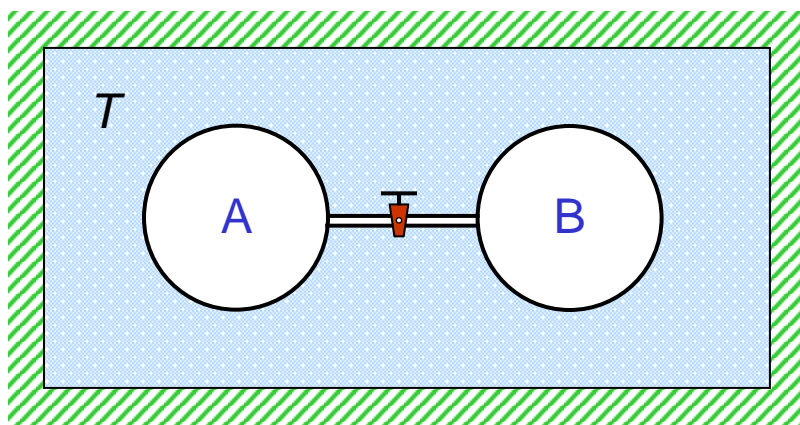# The Joule Expansion Experiment

For a closed system, the state function U is determined by T and V alone:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Joule tried to measure this partial derivative.

1. Gas in A, vacuum in B.

2. Open valve.

3. Any change in T?

He found no change in temperature when the gas expanded from V_A to $V_A + V_B$, i.e. $q = 0$. Also, no work was done (free expansion), so $w = 0$. Conclusion: $\Delta U = 0$ and hence

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{or} \qquad U = U(T) \quad \text{only}$$

Strictly only true for ideal gases.

Not true for liquids and solids, but since $\Delta U \approx \left(\partial U / \partial V\right)_T \Delta V$ and ΔV is very small, the effect of ΔV on U is usually ignored.

Pressure Dependence of Enthalpy

For a closed system, the state function H is determined by T and P alone:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$= C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

For ideal gases $\quad H = U + PV = U + nRT$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$$

Not true for real gases, liquids and solids!

$$dH = dU + PdV + VdP$$

$$C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV + VdP$$

At fixed temperature, $dT = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = \underbrace{\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T}_{\text{small for liquids and solids}} + V \approx V$$
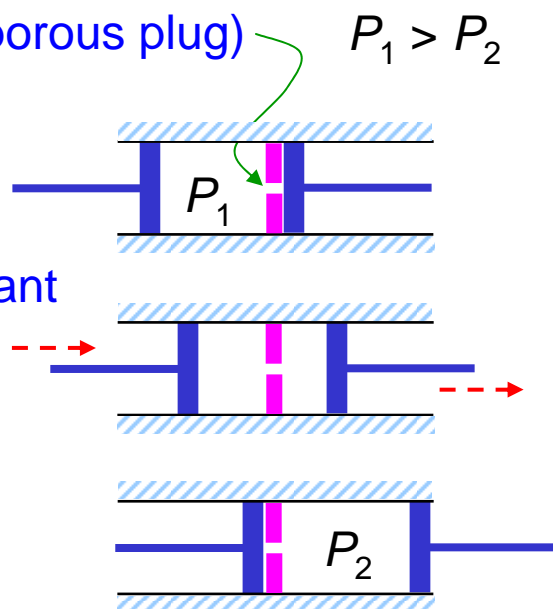
Investigate real gases at constant enthalpy, i.e. $dH = 0$

$$\Rightarrow \quad \left(\frac{\partial H}{\partial P}\right)_T = -C_P \left(\frac{\partial T}{\partial P}\right)_H$$

The Joule-Thomson Experiment

Joule-Thomson Coefficient $\quad \mu_{JT} = \left(\dfrac{\partial T}{\partial P} \right)_H$

Pump gas through throttle (hole or porous plug) $\quad P_1 > P_2$

Keep pressures constant
by moving pistons.

