

$$\epsilon = \frac{\text{work done}}{\text{heat in from } T_h} = 1 - \frac{q_1}{q_3}$$

$$= 1 - \frac{T_c}{T_h}$$

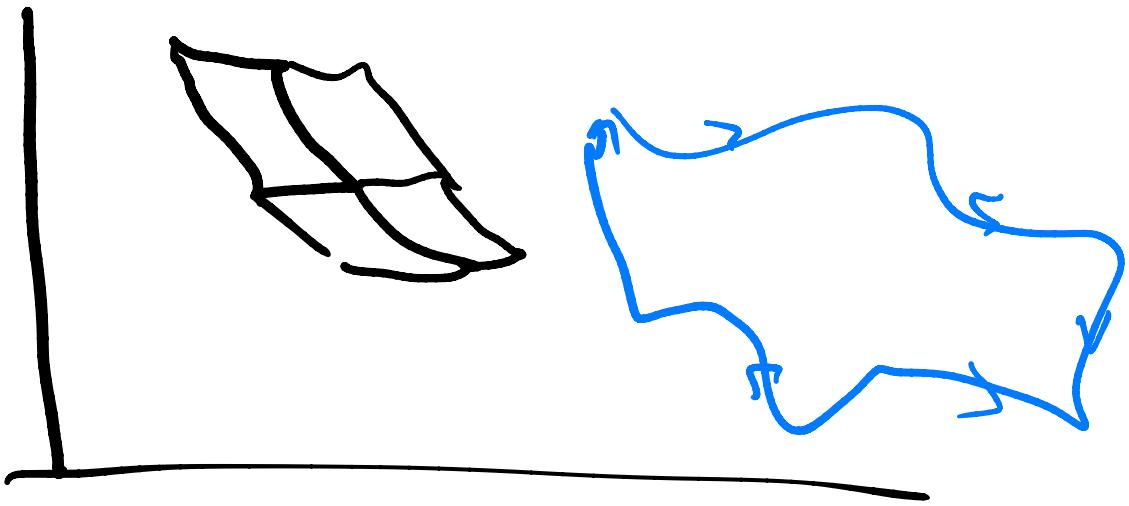
$$\frac{q_3}{q_{f1}} = -\frac{T_c}{T_h} = -\frac{T_3}{T_1}$$

$$\Rightarrow \frac{q_1}{T_1} + \frac{q_3}{T_3} = 0$$

suggests is a quantity  $\sim \frac{q}{T}$

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*

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

$$dS \equiv \frac{dg^{\text{rev}}}{T} \quad \text{state function}$$

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

for any path

$$\oint dS = 0$$

# Entropy for reversible processes

## ① Const P expansion



$$dE = dq + dw$$

$$dq = C_p dT$$

$$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \int_i^f \frac{C_p}{T} dT = C_p \ln\left(\frac{T_f}{T_i}\right)$$

if  $C_p$  is constant

ideal gas  $T = PV/nR$   $\Rightarrow C_p \ln\left(\frac{V_f}{V_i}\right)$  (i.g.)

