

$$\begin{aligned}
 \epsilon &= \frac{\text{work done}}{\text{heat in from } T_h} = 1 - \frac{q_4}{q_3} \\
 &= 1 - T_c/T_h
 \end{aligned}$$

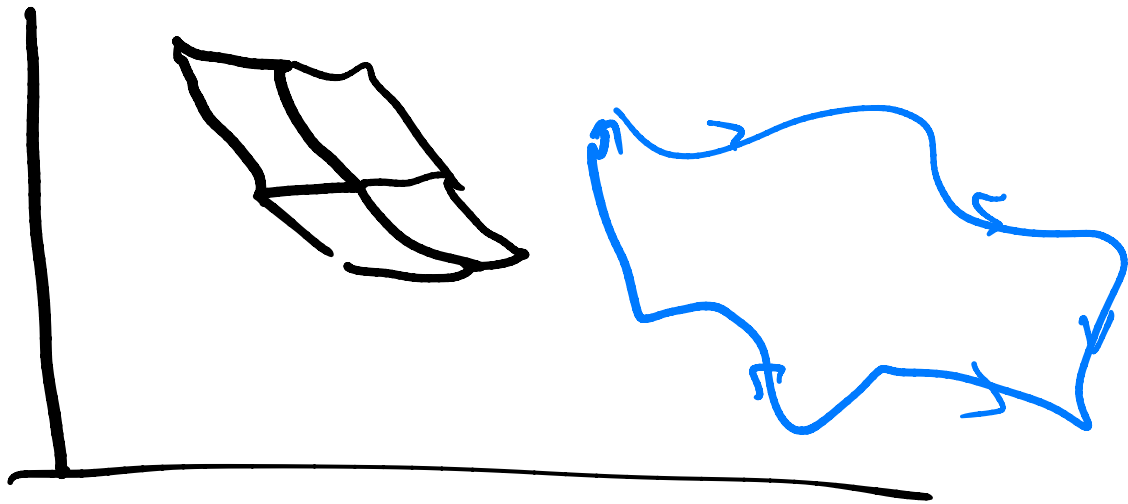
$$q_3/q_1 = -\frac{T_c}{T_h} = -\frac{T_3}{T_1}$$

$$\Rightarrow q_1/T_1 + q_3/T_3 = 0$$

suggests is a quantity  $\sim q/T$

which is a state function

(see book)



any closed cycle can be made of  $\infty$  small  
cannot cycles

$$\sum q_i / T_i = 0$$

↙ arbitrary cycle

$$\oint \frac{dq_{rev}}{T} = 0 \quad \text{define}$$

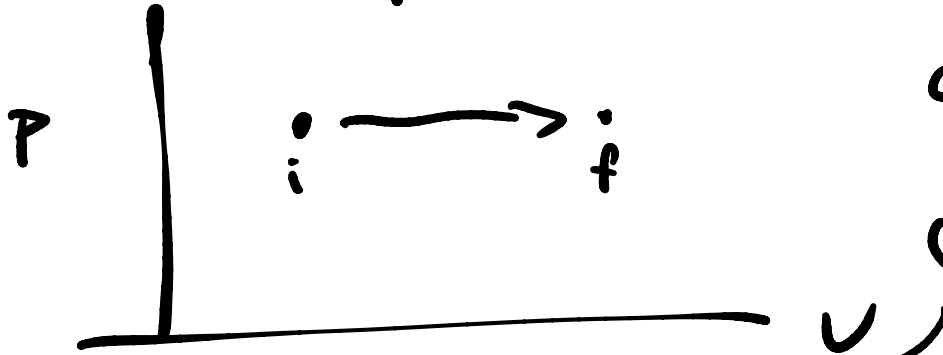
$$dS \equiv dq_{rev}/T \quad \text{state function}$$

$$\Delta S_{a \rightarrow b} = \int_a^b dS = \int_a^b \frac{dq_{rev}}{T}$$

$$\oint dS = 0 \quad \text{for any path}$$

# Entropy for reversible processes

① Const P expansion



$$dE = dq + dw$$

$$dq = C_p dT$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \int_i^f \frac{C_p dT}{T} \quad \leftarrow \text{if } C_p \text{ is constant} = C_p \ln\left(\frac{T_2}{T_1}\right)$$

ideal gas  $T = PV/nR$   $\rightarrow = C_p \ln(V_2/V_1)$  (ig)

