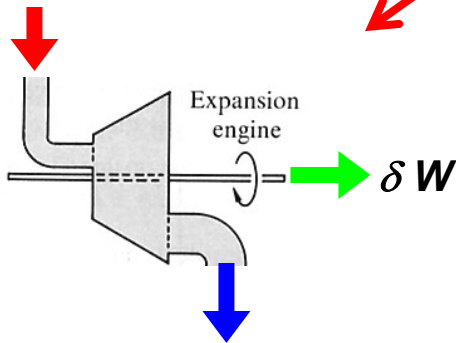
# Cooling of Gases



constant  $\Delta P = P_1 - P_2$ .

(a) an “expansion engine”  
( $\delta W \neq 0$ );

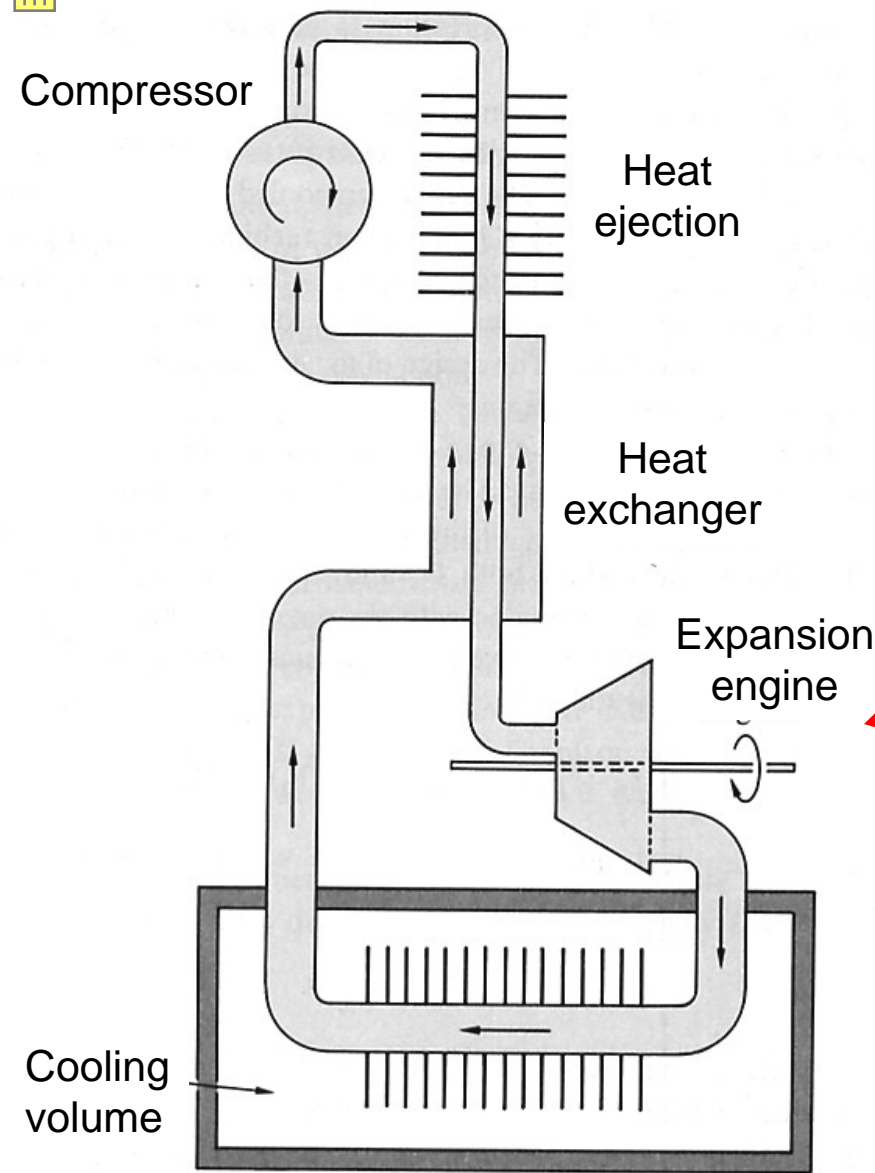
$$H_1 = U(T_1) + P_1 V_1$$



$$H_2 = U(T_2) + P_2 V_2$$

(b) a porous membrane  
or a constriction.  
( $\delta W = 0$ ).

$$H_1 - H_2 = (U_1 + P_1 V_1) - (U_2 + P_2 V_2) = \delta W$$



# Simple Expansion Refrigerator

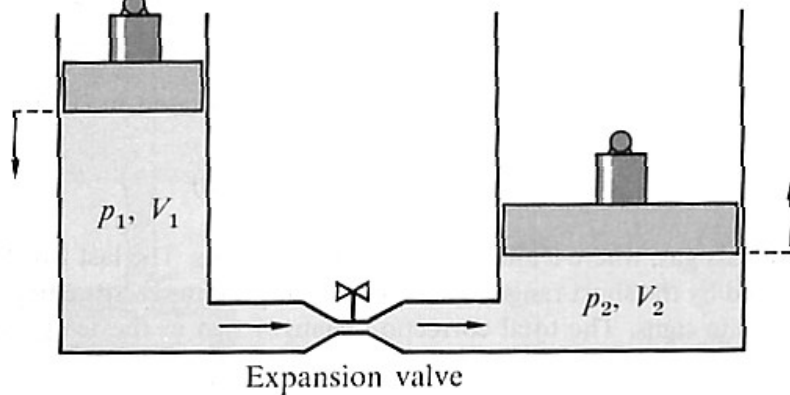
This process works for both *ideal* and *real* gases.

