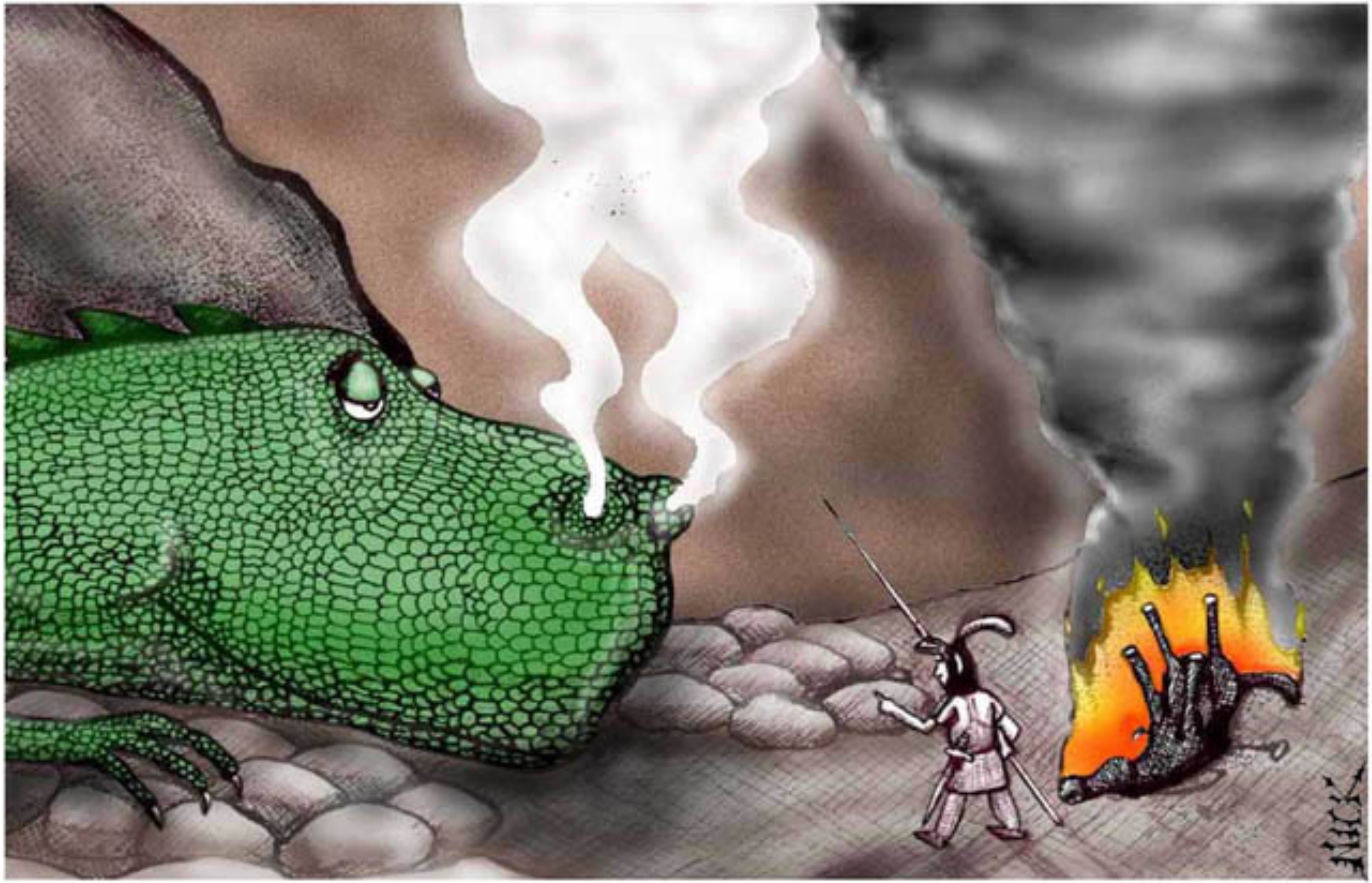


"I suppose you think that's funny..."

Life is a *dynamic* process.

- It involvs a constant change
- There are several fundamental molecular processes of change