② const volume

$$dq = C_v dT$$

$$\Delta S = C_v \ln(T_2/T_1)$$

③ const T,  $dE = 0$ ,  $dq = -w = PdV$

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T} = \int_1^2 \frac{P dV}{T} = nR \int \frac{1}{V} dV$$

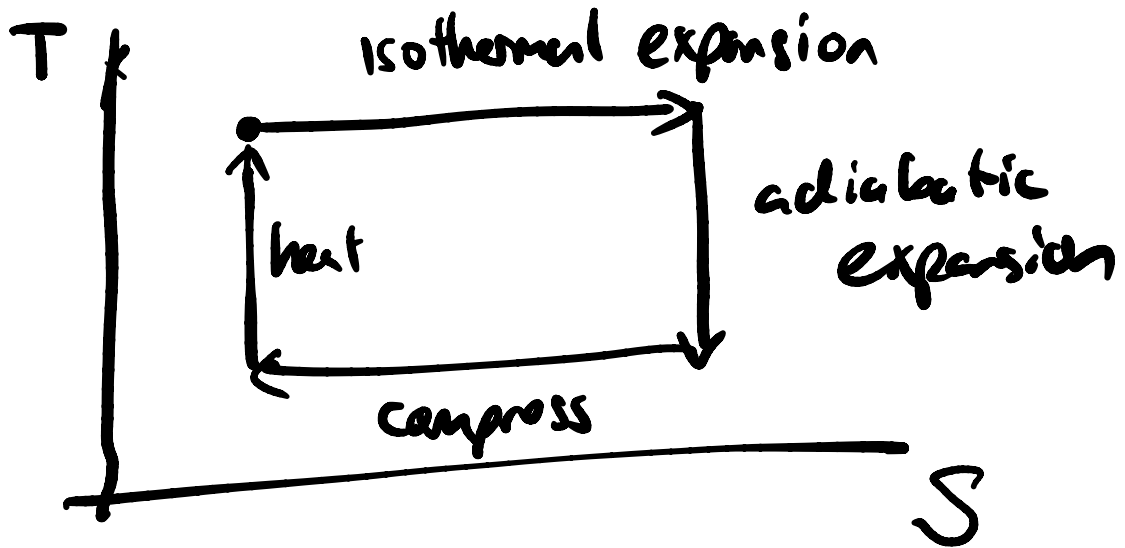
$\hat{=} \frac{nR}{V} = nR \ln(V_2/V_1)$

