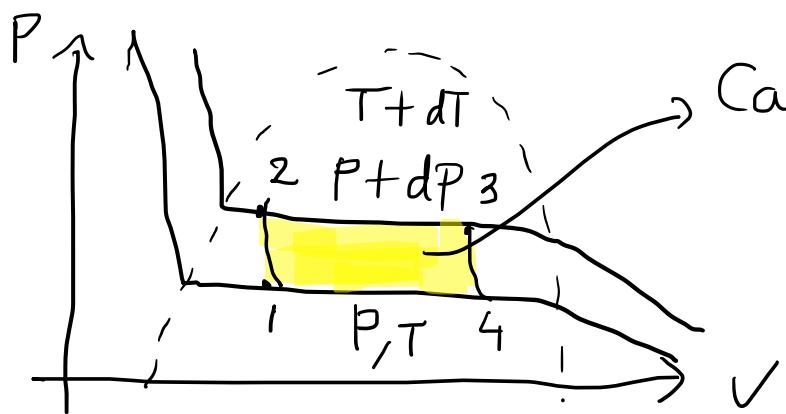


Clausius Clapeyron eqn:

$$\left(\frac{dP}{dT} \right) = \frac{\lambda}{T(v_2 - v_1)}$$



Carnot cycle

$1 \rightarrow 2 \quad \} \text{ adiabatic curves}$
 $3 \rightarrow 4 \quad \}$

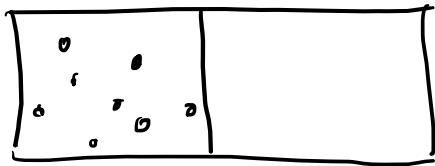
$$|W| = dP_m \Delta v, \quad \{$$

$$|Q_H| = m\lambda \quad \}$$

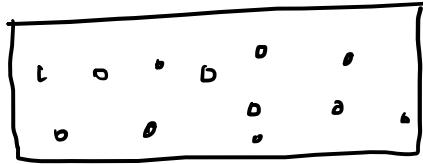
$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T}{T+dT} \approx \frac{dT}{T}$$

$$\frac{dP_m \Delta v}{m \lambda} = \frac{dT}{T} \rightarrow \boxed{\left(\frac{dP}{dT} \right) = \frac{\lambda}{T(\Delta v)}} \quad \begin{matrix} \swarrow \\ \text{C-C eqn.} \end{matrix}$$

Revisit free expansion (adiabatic)



