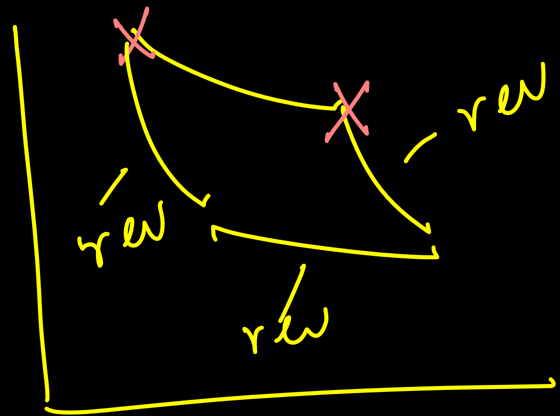
Irreversible Carnot



$$(-w_{rev}) > (-w_{irr})$$

$$\Delta U = (q + w)_{rev} = (q + w_{irr})$$

$$q_{irr} < q_{rev}$$

$$\varepsilon = 1 + \frac{q_2^{rev}}{q_1^{irr}} < 1 + \frac{q_2^{rev}}{q_1^{rev}}$$

$$q_{rev} + w_{rev} = q_{irr} + w_{irr}$$

$$q_{rev} - w_{irr} = q_{irr} - w_{rev}$$

$$\frac{dq_{rev}}{T} > \frac{dq_{irr}}{T}$$

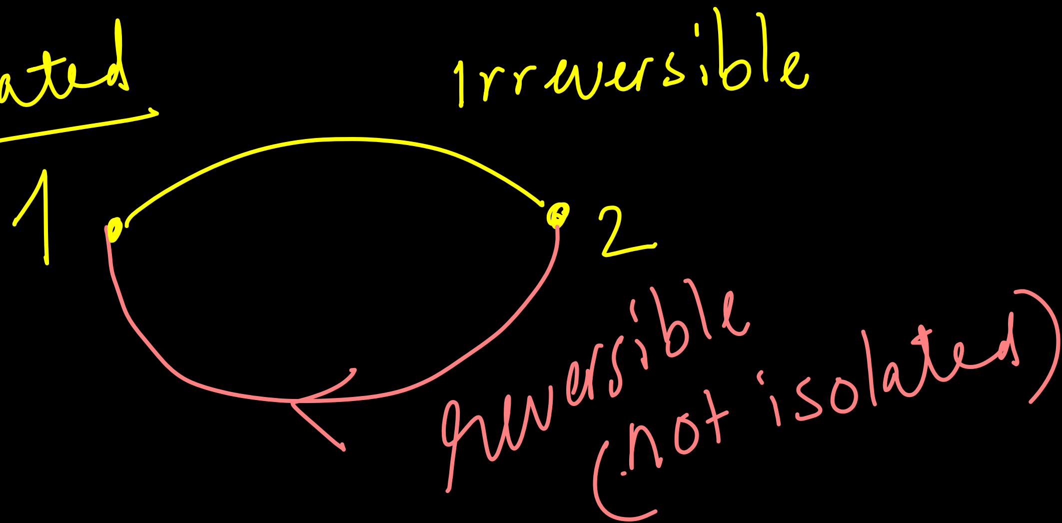
$$\frac{dq_{irr}}{T} < \frac{dq_{rev}}{T}$$

$$\oint \frac{dq_{irr}}{T} < 0$$

$$\boxed{\oint \frac{dq}{T} \le 0}$$

Clausius Inequality

Isolated



$$q^{irr} = 0$$

$$\oint \frac{dq}{T} \le 0$$

$$\overset{0}{\cancel{\int_1^2 \frac{dq^{irr}}{T}}} + \int_2^1 \frac{dq^{rev}}{T} \le 0$$

