Module 2

Laws of Thermodynamics-Caratheodory's Formulation

Lecture 2.1

The Concept of Work

CONCEPT OF WORK

Momentary effort to bring about a change of state of a system : FORCE

TOTAL INTEGRATED EFFORT : WORK

SIGN CONVENTION ADOPTED BY IUPAC IN 1970 : <u>Work input</u> to a system <u>is +ve</u>

DEF. $$W' = \int_I^F -f''dx''$$

Work done on system

Gen. Force of surrounding

Change in coord. of surroundings

CONCEPT OF WORK

If condition of interaction is x′+x″ = Const.

$$W' = \int_I^F f''dx'$$

Further, if the process is a sequence of eqlbm. states (i.e. quasi-equilibrium),

$$f'' = f' \quad \& \quad W' = \int_I^F f'dx'$$

CONCEPT OF WORK

Isothermal Expansion of an ideal gas

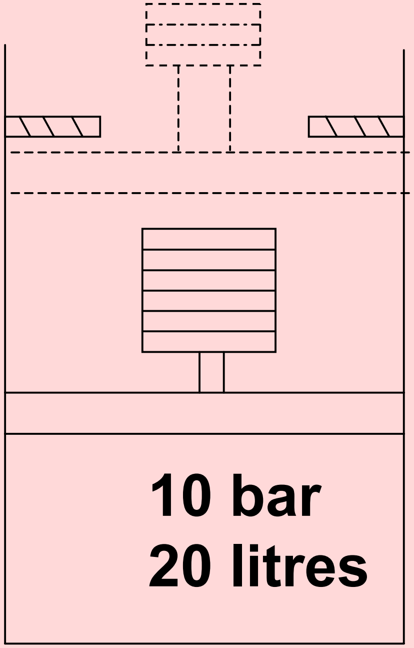
Final Press = 1 bar

(i) Sudden expansion 10 bar $\rightarrow$ 1 bar

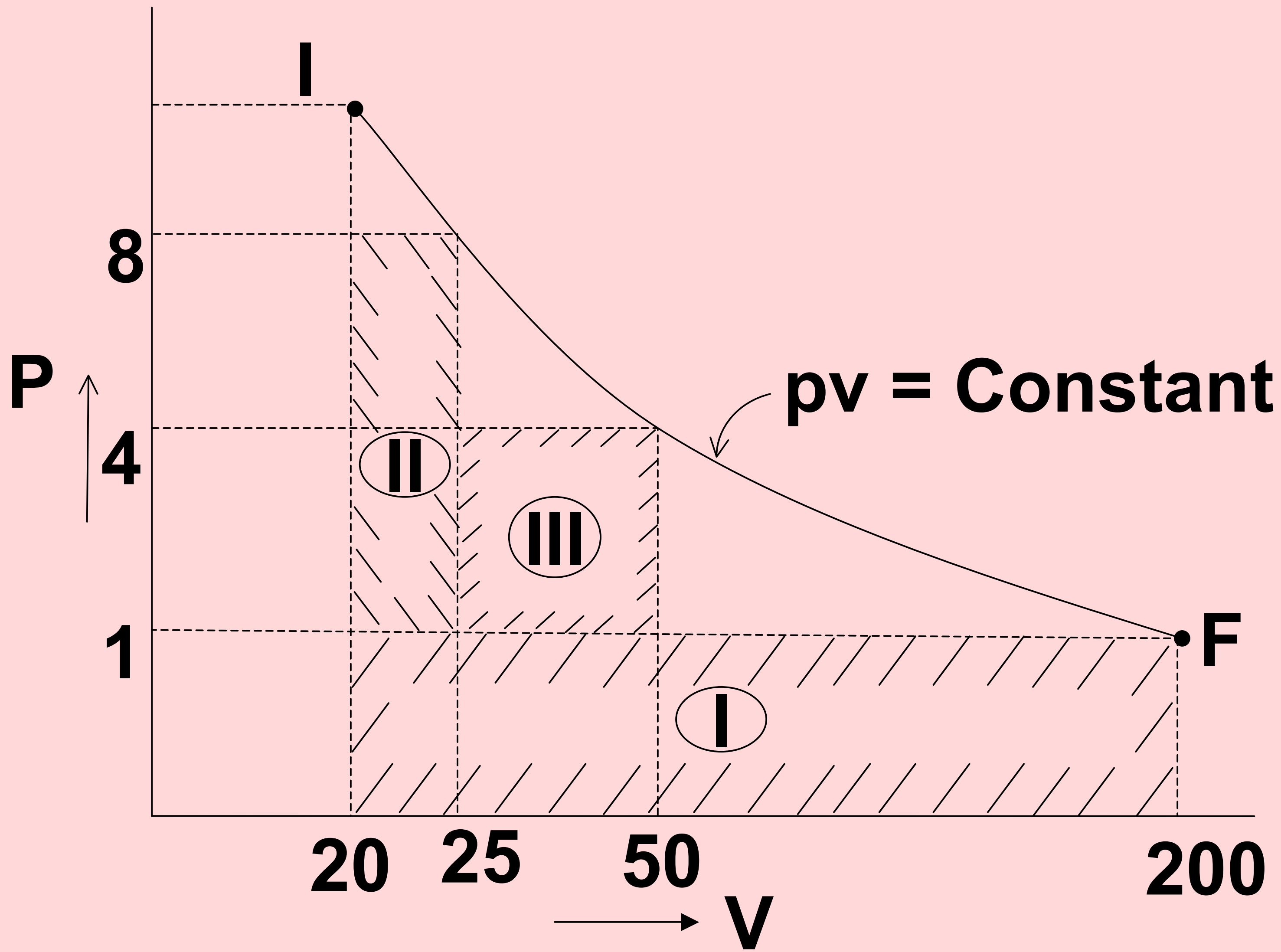
(ii) 10 $\rightarrow$ 8 $\rightarrow$ 1 bar

(iii) 10 $\rightarrow$ 8 $\rightarrow$ 4 $\rightarrow$ 1

(iv) Quasi-equilibrium



CONCEPT OF WORK



CONCEPT OF WORK

Work required for atomizing 1 kg of water isothermally?

$$\{\sigma = .07\frac{N}{m} \quad d \sim 60\mu\}$$

$$W'_{on} = \int_i^f \sigma dA = \sigma(A_f - A_i)$$

A_f ?

$$N.\frac{\pi}{6}(60\times10^{-6})^3 \times 1000 = 1kg \qquad N = 8.842\times10^9 \ drops$$

$$A_f = \pi(60\times10^{-6})^2 \times N = 100m^2$$

CONCEPT OF WORK

A_i ? **enters nozzle thro a pipe of 15mmϕ**

$$\frac{\pi}{4} d^2 .L.\rho = 1kg \qquad A_i = \pi dL$$

$$\frac{A_i}{1} = \frac{\pi dL}{\pi/4 d^2 L\rho} = \frac{4}{d\rho} = .267m^2$$

$$W' = .07(100 - .267)J = 6.98J$$

End of Lecture

Lecture 2.2

The First Law

FIRST LAW :-

Simplified Caratheodory's formulation

The amount of <u>work</u> required <u>for adiabatically changing</u> a system from an initial state I to a final state F <u>is always the same</u> independent of the path choosen, nature of interaction & any other circumstances.