$$\leftarrow \delta W = H_1 - H_2$$

For an ideal monatomic gas:

$$H = \frac{5}{2} N k_B T \quad T_1 - T_2 = \frac{2}{5} \frac{W}{N k_B}$$

# The Joule-Thomson Process



(b) **Throttling** process

$$H_1 - H_2 = \delta W = 0$$

- Irreversible!!
- Real gases only

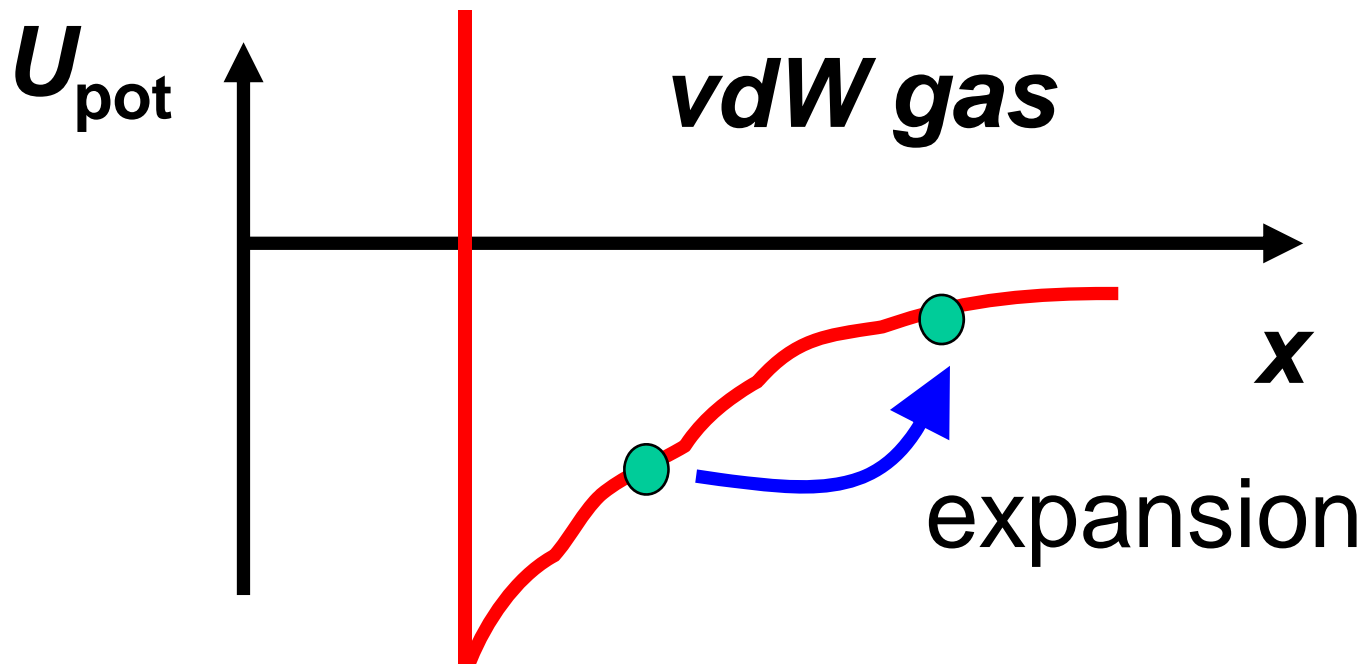
**Isenthalpic expansion:**  $H_1 = H_2$

For an **ideal** gas, :  $H = \frac{f + 2}{2} N k_B T$

$$\Delta H = 0 \quad \Rightarrow \quad \Delta T = 0$$



# The JT Process in Real Gases (low density)

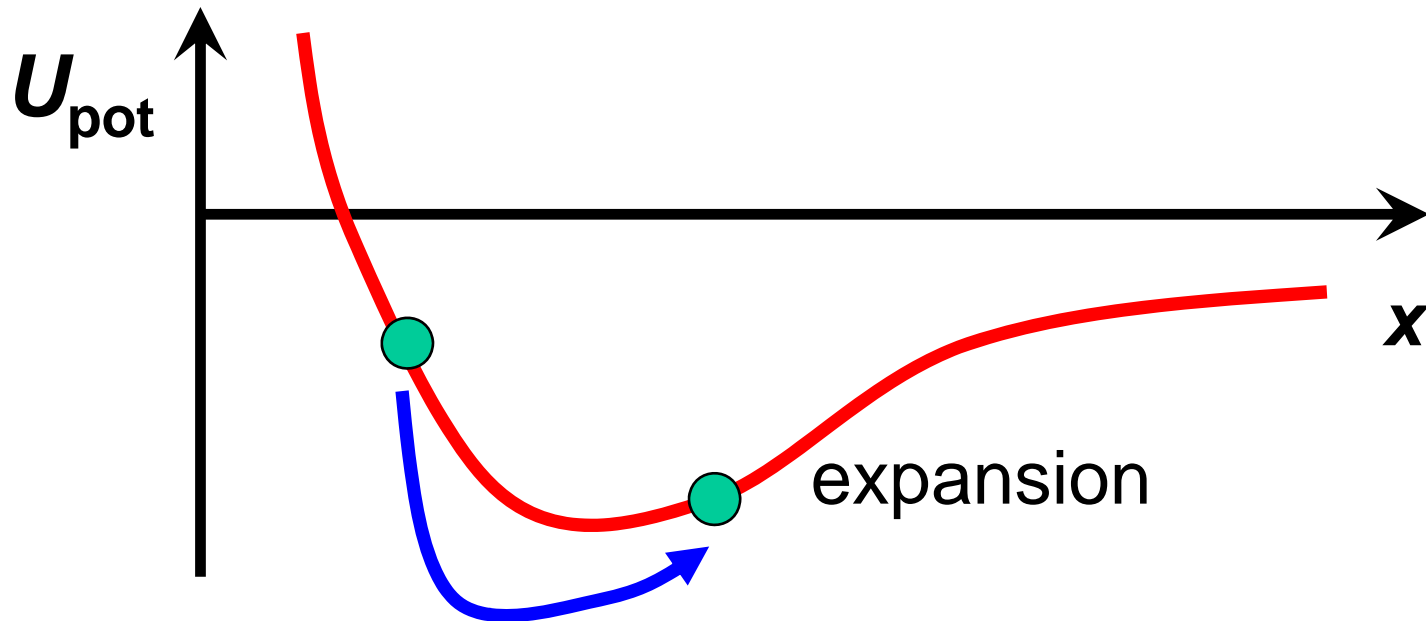