② const volume

$$dq = C_V dT$$

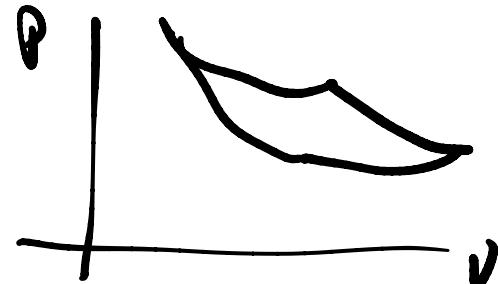
$$\Delta S = C_V \ln(T_2/T_1)$$

③ const T,  $dE = 0$ ,  $dq = -\omega = PdV$

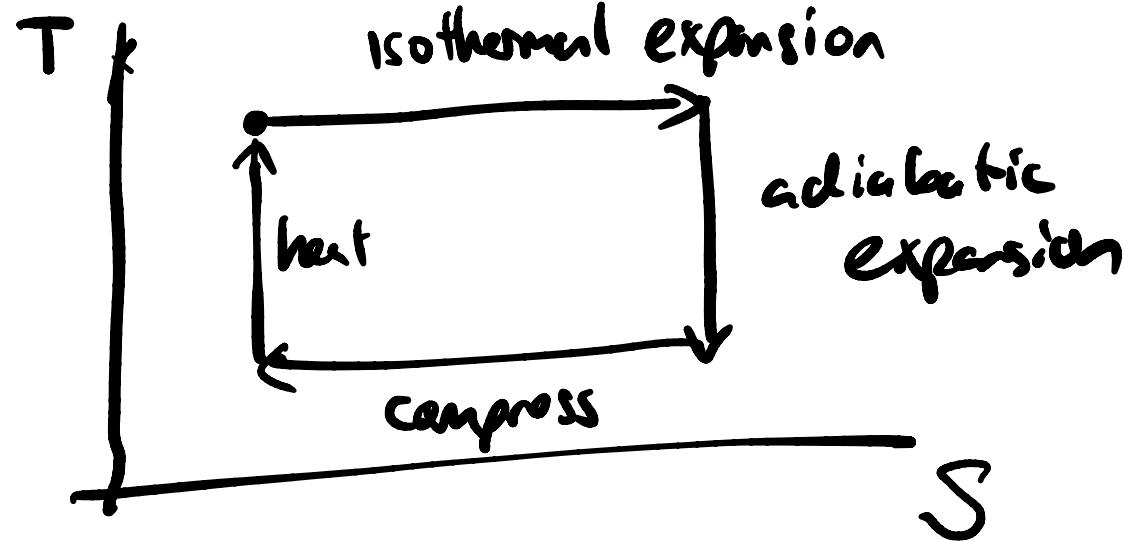
$$\Delta S = \int_{1}^{f} \frac{dq}{T} = \int_{1}^{f} \frac{P}{T} dV = nR \int \frac{1}{V} dV$$
$$= \frac{nR}{V} = nR \ln(V_2/V_1)$$

④ adiabatic :  $dq = 0$

$$dS = dq/T = 0$$



cannot  
cycle



# Equilibration of temperature



$$\mathcal{E} = \mathcal{E}_A + \mathcal{E}_B \Rightarrow d\mathcal{E}_A = -d\mathcal{E}_B$$

$$d\mathcal{E} = d\mathcal{E}_A + d\mathcal{E}_B$$

||  
0

$$dE = \cancel{dq} + \cancel{\omega} - PdV \rightarrow 0$$

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

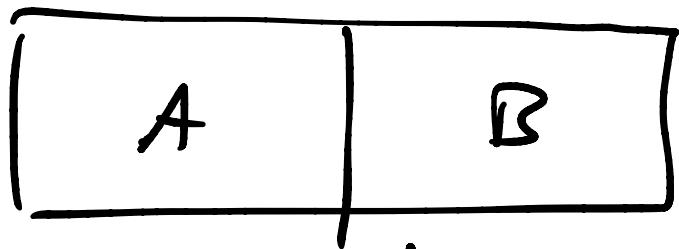
$$dS_B = \frac{dq_B}{T_B}$$

$$dE_B = -dE_A$$

$$dS = dS_A + dS_B$$

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

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



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

$$T_A > T_B : dE_A < 0$$

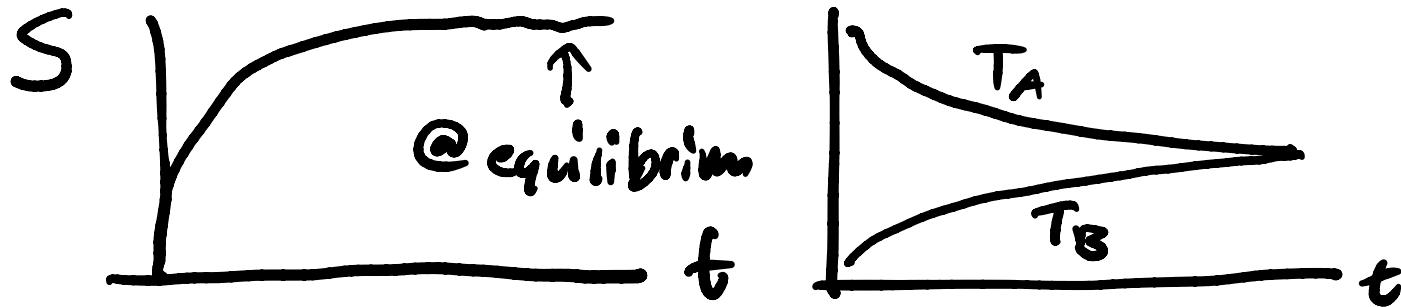
$$\left( \frac{1}{T_A} - \frac{1}{T_B} \right) < 0$$

$$dS > 0$$

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

$$dS = dS_{\text{produced}} + dS_{\text{exchange}}$$
$$= dS_{\text{prod}} + \frac{\delta q}{T}$$