It must be a measure of change in some property

$$E'_F - E'_I = \underbrace{W'_{ad}}_{\uparrow} = -\int_I^F f_i'' dx_i''$$

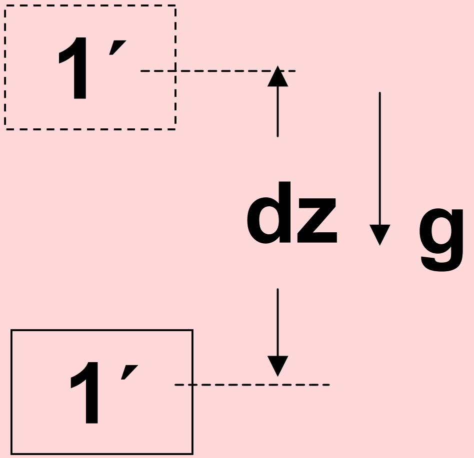
State fn.

fn. of states I & F only

CONCEPT OF ENERGY

Consistency of this definition of energy <u>with other 'sciences'</u>

- <u>Potential Energy</u>



Change in energy of object in process 1-1´

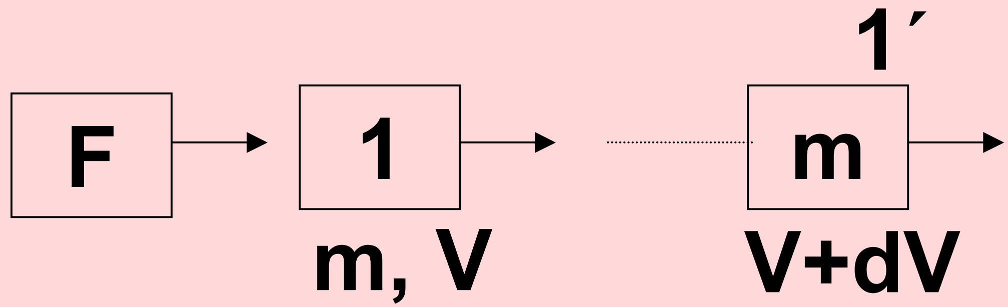
E´-E = adiabatic work done on object

= mg dz

or $\Delta E = mg \, . \, \Delta Z$ = P.E. Change.

Consistency of this definition of energy <u>with other ‘sciences’</u>

- <u>**Kinetic Energy**</u>



Change in energy of object in process 1-1´

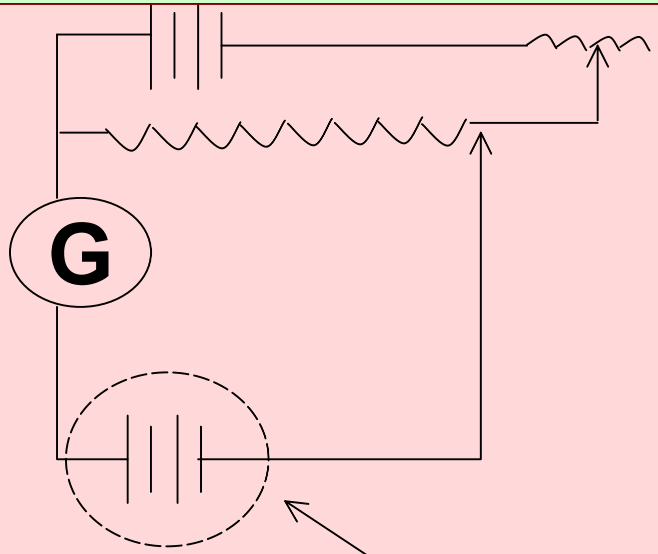
E´-E = adiabatic work done on object

$$= F \times dist = \left(m\frac{dV}{dt} \right)(Vdt) = mVdV = d\left(\frac{1}{2} mV^2 \right)$$

or ΔE = Δ.K.E

Consistency of this definition of energy <u>with other 'sciences'</u>

- **<u>Electrical Energy</u>**



Change in energy of object in process 1-1´

Object Q → Q + dQ

1 1´

E´-E = adiabatic work done on object = V. dQ

= V.I.dt.

= Electrical Energy

THE CONCEPT OF HEAT

HEAT : **Energy increase of an object in any process reduced by the work done upon it.**

$$Q = E_F - E_I - W_{on}$$

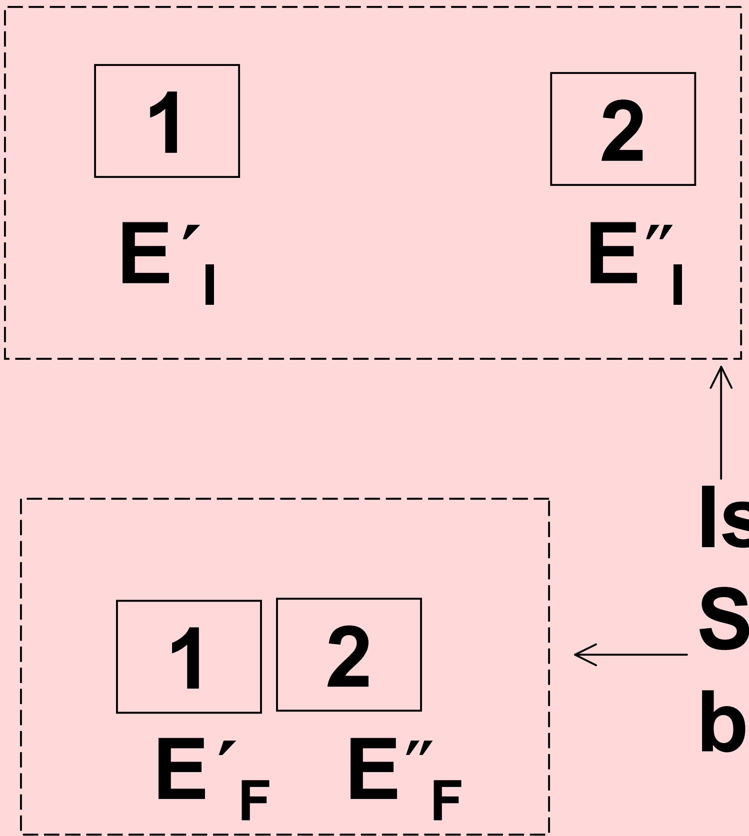
Consistency of this definition with other branches of science

