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.,***

a main REASON why you are studying thermodyamics

Concept of **State** of a System:

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

synonyms:
state property ≡ state function ≡ state variable
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 state functions,** 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., NOT on 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*.

Recall, if we compare:

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

We cannot tell which is which.

We believe that molecules have no memory!

How many variables required to specify a state?

Typically , NATURE is such that <u>any</u> state of <u>any</u> system is determined completely by <u>any 3 state variables.</u>
(in the absence of large external forces)
U depends on p, V, T, n, C; but all of those depend on U
but if <u>*any*</u> 3 are set, ALL the others are set too.

Thus: We may <u>choose</u> 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.

<u>This is possible by Equations of State</u>

example, ideal gas: $pV = nRT$

n = mols, p = pressure, V = volume, T = absolute temp.

R = "gas constant" = 8.3145 J mol^{-1} K-1

= 0.08145 L bar mol^{-1} K-1

=0.0821 L atm mol^{-1} K-1

$$\text{Note that } V = \frac{nRT}{p} = V(n,T,p),$$

$$p = \frac{nRT}{V} = p(n,T,V),$$

$$n = \frac{pV}{RT} = n(T,p,V)$$

Also, recall that $U=(3/2)nRT$.

Therefore: $V= nRT/p = (2/3)U/p$

<u>Some **restricted paths** and their names</u>

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 :** $\mathbf{q = 0}$

Cyclic (final state = initial state) **Δ(any STATE variable = 0)**
(but q and w are not necessarily =0)

EACH of the above may be spontaneous **(happen FAST, *irreversible*)** or carried out **very SLOWLY**, *nearly* at **<u>equilibrium</u>** ***("reversibly")***

<u>Reversible</u> paths are super <u>SPECIAL</u> in thermodynamics.
What is reversible? Why is this important?

Just what is so Special?

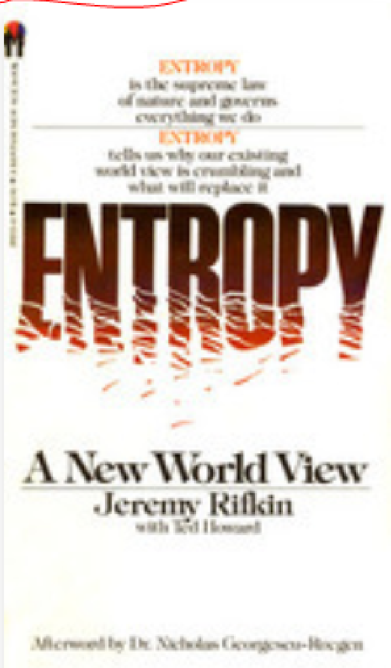
Characteristics	**Consequences**
virtual equilibrium at all times	Measurements and calculations are possible.
forces are virtually balanced	***Maximum possible work*** is done **by** system if the process is naturally **spontaneous** i.e., w is **most** negative (least positive) possible and q is **least** negative (most positive) possible
Infinitesimal change in external force *changes direction* of process.	***Minimum possible work*** is required to **force** a process that is naturally **non-spontaneous**

In Chapter 3:

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

ΔS_{univ} = 0 during a reversible process

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



Want to Read

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Entropy

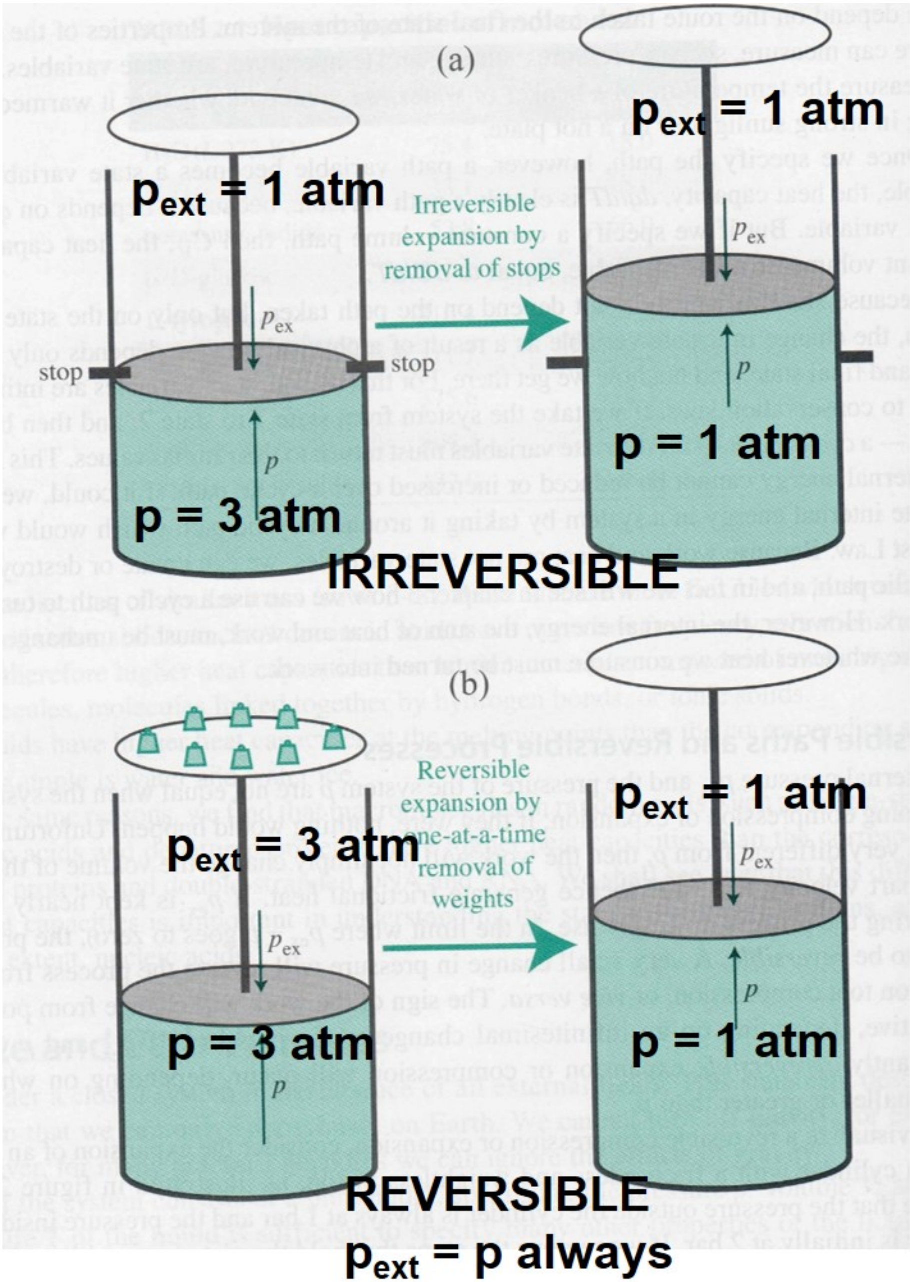
by Jeremy Rifkin, Ted Howard

3.77 · Rating details · 249 Ratings · 20 Reviews

Non-fiction book by Jeremy Rifkin and Ted Howard, with an Afterword by Nicholas Georgescu-Roegen.

In the book the authors seek to analyse the world's economic and social structures by using the second law of thermodynamics, that is, the law of entropy. The authors argue that humanity is wasting resources at an increasing rate, and that will lead to the destruction of our c ...more

Fig. 11
Comparison of reversible vs. irreversible expansions of gas in cylinder.



