

2nd Law & Entropy

Reminder: Quiz (BT 202)

Date: 9th Sept 2022 (Friday)

Time: 5 PM – 6 PM

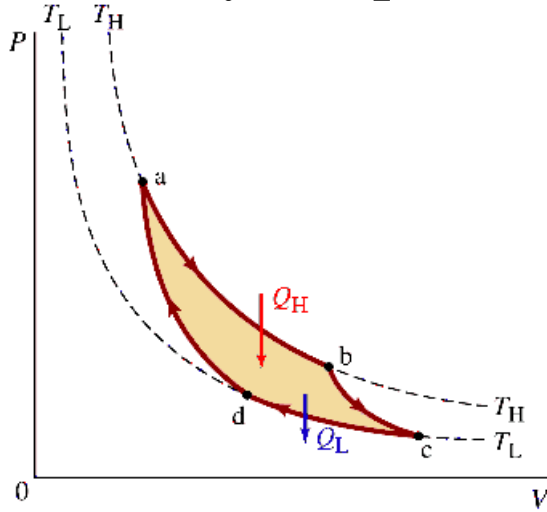
Venue: Lecture Hall 1

Syllabus: Up to Lecture 8 (L7.pdf)

10 Marks

Limitation of 1st Law

> For a cyclic process Heat can be completely converted into heat.



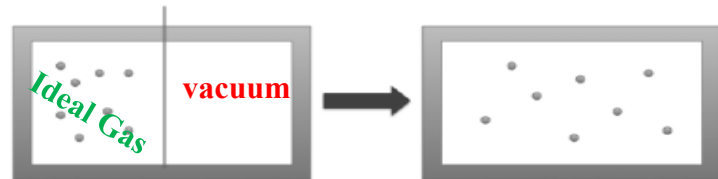
$$\Delta U = q + w$$

$$\Rightarrow 0 = q + w \text{ (cyclic process)}$$

$$\Rightarrow q = -W \text{ (cyclic process)}$$

In reality although work can be completely converted into heat but the opposite is not true.

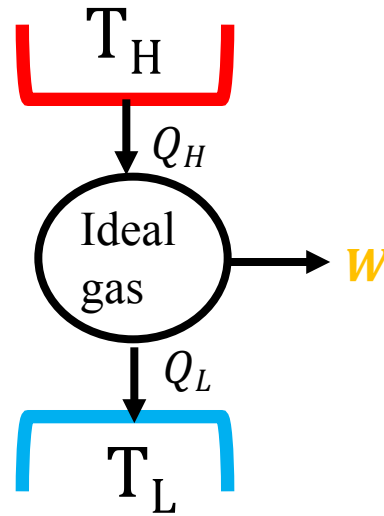
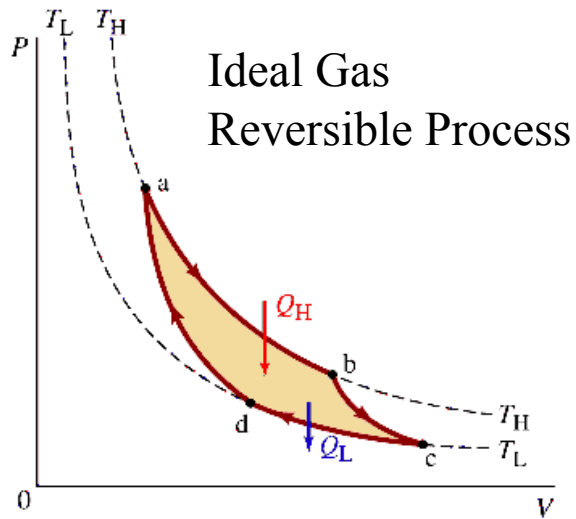
> Directionality of a process is not known.



In reality opposite direction does not happen spontaneously.

(free expansion) $\Delta U = 0, W=0, q=0$

What is the efficiency of this engine?



$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$$Q_H = nR T_H \ln(V_b/V_a)$$

$$Q_L = nR T_L \ln(V_c/V_d)$$

Lecture 9_Tutorial02

$$TV^{(nR/C_v)} = C \quad \text{Lecture 7}$$

$$T^{(C_v/nR)}V = C'$$

- $T_H^{(C_v/nR)} V_b = T_L^{(C_v/nR)} V_c$
- $T_H^{(C_v/nR)} V_a = T_L^{(C_v/nR)} V_d$

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L \ln(V_b/V_a)}{T_H \ln(V_c/V_d)}$$