$$\int_2^1 dS \leq 0 \qquad \Delta S(2 \to 1) \leq 0$$

$$\Delta S \geq 0$$

ISOLATED

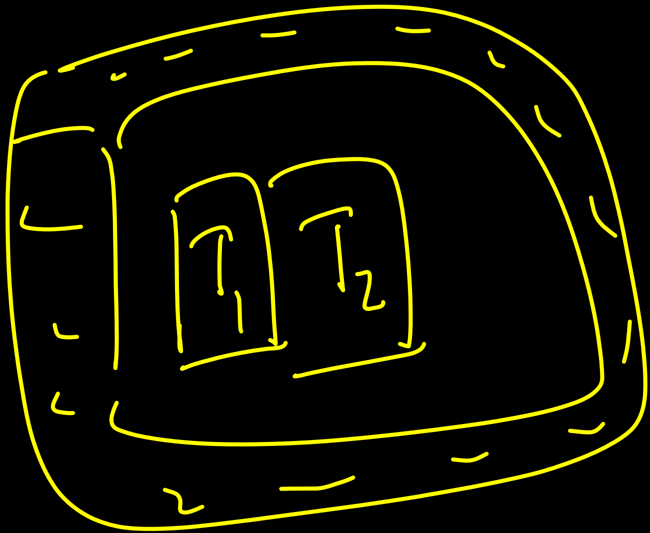
$\Delta S > 0$ spontaneous, irreversible

$\Delta S = 0$ reversible, equilibrium

$\Delta S < 0$ impossible

2nd Law

Entropy of the universe increases.



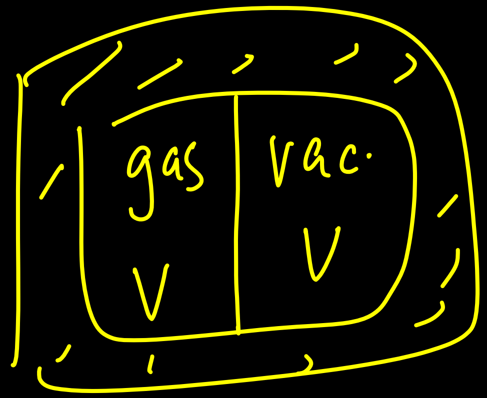
$$dS = dS_1 + dS_2$$

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} = dq_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

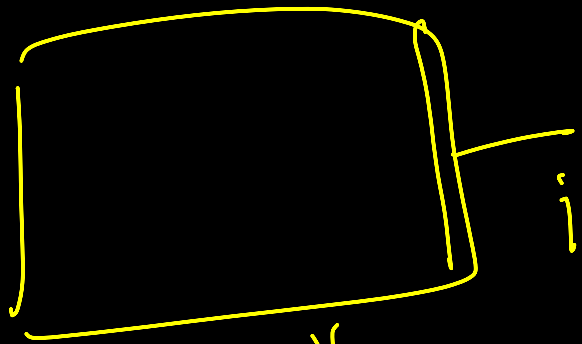
$$dS = dq_1\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Joule expansion — Ideal gas

$$\text{gas}(V, T, p) \xrightarrow[\text{irr.}]{\text{ad.}} \text{gas}\left(2V, T, \frac{p}{2}\right)$$



$$\Delta U = 0, \quad w = 0, \quad q = 0$$



isothermal compression, rev.

$$\int \frac{dq_{rev}}{T} = \int_{2V}^{V} \frac{-dw_{rev}}{T} = \int_{2V}^{V} \frac{+p\,dV}{T} = nR\int_{2V}^{V} \frac{dV}{V}$$