$$U(T, V) = U_{\text{kin}}(T) + U_{\text{pot}}(V)$$

$$\Delta H = 0, \Delta V > 0 \Rightarrow \Delta T < 0$$

# The JT Process in Real Gases (high density)

At **high densities**, the effect is reversed: the sign of  $\Delta T$  depends on initial  $T$  and  $P$ .

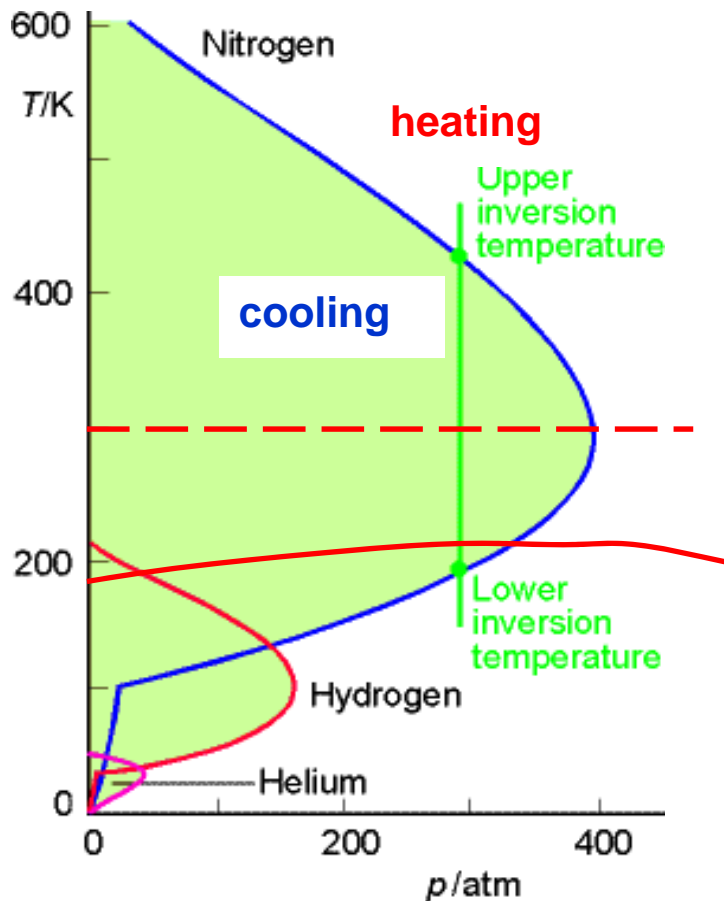


$$\Delta H = 0, \Delta V > 0 \Rightarrow \Delta T > 0$$



# The JT Process in Real Gases (cont.)

All gases have **two inversion temperatures**: in the range between the upper and lower inversion temperatures, the JT process **cools** the gas, outside this range it **heats** the gas.