Synthesis $$A + B \Rightarrow C$$

Lysis $$P \Rightarrow Q + R$$

Biochemistry

Transport $$X_{environment_1} \Rightarrow X_{environment_2}$$

Association/disassociation $$A + B \Leftrightarrow AB$$

Biophysics

Thermodynamics

Greek: *therme* : heat
dynamis: power

The science of Energy

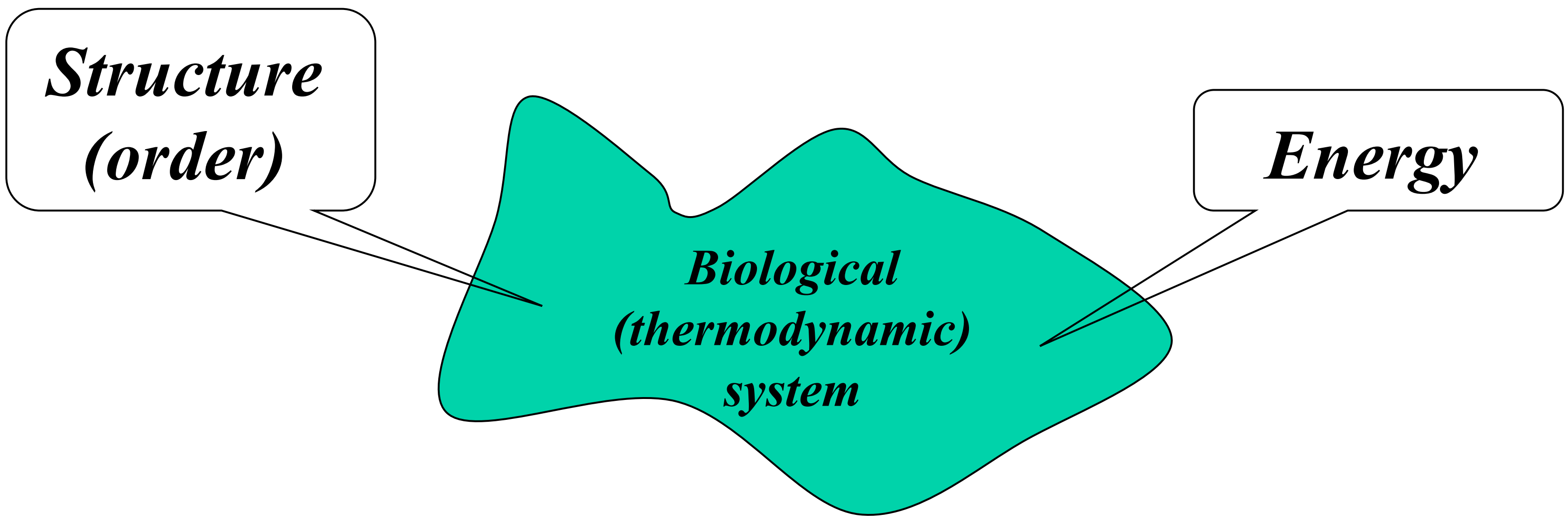
- forms and transformations of energy
- the relation between energy and matter

- *The laws of thermodynamics **describe states**.*
- *Predicts **the energetic limitations** on state changes of systems of molecules.*
- *Predicts **the relative molecular populations** of energetically accessible states.*
- *Predicts **the direction of the reactions** that link these states.*

Does NOT predict rate!

Thermodynmics involves defining the system

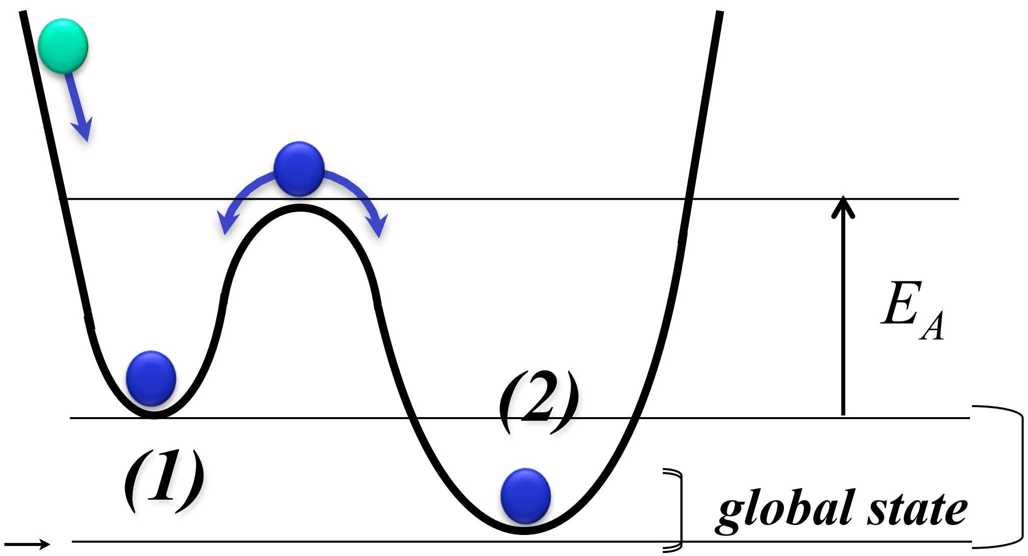
A system is a set of individual *components* that are linked by *relationships* of some kind to form a whole.



Biological (Thermodynamic) System

***Kinetics*:**

How fast the system can reach equilibrium between state (1) and state (2)?



