INTRODUCTION TO Thermodynamics

This Presentation was Developed

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Why Study Thermodynamics

Thermodynamics is the oldest and most clearly formulated branch of Engineering and physics. Thermodynamics includes the study of heat, work, and temperature and their relation to energy, entropy, and the physical properties of matter and radiation.

The behavior of these quantities is governed by the four laws of thermodynamics, which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics plays a large role in all areas of engineering involved in the production and distribution of electrical energy.

Definitions

Energy: is the quantitative property that is transferred to a body or to a physical system, recognizable in the performance of work

Heat: In thermodynamics, **heat** is energy in transfer between a thermodynamic system and its surroundings by modes other than thermodynamic work and transfer of matter.

Work: Thermodynamic work is the most important process by which a thermodynamic system can interact with and transfer energy to its surroundings. This results in externally measurable macroscopic forces on the system's surroundings, which can cause mechanical work, to lift a weight, for example.

Temperature: Thermodynamic temperature is defined in terms of a macroscopic Carnot cycle. Thermodynamic temperature is of importance in thermodynamics because it is defined in purely thermodynamic terms. SI temperature is conceptually far different from thermodynamic temperature. Thermodynamic temperature was rigorously defined historically long before there was any knowledge of microscopic particles such as atoms, molecules, and electrons.

Definitions

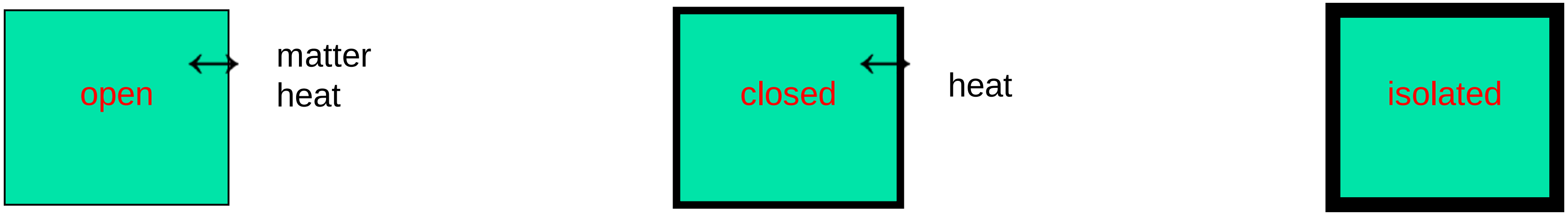
- **State** - Refers to the energy content of a given system. The state is defined by specifying certain variables such as temperature, pressure, volume and composition.
- State Variables specifically refer to the change inherent if a reaction proceeds because of a change in state
- State variables are either extensive or intrinsic
- Extensive → variables which are proportional to the quantity of matter (such as volume)
- Intrinsic → variables which are independent of quantity, that instead describe the whole system (such as density, temperature, and concentration)

Energy

The total energy of a system can be subdivided and classified into potential energy, kinetic energy, or combinations of the two in various ways. Kinetic energy is determined by the movement of an object – or the composite motion of the object's components – while potential energy reflects the potential of an object to have motion, generally being based upon the object's position within a field or what is stored within the field itself.

Systems

- System – the PART of the universe that is under consideration. It is separated from the rest of the universe by it’s boundaries
  - Open system → when matter CAN cross the boundary
  - Closed system → when matter CANNOT cross the boundary
  - Isolated → Boundary seals matter and heat from exchange with another system

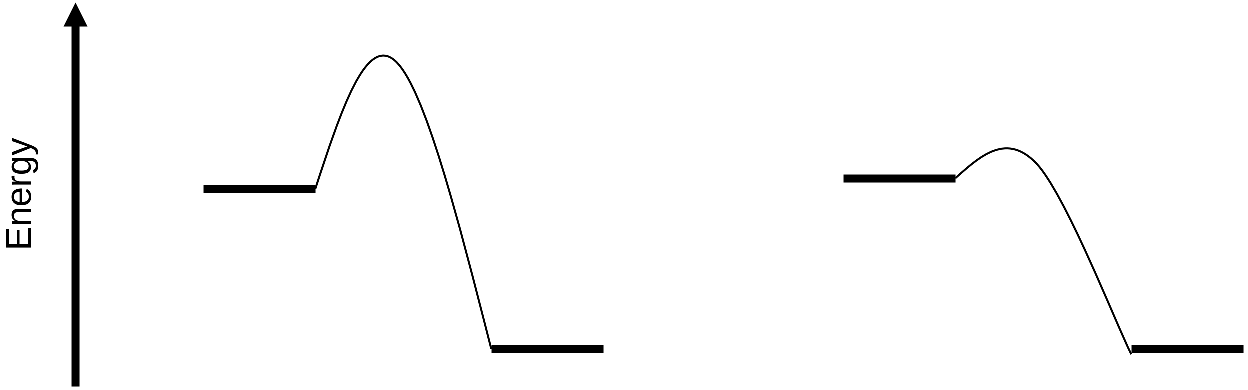


Picking a system

- The investigator picks the system
- It can be as large or as small as you want it to be, proper definition of the system is important to address the reactions you want to
- Leaving out gases or sediments or melts or other can make a problem simpler/tractable or more inaccurate…