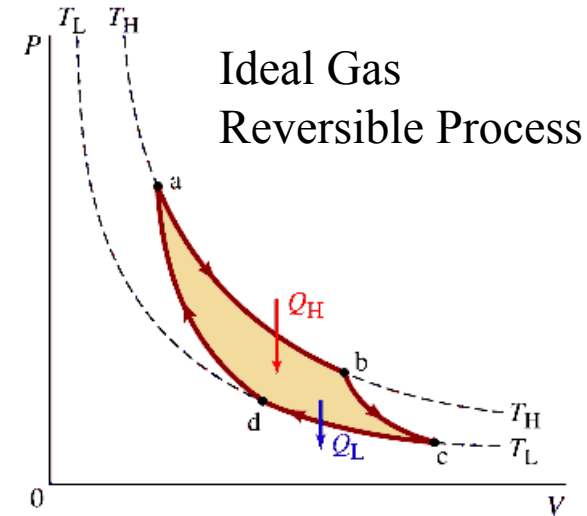
$$= 1 - \frac{T_L}{T_H}$$

Maximum Efficiency < 1

$$\frac{Q_L}{Q_H} = \frac{T_L \ln(V_b/V_a)}{T_H \ln(V_c/V_d)} = \frac{T_L}{T_H}$$

$$\Rightarrow \frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

$$\Rightarrow \frac{Q_L}{T_L} = \frac{Q_H}{T_H}$$



Interesting theoretical issue:

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

Heat input at stage a → b

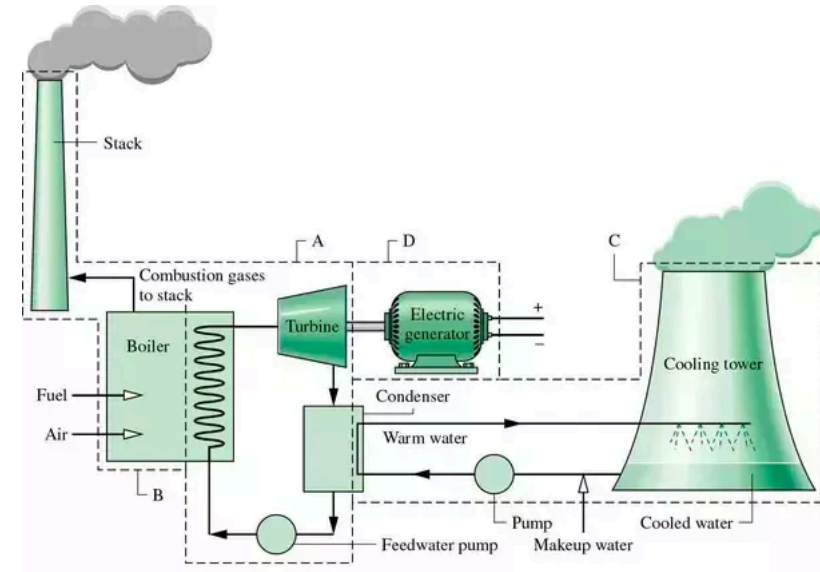
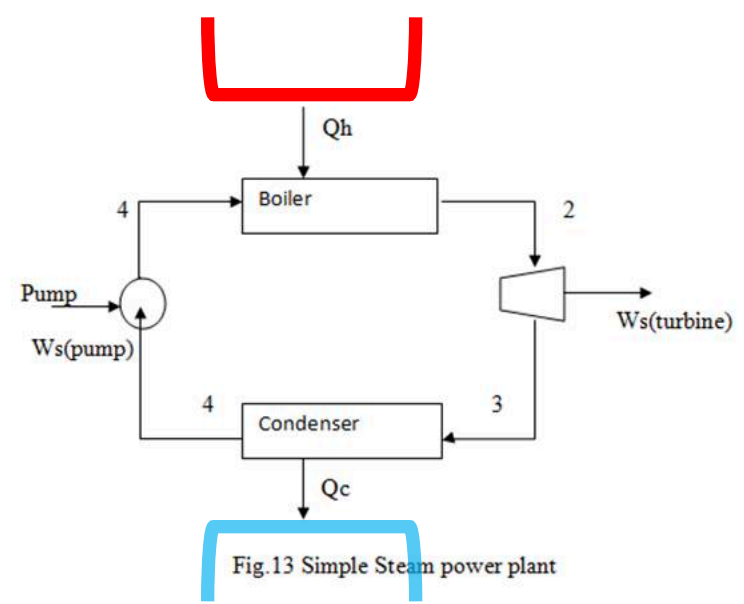
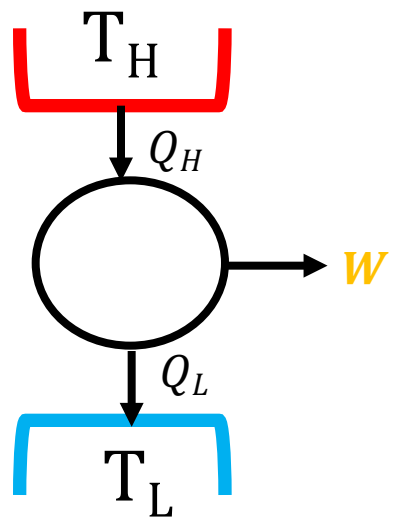
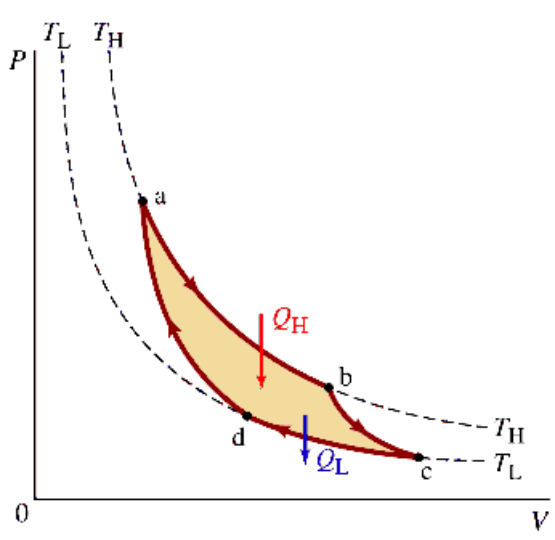
Heat extracted at stage c → d