$$\sum \vec{F} = 0$$

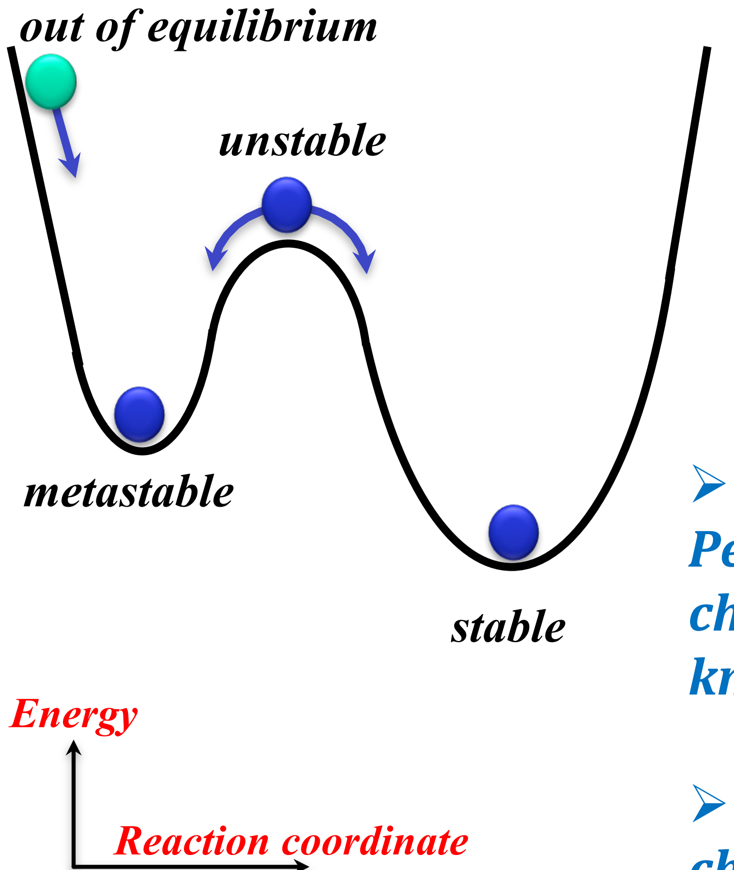
- ***Kinetic pathway – comprehensive description of structure and temporal order of intermediates and the rates***
- ***Kinetic mechanism – describes the nature of intermediates***

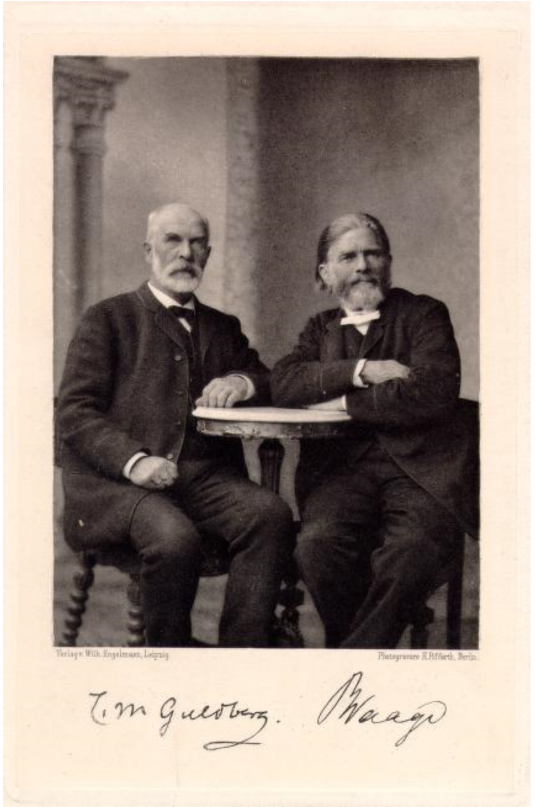
***Equilibrium thermodynamics*:**

How the system is distributed between state (1) and state (2)?

Equilibrium (state of balance):