Consistency of this definition of heat with our common idea of heat transfer between two objects

$E_I = E'_I + E''_I$

{For overall system}

$E_F = E'_F + E''_F$



Isolated System boundaries

Consistency of this definition of heat with our common idea of heat transfer between two objects

Since the overall system is isolated

$$E_I = E_F \quad \text{i.e.} \quad E'_I + E''_I = E'_F + E''_F$$

Re-arranging

$$(q''=)\ E''_F - E''_I = -\ (E'_F - E'_I) = (-q')$$

Since there is no work interaction, the quantity (q) indicates energy transfer in Thermal Interaction, commonly called "Heat Transfer".

Consistency of this definition of heat with our common idea of heat transfer between two objects

Above eq. clearly indicates that this energy transfer takes place from one object to another.

First Law

$$E_F - E_I = Q_{in} + W_{on}$$

Law of Conservation of Energy

If an object is taken through a sequence of processes which bring it back to the initial state

$$\sum Q_{in} + \sum W_{on} = 0 \qquad \sum Q_{in} = -\sum W_{on} = \sum W_{by}$$

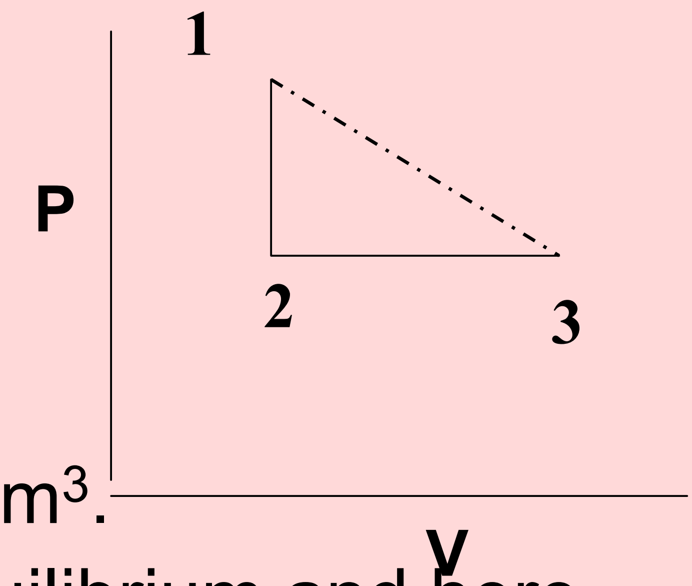
End of Lecture

Lecture 2.3

The First Law - Examples

THE FIRST LAW -- EXAMPLES

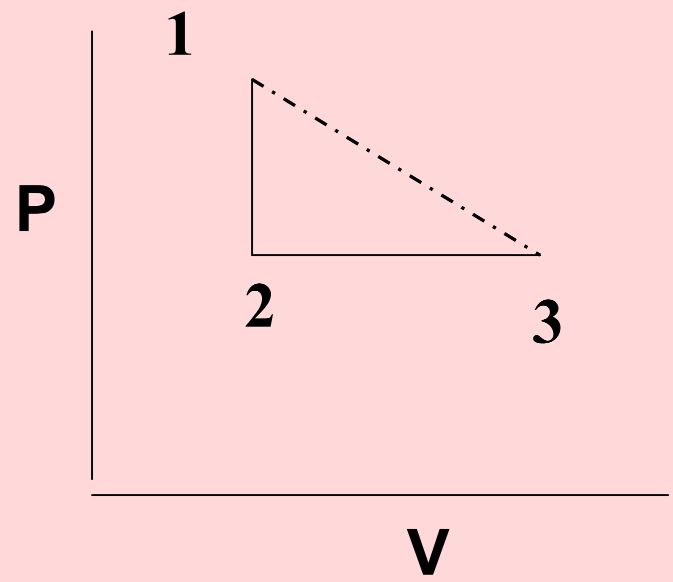
- cycle undergone by an ideal gas confined within a piston and cylinder. Processes 1-2 and 2-3 are quasi equilibrium processes with P_1=5 bar, V_1=.1 m^3; P_2=1 bar, V_3=0.2 m^3. Process 3-1 is not quasi equilibrium and here 30 kJ of work is done on the gas.



THE FIRST LAW -- EXAMPLES

- W_{12} =0; W_{23}=$(-10^5)(.2-.1)$
  W_{23} =-10kJ; W_{31}=30kJ

$$\sum W_{on} = -\sum Q_{in} =$$
$$-10+30=20kJ$$



Net Q_{in} = -20kJ

Net work input to the cycle
=> Refrigeration cycle

THE FIRST LAW --EXAMPLES

A Car battery is being charged by connecting to a charger at 15V.

During half an hour of charging process current drops linearly from 2 amp to 1 amp and the energy of the battery is increased by 35 kJ.

What is the heat transfer during the process?

THE FIRST LAW --EXAMPLES

$$W'_{on} = \int_i^f f'' \, dx' = (15V) \; (\Delta Q)$$

$$I = \frac{dQ}{dt}$$ **is varying during the process**

$$\therefore \Delta Q = \int_i^f dQ = \int_i^f I \; dt = \int_i^f \left(2 - \frac{t}{1800} \right) \; dt$$

$$= \left(2t - \frac{t^2}{3600} \right)_0^{1800} = 2700 \;\; Coulombs$$

THE FIRST LAW --EXAMPLES

$$\therefore W'_{on} = 15 \times 2700 J = 40.5 kJ$$

$$Q_{in} = E_F - E_I - W_{on}$$

$$= 35 - 40.5 = -5.5 kJ$$

$\therefore$ **Heat lost by the battery = 5.5 kJ**

THE FIRST LAW -- EXAMPLES

- Show that the Hess's Law is a direct consequence of the first Law.
- Using Hess's Law evaluate the heat effect of the reaction of incomplete combustion of solid C into CO.

  Given in the complete combustion of C 406 kJ/kmol of heat are evolved.

  While in the combustion of CO into CO_2 285 kJ/kmol of heat are evolved.

