

TODAY

1. Concept of **STATE** of a system
2. **State** functions (U,V, T, p...) vs. **path** functions (q, w)
3. **Changes** in state functions are *independent* of path
4. **Reversibility:**
Reversible paths are key to life processes and the economy, *i.e.*,

the main REASON why you are studying thermodynamics

Concept of State of a System:

If a system is at equilibrium (properties do not change measurably over time), the **properties define the state**.

state variable \equiv state function \equiv state property

Examples: U, V, T, p, C, concentrations, S, H*, G* .
(energy, volume, temperature, pressure, heat capacity, concentrations, entropy, enthalpy, and Gibbs energy)

(* enthalpy and Gibbs energy are human-defined for convenience)

but q and w are NOT state functions (of the system).

(Recall, they are two types of energy observed in the surroundings during a change of state of the system.)

Changes in state variables (functions), e.g.,
 ΔU , ΔH , Δp , ΔT , ΔV , ...

depend only on the initial and final states

NOT on path, i.e., the manner in which the system gets from state 1 to state 2.

In contrast, recall that q and w do depend on the path.

How many variables required to specify a state?

Typically, NATURE is such that any state of any system is determined completely by **any 3 state variables.**

(in the absence of external fields)

U depends on p , V , T , n , C ; but all of those depend on U
but if any 3 are set, ALL the others are set too.

Thus: We may choose to express U as a function of any 3 variables, e.g., $U = U(p, V, T) = U(n, T, V) = U(n, p, V) = U(C, T, V)$...
or $V = V(U, p, V) = V(n, T, p)$, etc.

Recall, if we compare:

water heated from 0 to 100 °C with a **hot plate** ($q=+$, $w=0$)
with water heated from 0 to 100 °C by **stirring** ($q=0$, $w=+$)

You will not be able to tell which is which.

We believe that molecules have no memory!

Some restricted paths and their names

Constant temperature \equiv isothermal : $\Delta T = 0$

Constant Pressure \equiv isobaric : $\Delta p = 0$ (usually say “constant pressure”)

Constant Volume \equiv isochoric : $\Delta V = 0$ (usually say “constant volume”)

Thermally insulated \equiv adiabatic : $q = 0$

Cyclic (final state = initial state) $\Delta(\text{any STATE variable} = 0)$
(but q and w are not necessarily $=0$)

EACH of the above may be spontaneous (*irreversible*)
or carried out very nearly at equilibrium (“*reversibly*”)

Reversible paths are super SPECIAL in thermodynamics.

What is reversible? Why is this important?

Just what is so Special?

Characteristics

virtual equilibrium at all times

forces are virtually balanced

Infinitesimal change in external force changes direction of process.

$\Delta S_{\text{univ}} = 0$ during a reversible process

Consequences

Measurements and calculations are possible.

Maximum possible work is done **by** system if the process is naturally **spontaneous** i.e., w is **most** negative (least positive) possible and q is **least** negative (most positive) possible

Minimum possible work is required to **force** a process that is naturally **non-spontaneous**

In Chapter 3:

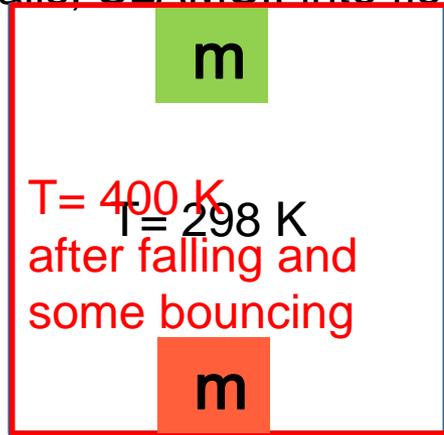
Entropy change of **system** : **$\Delta S = q_{\text{rev}}/T$**

Because a tiny + or - change will make the reaction spontaneous in either the forward or backward direction.
[Think LeChatelier!]

Contrasting irreversible and reversible

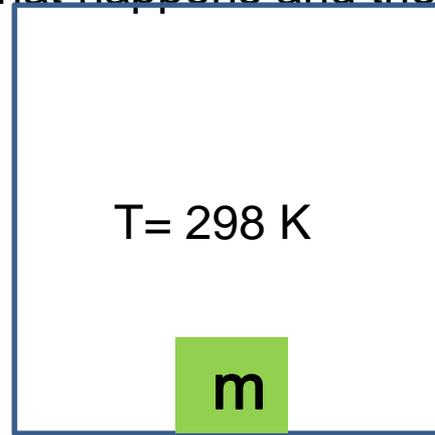
Consider the process of a falling object of mass = m , with $T = 298\text{ K}$ before and after, with **surroundings at $T = 298\text{ K}$. No insulation.**

Mass falls, SLAMS!! into floor. Describe what happens and the new state.



State 1

cooling
→



State 2

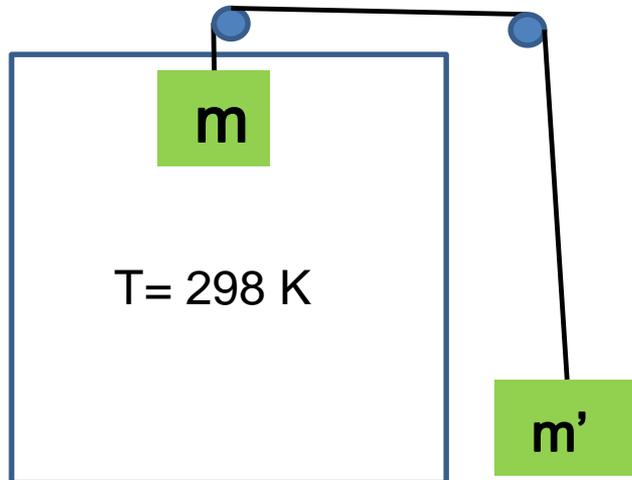
Path 1,

$$\Delta U = ? -mgh$$

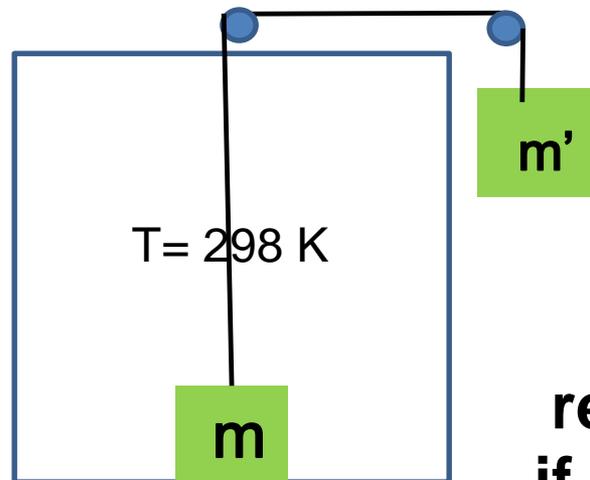
$$w = ? \quad 0$$

$$q = ? \quad -mgh$$

irreversible



State 1



State 2

Path 2,

$$\Delta U = ? -mgh$$

$$q = ? \quad 0$$

$$w = ? \quad -mgh$$

reversible
if m' is almost = m

NOW, find a **reversible** path