$$\sum \vec{F} = 0$$

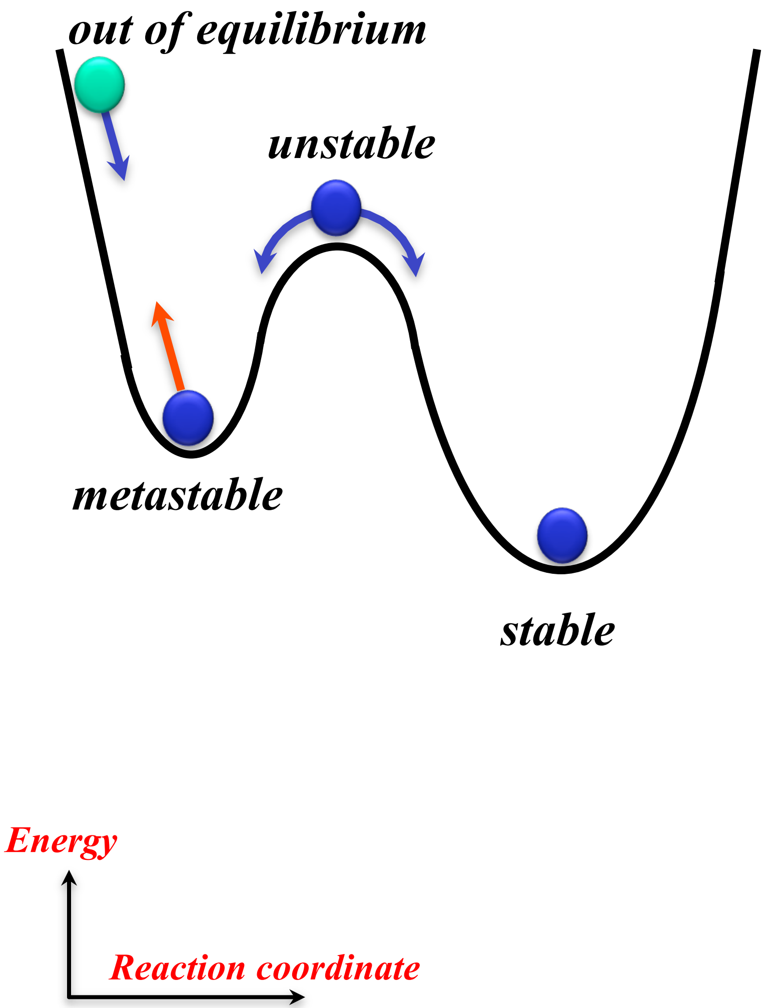


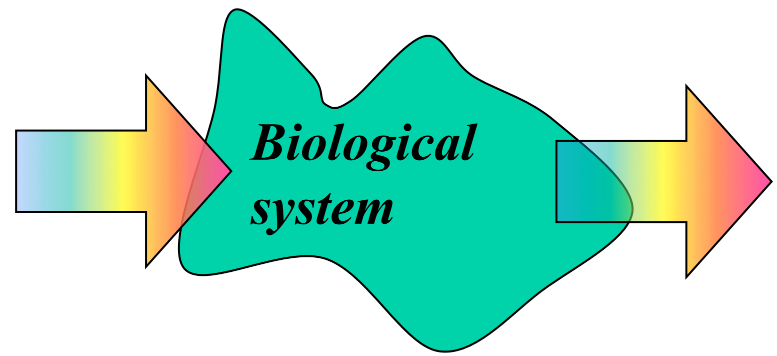


- ***In 1864 Cato Maximilian Guldberg and Peter Waage first proposed the concept of chemical equilibria, which latter became known as the law of mass action***

- ***Chemical equilibrium depends both on the chemical nature of reactants and on the relative amounts of each reactant present in the reaction mixture***

Life is an out of Equilibrium Process





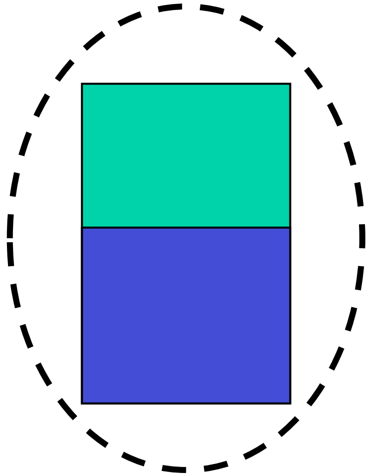
Steady-state
(constant force; constant rate):

$$\sum \vec{F} = const$$

$$\frac{\partial [property]}{\partial t} = 0$$

The difference between Life and Death

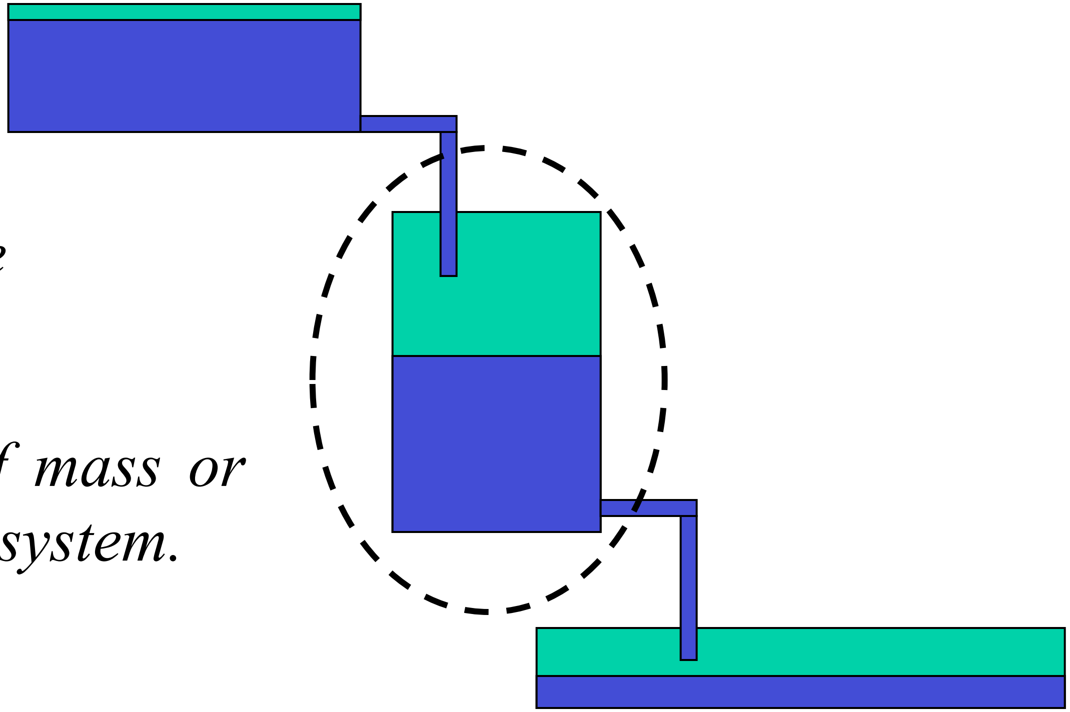
Equilibrium



(a) *The state variables are independent of time.*

(b) *There is no flux (no dissipation) of mass or energy across the boundaries of the system.*

Steady-state



(a) *The state variables are independent of time.*

(b) *There is a net flux of mass or energy moving across the system.*

State of the system

- A certain number of variables specify the state of the system.

  (a) ***intensive variables*** – ***independent of the size of the system*** **(**density, dielectric constant, molar free energy, chemical potential, pressure, specific heat and temperature)

  (b) ***extensive variables*** – ***dependent on system size*** **(**the mass, energy, enthalpy, entropy and volume)

The state of a system is defined when all of its properties can be specified.

Specification of the state of the system allows to reproduce it exactly.