HESS'S Law

The amount of Heat evolved / absorbed in any chemical reaction occurring at a constant volume/ pressure is independent of any intermediate reactions and is determined only by the initial and final states of the reacting substances

End of Lecture

Lecture 2.4

The Second Law

THE SECOND LAW …… BACKGROUND

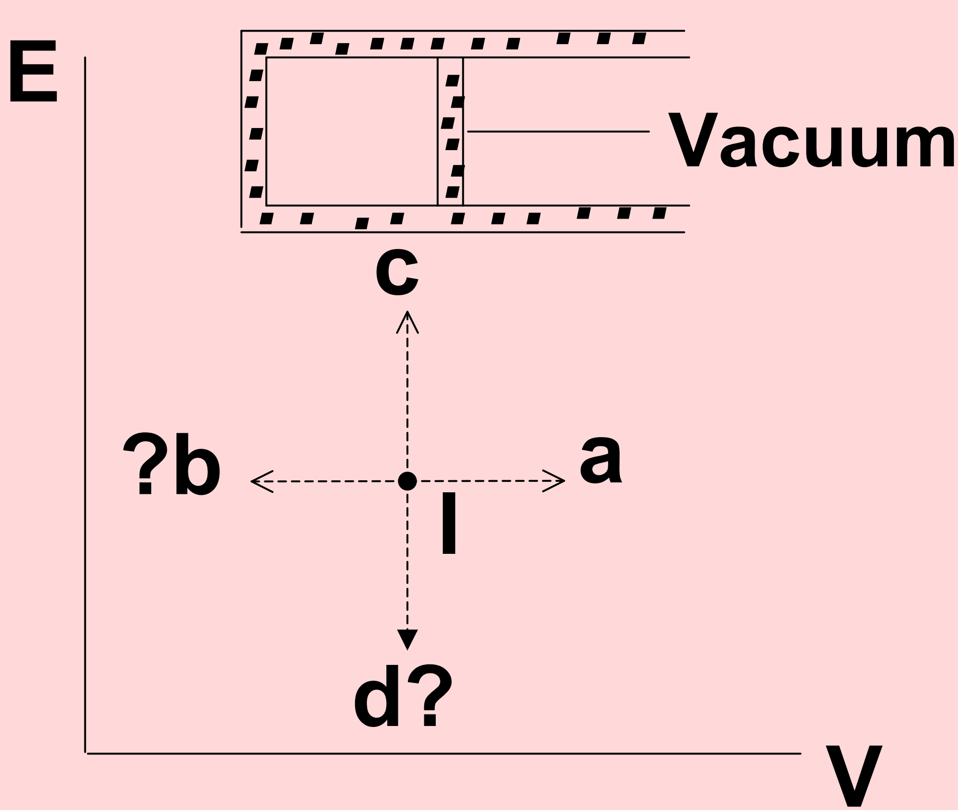
Accessibility of States

- What does 1st law tell us?

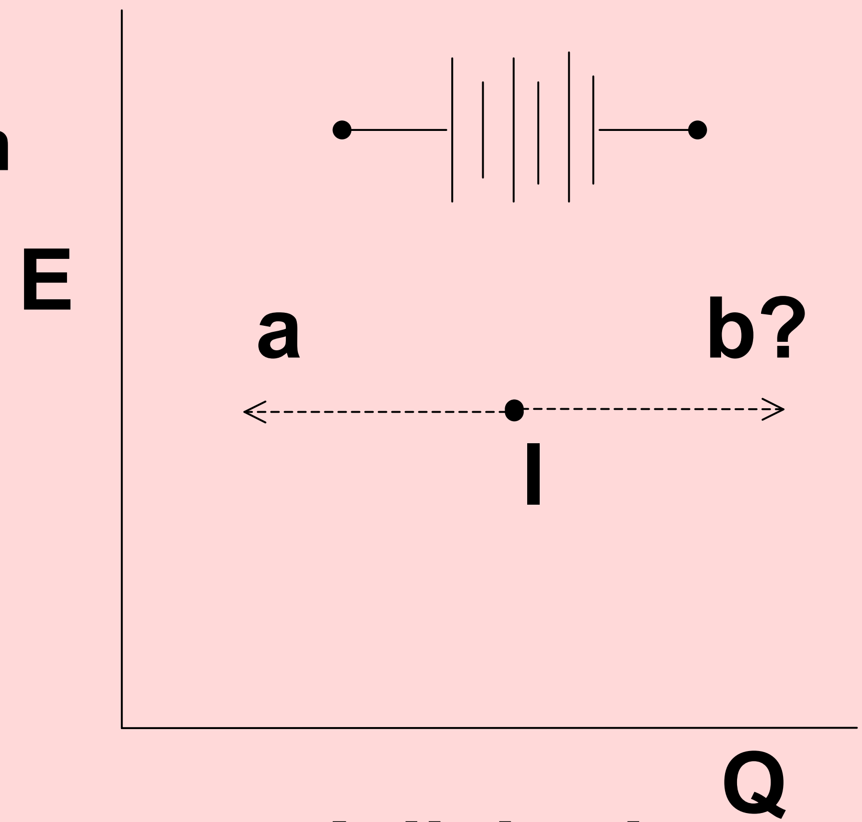
- Limitation of accessibility under adiabatic conditions.

If there are no constraints all states are accessible.

THE SECOND LAW …… BACKGROUND



Adiabatic interactions of a compressible fluid



Adiabatic interactions of a battery

What do we learn from these examples?

- **In the immediate neighbourhood of any state of an object there are other states that can not be reached form there by an adiabatic process.**

