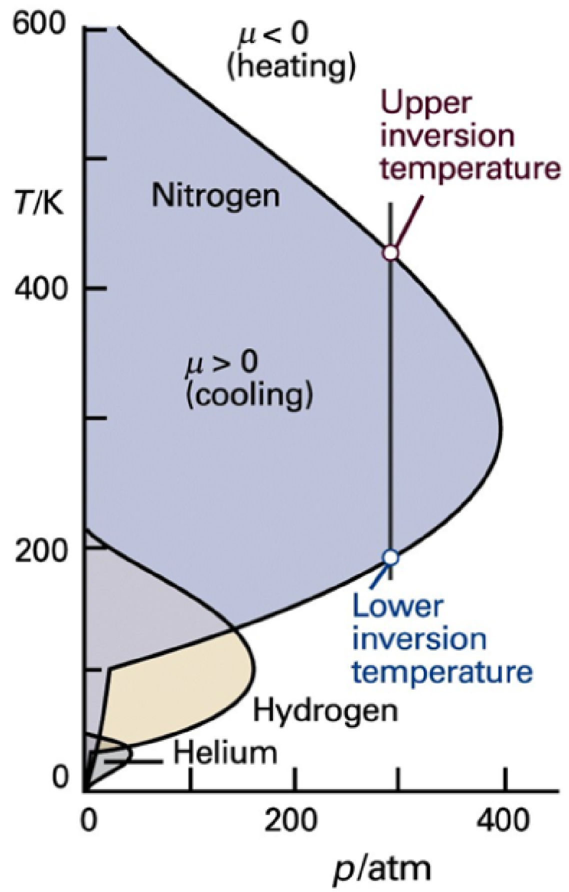


Figure 2-32
Atkins Physical Chemistry, Eighth Edition

$$w = -nRT \ln \frac{V_f}{V_i}$$

$$dU = đq + đw$$

$$= C_{path}\, dT - P_{ext}\, dV$$

$\Delta U = \text{slope}\, \Delta T$

$U(T, V)$; $dU = \left(\frac{\partial U}{\partial T}\right)_V dT$

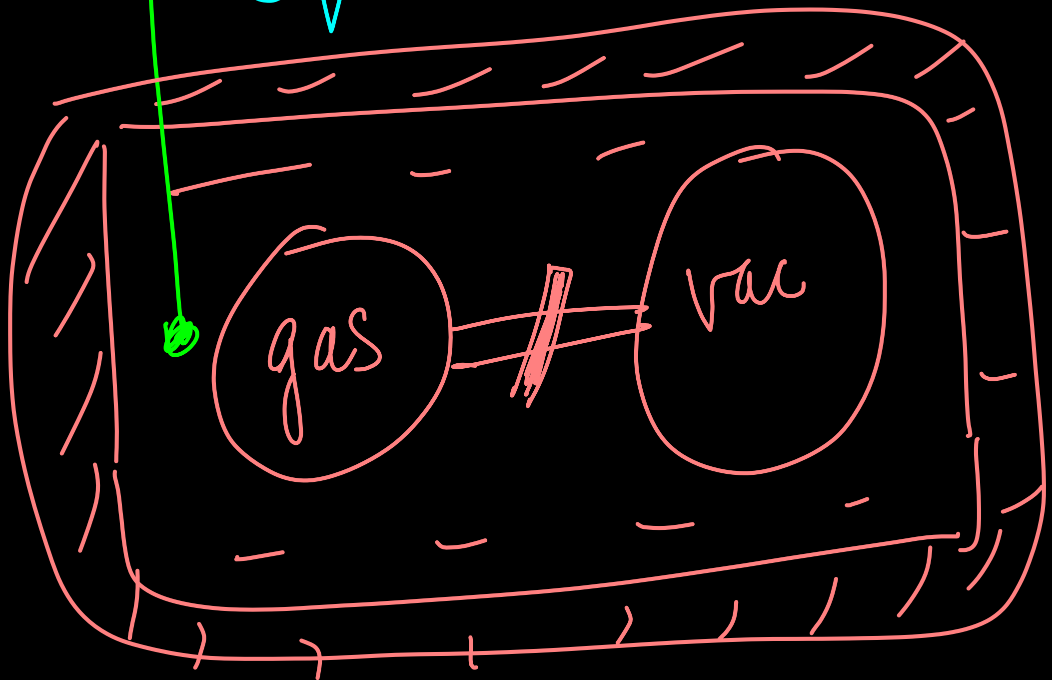
$\left(\frac{\partial U}{\partial T}\right)_V = \text{slope}$

$\Delta U = \left(\partial U / \partial T\right)_V \Delta T$

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

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

C_V $\qquad$ π_T



Joule's expansion

$q = 0$, $w = 0$, $dU = 0$

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

$$\left(\frac{\partial U}{\partial V}\right)_T dV = -C_v\, dT$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -C_v \left(\frac{\partial T}{\partial V}\right)_U = 0$$

$= \eta_J$ Joule coeff.