State Functions

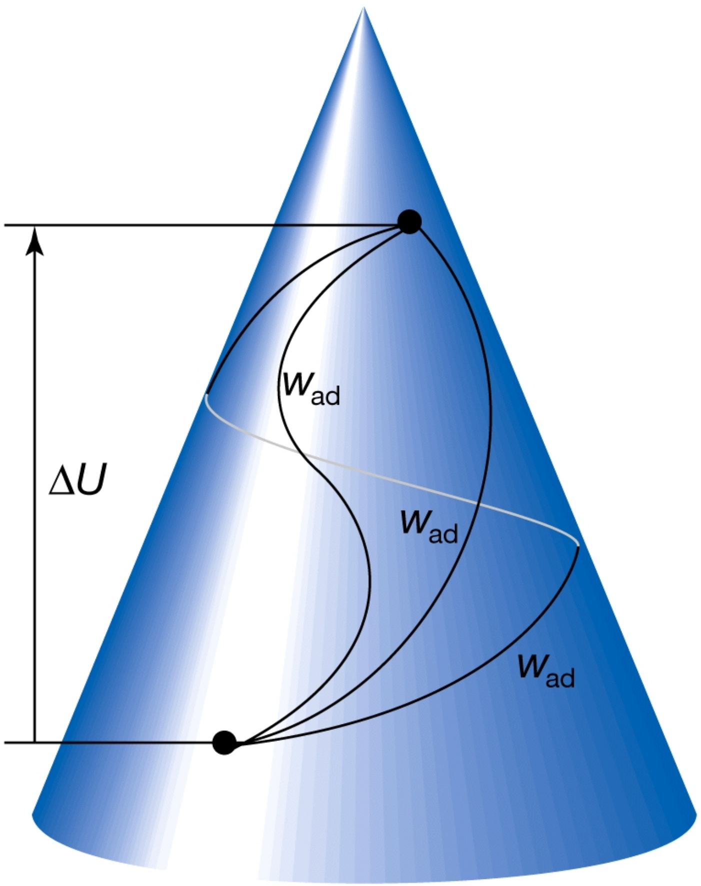
$$\int_1^2 dy = y_2 - y_1$$

- Change of y between two states is independent of the pathway that links the states, i.e. the infinitesimal change of y, ***dy***, is a ***perfect differential.***

- The function y is then a state function.

- The value of the state function is unique for a given state.

- Clearly definable only for systems in equilibrium.



Low of conservation

The law of conservation of mass *(matter) was postulated in 1748 by Lomonosov and later unambiguously formulated by Lavoisier.*

"All changes in nature are such that inasmuch is taken from one object insomuch is added to another."

Mikhail Lomonosov

Antoine Lavoisier

The total mechanical energy of the system is conserved

$$U = constant = E_{kin} + E_p$$

The mean kinetic energy of the molecule relates to its temperature: $E_{kin} = \frac{1}{2} m\bar{v}^2 = \frac{3}{2} k_B T$

Potential energy of biological system reflects its capacity to cause an effect.

Internal energy (U)

$$\Delta U = U(2) - U(1) = \int_1^2 dU$$

It is a state function

- Kinetic Energy of Motion: Translation, Vibration, Rotation
- Chemical Energy (chemical bonds)
- Energy of Non-covalent Interactions

U is changed by changing the *state* of the system (*e.g.* T or P).

Although internal energy may not measurable, its *changes can be measured* with calorimetry.

The First Law of Thermodynamics

(conservation of energy)

Julius Robert von Mayer

Demonstrated the "mechanical equivalence of heat"

- Energy cannot be created nor destroyed.
- The total energy of the universe is a constant.
- Energy can be converted from one form to another or transferred from a system to the surroundings or vice versa.
- The energy of an isolated system is conserved

Heat and work are both considered as equivalent forms of energy

Addition of heat (δQ) and work (δW) to an isolated system must be reflected in a change of the energy of the system.