before



after

}

$$T_i = T_f \text{ (ideal gas)}$$

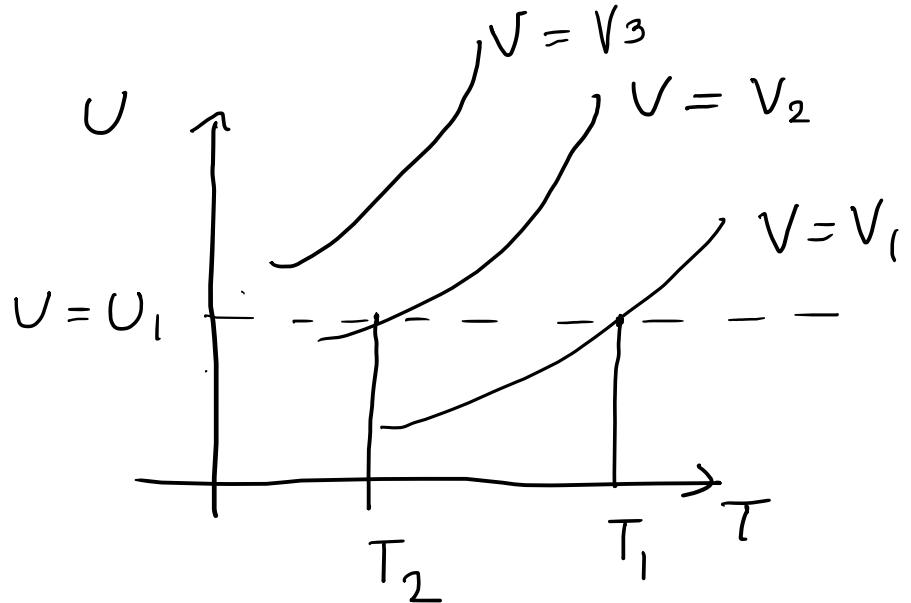
$$U(T_i, V_i) = U(T_f, V_f)$$

$$\Delta Q = \Delta W = 0$$

for ideal gases cannot cool gas by free expansion

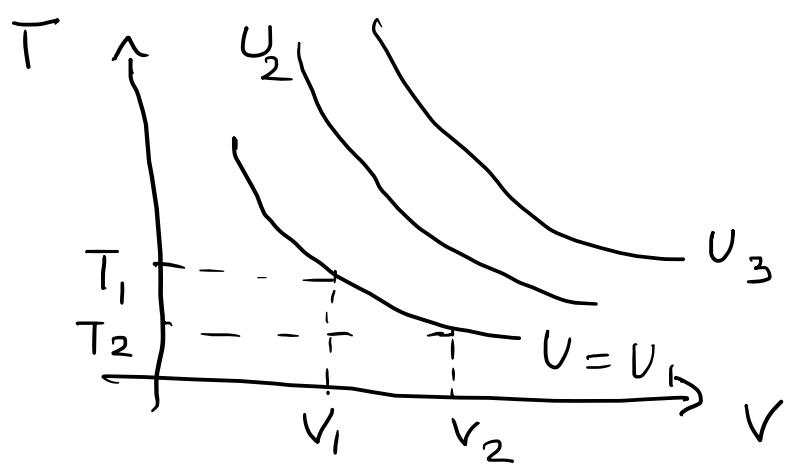
$$\text{Since } T_i = T_f$$

$$\text{Generally } U(T, V)$$



given these curves

$$T_2 < T_1 \quad \{V_2 > V_1\}.$$



Initial T_1, V_1 will determine a given curve $U = U_1$, (since $U = \text{const}$).

$$T_2 < T_1.$$

adiabatic free expansion of van der Waals' gas.

1 mole,

$$U(T_2, v_2) = U(T_1, v_1)$$

Recall we had derived in class

$$U(T, v) = c_v T - \frac{a}{v} + \text{const}$$

(assuming $c_v = \text{const}$
otherwise
 $\int c_v dT$)