④ adiabatic:  $dq = 0$

$$dS = dq/T = 0$$



Carnot  
cycle



# Equilibration of temperature



$$E = E_A + E_B \Rightarrow dE_A = -dE_B$$

$$dE = dE_A + dE_B$$
$$0 = 0$$



$$dE = dq + dw - PdV \rightarrow 0$$

$$dS_A = \frac{dq_A}{T_A}$$

$\swarrow dE$

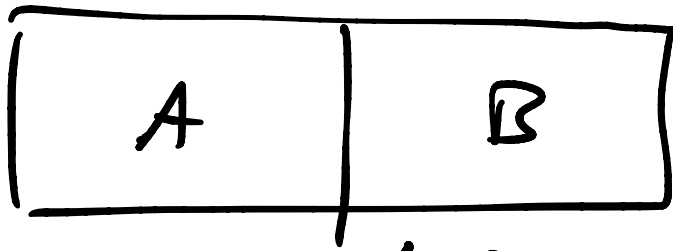
$$dS_B = \frac{dq_B}{T_B}$$

$$dS = dS_A + dS_B$$

$$= \frac{dE_A}{T_A} + \frac{dE_B}{T_B}$$

$$dS = dE_A \left( \frac{1}{T_A} - \frac{1}{T_B} \right)$$

$\swarrow dE_B = -dE_A$



$$dS = dE_A \left( \frac{1}{T_A} - \frac{1}{T_B} \right)$$

$$T_A > T_B : dE_A < 0$$

$$\left( \frac{1}{T_A} - \frac{1}{T_B} \right) < 0$$

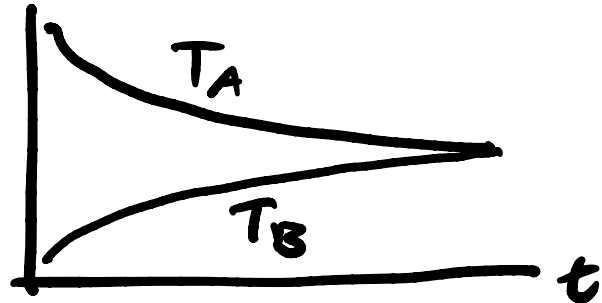
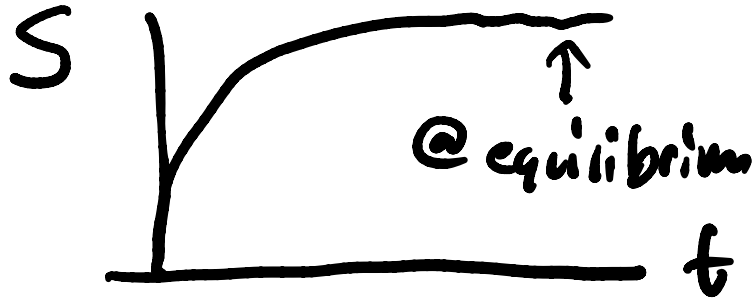
$$dS > 0$$

For a closed system

Entropy can be produced!

$$dS = dE_A \left( \frac{1}{T_A} - \frac{1}{T_B} \right)$$

$$\Rightarrow dS = 0 \text{ when } T_A = T_B$$



# Isolated system

$dS > 0$  for a spontaneous process

$dS = 0$  for a reversible process

spontaneous processes continue  
until Entropy is maximized

For an irreversible process:  
Entropy is produced

What about a non-isolated system

$$dS = dS_{\text{produced}} + dS_{\text{exchange}}$$

$$= dS_{\text{prod}} + \frac{dq_{\text{ex}}}{T}$$

Reversible:  $dS_{\text{prod}} = 0$        $dS = \frac{dq_{\text{ex}}^{\text{rev}}}{T}$

Irreversible  $dS_{\text{prod}} > 0 \Rightarrow dS > \frac{dq_{\text{ex}}^{\text{ir}}}{T}$