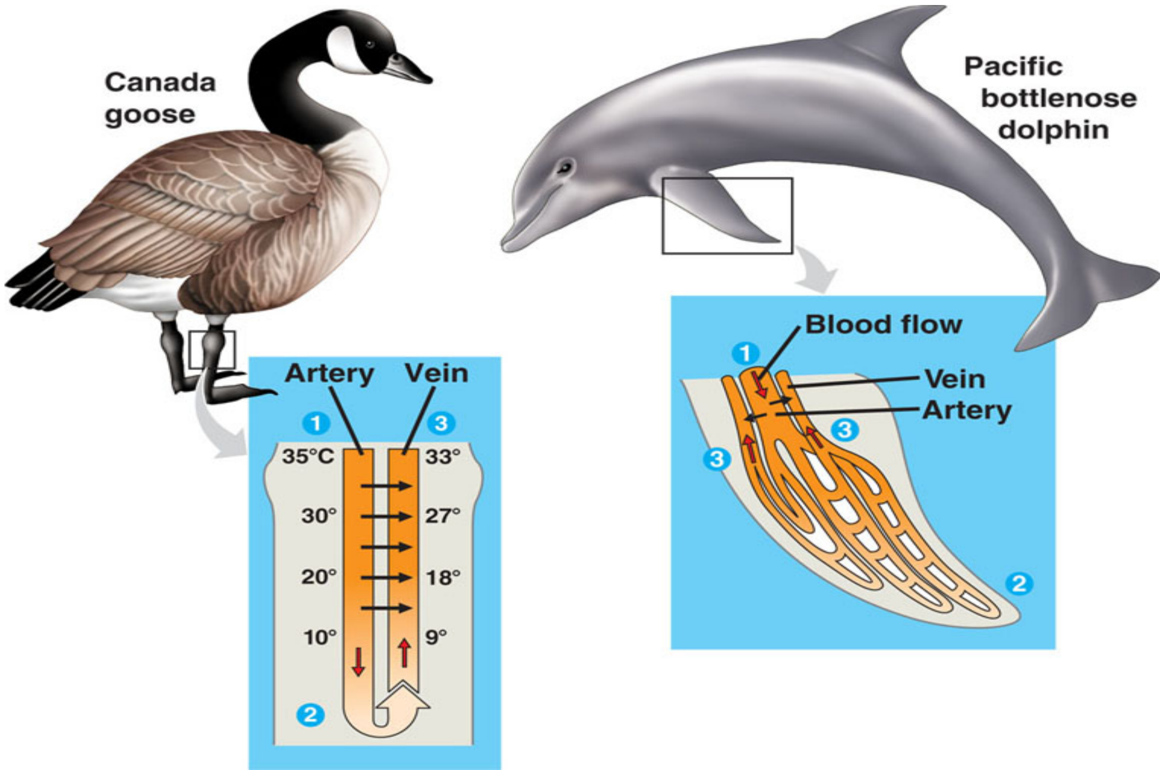
$$\boxed{dU = \delta q + \delta w}$$

Fluxes

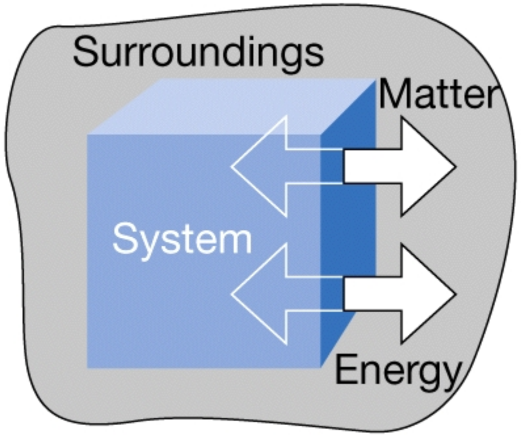
*Universe = **System** + Surroundings*

It does not matter what is in the system, only what enters and leaves the box.

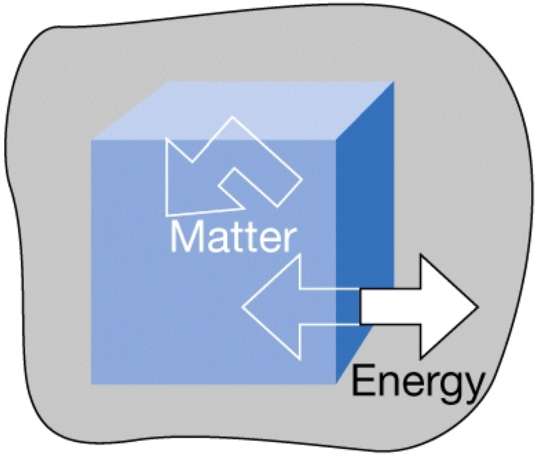
A system is defined by its boundary



Classes of Systems

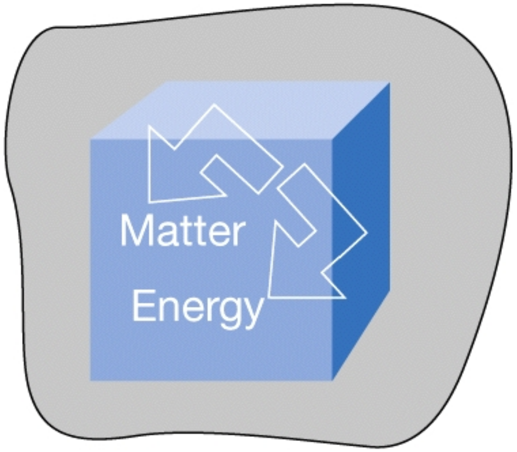


Open systems - both energy and mass cross the boundary.



Closed systems - energy, but not mass cross the boundary

Isolated systems - neither energy nor mass cross the boundary



Sign convention

Energy caming in is positive

Energy gowing out is negative

Proces	***Sign***
Work done by the system on the surrounding	–
Work done on the system by the surrounding	+
Heat absorbed by the system from the surrounding (endothermic process)	+
Heat absorbed by the surrounding from the system (exothermic process)	–

Heat

Heat flowing across a system boundary causes the system to change.