Work done by system

$$-w = P_2 V_2 - P_1 V_1$$

Since $q = 0$

$$\Delta U = U_2 - U_1 = w = P_1 V_1 - P_2 V_2$$

$$\Rightarrow \quad U_2 + P_2 V_2 = U_1 + P_1 V_1$$

$$H_2 = H_1 \quad \text{constant enthalpy}$$

Measure change in T of gas as it moves from side 1 to side 2.

$$\mu_{JT} = \left(\dfrac{\Delta T}{\Delta P} \right)_{\Delta P \to 0}$$
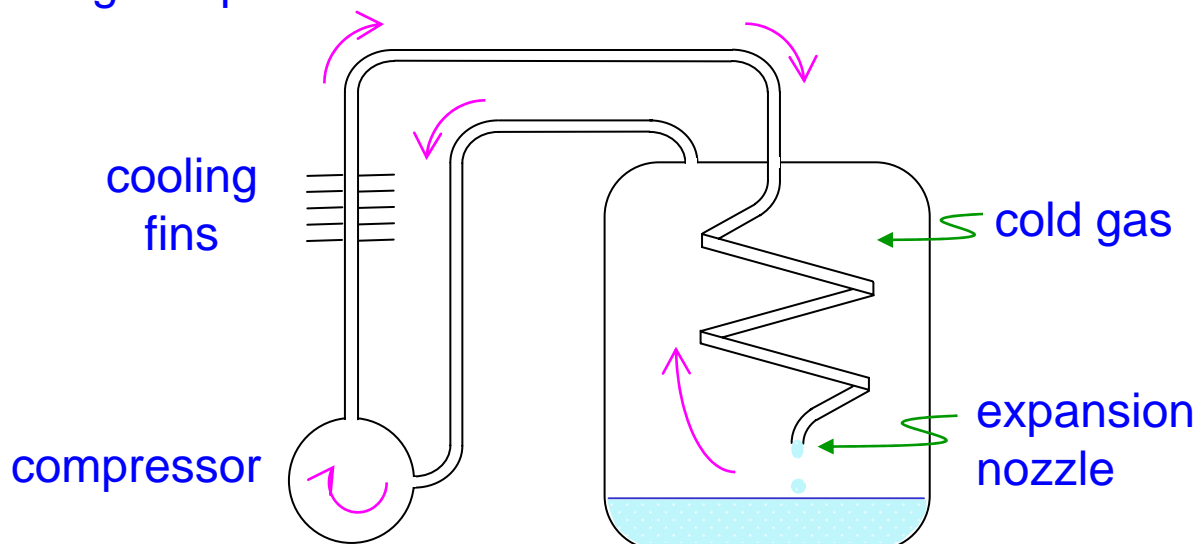
A modern, more direct experiment
uses similar apparatus but with a
heater to offset the temperature drop.

$$\left(\dfrac{\partial H}{\partial P} \right)_T = \lim_{\Delta P \to 0} \left(\dfrac{q}{\Delta P} \right)$$
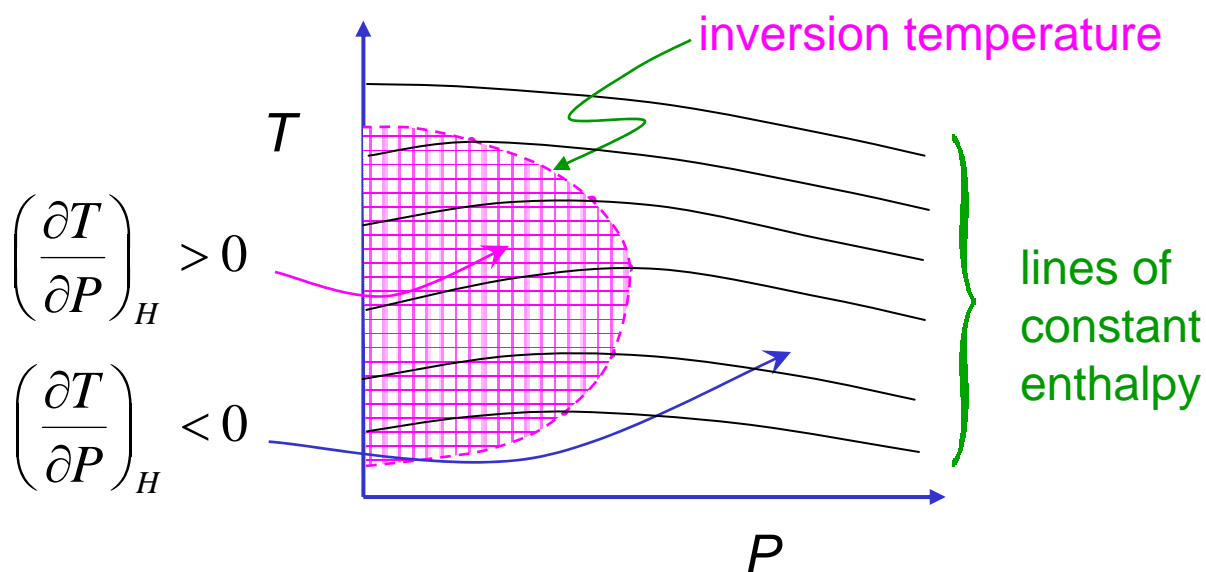
The Linde Refrigerator