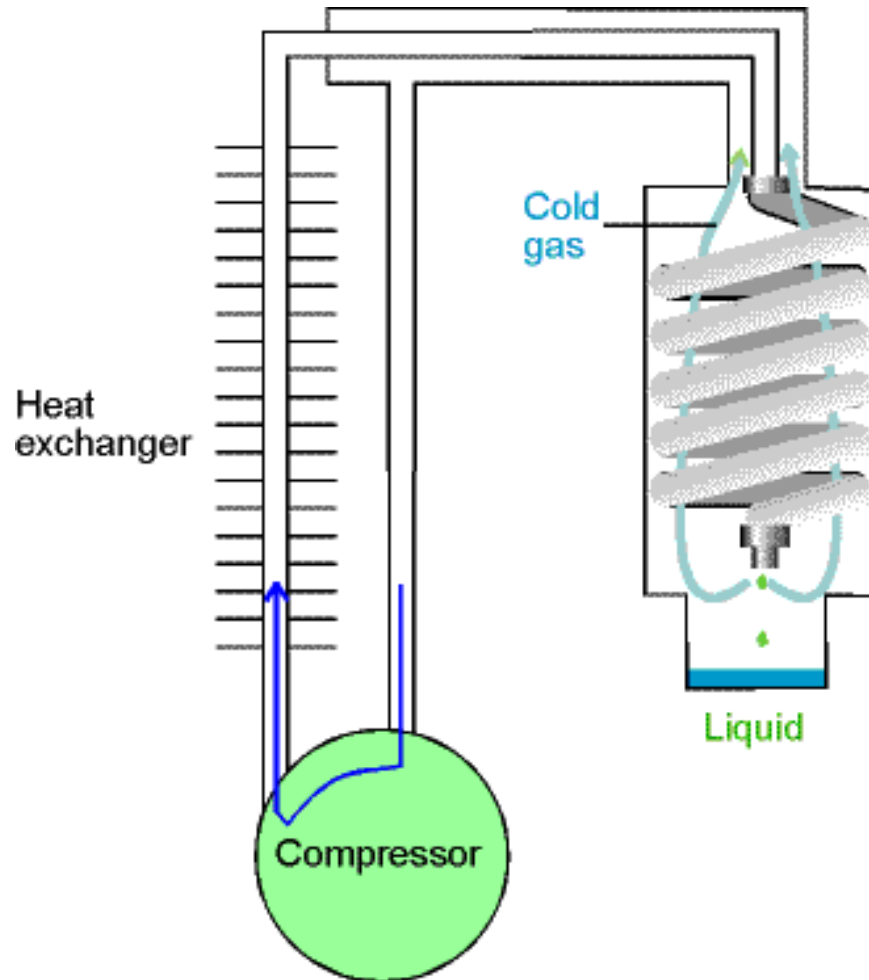


Gas	boiling $T$ ( $P=1$ bar)	inversion $T$ @ $P=1$ bar
CO <sub>2</sub>	195	(2050)
CH <sub>4</sub>	112	(1290)
O <sub>2</sub>	90.2	893
N <sub>2</sub>	77.4	621
H <sub>2</sub>	20.3	205
<sup>4</sup> He	4.21	51
<sup>3</sup> He	3.19	(23)



# Liquefaction of Gases

For air, the inversion  $T$  is above RT. In 1885, Carl von Linde liquefied air in a liquefier based solely on the JT process:



Linde  
refrigerator

# “Efficiency” of liquefaction

**Estimate of efficiency**: let 1 mole of gas enter the liquefier, suppose that the fraction  $\lambda$  is liquefied.

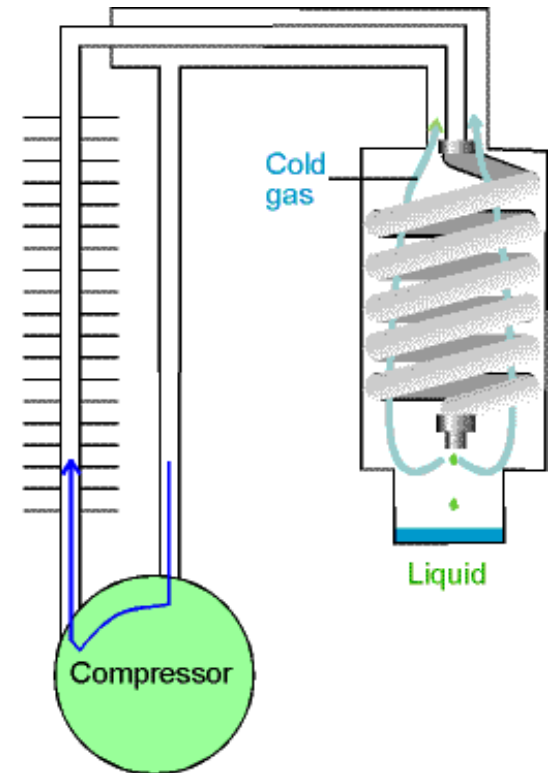
$$H_{in} = \lambda H_{liq} + (1 - \lambda) H_{out}$$

$$H_{in} = H(T_{in}, P_{in}) \quad H_{out} = H(T_{out}, P_{out})$$

$$\lambda = \frac{H_{out} - H_{in}}{H_{out} - H_{liq}}$$

Liquefaction takes place if

$$H_{out} = H(T_{out}, P_{out}) > H_{in} = H(T_{in}, P_{in})$$



## Example (Pr. 4.34, Pg 143)

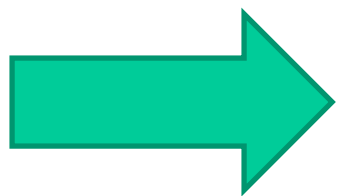
The fraction of  $N_2$  liquefied on each pass through a Linde cycle operating between  $P_{in} = 100$  bar and  $P_{out} = 1$  bar at  $T_{in} = 200$  K:

$$\lambda = \frac{H_{out} - H_{in}}{H_{out} - H_{liq}}$$

$$H_{in}(100\text{bar}, 200\text{K}) = 4442 \text{ J/mole}$$

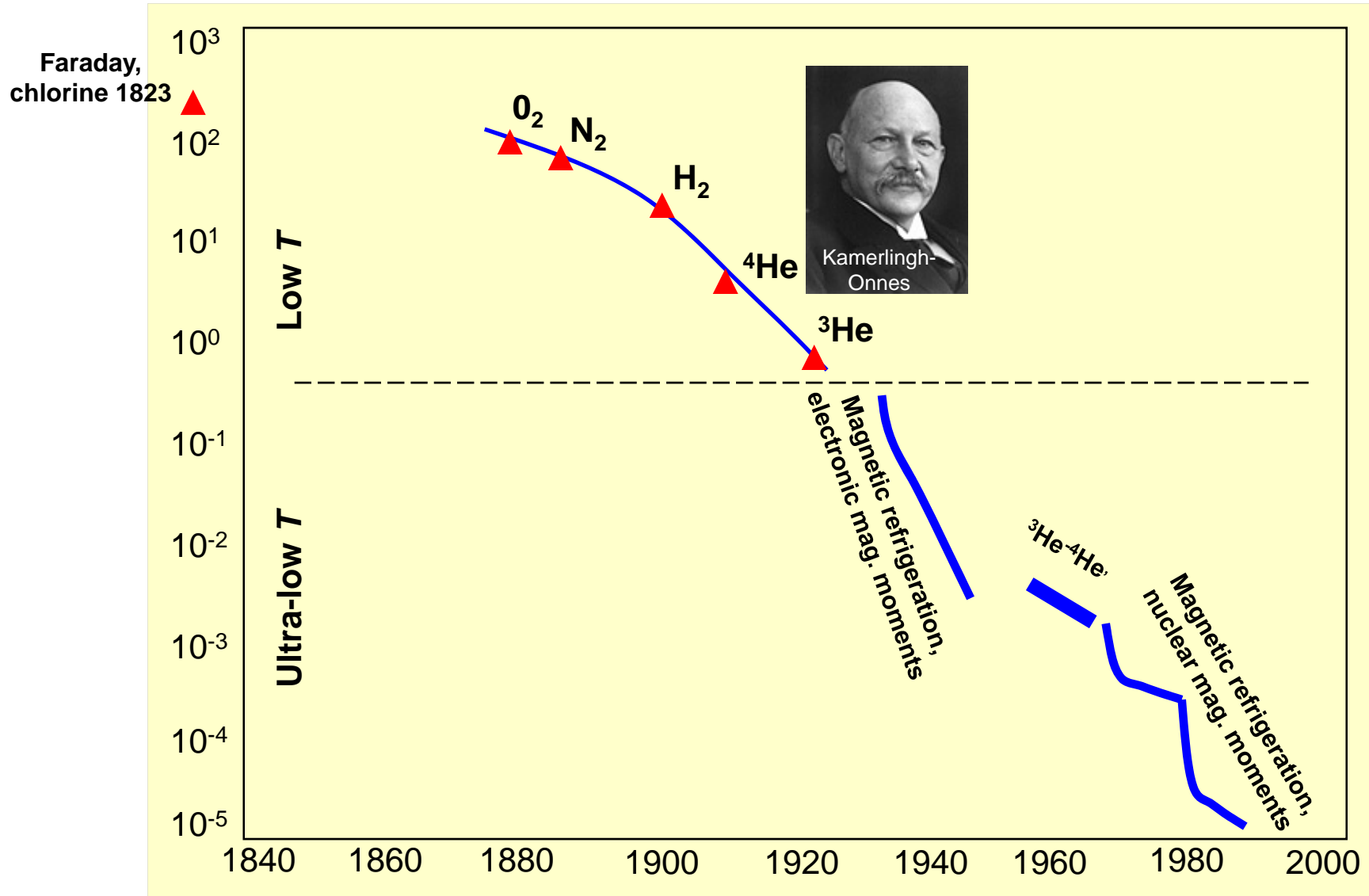
$$H_{out}(1\text{bar}, 200\text{K}) = 5800 \text{ J/mole}$$

$$H_{liq}(1\text{bar}, 77\text{K}) = -3407 \text{ J/mole}$$



$$\lambda = \frac{5800 - 4442}{5800 - (-3407)} = 0.15$$

# Historical Development of Refrigeration



# Cooling by Evaporation of Liquids

$$\delta Q = \frac{dn}{dt} [H_{liq} - H_{vap}] = \frac{dn}{dt} L_{vap}$$

$\delta Q$  – the cooling power,  $dn/dt$  – the number of molecules moved across the liquid/vapor interface



Usually a pump with a constant-volume pumping speed is used, and thus the mass flow  $dn/dt$  is proportional to the vapor pressure.

$$\frac{dn}{dt} \propto P_{vap}(T) \propto \exp\left(-\frac{1}{T}\right) \quad \text{Pr. 5.35}$$