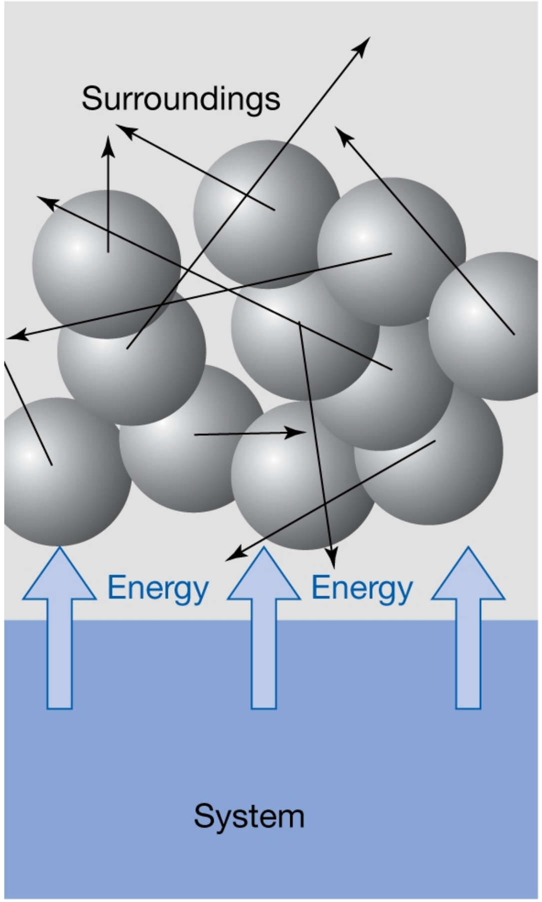
$$q = C\left(T_f - T_i\right)$$

It is NOT a state function

Generates thermal motion

- Boltzmann thermal energy is fundamental in biological processes.

- Gives limit on which biological signals can be detected and transmitted.



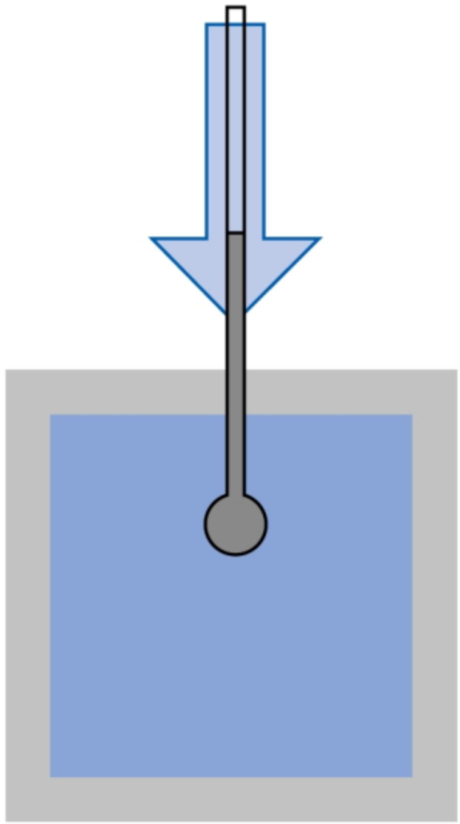
Equipartition Theorem

- 1/2 $k_B T$ thermal energy per degree of freedom
- average thermal velocity: $$\frac{3}{2} k_B T = \frac{1}{2} m v^2$$

Processes – energy flow

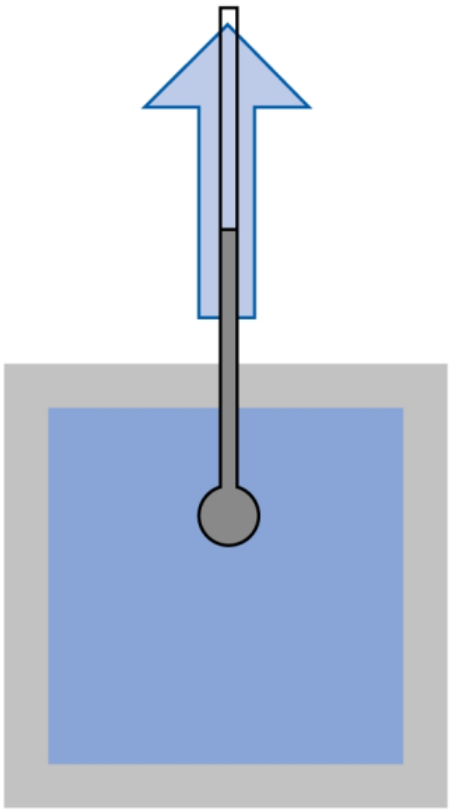
Endothermic *process*

absorbs energy as heat



Exothermic *process*

release energy as heat



Heat capacity

$$\boxed{C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}}$$

$V = const$

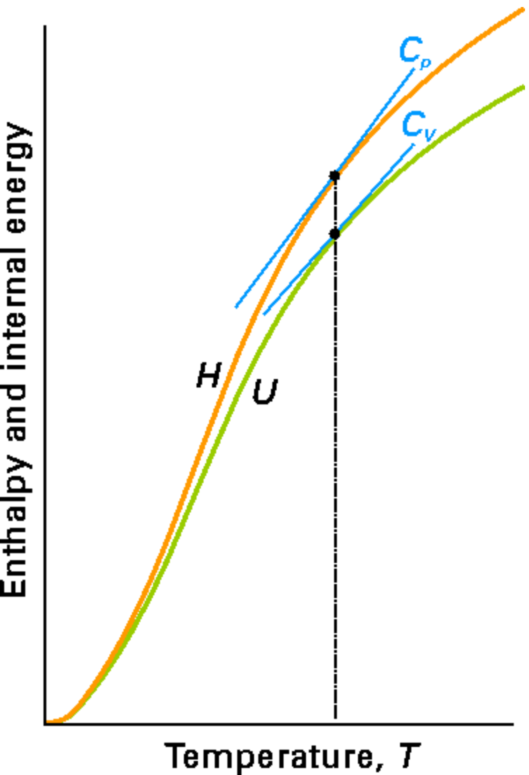
$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

the heat capacity at constant volume

$P = const$

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

the heat capacity at constant pressure



The amount of heat required to produce a one degree change in temperature in a system.