Full cycle

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

A NEW STATE VARIABLE: $\Delta S = \frac{Q}{T}$

Cyclic process $\Delta S = 0$



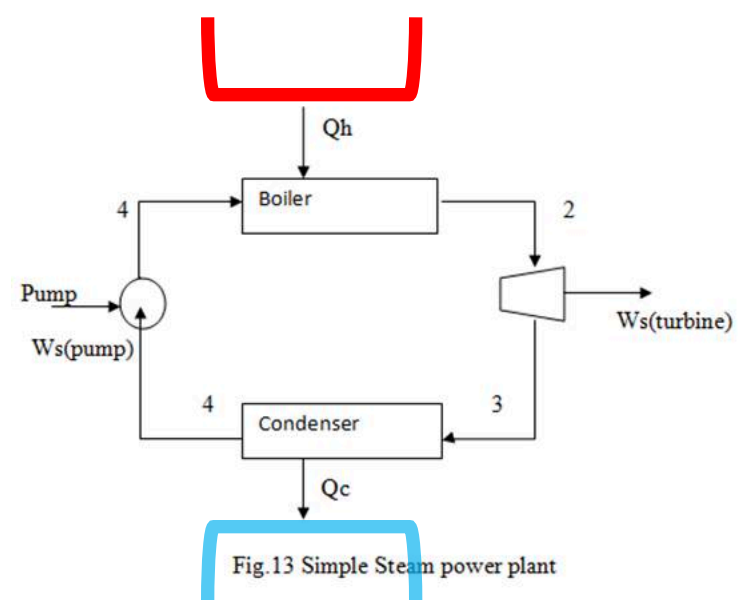
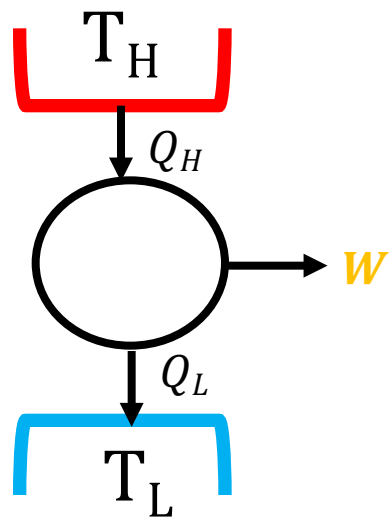
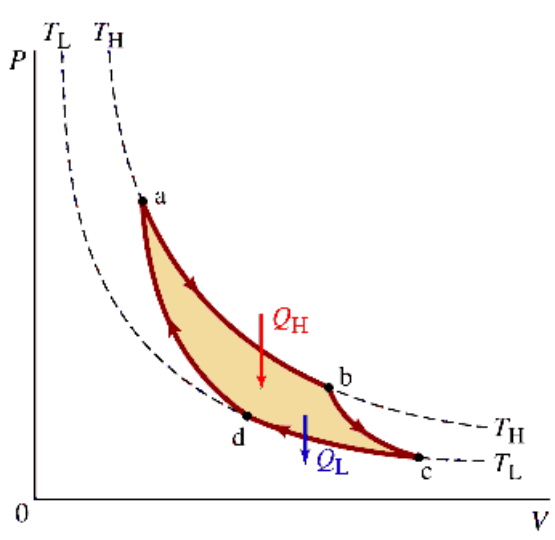
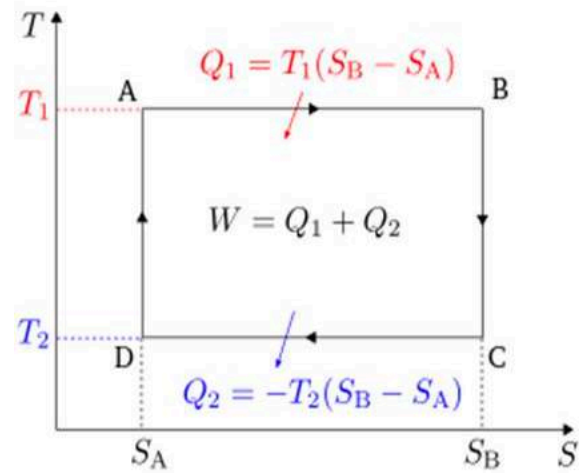
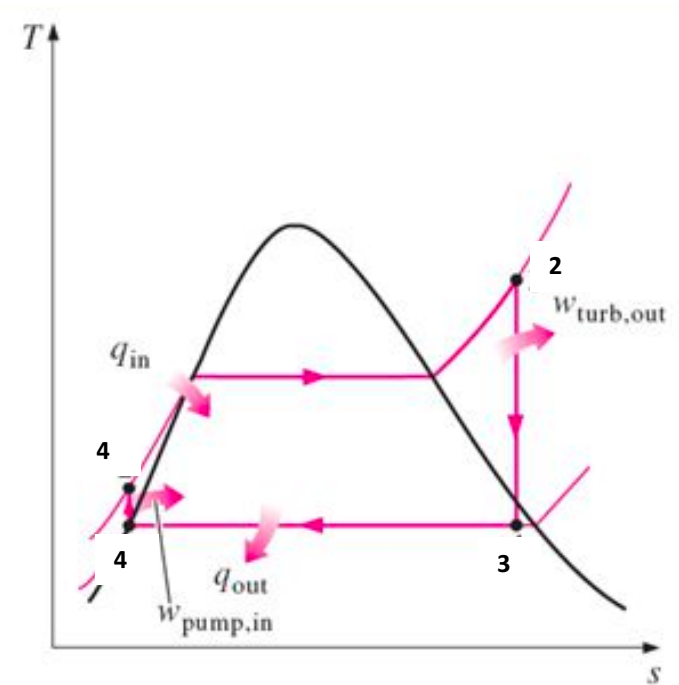