IRREVERSIBLE→

p = changes 3 atm to 1 atm

but p_{ext} = 1 atm and *constant*

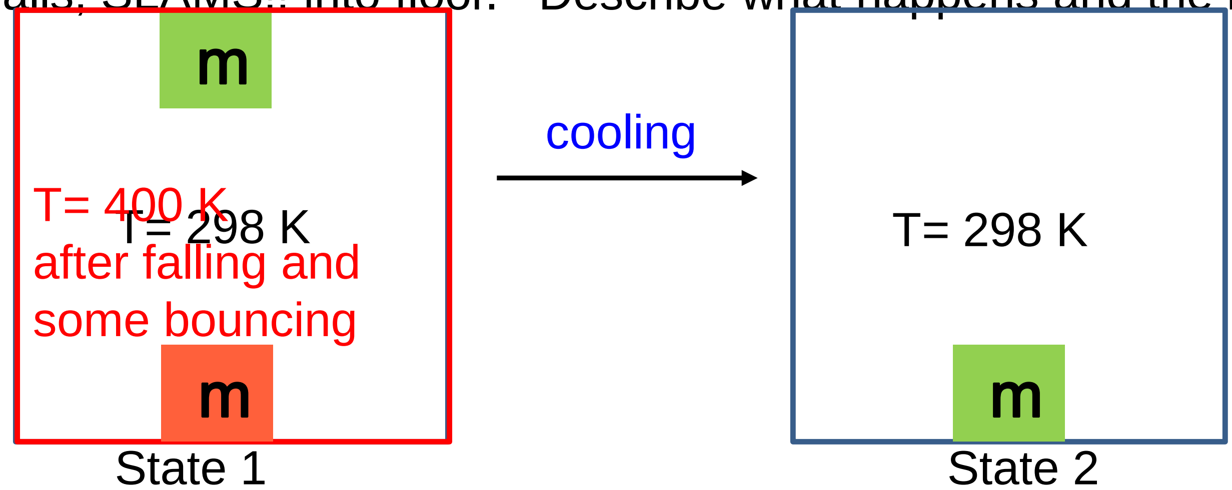
REVERSIBLE→

p_{ext} = p during entire expansion
by removing grains of sand from piston.
Adding one grain of sand reverses direction

Contrasting irreversible and reversible: part 2: Falliing Mass

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

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



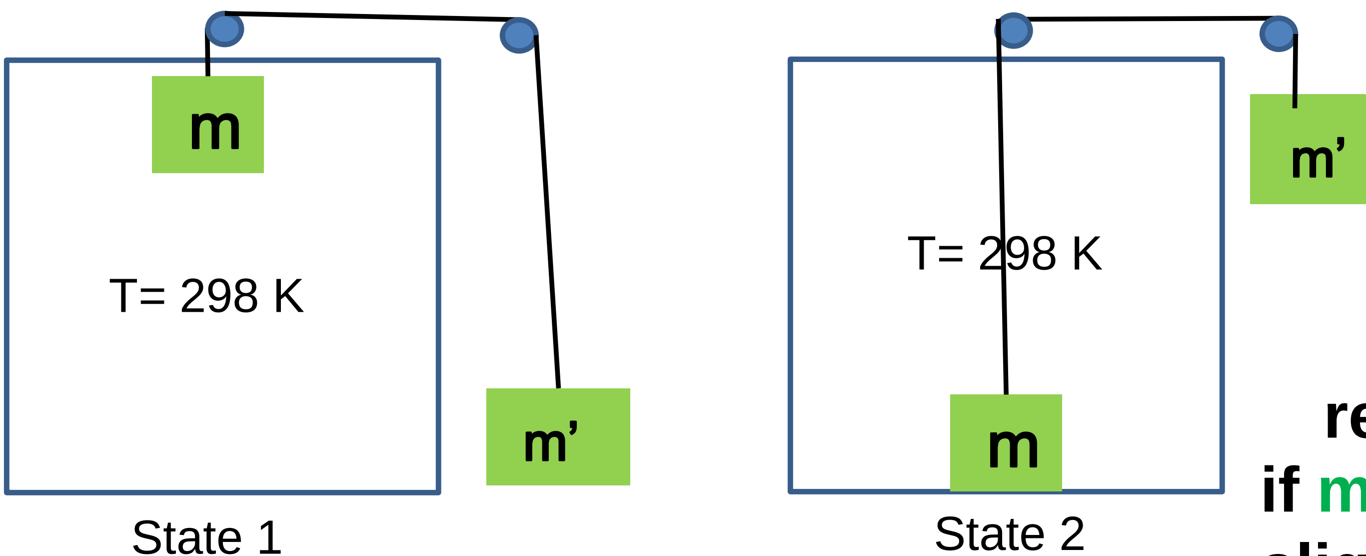
Path 1,

ΔU = ? -mgh

w = ? 0

q = ? -mgh

irreversible



Path 2,

ΔU = ?-mgh

q = ? 0

w= ? -mgh

reversible if m' is very slightly less than m

NOW, find a **reversible** path