Work

It depends on Path

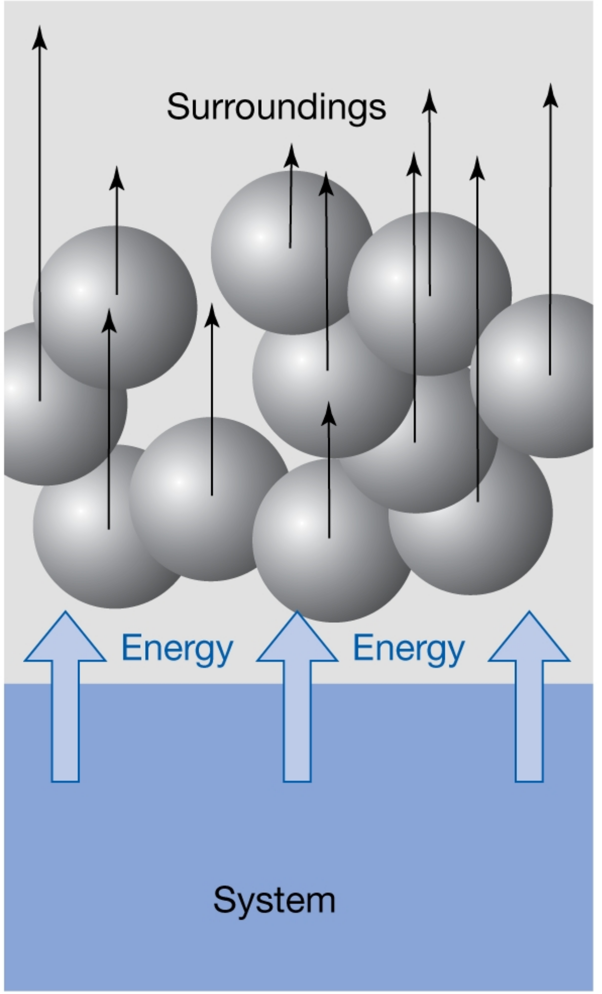
It is NOT a State Function!

The work is a product of an intensive and extensive variables, i.e., **μdn**, **φdq**, and **pdV**, etc.,

Organized motion

- F0/F1 ATPase turns in mitochondria – molecules acting in concert

- Doing work is equivalent to raising a weight.



For any process, the maximum work is obtained when the process is carried out reversibly.

Carnot's Principle – fluxes of energy

Sadi CARNOT (1825)

A steam machine needs 2 sources of heat:

a hot one: *temperature* T_h

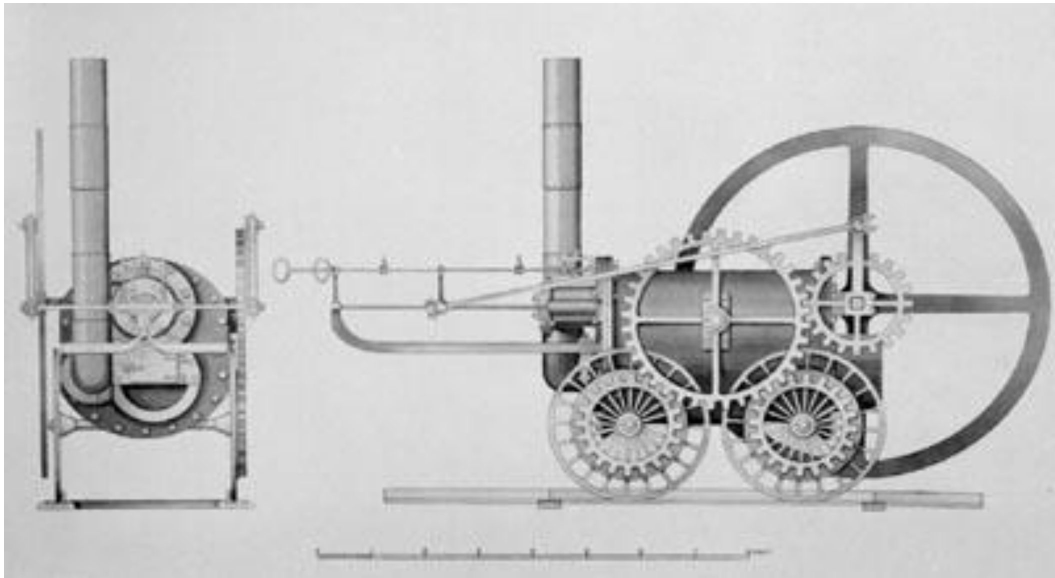
a cold one: *temperature* T_c

$$T_h > T_c$$

The equivalence between heat and work.

$$1cal = 4.184\frac{kgm^2}{s^2} = 4.184 Jules$$

The technical revolution has started.



Other Types of Work

Surface Expansion $dW_{surf} = \gamma\, dA$

Electrical $dW_q = \mathrm{E}dq$

Mechanical work $dW = \mathrm{F}dx$

Grawitational work $dW = \mathrm{mg}dh$