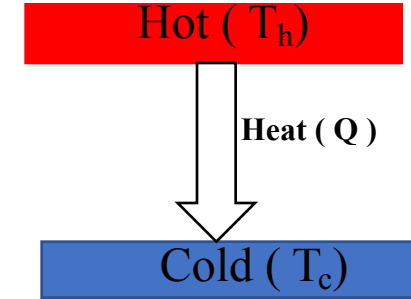
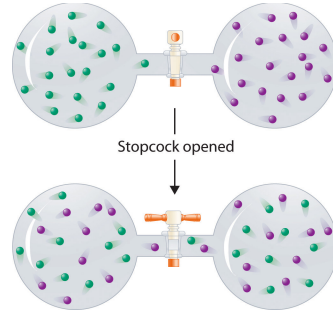
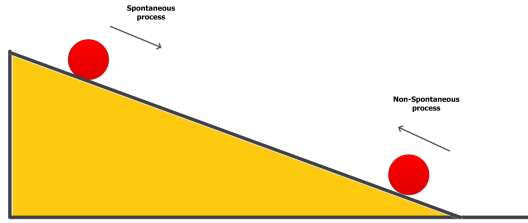
Fig.13 Simple Steam power plant



Carnot Cycle

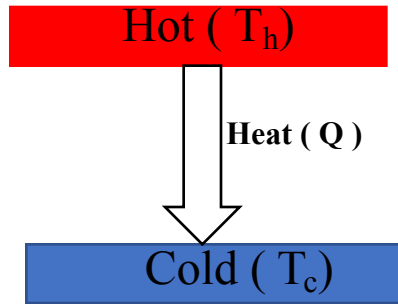


For any spontaneous process, entropy= S of the universe increases

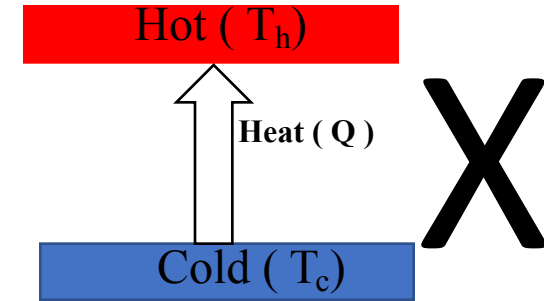


Things can happen in both direction : No restriction from 1st Law

2nd Law explain the arrow of Time



Lets define a quantity = $\Delta S = \frac{Q}{T} = \frac{\text{Heat}}{\text{Temp}}$



Case I: Heat flow from Hot → Cold

$$\Delta S = -\frac{Q}{T_h} + \frac{Q}{T_c} > 0$$

Case II: Heat Flow from Cold → Hot

$$\Delta S = \frac{Q}{T_h} - \frac{Q}{T_c} < 0$$

Case III ($T_h=T_c$), Equilibrium

$$\Delta S = \frac{Q}{T_h} - \frac{Q}{T_c} = 0$$

change in entropy greater than or equal to zero

$$dS \geq 0$$

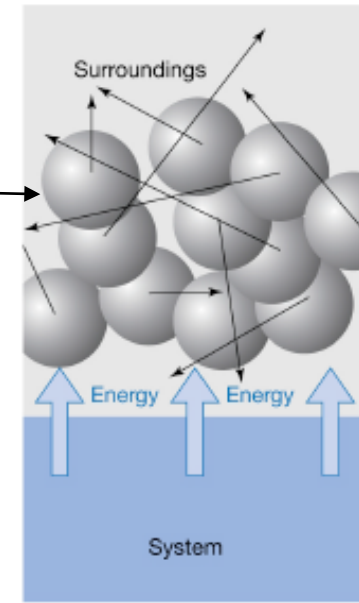
- Energy is conserved for all cases I, II, III
- $\Delta S_{\text{universe}} \geq 0$, Not only explain why things happen in one direction but also quantitative.