$dS \geq \frac{dq_{\text{ex}}}{T}$  for any process

$$\Delta S = \int_a^b dS \geq \int_a^b dq/T \quad (\text{second law})$$

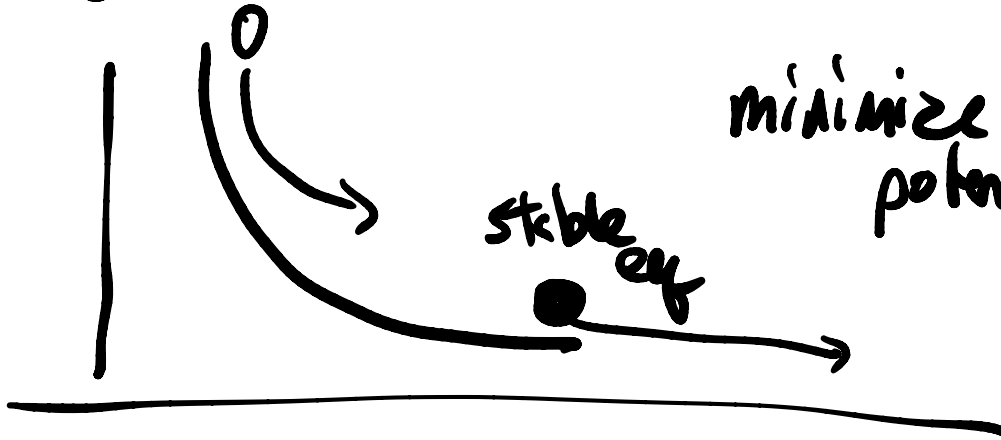
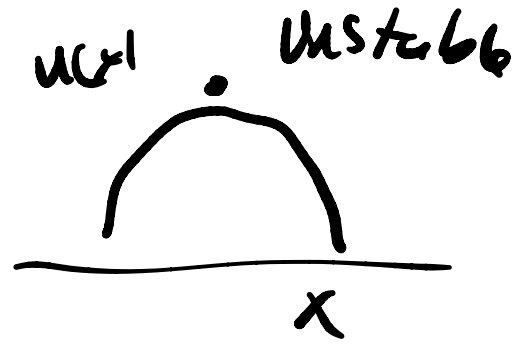


universe is a closed system

$$dS_{\text{univ}} \geq dq/T \geq 0$$

"Thermodynamic potential"

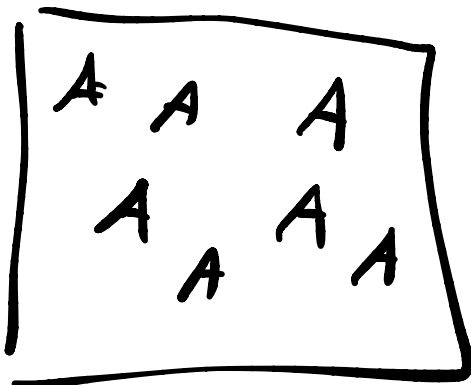
Entropy as T.P.