$U_1 = U_2$ for free expansion

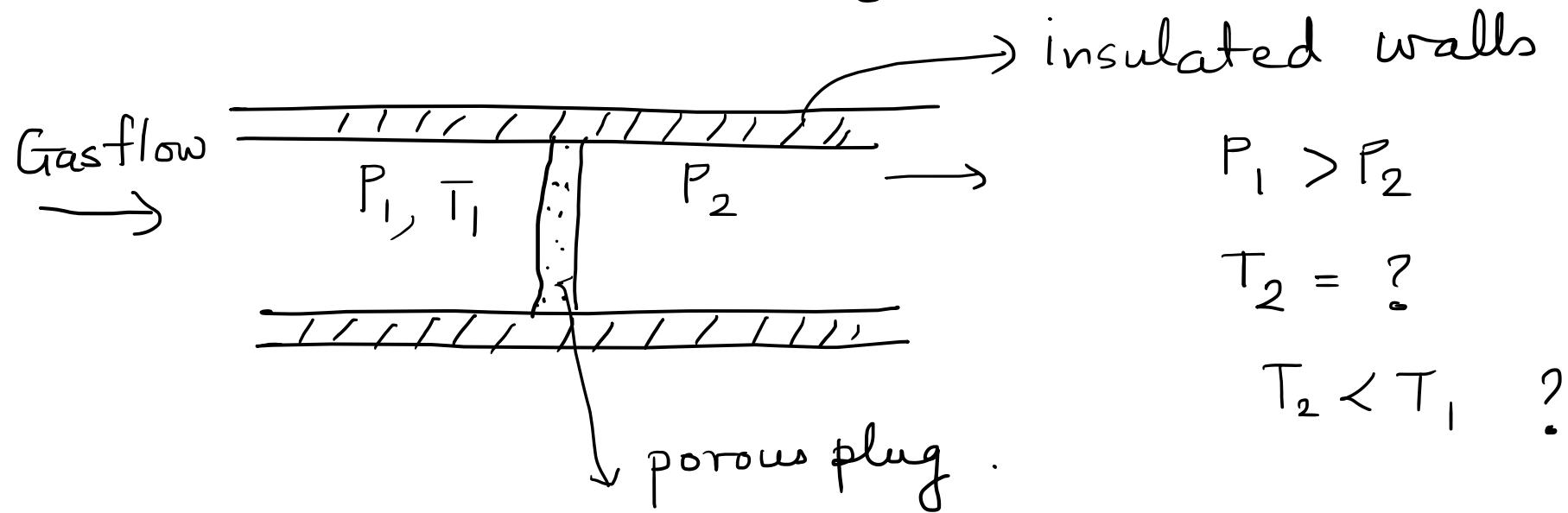
$$c_v (T_2 - T_1) = a \left(\frac{1}{v_2} - \frac{1}{v_1} \right), \quad \text{but } v_2 > v_1$$

