WHAT DO WE KNOW?

$$C_V \equiv \frac{đq_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V ; \quad \Delta U = q_V$$

$$C_p \equiv \frac{đq_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p ; \quad \Delta H = q_p$$

$$dU = đq + đw \quad \text{FIRST LAW}$$

$$H = U + pV$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

T(V, P) OR P(V, T) OR V(T, P)

$$\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V}$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{+\alpha}{\kappa}}$$

$U(T,V)$

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

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

$H(T,P)$

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

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

$\boxed{\text{WORK}}$

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV$$

a) CONSTANT V $(dV=0)$

$$W = 0$$

b) CONSTANT P_{ext}

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV = -P_{ext}(V_f - V_i)$$

c) CONSTANT T AND Reversible PATH

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV = \int_{V_i}^{V_f} P(T,V)\, dV$$

FREE EXPANSION

$$\Delta T = 0 \qquad \Delta V \neq 0$$

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

$$\Delta U \sim \Delta T \Rightarrow dU = 0$$

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad !}$$

$$\Rightarrow \quad dU = C_V dT$$

$$\Delta U = C_V (T_f - T_i)$$ FOR ANY PATH

Kinetic Theory

$$U = n \frac{3}{2} RT \quad \text{(IDEAL GAS)}$$

$$\left(\frac{\partial U}{\partial T}\right) = n \frac{3}{2} R = C_V \Rightarrow \boxed{\bar{C}_V = \frac{3}{2} R}$$

EXP $\quad q_p > q_V \qquad C_p > C_V$

CONST PRESSURE PATH

$$q_p = n \bar{C}_p \Delta T$$

$$\Delta U = q_p - P_{ext} \Delta V$$

i) REVERSIBLE

$$\boxed{\Delta U = n\bar{C}_v \Delta T}$$

$$= q_p - P\Delta V \quad (P\Delta V = nR\Delta T)$$

$$= n\bar{C}_p \Delta T - nR\Delta T$$

$$\boxed{= n(\bar{C}_p - R)\Delta T}$$

$$\Rightarrow \boxed{\bar{C}_p = C_v + R = \frac{5}{2}R}$$

FOR AN IDEAL GAS AND A REVERSIBLE ADIABATIC PATH

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

$$P_f V_f^{\gamma} = P_i V_i^{\gamma}$$

$$\frac{T_f}{T_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1-\gamma}{\gamma}}$$

$U(T,P) \quad U(T,V)$

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

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

BUT $V(T,P)$ AND

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

THEREFORE

$$dU = \left[\left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP$$

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

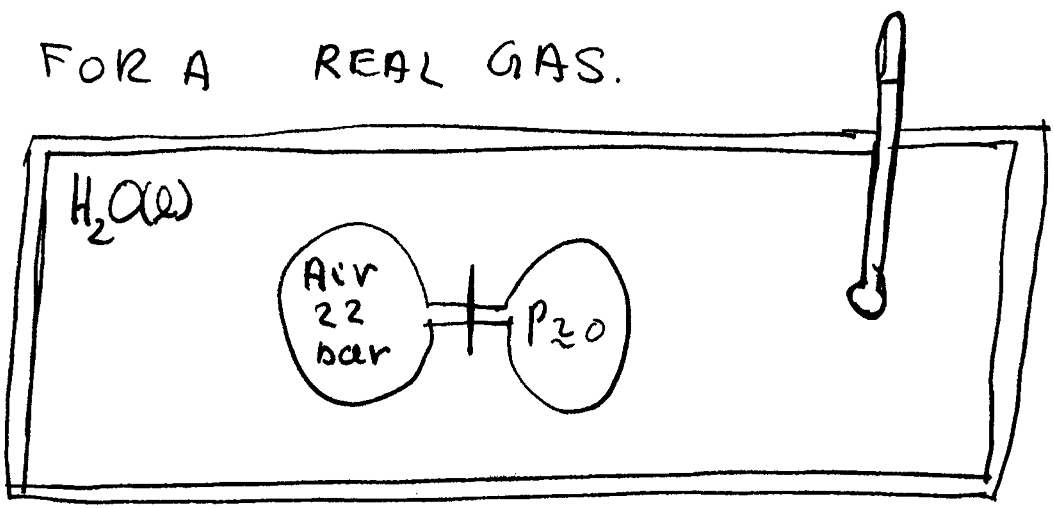
$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

THE JOULE EFFECT

IN 1845 JOULE PUBLISHED AN EXPERIMENT THAT WAS DESIGNED TO DETERMINE WETHER

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

FOR A REAL GAS.



$$dU = dq + dw$$

$$= dq - P_{ext}\, dV = dq$$

$$= C_v\, dT$$

$dT \approx 0 \Rightarrow dU = 0$

↑ EXPERIMENTAL ACTUALLY $\Delta T = 2 \times 10^{-5}$ K

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

BUT $dT = 0$

$$0 = \left(\frac{\partial U}{\partial V}\right)_T dV$$

SINCE $dV \neq 0$

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

CONSEQUENCES.