ENTROPY CHANGE AND TEMPERATURE

$$dS = \frac{\delta q_{rev}}{T}$$

Entropy is related to the disorder of a system. If you add energy as heat to a system, then its entropy increases because the thermal disorder increases.

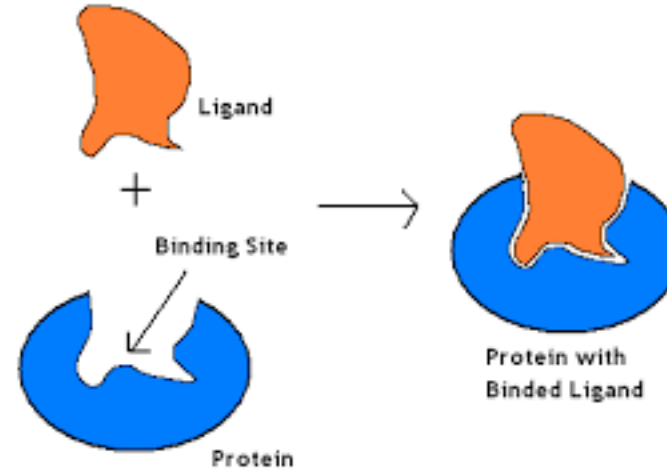
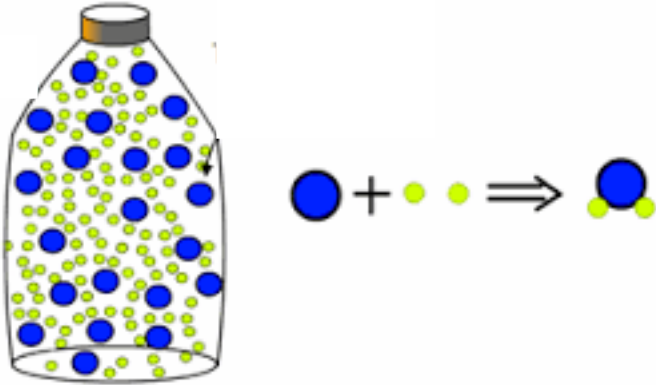
Note that the same heat delivered at lower T contributes more to an entropy increase than heat delivered at a higher T .



Average kinetic energy

Very strange quantity: (Randomness/Temp) and state function

Why do we need a quantitative equation?



$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

Apparent contradiction of 2nd Law of thermodynamics ?

- crystallization
- Life on earth

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$$

Need to calculate $\Delta S_{\text{surrounding}}$ all the time ! 🤔

$$\Delta S_{\text{surrounding}} = \frac{Q_{\text{surrounding}}}{T} = \frac{-Q_{\text{system}}}{T}$$

[At constant Pressure]

$$\Delta S_{\text{surrounding}} = \frac{-Q_{\text{system}}}{T} = \frac{-Q_p}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

Lets try to get rid of surrounding entropy ?

2nd Law, $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$

$$\Rightarrow \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T} \geq 0$$

$$\Rightarrow T \Delta S_{\text{system}} - \Delta H_{\text{system}} \geq 0$$

$$\Rightarrow -(-T \Delta S_{\text{system}} + \Delta H_{\text{system}}) \geq 0$$

$$\Rightarrow (-T \Delta S_{\text{system}} + \Delta H_{\text{system}}) \leq 0$$

At constant pressure and temperature ?

$$\Rightarrow \Delta(H_{\text{system}} - TS_{\text{system}}) \leq 0$$

$$\Rightarrow \Delta(H - TS) \leq 0$$

No Surrounding term; System only term.
predict spontaneity based on system (G).

$$\Rightarrow \Delta G \leq 0 \quad (2^{\text{nd}} \text{ law in terms of system})$$

(G = H - TS = Gibbs Free Energy = STATE FUNCTION)

At constant volume and temperature ?

$$\Delta S_{\text{surrounding}} = \frac{-Q_{\text{system}}}{T} = \frac{-Q_v}{T} = \frac{-\Delta U_{\text{system}}}{T}$$

$$\text{2nd Law, } \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$$

$$\Rightarrow \Delta S_{\text{system}} - \frac{\Delta U_{\text{system}}}{T} \geq 0$$

$$\Rightarrow \Delta(U_{\text{system}} - TS_{\text{system}}) \leq 0$$

$$\Rightarrow \Delta(U - TS) \leq 0$$

$$\Rightarrow \Delta A \leq 0$$

(**A = U - TS = Helmholtz Free Energy = STATE FUNCTION**)