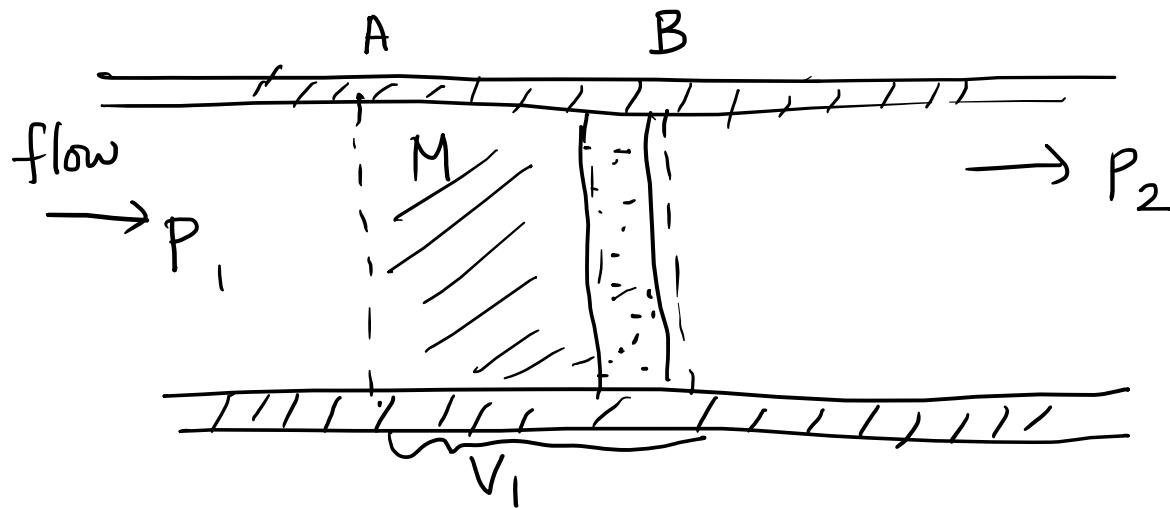
$T_2 < T_1 \rightarrow$ cooling

$$\frac{1}{v_2} < \frac{1}{v_1}$$

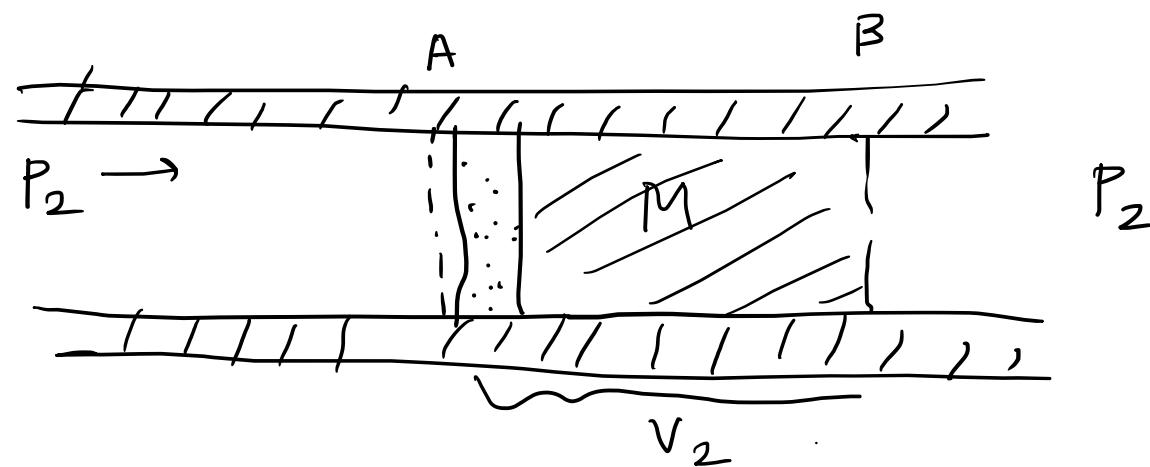
Alternative process for cooling gases : Joule - Thomson Process

Also known as Throttling





volume occupied
by constriction
negligible



$$\Delta U = U_2 - U_1 = U(P_2, T_2) - U(P_1, T_1)$$

mass M of gas does work $P_2 V_2$ displacing the gas to the right by vol. V_2 .

Net work done by mass M of gas

$$W = P_2 V_2 - P_1 V_1$$

But no heat is absorbed in the process.