Enthalpy, H

$$\text{gas}(p\ T_1\ V_1) \underset{\text{const } p}{\overset{\text{rev.}}{\rightleftharpoons}} \text{gas}(p\ T_2\ V_2)$$

$$\Delta U = q + w = q_p - p_{ext}\Delta V$$

$$\Delta U + \Delta(pV) = q_p$$

$$\Delta(U + pV) = q_p$$

$$\Delta H = q_p$$

$H(T, p)$

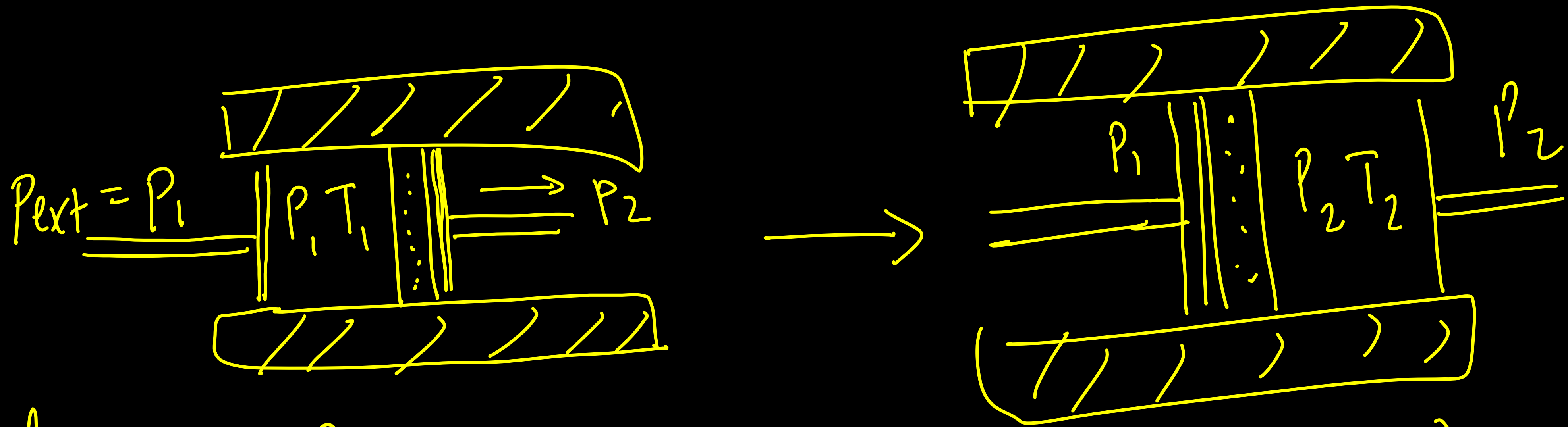
$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$C_p \, dT + \mu_T \, dp$$

$$đq_p = C_p \, dT$$

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$$ isothermal J-T coeff.

$$\mu = (\partial T/\partial p)_H$$ isenthalpic J-T coeff.



ad. $q = 0$

$$w = P_1 V_1 - P_2 V_2 = -\Delta(PV)$$

$$\Delta U = q + w = -\Delta(pV)$$

$$\Delta(U + pV) = 0 \qquad \Delta H = 0$$

$$-P_1(0 - V_1)$$

$$-P_2(V_2 - 0)$$

$$dH = C_p\, dT + \left(\frac{\partial H}{\partial p}\right)_T dp = 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T = - C_p \left(\frac{\partial T}{\partial p}\right)_H \quad \mu$$

$$\left(\frac{\Delta T}{\Delta p}\right)_H$$

Van der Waals gas

$$\left(\frac{\partial H}{\partial p}\right)_T \approx b - \frac{a}{RT} = 0$$

$$T = T_{inv} = \frac{a}{Rb}$$

Gas cools below the $T_{inv.}$

'Linde' refrigerators – J-T cooling