## Cryoliquids

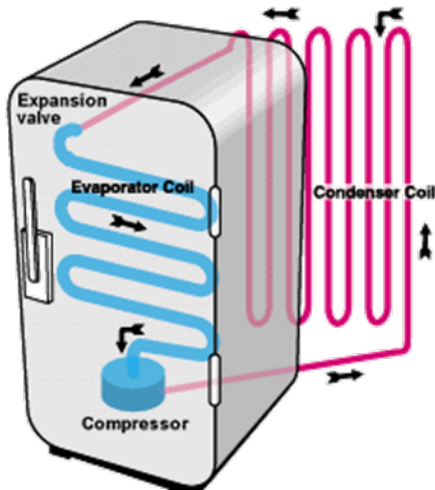
Substance	boiling T (P=1 bar)	melting T (P=1 bar)	Latent heat kJ/liter	Price \$ / liter
H <sub>2</sub> O	373.15	273.15	2252	
Xe	165.1	161.3	303	
O <sub>2</sub>	90.2	54.4	245	
N <sub>2</sub>	77.4	63.3	160	0.3
H <sub>2</sub>	20.3	14.0	31.8	
<sup>4</sup> He	4.21	--	2.56	8
<sup>3</sup> He	3.19	--	0.48	5x10 <sup>4</sup>

the cooling power diminishes rapidly with decreasing  $T$  (at  $T \rightarrow 0$ ,  $\delta S$  becomes small for all processes)

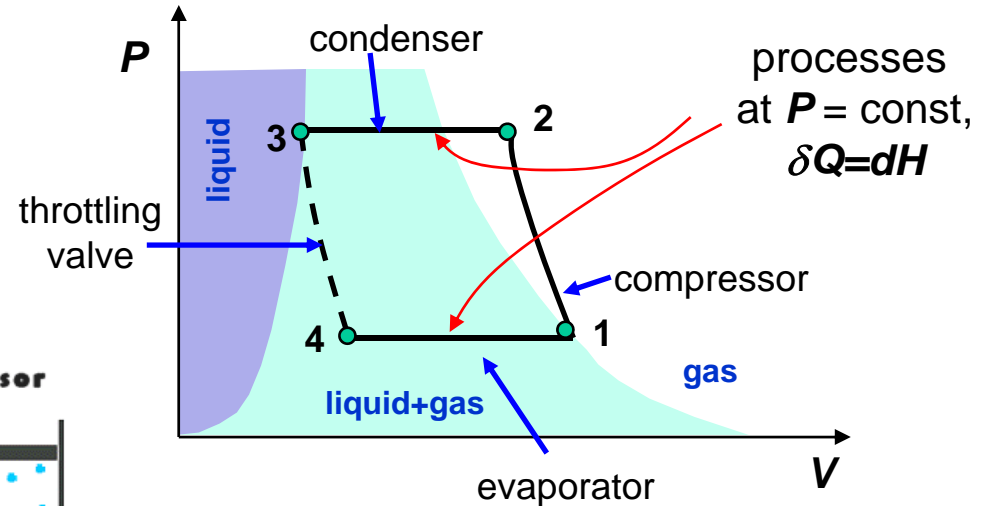
the evaporation cooling of Liquid Helium

$P$ , torr	10 <sup>-4</sup>	10 <sup>-3</sup>	10 <sup>-2</sup>	10 <sup>-1</sup>	1	10	100
$T(^4\text{He})$ , K	0.56	0.66	0.79	0.98	1.27	1.74	2.64
$T(^3\text{He})$ , K	0.23	0.28	0.36	0.47	0.66	1.03	1.79

# Kitchen Refrigerator

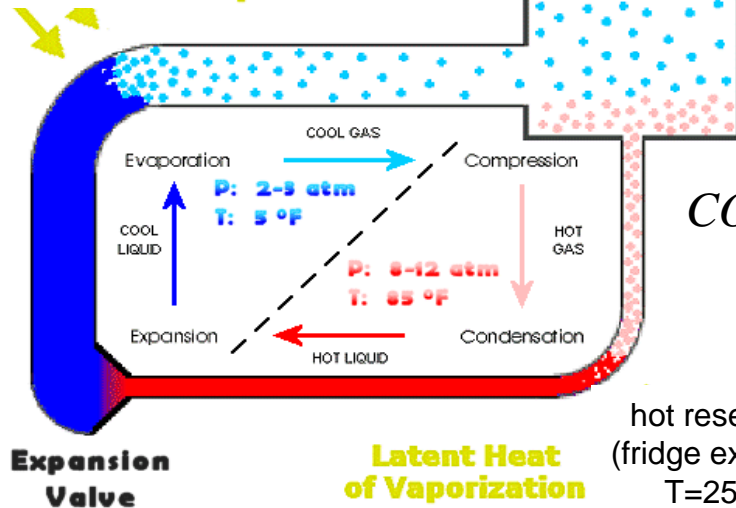


A liquid with suitable characteristics (e.g., Freon) circulates through the system. The compressor pushes the liquid through the condenser coil at a high pressure ( $\sim 10$  atm). The liquid sprays through a throttling valve into the evaporation coil which is maintained by the compressor at a low pressure ( $\sim 2$  atm).



cold reservoir  
(fridge interior)  
 $T=5^{\circ}\text{C}$

**Latent Heat of Vaporization**



**Latent Heat of Vaporization**

hot reservoir  
(fridge exterior)  
 $T=25^{\circ}\text{C}$

$$COP = \frac{Q_C}{Q_H - Q_C} = \frac{H_1 - H_4}{H_2 - H_3 - (H_1 - H_4)} = \frac{H_1 - H_4}{H_2 - H_1}$$

The enthalpies  $H_i$  can be found in tables.

