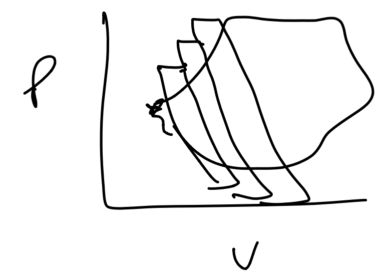
Entropy: State Function

$dS \equiv \frac{dq_{reversible}}{T}$



prescription for

Calculating dS or ΔS

For $q_{irreversible}$, can't use $\frac{dq_{irrev}}{T}$

$\Delta S > 0$ Irreversible Process in <u>Isolated</u> system

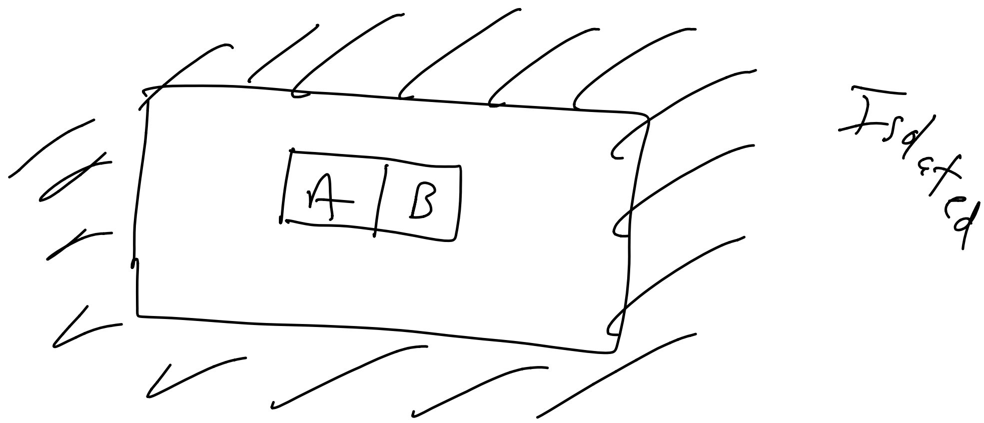
$\Delta S = 0$ Reversible Process in <u>Isolated</u> system

$\Delta S < 0$ Never less than zero in <u>Isolated</u> system

Isolated System

$T_A \neq T_B$

$T_A > T_B$



system = combo block A + B

$$dU = dq + \underline{dW} = 0$$

$$= dq_A + dq_B = 0$$

$$dq_A = -dq_B \longleftarrow$$

$$\underline{dS \sim \frac{dq}{T}} \qquad \underline{dS_A + dS_B} = dS_{TOTAL} = dS_{system}$$

$$dS_{system} = \frac{dq_A}{T_A} + \frac{dq_B}{T_B} \qquad dq_A = -dq_B$$

$$dS_{system} = dq_A \left[\frac{1}{T_A} - \frac{1}{T_B} \right] \longleftarrow$$

dq_A: (−) ; $\left[\frac{1}{T_A} - \frac{1}{T_B} \right]$: (−)

$T_A > T_B$

$$dS_{system} > 0$$

Irreversible

Spontaneous

<u>limiting condition:</u> $T_A \rightarrow T_B$

$$T_A = T_B + \varepsilon$$

(ε ← infinitesimal difference)

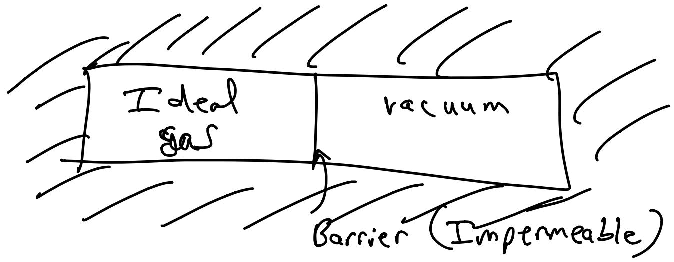
$$dS_{system} = dq_A \left[\frac{1}{T_A} - \frac{1}{T_B} \right]$$

in limiting condition $dS_{system} \rightarrow 0$

Reversible

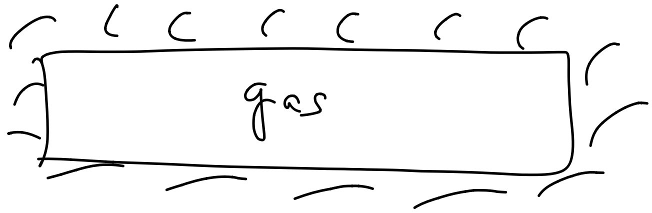
limiting to <u>Equilibrium</u>

Expansion of Ideal Gas



Initially

remove barrier



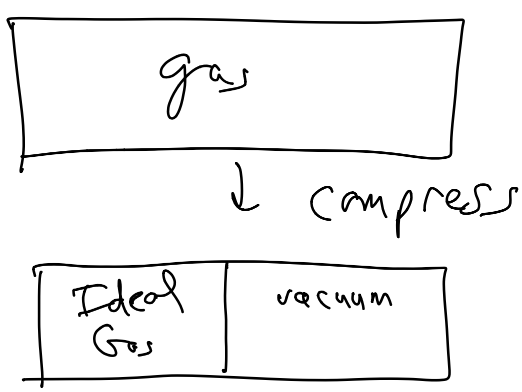
What is ΔS ?

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dq_{irrev}}{T}$$

← Can't use this Eqn. because $q_{irreversible}$

But!!!

I can construct a reversible process



Isothermally

Isothermal Compression of I.G.

$$dS = \frac{đq_{rev}}{T}$$

1st "Law" $dU = đq_{rev} + đw_{rev} = 0$

$$đq_{rev} = -đw_{rev}$$

$$= +p\,dV$$

$$= nRT\frac{dV}{V}$$

$$đq_{rev} = nRT\,d(\ln V)$$

$$dS = \frac{nRT}{T}\,d(\ln V)$$

$$dS = nR\,d(\ln V)$$ Iso T compression

$$\Delta S_{compression} = nR\int_{V_{uncomp}}^{V_{comp}} d(\ln V)$$

$$\Delta S_{compression} = nR\ln\left(\frac{V_{comp}}{V_{uncomp}}\right)$$

$$\boxed{\Delta S_{expansion} = -nR\ln\left(\frac{V_{comp}}{V_{uncomp}}\right)}$$

$$\Delta S_{expansion} > 0$$

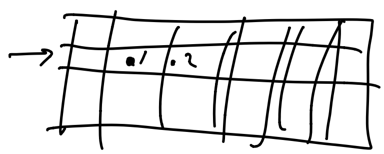
Irreversible Process

Spontaneous

$$\Delta S_{expansion} = nR\ln\left(\frac{V_{uncomp}}{V_{comp}}\right)$$

$V_{uncomp} = 2V_{compressed}$

$$\Delta S_{expansion} = nR\ln 2$$



m particles

N sites
containers