Property of Gibbs Free Energy ? What's the big deal ?

$$G = H - TS$$

$$\Rightarrow \Delta G = \Delta H - T\Delta S - S\Delta T$$

Substituting , $H = U + PV$

$$\Rightarrow \Delta G = \Delta(U + PV) - T\Delta S - S\Delta T$$

$$\Rightarrow \Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

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

$$\Rightarrow \Delta G = (Q + W) + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

Now, $W = W(PV) + W(nonPV) = - (P\Delta V + W_{nonPV})$

$$\Rightarrow \Delta G = Q - (P\Delta V + W_{nonPV}) + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

Definition of entropy: For a reversible process $\Delta S = Q/T$

$$\Rightarrow \Delta G = Q - (P\Delta V + W_{nonPV}) + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

$$\Rightarrow \Delta G = -W_{\text{nonPV}} + V\Delta P - S\Delta T$$

At constant pressure, Temp

$$\Rightarrow \Delta G_{P,T} = -W_{\text{nonPV}}$$

Free Energy:

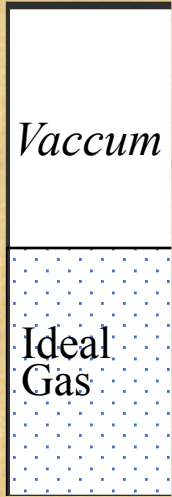
It is the portion of a system's energy that is able to perform work when temperature and pressure is uniform throughout the system, as in a living cell

- Free energy also refers to the amount of energy actually available to break and subsequently form other chemical bonds



Entropy calculations

- * Suddenly Remove Partition
- * Adiabatic expansion



V_1, T



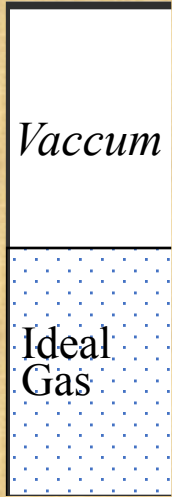
V_2

$$q = 0, \Delta S = \frac{Q}{T} = 0$$



Entropy calculations

- * Suddenly Remove Partition
- * Adiabatic expansion

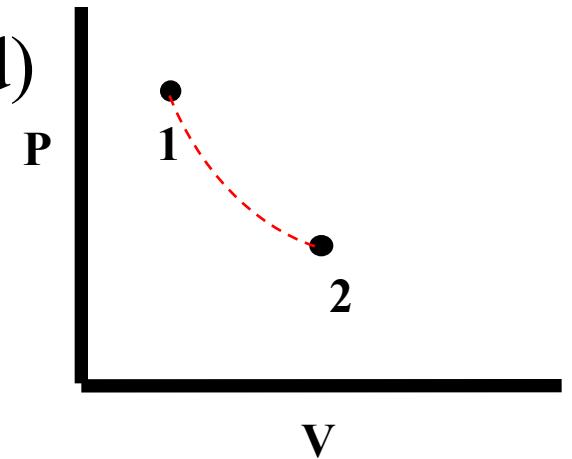


V_1, T



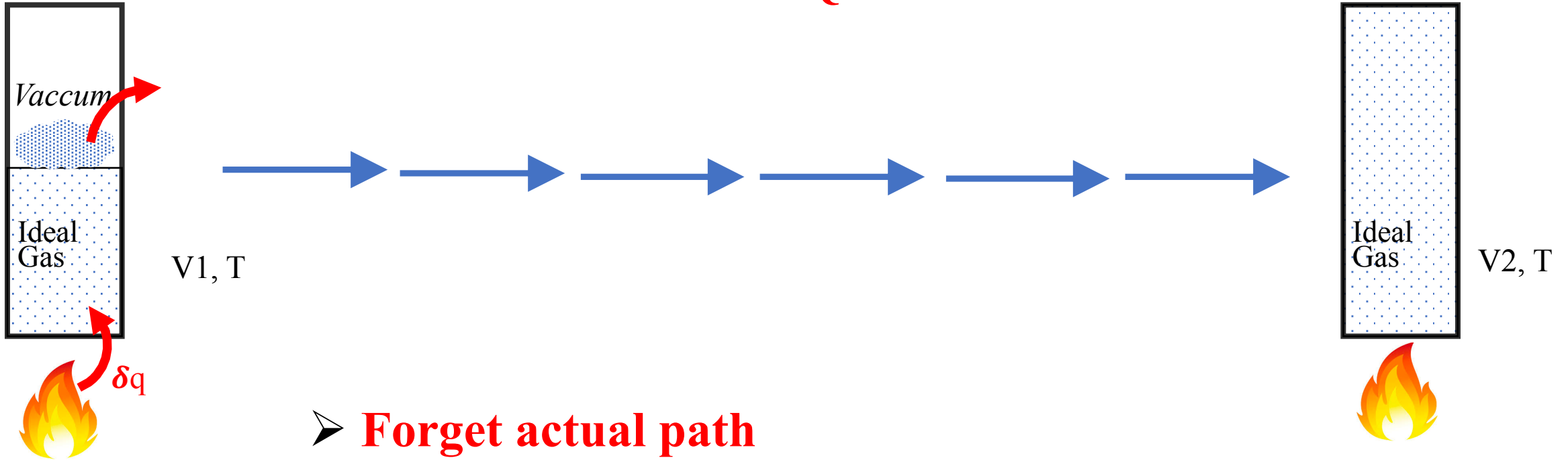
V_2, T

- GAS gone off from PV diagram
- After some time gas will settle down
- IDEAL Gas expanded freely ($T = \text{unchanged}$)