Further subdivision of the accessible states based on the nature of process

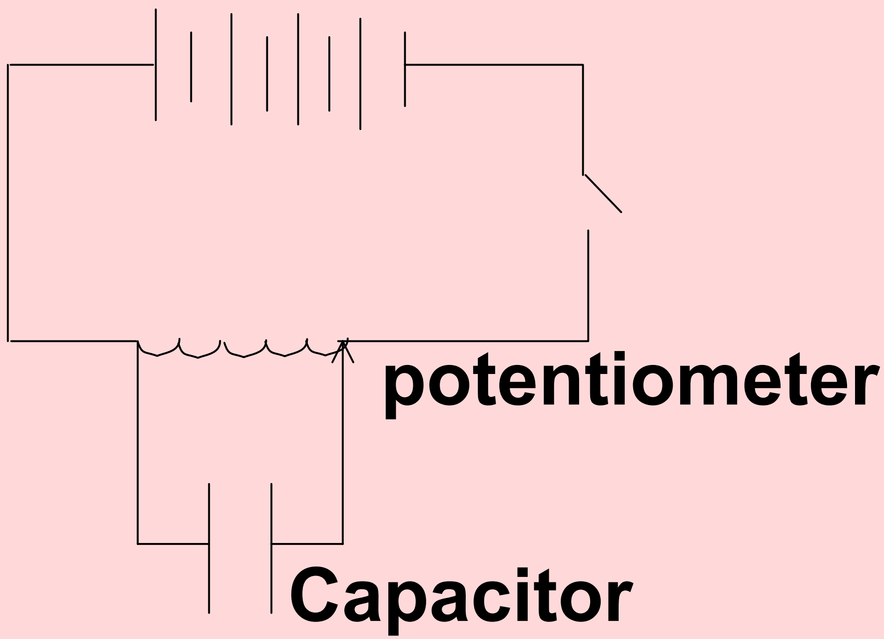
THE SECOND LAW …… BACKGROUND

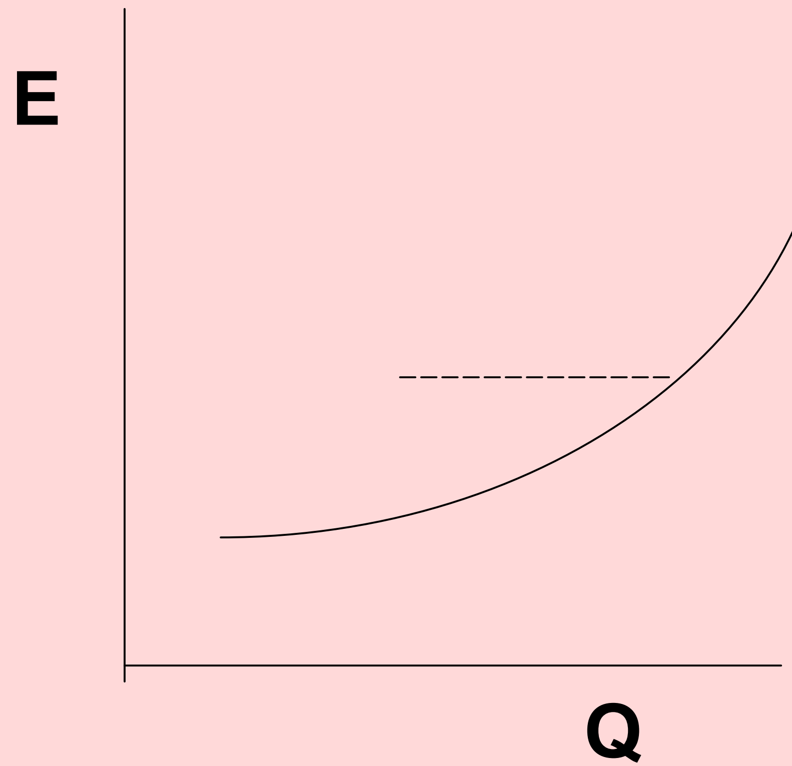
→ Reversible Process

An object is said to undergo a reversible process if, at any time during the process, both the object & the surroundings with which it interacts can be brought back to their initial states.

How to achieve it?

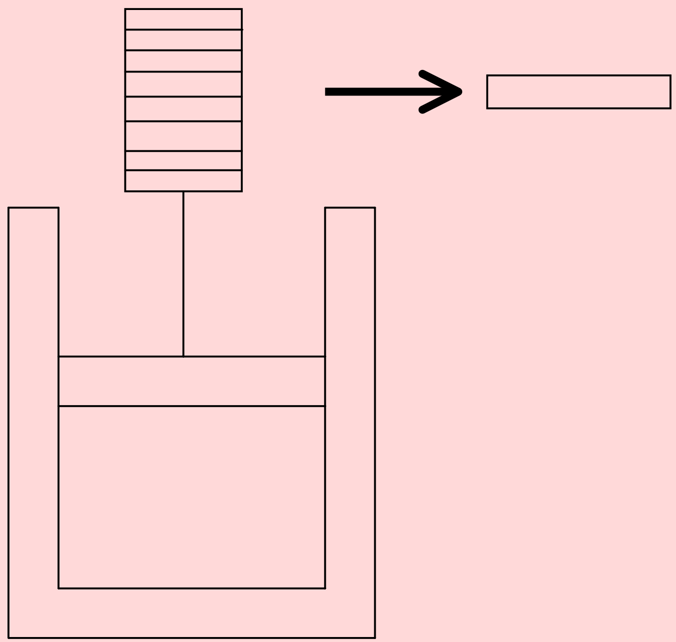
Reversible Processes



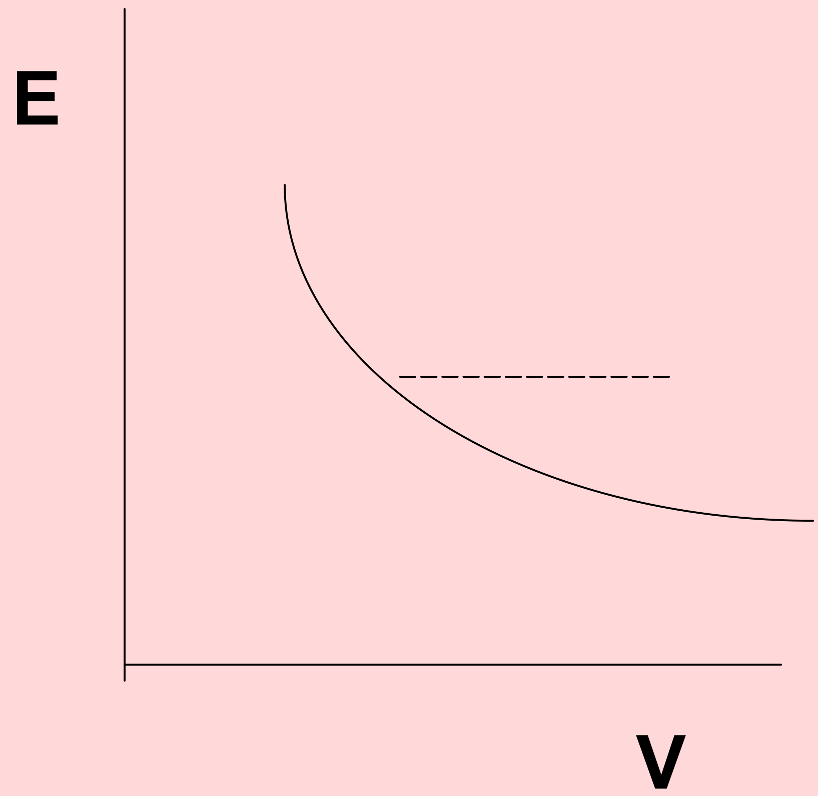


Reversible Charging of a Capacitor

Reversible Processes



Reversible adiabatic expansion of a Compressible Fluid



THE SECOND LAW

SECOND – LAW : CARTHEDORY'S FORMULATIONS

If we change the state of a system starting from an initial state I by adiabatic processes :