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

Irreversible  $dS_{\text{prod}} > 0 \Rightarrow dS > \frac{\delta q^{\text{irr}}}{T}$

$dS \geq \frac{\delta q}{T}$  for any process

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

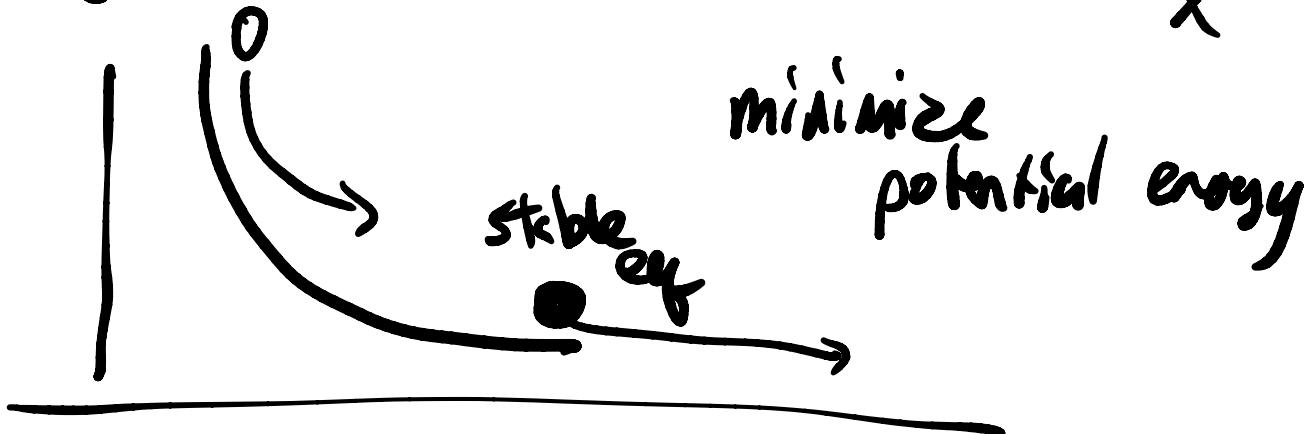
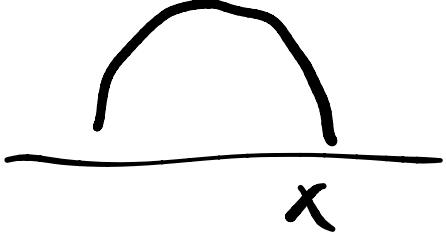


Universe is a closed system

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

"Thermodynamic potential"  $\psi(x)$ . unstable

Entropy as T.P.

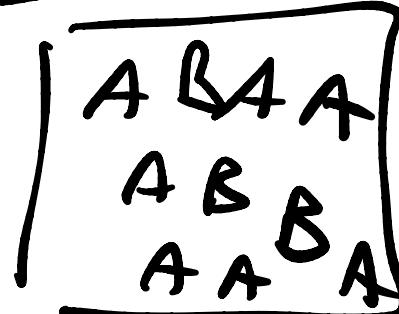
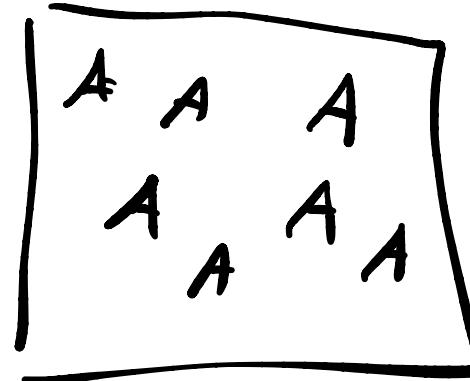