For most gases at room temperature $\mu_{JT} > 0$ so sudden (adiabatic) expansion results in a drop in T.

This is the basis of operation of the Linde refrigerator and gas liquefaction.

In general, μ_{JT} depends on T and can even change sign.

$$\left(\frac{\partial T}{\partial P}\right)_H > 0$$

$$\left(\frac{\partial T}{\partial P}\right)_H < 0$$

The Molecular Interpretation of *U*

What is *U*? Δ*U* can be related to thermochemical observables:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad \Delta U = \int_{T_1}^{T_2} C_V \, dT \quad \text{for ideal gases}$$

$$U(T) - U(0) = \int_0^T C_V \, dT$$

Can *U* be calculated from molecular properties?

$$U = \sum_{\text{molecules}} u = N <u> \quad \text{ignoring intermolecular forces}$$

Classically, *<u>* is given by the Equipartition Law:
"The average energy of each different mode of motion of a molecule is ½*kT*."

k = Boltzmann constant = R/L
= 1.381 × 10^{-23} J K^{-1}

Implicit in this "law" is the concept that there is no coupling between molecular modes of motion.

Total: $\quad u = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} (+\varepsilon_{\text{el}})$

Translation: $\quad \varepsilon_{\text{tr}} = \frac{1}{2}mv^2 = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2$

Rotation: $\quad \varepsilon_{\text{rot}} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$

Vibration: $\quad \varepsilon_{\text{vib}} = T + V = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$ per mode

no. of vib. modes $= \begin{cases} 3n-6 & \text{for non-linear molecules} \\ 3n-5 & \text{for linear molecules} \end{cases}$

The Molecular Interpretation of U (cont.)

When quantum effects can be ignored, the average energy of every quadratic term in the energy expression has the same value, ½*kT*.

Monoatomic gases

$$<u> = \tfrac{3}{2}kT, \quad \bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V = 1.5R$$

Diatomic gases

$$<u> = \left(\tfrac{3}{2}+1+1\right)kT, \quad \bar{C}_V = 3.5R$$

Linear polyatomics

$$<u> = \left(\tfrac{3}{2}+1+3n-5\right)kT$$

$$\text{e.g. for } n = 3, \ \bar{C}_V = 6.5R$$

Non-linear molecules

$$<u> = \left(\tfrac{3}{2}+\tfrac{3}{2}+3n-6\right)kT$$

$$\text{e.g. for } n = 3, \ \bar{C}_V = 6.0R$$

Experimental observations do *not* agree with these predictions, except for monoatomic gases. In particular:

- The predicted values are too high.

- Experimental values are temperature-dependent.

Accurate calculations are provided by statistical mechanics, where it can be shown that the equipartition principle only holds in the limit of high temperature, specifically for the condition $kT >> \Delta E$, where ΔE is the appropriate spacing of energy levels.

