MORE FORMALLY:

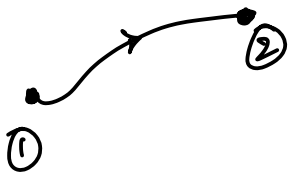
There exists a state function $S(U, X_i)$ which monotonically increases with U and for which:

$$dS_{system} \geq \frac{\delta Q}{T}$$

$$\Rightarrow \Delta S_{system} \geq \int_A^B \frac{\delta Q}{T}$$

* The second law imposes directionality to processes.

Consider a system going from ① → ②. ① & ② are infinitesimally close together if ① → ② is allowed.



$$dS_{①\to②} = dS_2 - dS_1 \geq \frac{\delta Q_{①\to②}}{T} \quad (*)$$

Consider the reverse path

for the path going from ② → ①

$$dS_{②\to①} = dS_1 - dS_2 \geq \frac{\delta Q_{②\to①}}{T}$$

Multiply * by (-1) throughout

$$dS_{②\to①} \leq \frac{\delta Q_{②\to①}}{T}$$

The two inequalities cannot both be true

Only true for REVERSIBLE paths where $dS = \delta Q/T$

Most paths can only go one way!

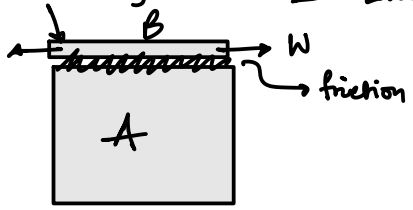
* What is entropy, why the inequality?

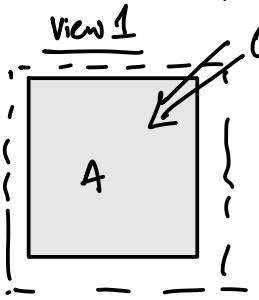
1st Law: $\Delta U = Q + W$

2nd Law: $dS \geq \frac{\delta Q}{T}$ if reversible: $dS = \frac{\delta Q}{T}$

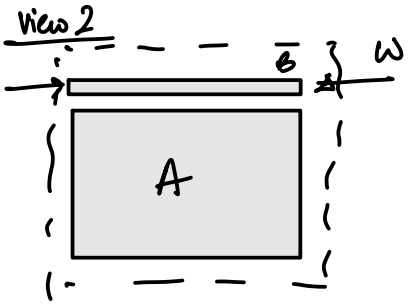
why the inequality?

Alternate way to think about 2nd Law: $dS = \frac{\delta Q}{T} + \text{positive quantity}$ ← energy delivered in other forms but dissipated as heat.





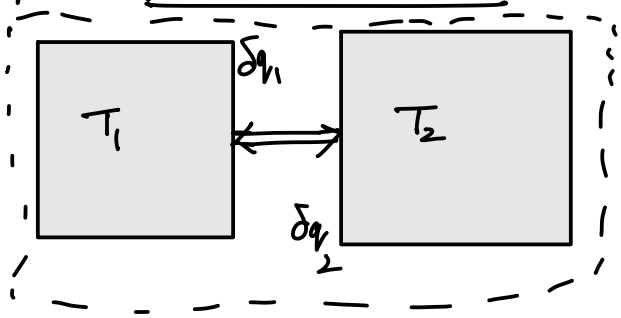
$dS = \delta Q/T$ (Assume reversible...)



$dS \geq \frac{\delta Q}{T} = 0$ ← These 2 statements are consistent

The reason for the inequality is that the 2nd Law needs to be applicable to ANY system boundary.

* Consequences of the 2nd Law for thermal eqm:



1st Law: $\delta q_1 + \delta q_2 = 0 \Rightarrow \delta q_1 = -\delta q_2$

$dS_{total} = dS_1 + dS_2 \geq 0$

$dS_{total} = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} \geq 0$

$\Rightarrow \delta Q_1 \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \geq 0 \Rightarrow \boxed{\delta Q_1 \left[\frac{T_2 - T_1}{T_1 T_2}\right] \geq 0}$