$$Q = 0$$

$$\Delta U + W = Q = 0$$

$$U_2 - U_1 + P_2 V_2 - P_1 V_1 = 0$$

$$\underbrace{(U_2 + P_2 V_2)}_{H_2} = \underbrace{(U_1 + P_1 V_1)}_{H_1}$$

$$\boxed{H_2 = H_1}$$

isenthalpic process

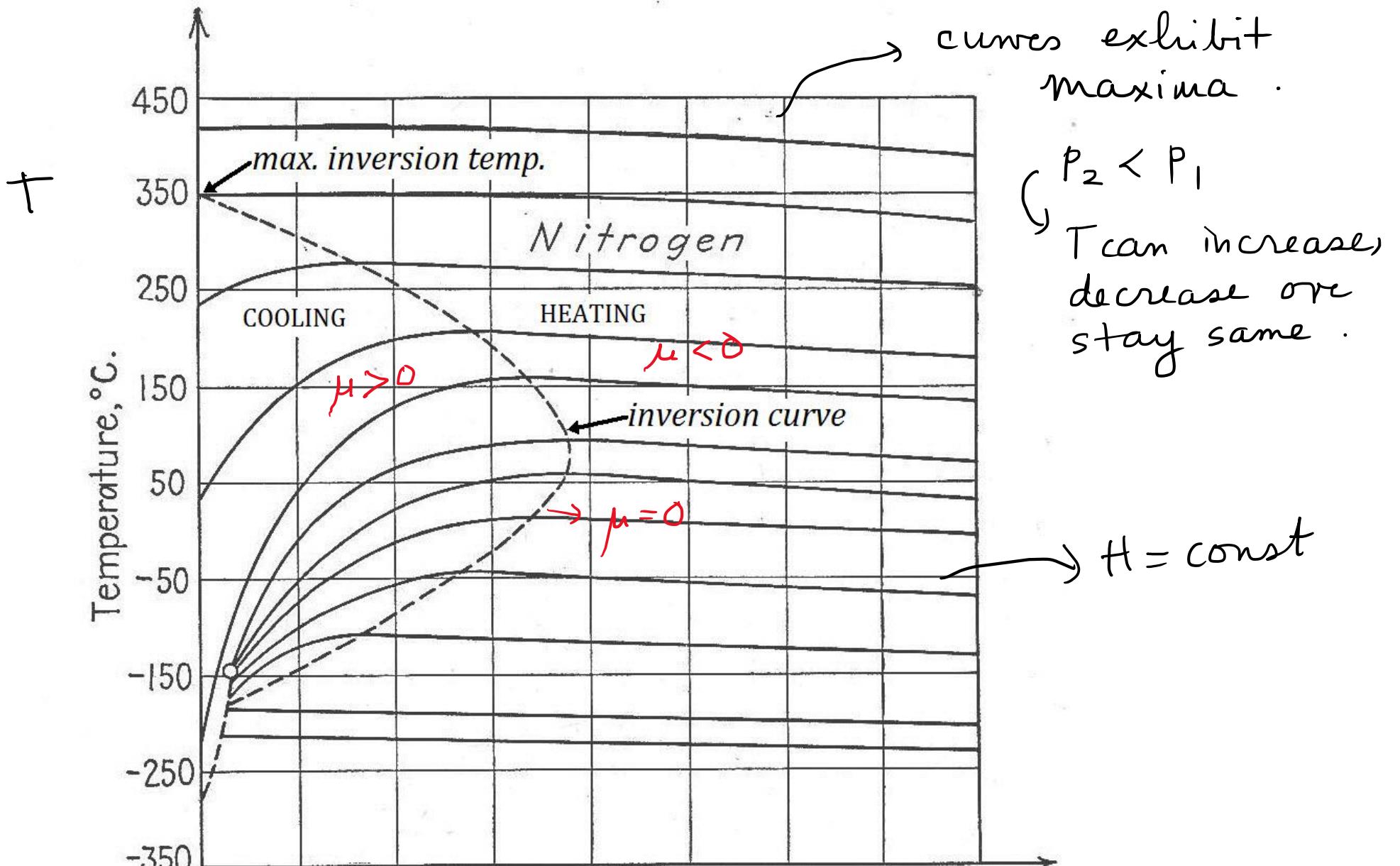
Ideal gas

$$H(T_2, P_2) = H(T_1, P_1)$$

$$H(T_2) = H(T_1).$$

$$\boxed{T_2 = T_1} \rightarrow \text{no cooling!}$$

$$\begin{aligned} H &= U + PV \\ &= U(T) + nRT \\ &= H(T). \end{aligned}$$



$$\mu = \left(\frac{\partial T}{\partial P} \right)_H$$

J-T coefficient

T will decrease if $\mu > 0$

T will not change if $\mu = 0$

T will increase if $\mu < 0$

$$dU = Tds - pdv$$

$$dH = d(U + PV) = Tds + Vdp.$$

$$dH = 0$$

$$0 = T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dp \right] + Vdp$$

$$= C_P dT + \left[T \left(\frac{\partial S}{\partial P} \right)_T + V \right] dp .$$

$$= C_P dT + \left[\left(-\frac{\partial V}{\partial T} \right)_P T + V \right] dp \quad \left\{ \begin{array}{l} \text{from Maxwell} \\ \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P \end{array} \right.$$

$$= C_P dT + [-V_B T + V] dp$$

$$C_p dT + [V - V\beta T] dp = 0$$

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_p} (T\beta - 1)}$$

ideal gas $T\beta = 1$, $\mu = 0 \rightarrow$ no cooling

$\mu > 0$, if $\beta > T^{-1}$, $\mu < 0$, $\beta < T^{-1}$

$\beta = T^{-1} \rightarrow$ inversion curve.

for cooling must $\mu > 0$

Max inv temp

$34^\circ K$ for He

$202^\circ K$ for H

$625^\circ K$ for N