

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 REASON for 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 to be defined*)

but q and w are **NOT** state functions.

(Recall, they are two different types of energy exchanged between system and 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.

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 SPECIAL in thermodynamics.

What is reversible? Why is this important?

Reversible Paths Are Special

Characteristics

virtual equilibrium at all times

forces are virtually balanced

Infinitesimal change in external force changes direction of 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**

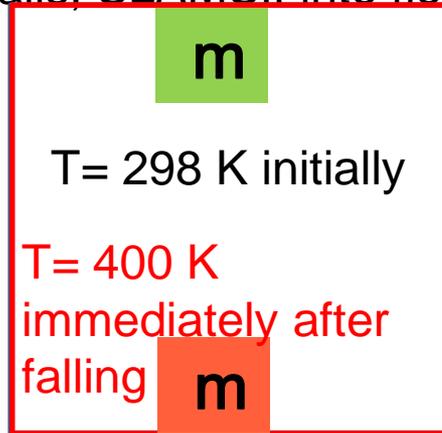
In Chapter 3

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

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

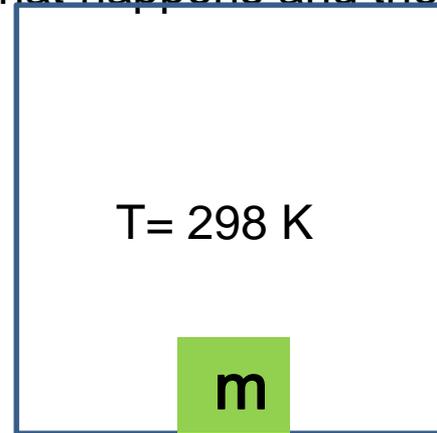
Consider the process of a falling object of mass = m , with $T = 298\text{ K}$ before and after, with surroundings at $T = 298\text{ K}$. No insulation.

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



State 1

cooling
→



State 2

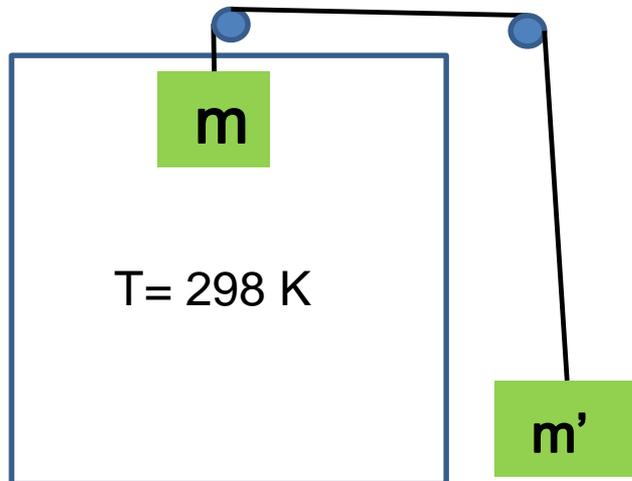
Path 1,

$$\Delta U = ? -mgh$$

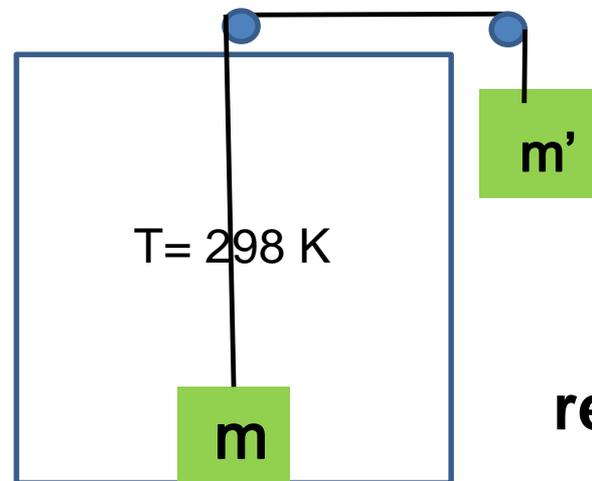
$$w = ? 0$$

$$q = ? -mgh$$

irreversible



State 1



State 2

Path 2,

$$\Delta U = ? -mgh$$

$$q = ? 0$$

$$w = ? -mgh$$

reversible

Find a **reversible** path

Spontaneous reactions can be harnessed to produce **“useful work”**
(also called non-pv work)

If not harnessed the only work is $w_{pv} = -p_{ext} \Delta V = -(1 \text{ bar}) \Delta V = \text{small}$

Consider burning gasoline: ΔU is large and negative

Unharnessed: $\Delta U = q + w$ so energy given off mostly as heat
(very exothermic), a waste unless heat is what you want.

This is totally irreversible ($H_2O + CO_2$ don't spontaneously make gasoline)

Harnessed: by enclosing the explosion in a cylinder and connecting
the piston to a crankshaft to turn the wheels so that the very high p pushes
against an opposing pressure that is just a little smaller **(nearly reversible)**

Now ΔU (almost) = $q_{rev} + w_{pv} + (w_{nonpv})_{rev}$, where
 $(w_{nonpv})_{rev}$ is large negative and q_{rev} is therefore a much smaller negative
Most of the large negative ΔU is useful work instead of heat.

The biochemical reactions in living systems are carried out in nearly reversible manner. Almost all the energy becomes useful work.
(it is not all ΔU . A large positive entropy change can give useful work.)