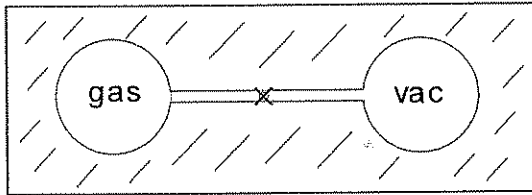


Joule Free Expansion of a Gas

(to get $\left(\frac{\partial U}{\partial V}\right)_T$)Adiabatic $q = 0$ Expansion into Vac. $w = 0$
($p_{\text{ext}} = 0$)

$$\text{gas } (p_1, T_1, V_1) = \text{gas } (p_2, T_2, V_2)$$

Since $q = w = 0 \Rightarrow dU \text{ or } \Delta U = 0$ Constant U

Recall $dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$

$$\left(\frac{\partial U}{\partial V}\right)_T dV_U = -C_V dT_U$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_V \left(\frac{\partial T}{\partial V}\right)_U \quad \text{measure in Joule exp't!} \quad \left(\frac{\Delta T}{\Delta V}\right)_U$$

Joule did this. $\lim_{\Delta V \rightarrow 0} \left(\frac{\Delta T}{\Delta V}\right)_U = \left(\frac{\partial T}{\partial V}\right)_U \equiv \eta_J \quad \therefore \boxed{dU = C_V dT - C_V \eta_J dV}$

Joule coefficient

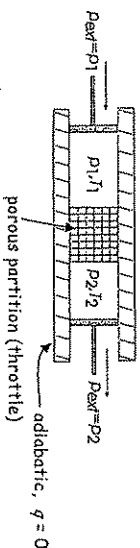
- For Ideal gas $\Rightarrow \eta_J = 0$ exactly
 $dU = C_V dT$ Always for ideal gas
 $U(T)$ only depends on T

The internal energy of an ideal gas depends only on temperature

Consequences $\Rightarrow \Delta U = 0$ For all isothermal expansions or compressions of ideal gases

$$\Rightarrow \Delta U = \int C_V dT \quad \text{For any ideal gas change in state}$$

$$\left(\frac{\partial H}{\partial p}\right)_T \Rightarrow \text{Joule-Thomson expansion}$$



$$\begin{aligned} w &= p_1 V_1 - p_2 V_2 \\ \Delta U &= q + w = p_1 V_1 - p_2 V_2 = -\Delta(pV) \\ \therefore \Delta U + \Delta(pV) &= 0 \Rightarrow \Delta(U + pV) = 0 \\ \therefore \Delta H &= 0 \end{aligned}$$

Joule-Thomson is a constant Enthalpy process.

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \Rightarrow C_p dT = -\left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = -C_p \left(\frac{\partial T}{\partial p}\right)_T \left(\frac{\Delta T}{\Delta p}\right)_H \leftarrow \text{can measure this}$$

Define $\lim_{\Delta p \rightarrow 0} \left(\frac{\Delta T}{\Delta p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT} \leftarrow \text{Joule-Thomson Coefficient}$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -C_p \mu_{JT} \quad \text{and} \quad dH = C_p dT - C_p \mu_{JT} dp$$

For an ideal gas: $U(T), \quad pV = nRT$

$$H = U(T) + pV = U(T) + nRT$$

only depends on T , no p dependence

$$H(T) \Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = \mu_{JT} = 0 \quad \text{for an ideal gas}$$

For a van der Waals gas:

$$\left(\frac{\partial H}{\partial p}\right)_T \approx b - \frac{a}{RT} \Rightarrow \mu_{JT} \approx \frac{2a}{RT} - b = 0 \quad \text{when} \quad T = T_{inv} = \frac{2a}{Rb}$$

$$1. \quad \text{If } \frac{2a}{RT} < b \Rightarrow T > \frac{2a}{Rb} = T_{inv}$$

$$\text{then } \left(\frac{\Delta T}{\Delta p}\right)_H < 0 \quad \text{so if } \Delta p < 0 \quad (p_2 < p_1) \\ \text{then } \Delta T > 0$$

gas heats up upon expansion.

$$2. \quad \text{If } \frac{2a}{RT} > b \Rightarrow T < \frac{2a}{Rb} = T_{inv}$$

$$\text{then } \left(\frac{\Delta T}{\Delta p}\right)_H > 0 \quad \text{so if } \Delta p < 0 \\ \text{then } \Delta T < 0$$

gas cools upon expansion.

$$T_{inv} \gg 300K \quad \text{for most real gases.}$$

\Rightarrow Use J-T expansion to liquefy gases