if $T_2 > T_1 \Rightarrow \delta Q_1 > 0$

$T_1 > T_2 \Rightarrow \delta Q_2 < 0$

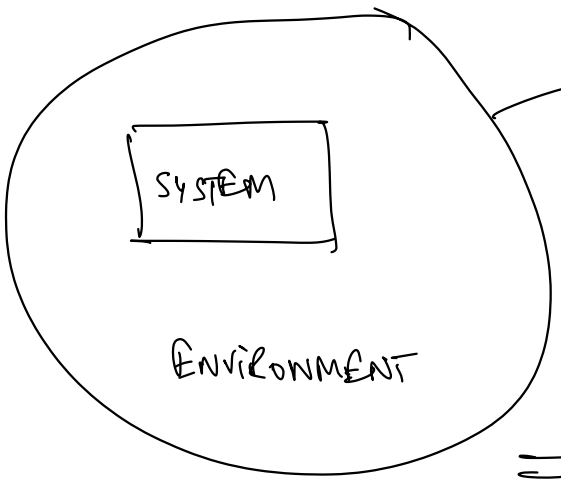
Irreversibility / Reversibility of the process

* Entropy is not CONSERVED

* Universe = isolated $\rightsquigarrow$ $\Delta S_{universe} \geq 0$ for any spontaneous process

gives time a "direction"

* CONSIDER:



$\Delta S_{universe} \geq 0$

$\Delta S_{Universe} = \Delta S_{env} + \Delta S_{system}$

$\Delta S_{environment} + \Delta S_{system} \geq 0$

$\Rightarrow$ if $\Delta S_{system} < 0$

$\Delta S_{environment} > |\Delta S_{system}|$ & $\Delta S_{environment} > 0$

$\Rightarrow$ if $\Delta S_{system} > 0$

$\Delta S_{environment} > -|\Delta S_{system}|$

ENTROPY CAN DECREASE $\Rightarrow$ Only has to increase for adiabatic systems.

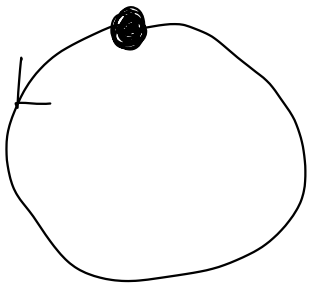
CONSEQUENCES:

① $\delta W_{reversible} < \delta W_{irreversible}$

② Limits in conversion of heat to work

In a cyclic reversible process $Q = 0$ & $W = 0$

Consider a cyclical reversible process:



$$\Delta S = \oint \frac{\delta Q}{T} = 0 \longrightarrow S \text{ is a state variable}$$

$$\Rightarrow Q = 0 \text{ @ constant temperature}$$

1st Law: $\Delta U = Q + W = 0$

$Q = 0 \Rightarrow W = 0$ } Cannot extract work at constant temperature

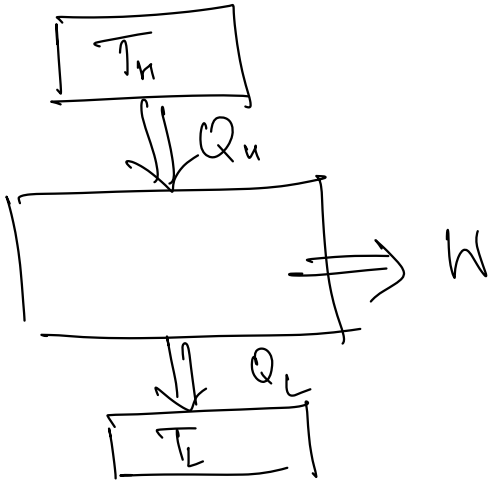
SOLUTION → Two temperatures T_H & T_L

$T_H > T_L$

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \Rightarrow Q_L = \frac{T_L}{T_H} Q_H$$

$$\Delta U = 0 = Q_H + Q_L + W$$

$$\Rightarrow W = -(Q_H + Q_L) = -\left(1 - \frac{T_L}{T_H}\right) Q_H$$



if $W < 0$

$Q_H > 0$

Since this is a reversible process W is the maximum work we can extract from 2 reservoirs

efficiency: $\eta = -\frac{W}{Q_H}$ ← this is the work you are getting

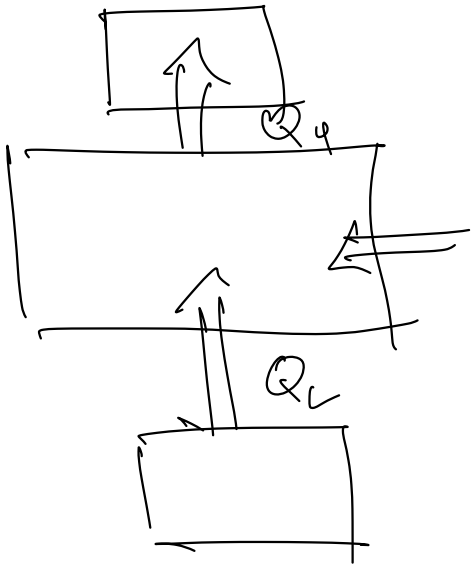
← how much you "pay"