AT THE SAME T, TWO SYSTEMS WITH DIFFERENT V HAVE EQUAL U.

$$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V = -1$$

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

$$\left(\frac{\partial T}{\partial V}\right)_U = 0$$

$$H = U + PV$$

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

FOR A <u>PERFECT GAS</u>

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

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

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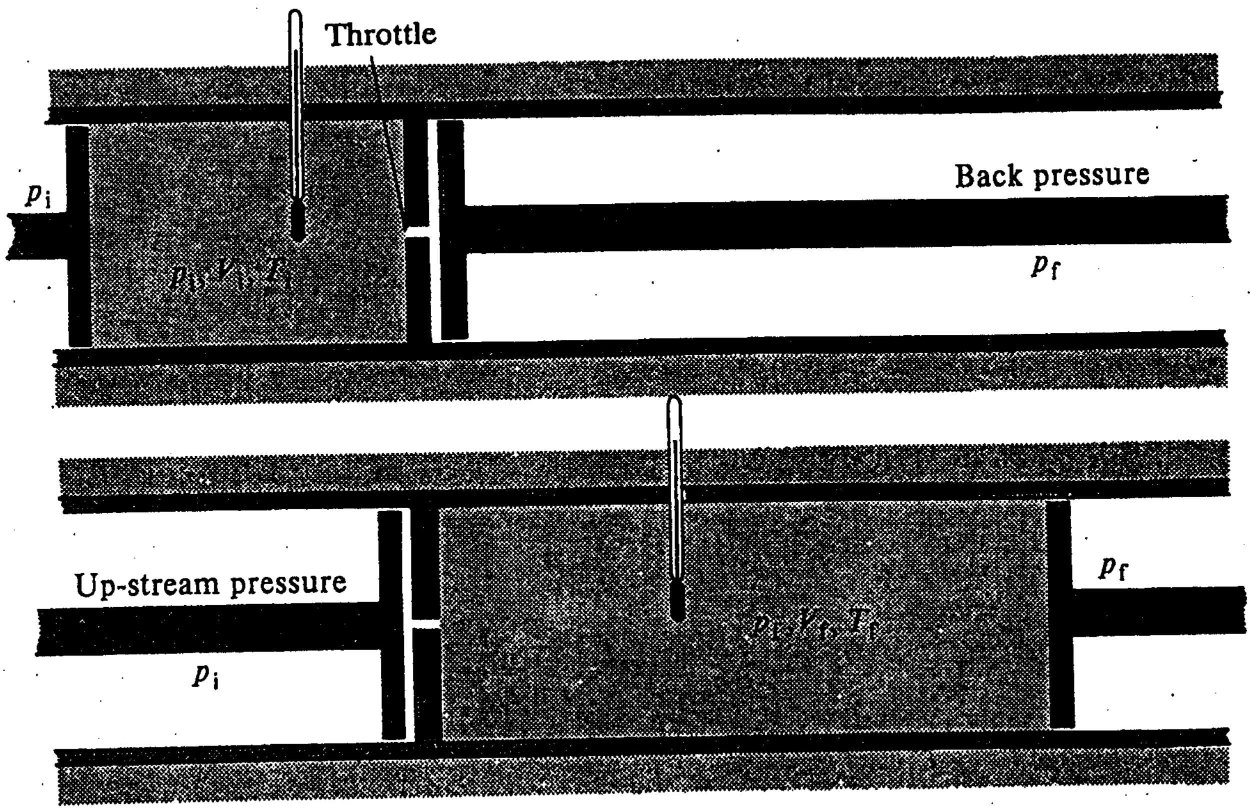

LEFT

WORK IS DONE ON THE GAS

$$W_L = -P_i(0 - V_i) = P_i V_i$$

$$W_R = -P_f(V_f - 0) = -P_f V_f$$

TOTAL WORK $\quad W = P_i V_i - P_f V_f$

THE PROCESS IS ADIABATIC

$$\Delta U = 0 = W$$

$$U_f - U_i = P_i V_i - P_f V_f$$

$$H_f = U_f + P_f V_f = U_i + P_i V_i = H_i$$

H CONSTANT

FOR THIS PROCESS

$$\Delta H = 0$$

AND WE CAN MEASURE T AND P. WE GET

$$\lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P}\right)_H = \left(\frac{\partial T}{\partial P}\right)_H \equiv \mu_{JT}$$

μ_{JT} MEASURABLE PROPERTY.

$C_p > C_v$

$$H = U + PV$$

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

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

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

$$dH = \left[C_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

$$+ \left[V + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial P}\right)_T\right] dP$$

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T$$

$$H(T, p)$$

$$\left(\frac{\partial H}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T = -1$$

$$-C_p \left(\frac{\partial T}{\partial p}\right)_H = + \frac{1}{\left(\frac{\partial p}{\partial H}\right)_T}$$

$$\boxed{-C_p \mu_{JT} = \left(\frac{\partial H}{\partial p}\right)_T}$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p} \; !$$

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \frac{V}{V}$$

$$\boxed{C_p = C_V + TV\frac{\alpha^2}{k}}$$

$$-C_p \mu_{JT} = V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T$$

$$= V - T\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{\mu_{JT} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]}$$