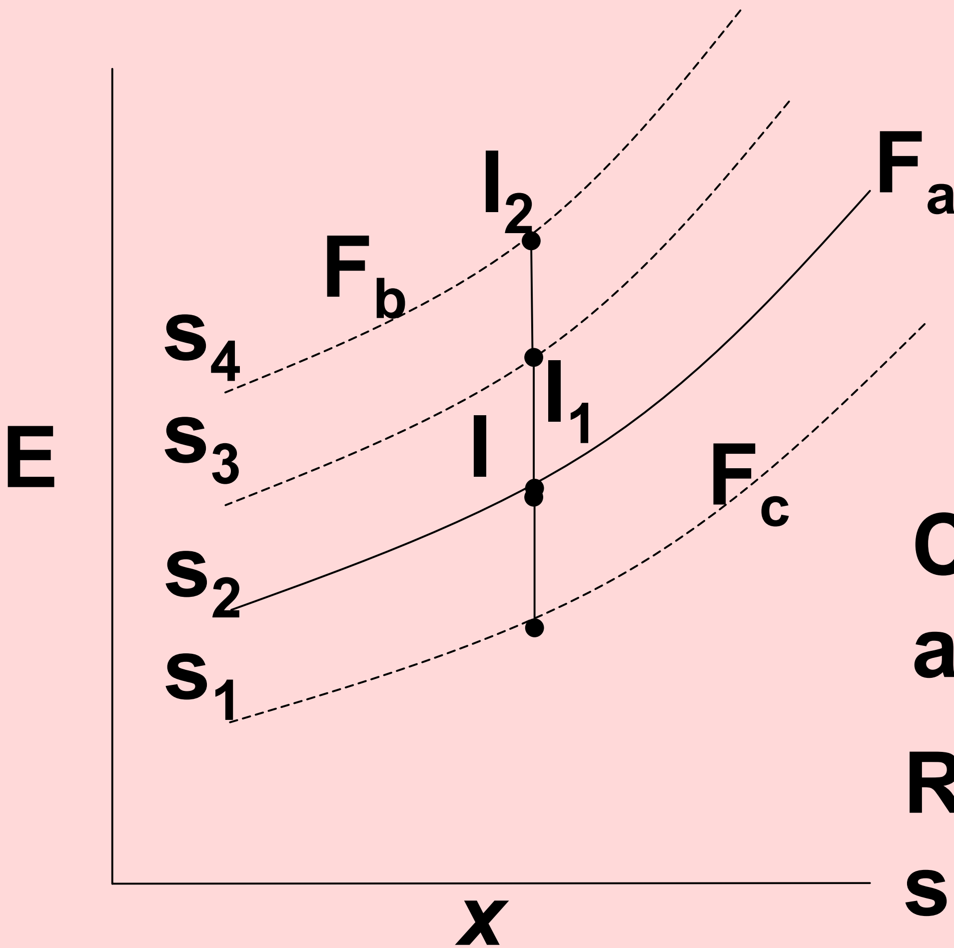
(a) There exist a set of states <u>F_a</u> that can be reached <u>reversibly</u>,

(b) There is also a set of states <u>F_b</u> that can be reached only <u>irreversibly</u>,

(c) There is a set of states <u>F_c</u> that <u>cannot be reached adiabatically</u> at all.