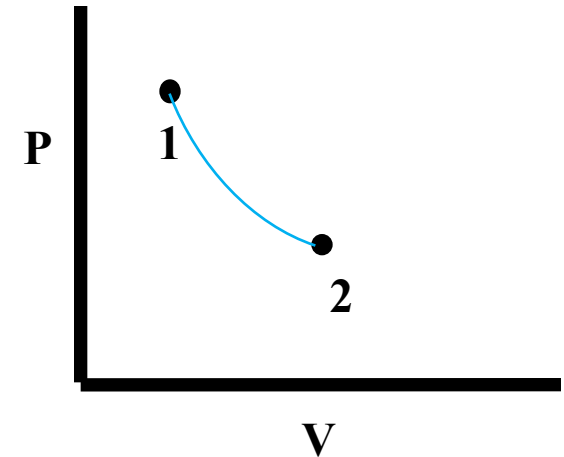


CALCULATION NEED EQUILIBRIUM PATH

CALCULATION NEED EQUILIBRIUM PATH

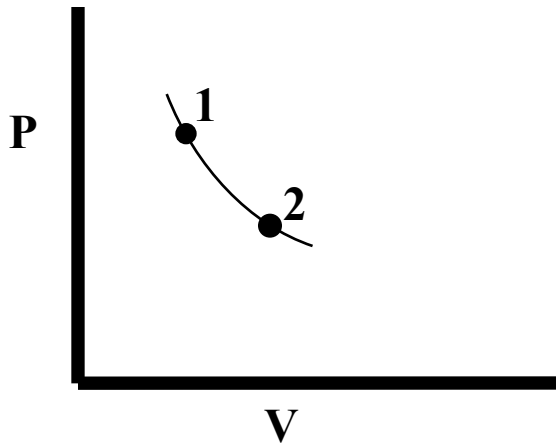


- **Forget actual path**
- Design a path which follows the eqm path and in the PV diagram.



REMINDER (LECTURE 5)

First Law and Isothermal expansion (Ideal gas)



$$\Delta U = q + w \quad (\text{No non-mechanical work})$$

Isothermal reversible Expansion

IDEAL GAS (Internal energy is a function of Temperature only)

