$$đw = -p_{ext}\, dV$$

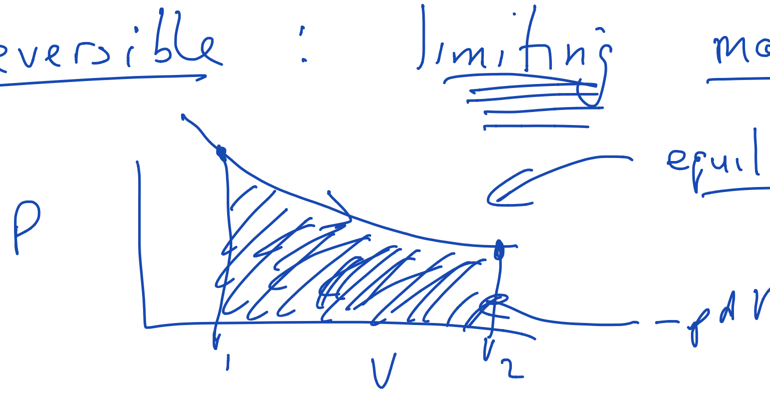
total volume

$$\boxed{V_m = \frac{V_{TOTAL}}{n}}$$

$$V = n V_m$$

Reversible : limiting max work

equilibrium states

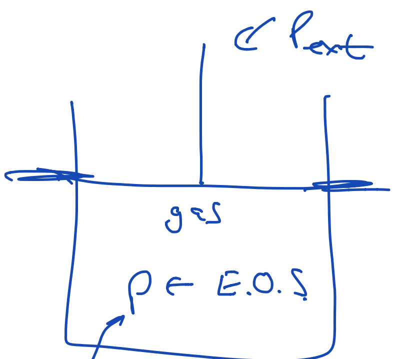


$1 \to 2 \to 1$ no change in system + surroundings

no net work

no net heat exchange

$A + B \rightleftharpoons C + D$ equilibrium



equilibrium internal pressure

$$P_{ext} = p + \delta p$$

$$đW = -P_{ext}\, dV$$

$$đW = -(p + \delta p)\, dV$$

$$đW = \underbrace{-p\,dV}_{\text{negative}} \underbrace{- \delta p\, dV}_{\text{positive}}$$

expansion $V_2 > V_1$ $\delta p < 0$

Reversible : <u>idealization</u>

hard to establish in <u>practice</u>

$$dU = đq + đW$$

$$dU = C_{path}(T)\,dT - P_{ext}\,dV$$

constant volume process ?

$$dU = C_{path}(T)\,dT$$

constant Temp $dU = -P_{ext}\,dV$

Adiabatic: $dU = đW_{reversible}$

U state fn. depends on T, V

$U(T, V)$

TOTAL Differential of $U(T, V)$

$$\boxed{dU(T,V) = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{\text{partial differential}} dT + \left(\frac{\partial U}{\partial V}\right)_T dV}$$

hold V constant while differentiating

Constant volume:

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

$$dU(T,V) = đq_V - \cancel{P_{ext}\, dV}$$

const. vol. heat interaction.

$$đq_V = \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$đq_V = C_V(T)\, dT$$

$$\boxed{C_V(T) \equiv \left(\frac{\partial U(T,V)}{\partial T}\right)_V}$$ definition

At constant volume:

$$\boxed{\begin{aligned} dU(T,V) &= đq_V \\ \therefore\ \Delta U(T,V) &= q_V \end{aligned}}$$

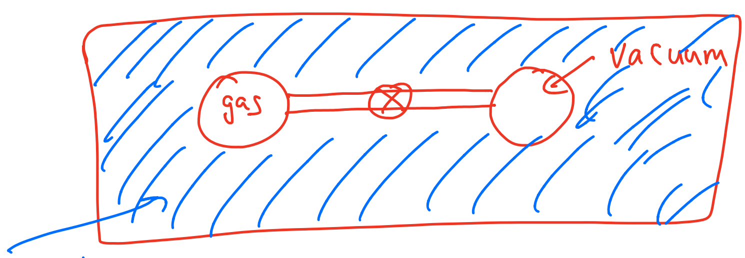
Total differential of $U(T,V)$

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

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

what is this?

Joule Free Expansion



insulation

system: gas

process: open stopper; let gas flow into vacuum

Apply 1st "Law" $dU = \cancel{đq}^{\,0} + \cancel{đw}^{\,0} = 0$

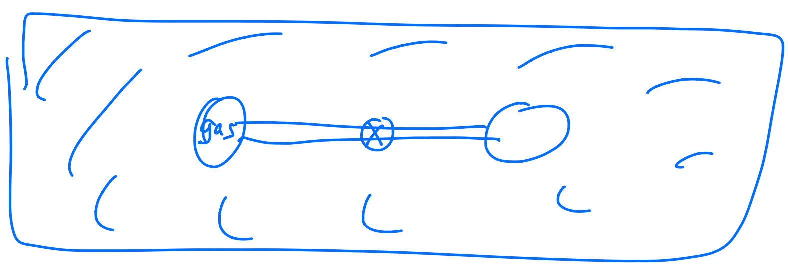
constant U process !!!!!

$$dU(T,V) = C_v(T)\, dT_u + \underline{\left(\frac{\partial u}{\partial v}\right)_T} dV_u = 0$$

$$-C_v(T)\, dT_u = \left(\frac{\partial u}{\partial v}\right)_T dV_u$$

$$-C_v(T)\, \frac{dT_u}{dV_u} = \left(\frac{\partial u}{\partial v}\right)_T$$

$$\boxed{-C_v(T) \left(\frac{\partial T}{\partial v}\right)_u = \left(\frac{\partial u}{\partial v}\right)_T}$$



vary ΔV

$$\lim_{\Delta V \to 0} \left(\frac{\Delta T}{\Delta V}\right)$$