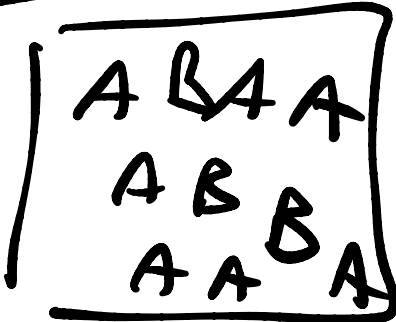
minimize  
potential energy

stable eq

Σ a reaction coordinate  
how far are we all from equilibrium

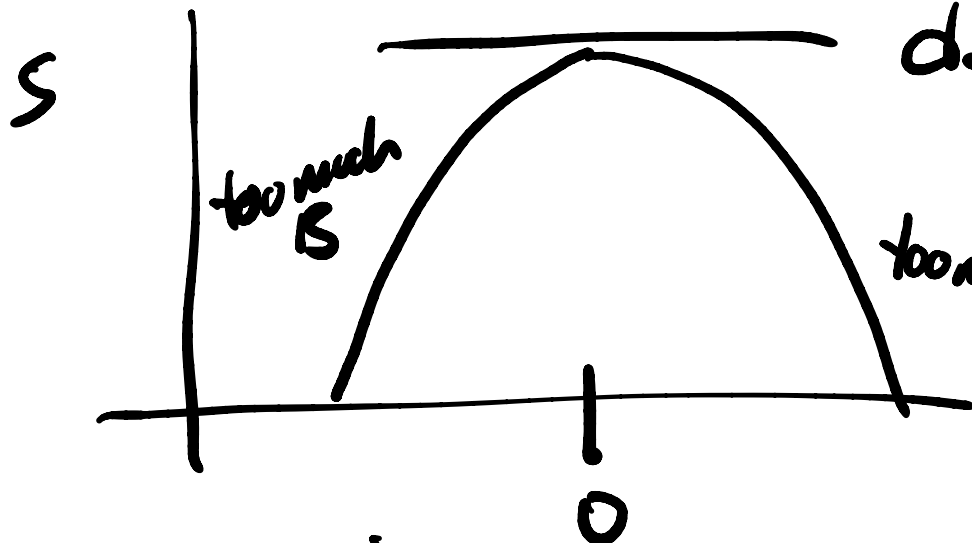


$$\xi = [A] - [A]_{\text{equil}}$$



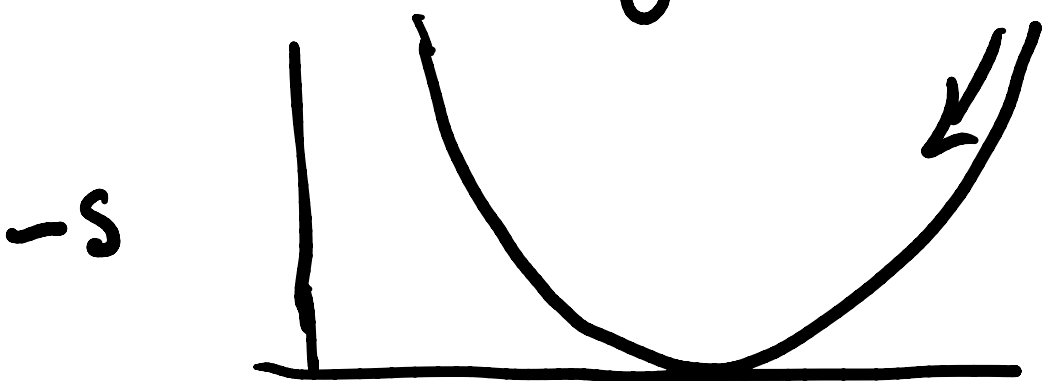


entropy is maximized for a spontaneous process



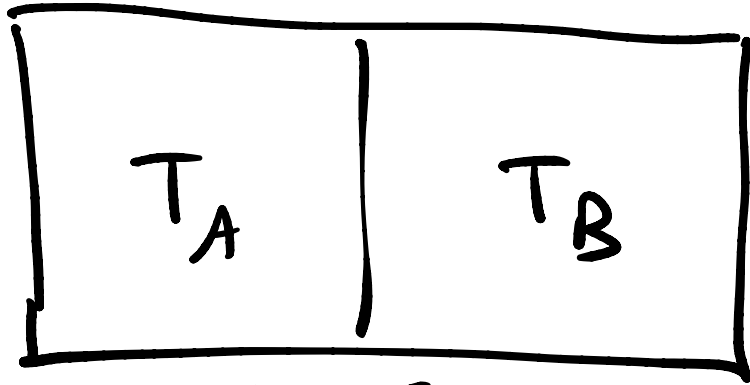
$$dS/d\xi = 0$$

$$F = -\frac{\partial \mathcal{F}}{\partial x}$$



"potential"  
for the reaction

# Example entropy problem



I.G.

$$\hookrightarrow T_f = \frac{T_A + T_B}{2}$$

Entropy change of process? <sup>2</sup>

Irreversible, but Entropy is state func.

$$\Delta S_{irr} = \Delta S_{rev}$$

$$\Delta S_A = C_V \ln \left( \frac{T_f}{T_A} \right) \quad T_f = \frac{T_A + T_B}{2}$$

$$\Delta S_B = C_V \ln \left( \frac{T_f}{T_B} \right)$$

$$\Delta S = \Delta S_A + \Delta S_B$$

$$= C_V \ln \left( \frac{T_f \cdot T_f}{T_A T_B} \right) = C_V \ln \left( \frac{(T_A + T_B)^2}{4 T_A T_B} \right) \quad \downarrow > 0$$

$$\text{if } T_A = T_B \Rightarrow \Delta S = 0 \quad / \quad T_A, T_B > 0$$