$$\Delta U = 0$$

$$\Rightarrow 0 = q + w$$

$$\Rightarrow q = -w$$

$$\Rightarrow q = -[-nRT \ln(V_2/V_1)]$$

$$\Rightarrow q = nRT \ln(V_2/V_1)$$

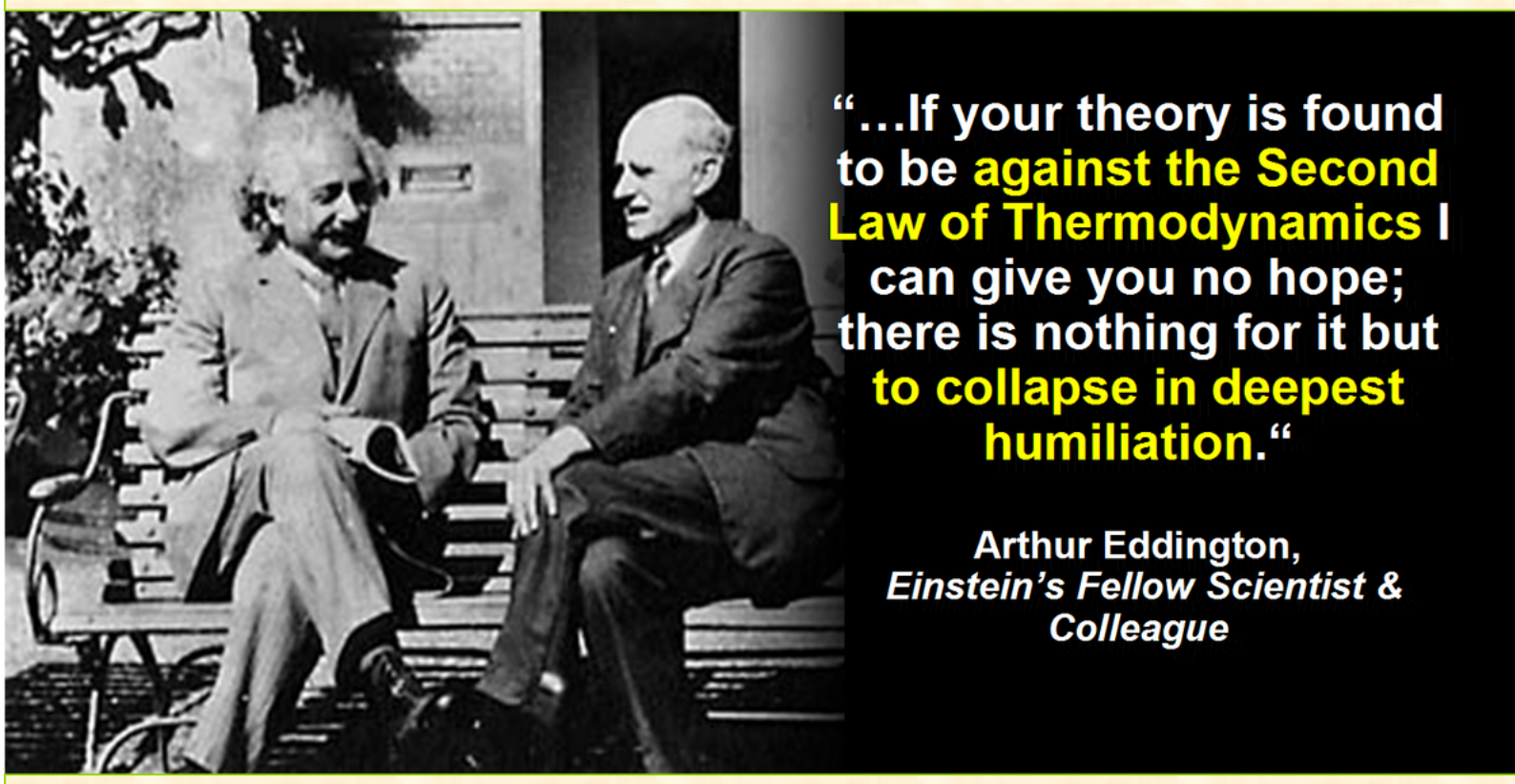
Makes sense, $q = +Ve$ (heat added)

$w = \text{Negative}$ (work is done by the gas)

$$\Delta S = \frac{Q}{T} = \frac{nRT \ln (V_2/V_1)}{T}$$

$$\Delta S = nR \ln (V_2/V_1) > 0$$

Conclusion: The way we computer the entropy change is not the way the process actually happens. (STATE FUNCTION)



“...If your theory is found to be **against the Second Law of Thermodynamics** I can give you no hope; there is nothing for it but **to collapse in deepest humiliation.**”

Arthur Eddington,
Einstein's Fellow Scientist & Colleague

1882- 1944

Physical insight

$$\Delta S = nR \ln(V_2/V_1) > 0$$
$$= (N/N_A)R \ln(V_2/V_1) > 0$$

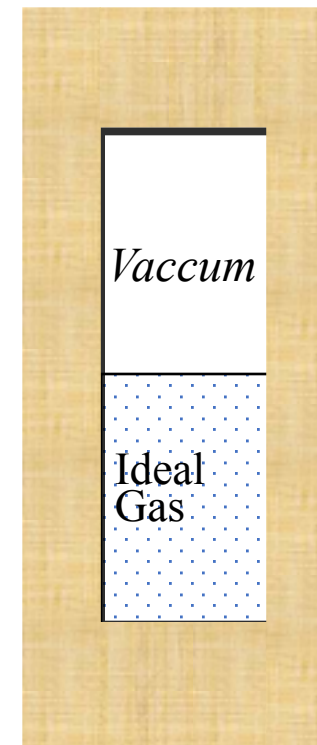
N = Number of gas particles

N_A = Avogadro's number

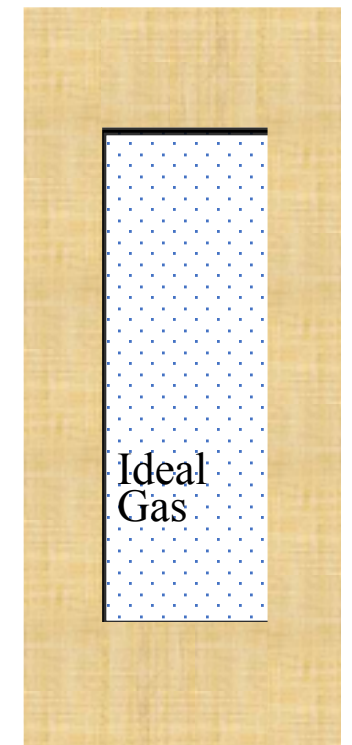
K_B = Boltzmann Constant

$$\text{Say, } V_2/V_1 = 2$$

$$\Delta S = N (R/N_A) \ln(2) > 0$$
$$= N K_B \ln 2$$



V_1, T



V_2, T

$$(V_2 = 2V_1)$$

$$\Delta S = K_B \ln 2^N$$

$$\Delta S = K_B \ln (2 \times 2 \times 2 \times 2 \dots 2^{\text{nth}})$$