Equipartition $\equiv$ free transfer of energy between modes

Temperature Dependence of C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad \text{where} \quad U - U_0 = N\left(<\varepsilon_{\text{tr}}> + <\varepsilon_{\text{rot}}> + \dots\right)$$

$$= C_V^{\text{tr}} + C_V^{\text{rot}} + C_V^{\text{vib}} + C_V^{\text{el}}$$
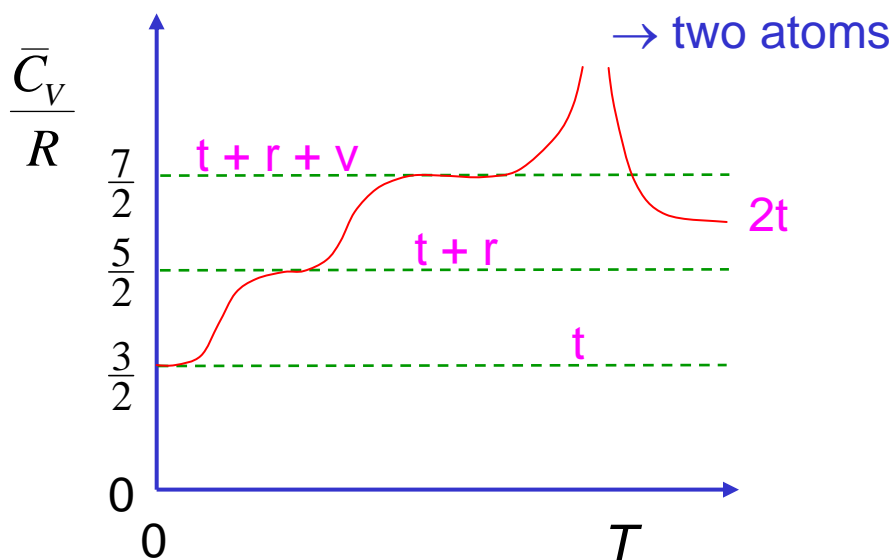
$\overline{C}_v^{\text{tr}} = 1.5R$ for all T

$$\overline{C}_v^{\text{rot}} = \begin{cases} R & - \text{ linear} \\ 1.5R & - \text{ non-linear} \end{cases} \quad \text{for } kT \gg \Delta\varepsilon_{\text{rot}}$$

$\overline{C}_v^{\text{rot}} = 0$ at very low T, where $<\varepsilon_{\text{rot}}> \to 0$

$\overline{C}_v^{\text{vib}} = R$ for each vibrational mode, at high T

$\overline{C}_v^{\text{el}} = 0$ *almost always*, since electronic excitation takes great energy

e.g. for a diatomic molecule:

Temperature Dependence of *H*

Interactions between molecules also contribute to the heat capacity of real systems. In particular, first-order phase changes often involve large energy changes. These are usually measured at constant pressure and expressed as enthalpies.
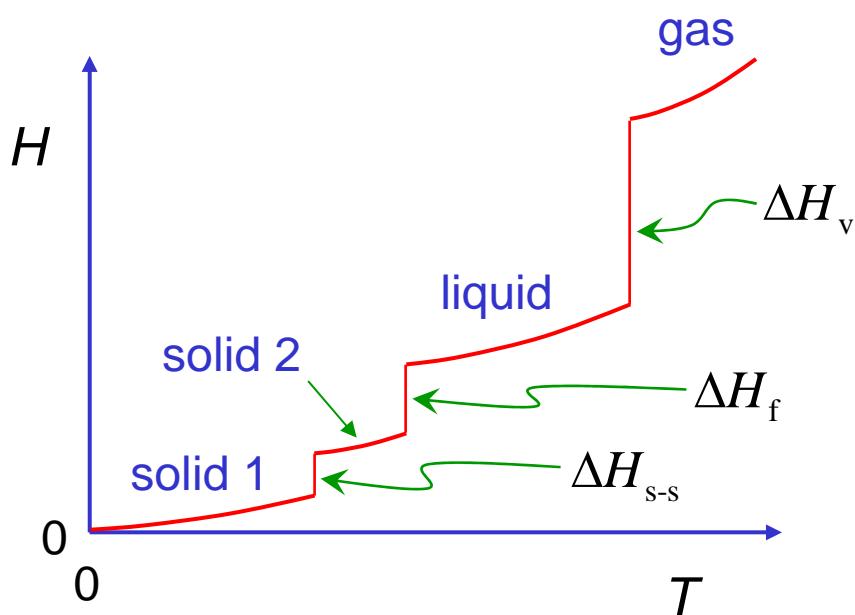
In general, $H = a + bT + cT^2 + \dots$ for each phase

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = b + 2cT + \dots$$