THE SECOND LAW

- The Implications of limited accessibility of some states



Simple Elect. System

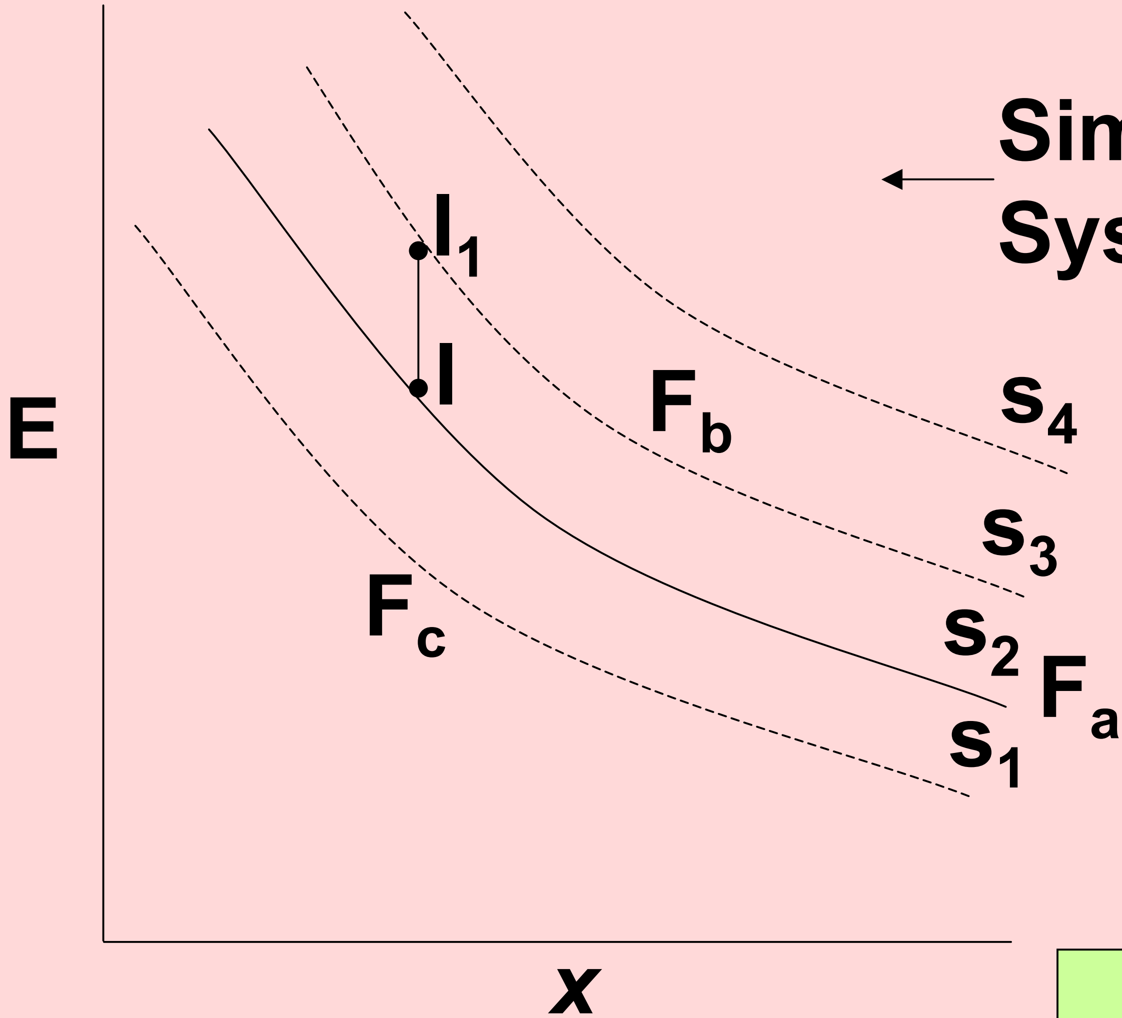
$x \equiv$ Charge

$E \equiv$ Energy

Can various reversible adiabats intersect?

Relationship between s_1, s_2, s_3, s_4?

THE SECOND LAW



Simple Compressible System

x ≡ Volume

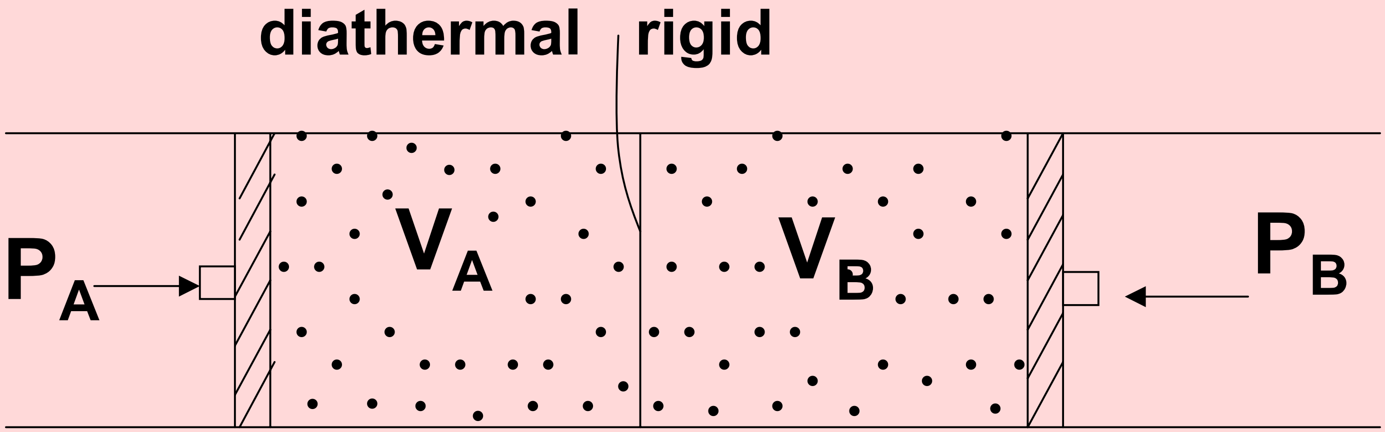
E ≡ Energy

$S \equiv Entropy$

E= E(S,x)

THE SECOND LAW

for a system defined by 3 - properties



State defined by E, V_A , V_B

Surfaces of constant empirical entropy

$$E = E(S, x_i)$$

What is Entropy?

- Equality of entropy at two states implies mutual accessibility of these states through reversible adiabatic processes
- Its relationship with other properties ?

End of Lecture

Lecture 2.5

The Second Law
…contd

THE SECOND LAW

SECOND – LAW : CARTHEDORY'S FORMULATION

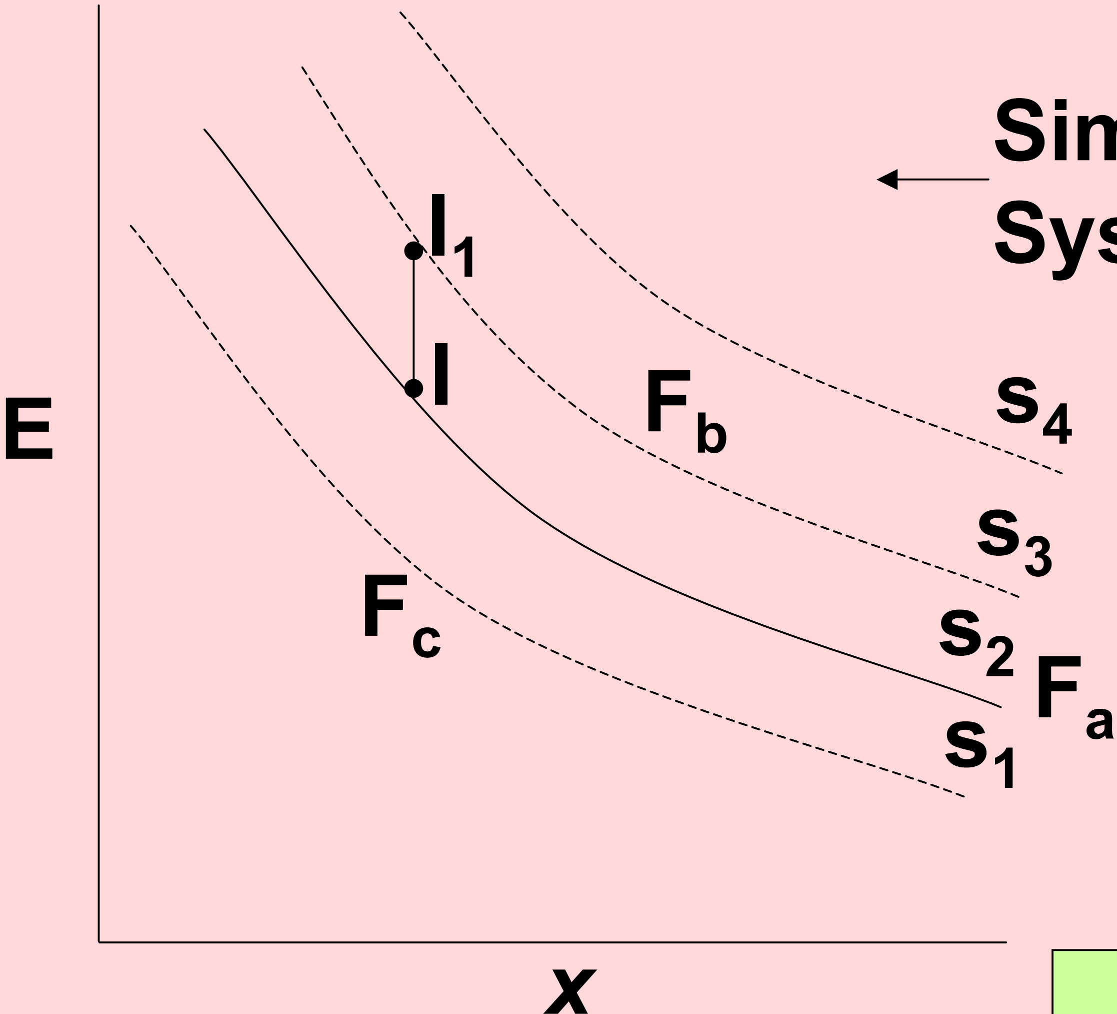
If we change the state of a system starting from an initial state I by adiabatic processes :