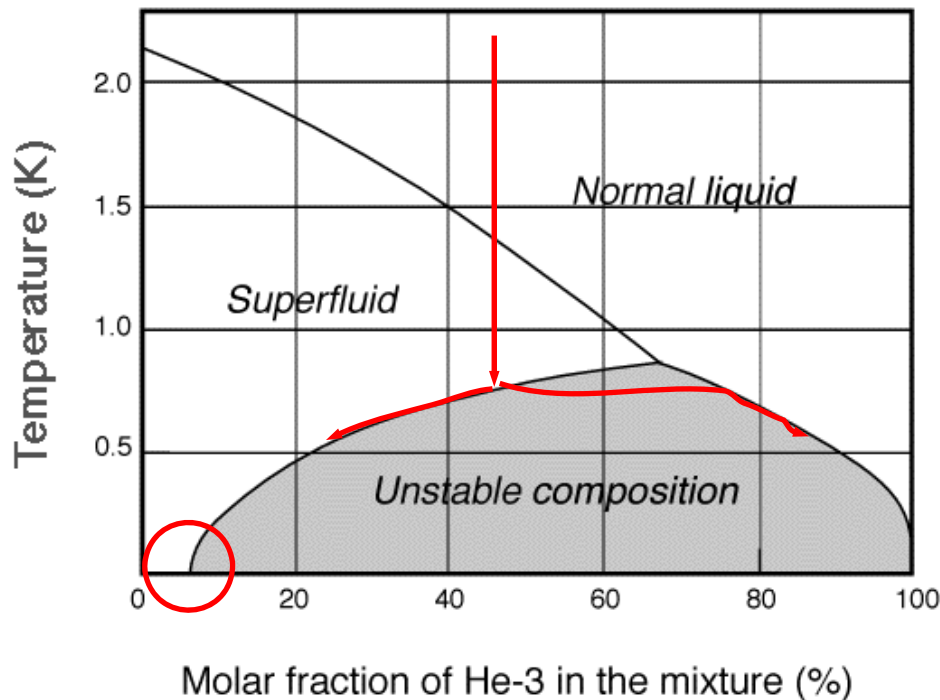
$$H_3 = H_4, \Rightarrow H_3^{\text{liquid}} = x \cdot H_4^{\text{liquid}} + (1-x) \cdot H_4^{\text{gas}}$$

$$S_2 = S_1 \rightarrow T_2 \rightarrow H_2(T_2, P_2)$$



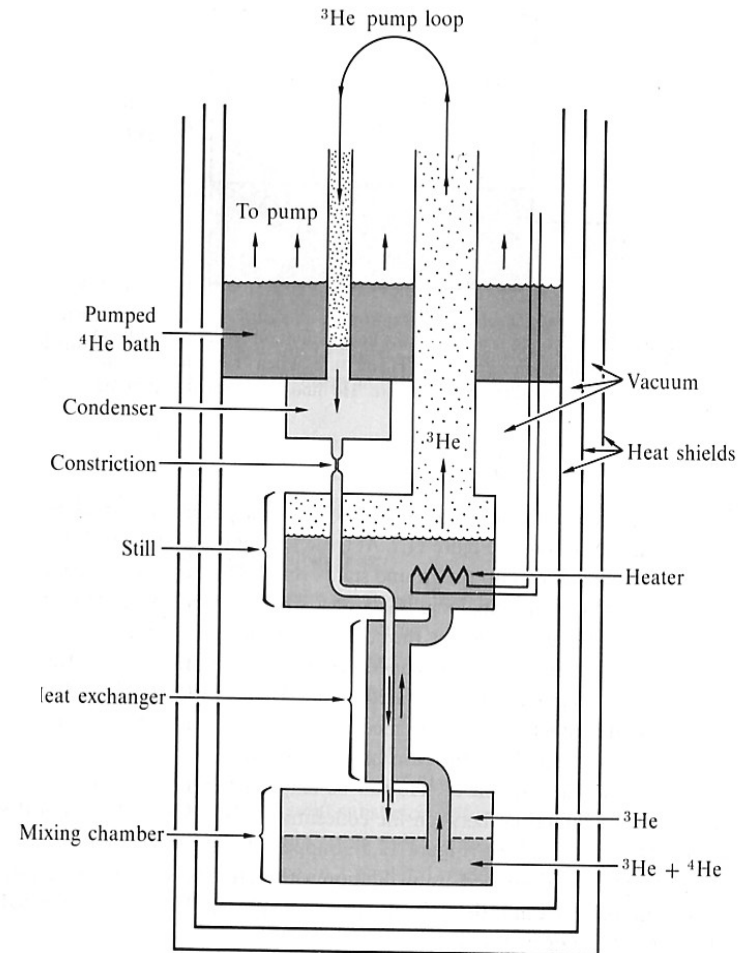
# Dilution Refrigerator (down to a few mK)

evaporation cooling with a **non-exponential** dependence  $P_{\text{vap}}(T)$

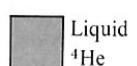
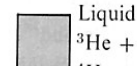
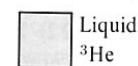
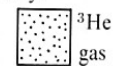


$$dQ(T) \propto \Delta H \cdot \frac{dn}{dt} \propto \left[ \Delta H \propto \int_0^T \Delta C dT \propto T^2 \right] \propto T^2$$

