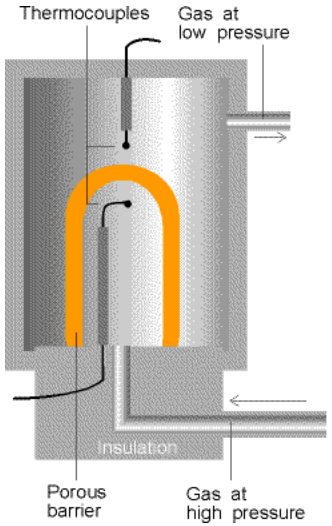
Important concepts

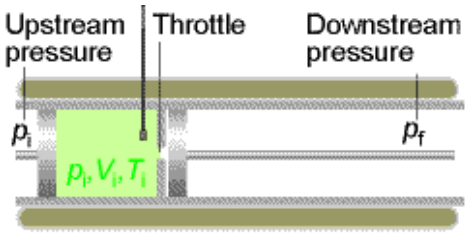
- State function U, H
- Reversible process
- Experiments / Mathematical derivation

Joule-Thomson experiments

The of real gases:

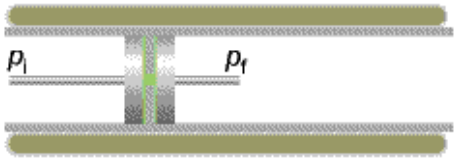
$Q=0$ $\qquad U_2 - U_1 = \Delta U = W$





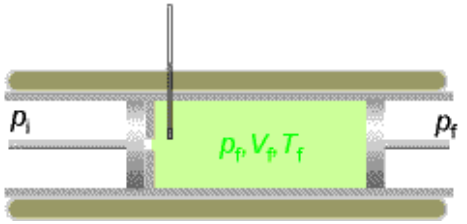
In compressing process:

$$W_1 = -p_1 \Delta V = p_1 V_1 \quad (\Delta V = 0 - V_1 = -V_1)$$



In expanding process:

$$W_2 = -p_2 \Delta V = -p_2 V_2 \quad (\Delta V = V_2 - 0 = V_2)$$

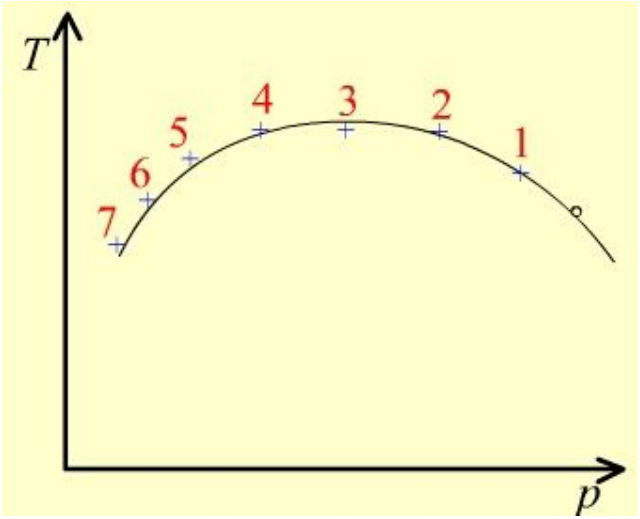


The enthalpy keep constant in the whole process

$$W = W_1 + W_2 = p_1V_1 - p_2V_2$$

so $$U_2 - U_1 = p_1V_1 - p_2V_2$$

and $$U_2 + p_2V_2 = U_1 + p_1V_1$$

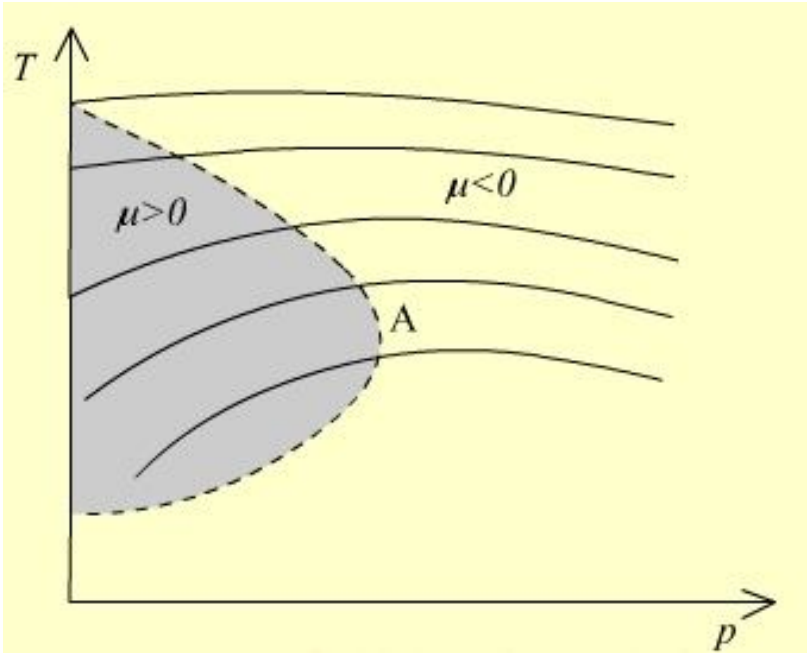


Experimentally determined isenthalpic curve

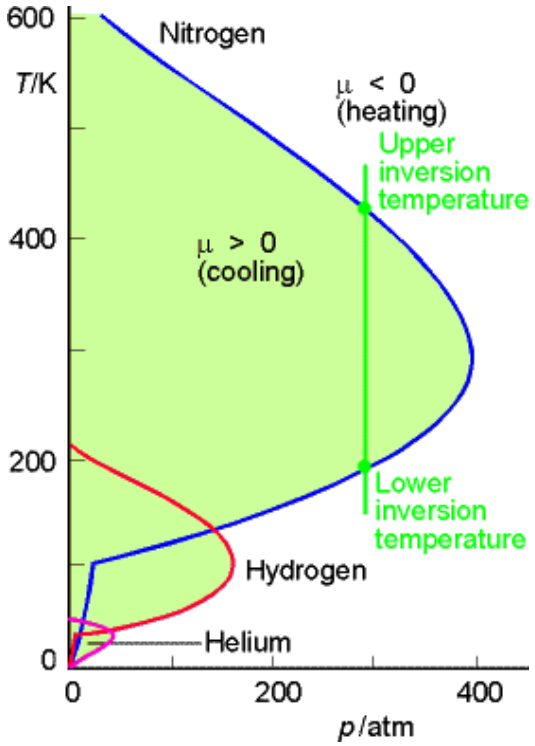
Define $$\mu_{\text{J-T}} = \left(\frac{\partial T}{\partial p}\right)_H$$

Joule-Thomson coefficient

Inversion temperature of real gases



Inversion curve



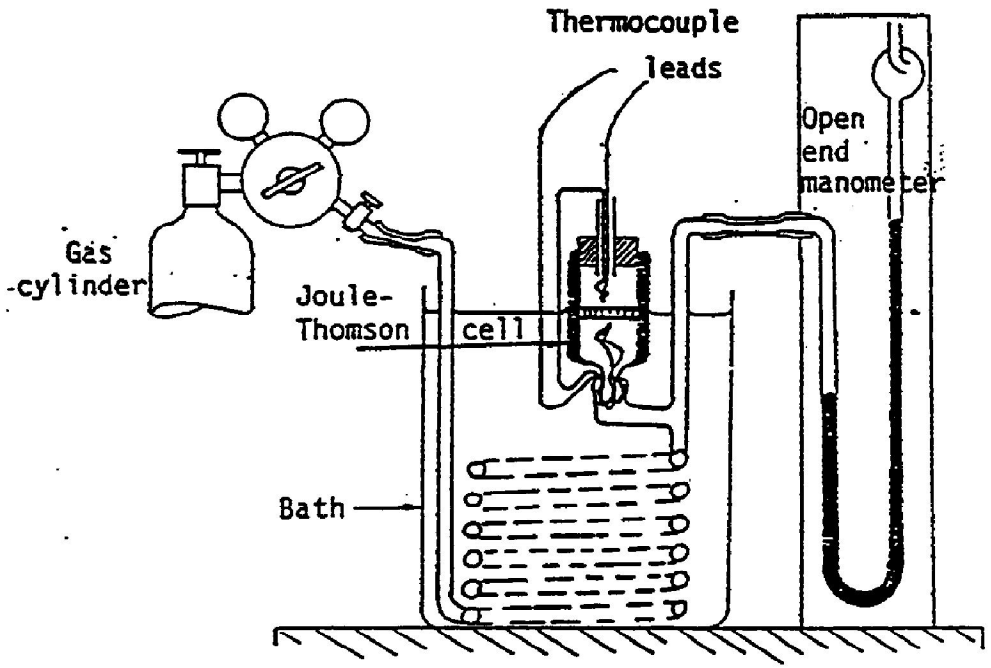
μ >0, P↓, △P<0, △T<0,T ↓decrease

μ =0, P↓, △P<0, △T=0,T not change

μ <0, P↓, △P<0, △T>0,T increase

He	40 K
N2	621 K
O2	764 K
Ne	231 K

273K, 1atm



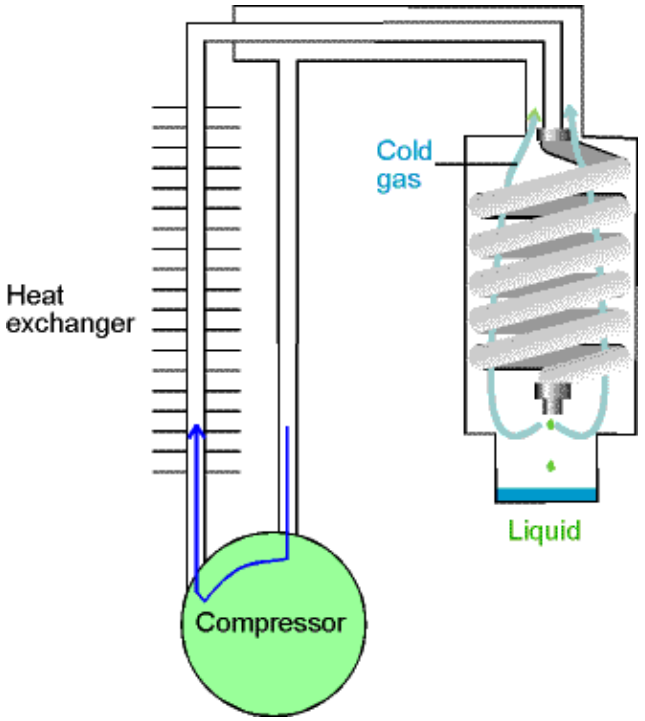
Joule-Thomson Apparatus

Gas	μ_{J-T}/K.MPa^{-1}
Ar	3.66
C6H14	-0.39
CH4	4.38
CO2	10.9
NH3	2.69
H2	-0.34

Application of the Joule-Thomson effect

Liquefying GASes using an isenthalpic expansion

Work principle of a refrigerator



Why μ>0, =0 or <0 ?

$$H = H(T, p) \qquad \mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$$

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \qquad \left(\frac{\partial T}{\partial p}\right)_H = \mu_{\text{J-T}},$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

$$H = U + pV,$$

$$\mu_{\text{J-T}} = -\left[\frac{\partial (U + pV)}{\partial p}\right]_T / C_p \quad = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right].$$