$\eta = \left[1 - \frac{T_L}{T_H}\right]$ ← CARNOT LIMIT

(eg) $T_H = 100^\circ C$ $\quad \eta = 1 - \frac{298}{373} \simeq 20\%$

$T_L = 25^\circ C$

HEAT PUMPS & EFFICIENCY:



$\eta = -\frac{Q_H}{W}$ ← what you want

↖ what you pay for it

$\eta = \frac{T_H}{T_H - T_L}$

$T_H = 25^\circ C$

$T_L = 0^\circ C$ $\longrightarrow$ $\eta = \frac{298}{25} = 11.92$

1 W of electricity generates 12 W of heat

electric heaters: 100% efficiency

cannot be more!

NATURAL GAS V/S ELECTRICITY:

Burn CH_4 $\longrightarrow$ $Q_{house} = \Delta H_{reaction}$

Alternately

gas $\longrightarrow$ electricity $\longrightarrow$ heat pump

Coefficient of performance $= \eta_{heat\ pump} \simeq 3$

power plant efficiency $= \eta_{pp} \simeq 0.4$

$$W_{electricity} = \eta_{pp} \Delta H_{reaction}$$

$$Q_{house} = \eta_{heat\ pump}\ \eta_{pp}\ \Delta H_{reaction}.$$

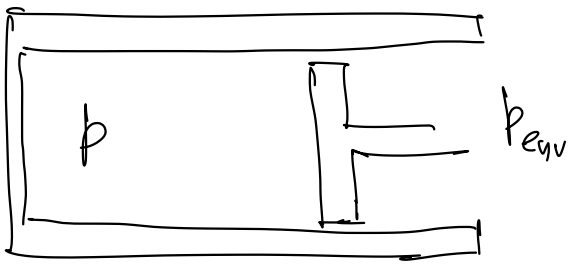
$$\boxed{Q_{house} = 1.2\ \Delta H_{reaction}}$$

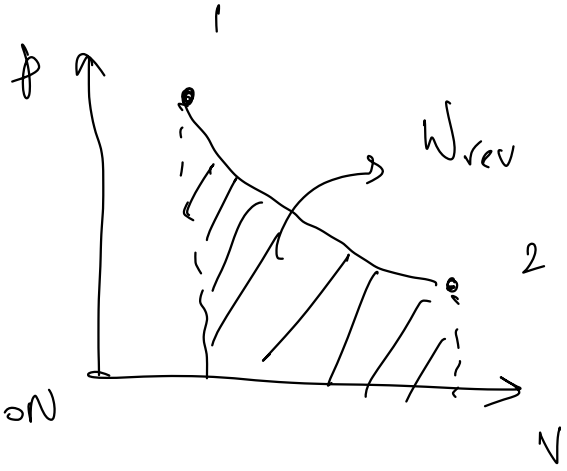
IDEAL GAS

Definition: $\begin{cases} pV = nRT \\ U = U(T) \end{cases}$ → not a function of p or V

↑ can derive from statistical mechanics

ILLUSTRATION OF 1ST AND 2ND LAW:





REVERSIBLE ISOTHERMAL EXPANSION

* $W_{rev} = \int_1^2 -p\,dV = -\int_1^2 \frac{RT}{V}\,dV$

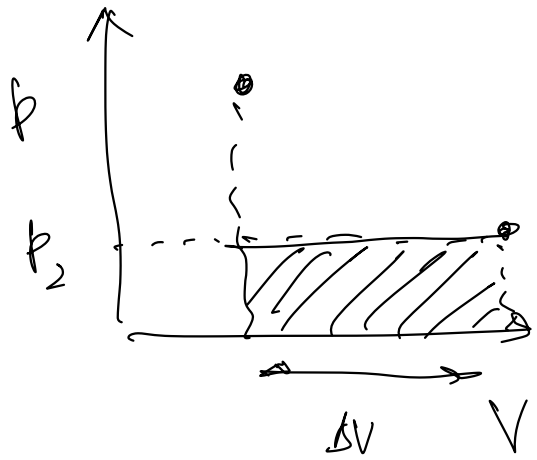
$= -RT \log\left(V_2/V_1\right)$

* $\Delta U = ? = 0$ → @ constant temperature
  ONLY TRUE FOR AN IDEAL GAS

* $Q = ?$ → $\Delta U = Q + W = 0 \Rightarrow Q = -W$

* $\Delta S = ?$ → $\Delta S = \frac{Q}{T} = R \log\left(V_2/V_1\right)$

IRREVERSIBLE EXPANSION:



* $W_{irreversible} = -p_2 \Delta V$
* $\Delta U = ? = 0$; since $T_1 = T_2$
* $Q = ?$

$$\Delta U = Q + W \Rightarrow Q_2 - W_{irreversible}$$

$$= p_2 \Delta V$$

* $\Delta S = ?$

⟶ same as reversible

$$\Delta S = R \log\left(V_2/V_1\right)$$

II Law: $\Delta S \geq \frac{Q}{T} \Rightarrow R\log\left(V_2/V_1\right) > \frac{p_2 \Delta V}{T}$

$$T = \frac{p_2 V_2}{R} = \frac{p_1 V_1}{R}$$

$$\frac{p_2 \Delta V}{T} = \frac{p_2 \Delta V \times R}{p_2 V_2} = \frac{V_2 - V_1}{V_2} R$$

$$= \left(1 - V_1/V_2\right) R$$

HEAT FLOW & HEAT CAPACITY:

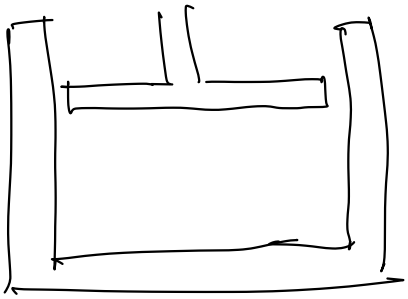
Heat = exchange of energy between system and environment due to ΔT

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{\delta Q}{dT}$$ ← heat introduced reversibly

$$\delta Q = dU - \delta W$$ → path dependent

δQ: path dependent

dU: path independent



- need to specify only 2-variables
  (eg) (T, V), (P, T), (P, V)
- U = state function
  $U(T,V)$, $U(P,T)$, $U(P,V)$

★ CONSTANT VOLUME PATH (control V & T):

$$\delta Q_V = dU + PdV \; ; \; dV = 0$$

$$\Rightarrow \delta Q_V = dU$$

$$C_V = \frac{\delta Q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$ ← response function

derived quantity from a state function

★ CONSTANT PRESSURE PATH (control p, T)

define: H = enthalpy = $U + pV$ ⟶ state function

$$dH = dU + p\,dV + V\,dp$$

$$dp = 0$$

$$\Rightarrow dH = \underbrace{dU + p\,dV}_{\delta Q}$$

$$C_p = \frac{\delta Q_p}{dT} \;;\quad \boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p}$$

Define: HEAT CAPACITY:

$$C \equiv \frac{1}{n}\frac{\delta Q}{dT}$$

infinitesimal heat flow needed to induce an infinitesimal temperature change.

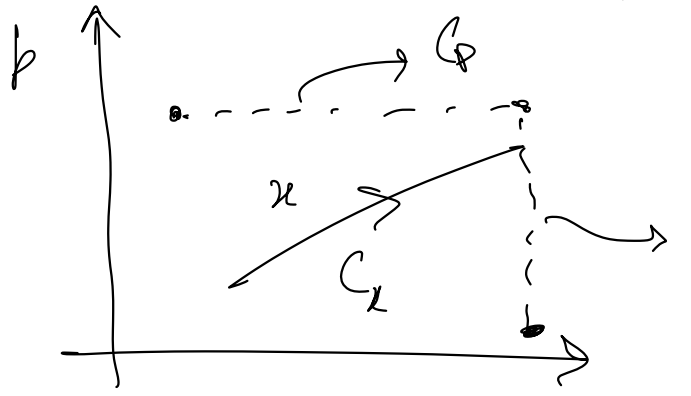
$\delta Q \longrightarrow$ path variable $\longrightarrow$ definition is incomplete!

$\longrightarrow$ path dependence

$$C_{path} \equiv \frac{1}{n}\left(\frac{\delta Q}{dT}\right)_{path}$$

(eg) ideal gas $\longrightarrow$ 2 variables out of (p, V, T) can be selected

$$C_p = \frac{1}{n}\left(\frac{\delta Q}{\partial T}\right)_p \qquad C_V = \frac{1}{n}\left(\frac{\delta Q}{dT}\right)_V$$



C_p & C_V are not the only heat capacities!

heat capacities can be defined along any path.