$\Delta H$  – the enthalpy difference between the  $^3\text{He}$ -rich and dilute phases



Key:

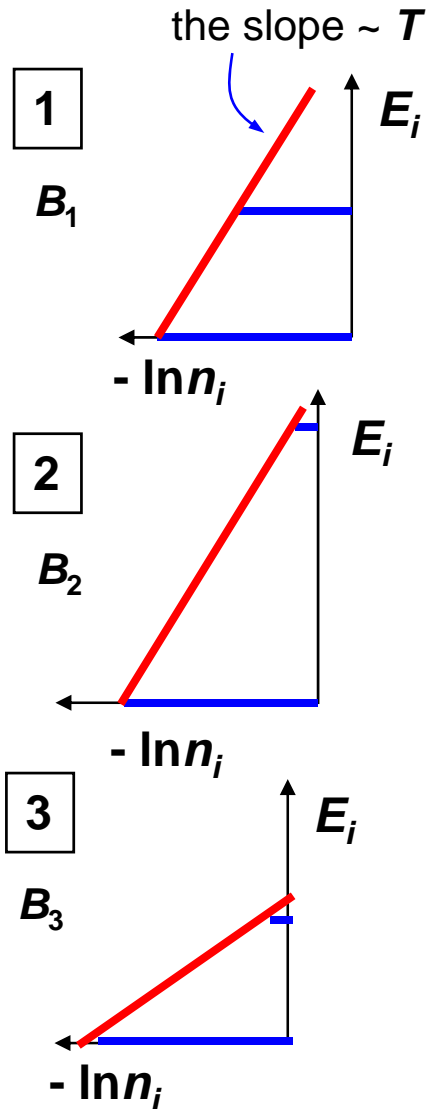


# Cooling by Adiabatic Demagnetization

Let's consider a quantum system with Boltzmann distribution of population probabilities for two discrete levels:

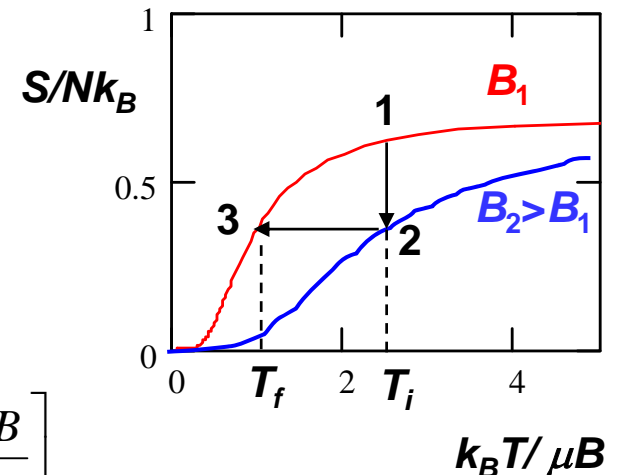
$$n_i \propto e^{-\frac{E_i}{k_B T}}$$

$$E_i = -k_B T \ln n_i$$



**1 – 2 - Isothermal** increase of  $B$  from  $B_1$  to  $B_2$ . The upper energy level rises because  $W$  has been done by external forces. If  $T = \text{const}$ , the work performed must be followed by population rearrangement, so that the red line is shifted, but its slope  $\sim T$  remains the same: e.g., if the magnetic field is increased, the population must decrease at the highest level and increase at the lowest –  $S$  decreases!

**2 – 3 - Adiabatic** decrease of  $B$  (the specimen is thermally isolated).  $S = \text{const}$ : the population of **each** level must be kept constant, while its  $E_i$  varies. The red line slope decreases –  $T$  decreases!



$$S\left(N, \frac{\mu B}{k_B T}\right) = N k_B \left[ \ln \left( 2 \cosh \frac{\mu B}{k_B T} \right) - \frac{\mu B}{k_B T} \tanh \frac{\mu B}{k_B T} \right]$$



## Nobel Prize in Physics 1997

# Laser cooling

- Very dilute gas (avoid condensing)
  - Momentum transfer from photons
- slowing down of molecules →  $T_{\text{K.E.}}$  decrease

$$P_{\text{photon}} = \frac{h}{\lambda}, \quad \Delta P_{\text{molecule}} \approx P_{\text{photon}}, \quad \langle \text{K.E.} \rangle = \frac{(P_{\text{molecule}})^2}{2m}$$
$$\Rightarrow \langle \text{K.E.} \rangle_{\text{min}} = \frac{(P_{\text{photon}})^2}{2m}$$

<http://www.colorado.edu/physics/2000/bec/lascool1.html>