minimize  
potential energy

a reaction coordinate  
how far are we from equilibrium

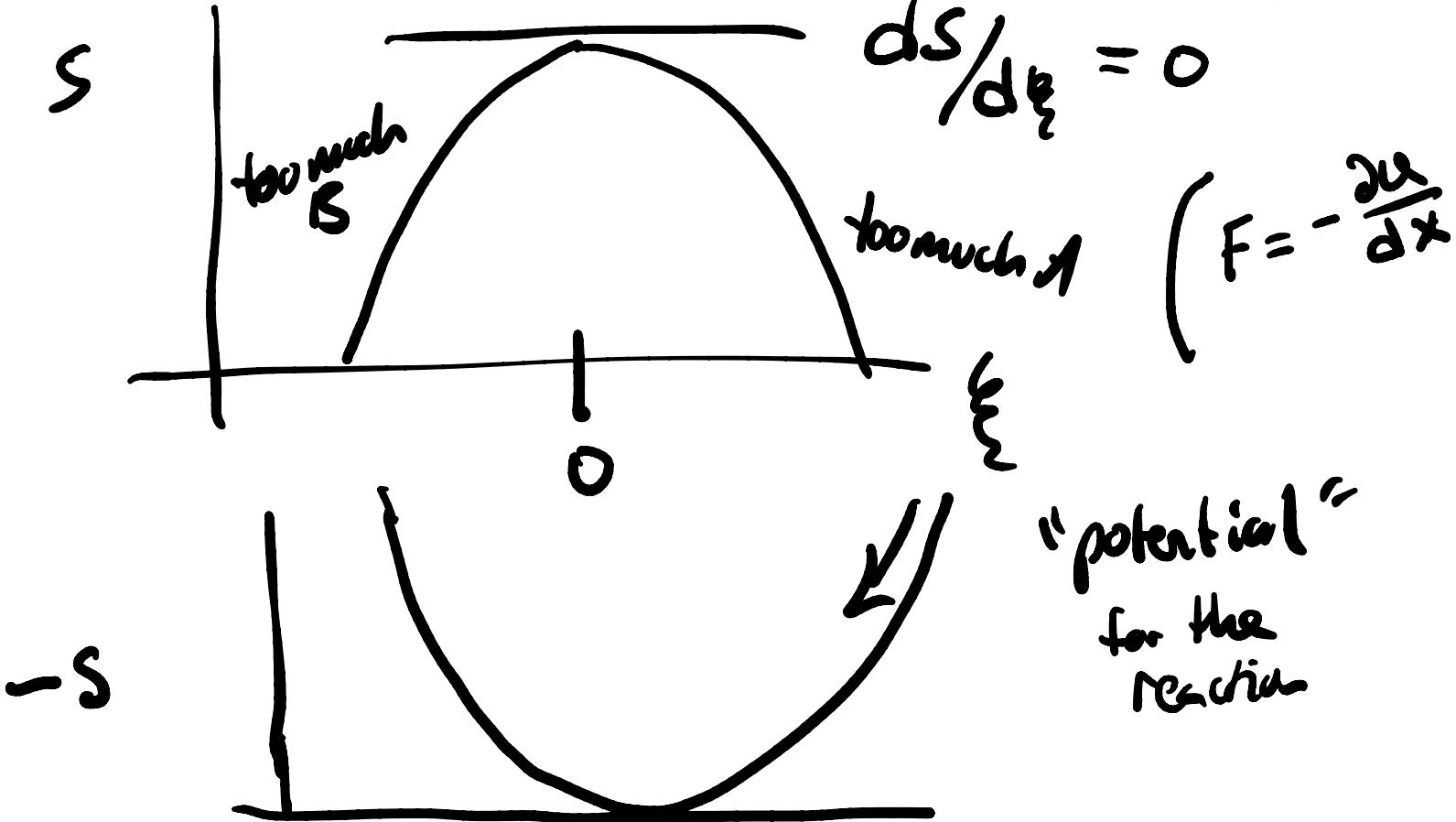


$$\xi = [A] - [A]_{\text{equil}}$$

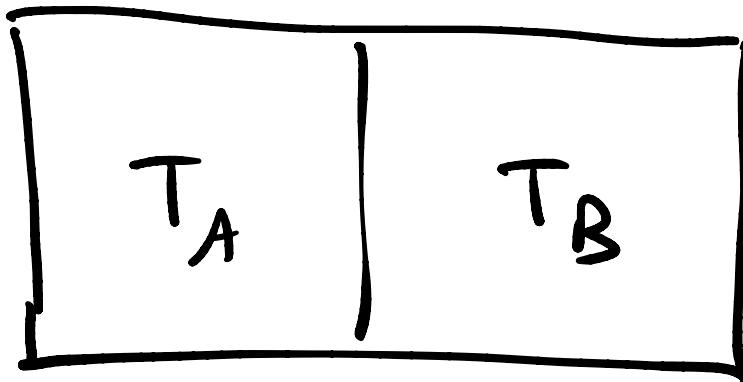


entropy is maximized for a spontaneous process

$$\frac{dS}{d\xi} = 0$$



## Example entropy problem



I.G.

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

Entropy change of process?

Irreversible, but Entropy is state func.

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

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

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

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

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

If  $T_A = T_B \Rightarrow \Delta S = 0$  /  $T_A, T_B > 0$