(a) There exist a set of states $\underline{F_a}$ that can be reached reversibly,

(b) There is also a set of states $\underline{F_b}$ that can be reached only irreversibly,

(c) There is a set of states $\underline{F_c}$ that cannot be reached adiabatically at all.

THE SECOND LAW



$x \equiv$ Volume

$E \equiv$ Energy

$S \equiv Entropy$

E= E(S,x)

What is Entropy?

- Equality of entropy at two states implies mutual accessibility of these states through reversible adiabatic processes
- Its relationship with other properties ?

…..understanding entropy

In general, $E = E(S, x_i)$

In the absence of thermal interaction $E = E(x_i)$

Can S be a generalised coordinate for thermal interaction ?

$\therefore$ Change in E between neighbouring states

$$dE = \left(\frac{\partial E}{\partial S}\right)_{x_i} dS + \sum_j \left(\frac{\partial E}{\partial x_j}\right)_{\substack{s, x_i \\ i \neq j}} dx_j$$

.....understanding entropy

First Law $$\Delta Q = \Delta E - \Delta W$$

For an adiabatic process; $\Delta Q = 0; \quad \Delta E = \Delta W$

For reversible process, $\Delta W = \sum_j f_j \Delta x_j$

For a reversible adiabatic process, S= const

therefore, since E= E(S,x_j) it follows :

$$\Delta E = \sum_j \left(\frac{\partial E}{\partial x_j} \right)_{s, x_{i \atop i \neq j}} \Delta x_j = \Delta W = \sum_j f_j \Delta x_j$$

…..understanding entropy

Since dx_j´s are arbitrary, this equation implies

$$f_j = \left(\frac{\partial E}{\partial x_j}\right)_{S,\, x_i,\, i \neq j}$$

Valid for all processes

Now, considering any arbitrary reversible process

$$\Delta Q = \Delta E - \Delta W$$

$$= \left\{ \left(\frac{\partial E}{\partial S}\right)_{x_i} \Delta S + \sum_j \left(\frac{\partial E}{\partial x_j}\right)_{S,\, x_i\ i \neq j} \Delta x_j \right\} - \sum_j f_j\, \Delta x_j$$

…..understanding entropy

$$\Delta Q = \left(\frac{\partial E}{\partial S}\right)_{x_i} \Delta S = \theta \Delta S$$

where

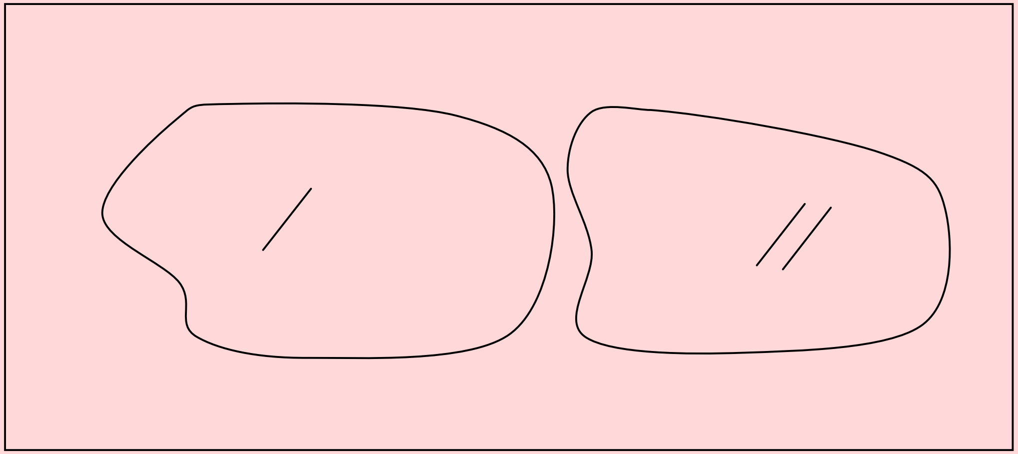
$$\theta = \left(\frac{\partial E}{\partial S}\right)_{x_i}$$

$$\therefore \Delta S = \frac{\Delta Q_{rev}}{\theta}$$

Physical significance of θ

.....understanding entropy

Consider an isolated system consisting of two objects undergoing ONLY thermal interaction



Clearly $E' + E'' = Const$ $\Delta E' + \Delta E'' = 0$

Since there is no work transfer from the first law it follows: $\Delta E = \Delta Q$

…..understanding entropy

Also $$\Delta E' = \left(\frac{\partial E'}{\partial S'}\right)_{x_i} \Delta S' \quad = \theta' \Delta S'$$

Similarly $$\Delta E'' = \theta'' \Delta S''$$

$$\therefore \quad \Delta S = \Delta S' + \Delta S'' = \frac{\Delta E'}{\theta'} + \frac{\Delta E''}{\theta''} = \left(\frac{1}{\theta'} - \frac{1}{\theta''}\right) dE'$$

…..understanding entropy

For Reversible change of states

$$\Delta S = 0, \quad \Rightarrow \quad \theta' = \theta''$$

Irreversible change

$$\Delta S > 0 \quad \Rightarrow \quad \theta' < \theta'', \quad \Delta E' > 0$$

$$\theta' > \theta'', \quad \Delta E' < 0$$

i.e. since here ΔE=ΔQ, this implies <u>heat flows to an object with smaller value of θ</u>. < c.f. definition of general force >

…..understanding entropy

Comparison with empirical Temperature

$$\theta = f(T)$$

Simplest Case : $\theta \equiv T$

$\therefore$ **In a reversible process** $\boxed{\Delta S = \dfrac{\Delta Q}{T}}$

T should be absolute temperature !

End of Lecture