$$= -nR \ln 2$$

$\Delta S = nR \ln 2$

$R \ln 2$ for the spontaneous process

Boltzmann

$S = k \ln W$ ← No. of microstates

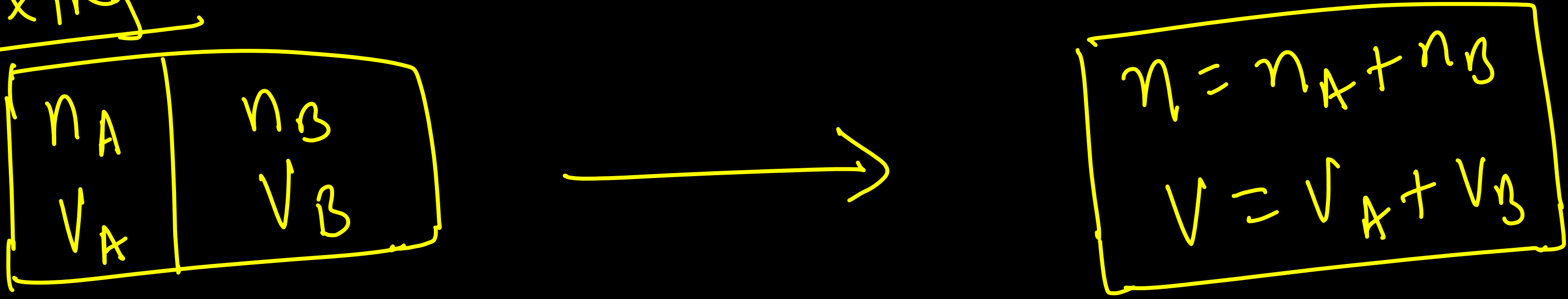
k: 1.381×10^{-23} J K^{-1}

$R = kN_A$

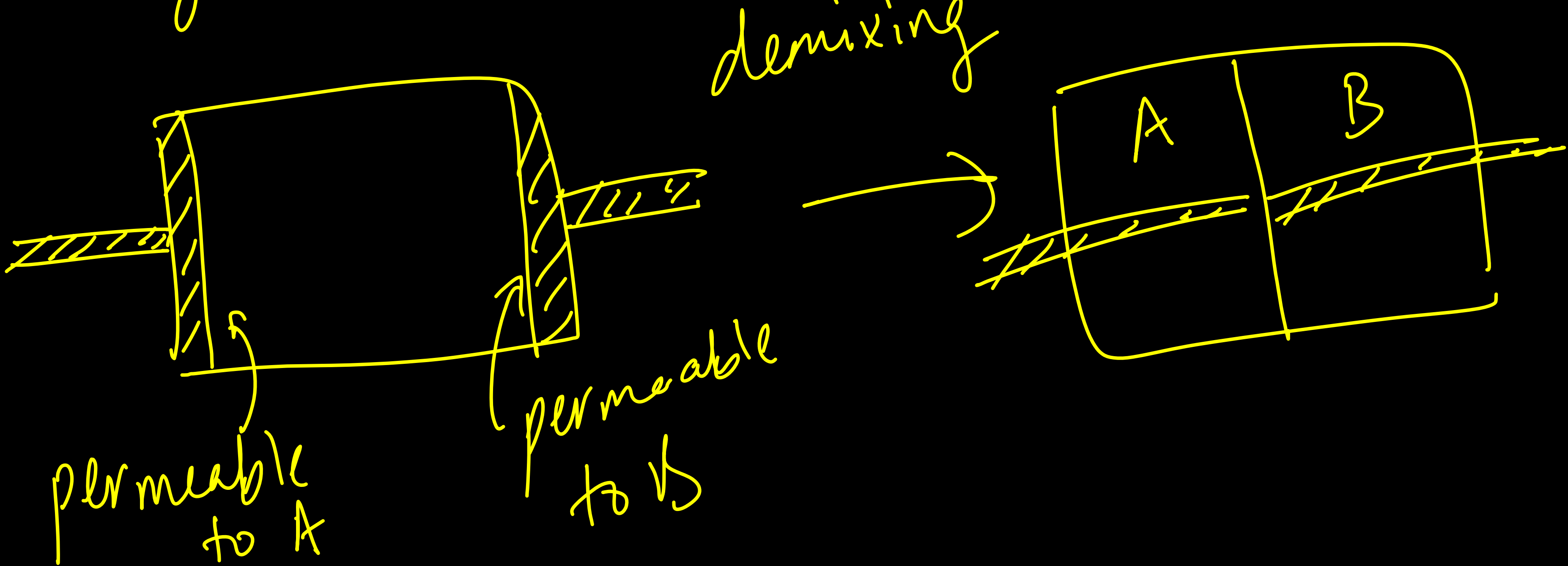
$k \ln c^{N_A} = N_A k \ln c$

$R \ln c$

Mixing



Ideal gases



I.G. $\Delta U = 0$ $\quad q_{rev} = -w_{rev}$ $\quad dw = -p_A \, dV_A - p_B \, dV_B$

$$\Delta S_{demix} = \int \frac{dq_{rev}}{T} = \int_{V}^{V_A} \frac{P_A}{T} dV_A + \int_{V}^{V_B} \frac{P_B}{T} dV_B \quad \text{---}$$

$$= n_A R \ln \frac{V_A}{V} + n_B R \ln \frac{V_B}{V}$$

mole fraction $X_A = \frac{n_A}{n}$ $X_B = \frac{n_B}{n}$

$$\Delta S_{demix} = nR \left[X_A \ln X_A + X_B \ln X_B \right]$$

$$\Delta S_{mix} = -nR \left[X_A \ln X_A + X_B \ln X_B \right]$$