Defining a system

- A system at equilibrium has measurable properties
- If the system changes from one equilibrium 'state' to another → these changes depend of the properties changed and not on the path (or exact process) the change went along



In thermodynamics, these 2 reactions are NOT different
Example: Catalysis does not affect thermodynamic calculations!

Processes

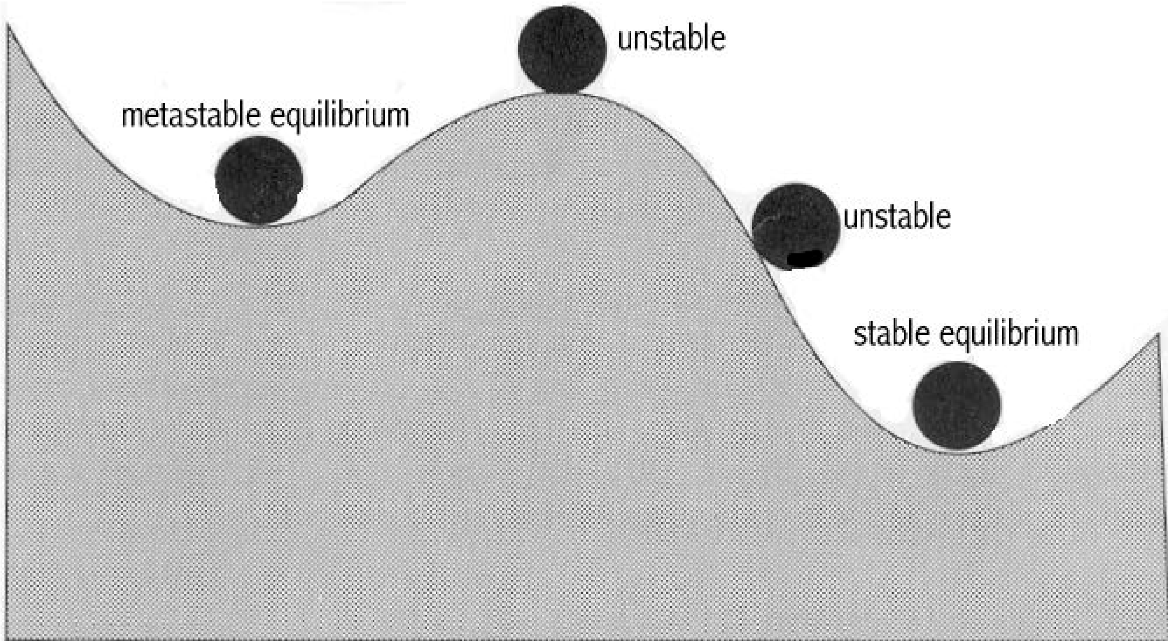
- The way a system changes states
  - Adiabatic → no heat exchange across boundaries of a system
  - Isobaric → constant pressure, but boundaries of the system can change (volume changes)

Equilibrium/ Reversibility

- Anything at equilibrium is theoretically undergoing forward and reverse reactions:
- A + B ↔ C
  - A + B → C **AND** C → A +B
- Equilibrium has 2 criteria:
  - Reaction does not appreciably change in time
  - Perturbation of that equilibrium will result in a return to the equilibrium

EQUILIBRIUM

- Stable equilibrium - System is at its lowest possible energy level.
- Metastable equilibrium - System satisfies above two criteria, but is not at lowest possible energy.



The historical perspective

- Benjamin Thompson, in 1798, proposed a link between work and heat generated from observing the boring of cannons

- Nicolas Carnot, in 1824, first proposed the concept of reversibility

- James Joule (a brewmaster), between 1840-1849 measured rising temperature from mechanical stirring – quantifying the relation between work and heat

Heat

- The origin of thermodynamics dealt with heat
- Thermo considers heat, and really ANY energy as though it were an indivisible fluid, always flowing from higher to lower energies
- Ergo → signs are + when energy flows from surroundings to the system and – when energy flows from system to surroundings

Work

- Work is another kind of energy
- Different from heat
- Can flow in and out of a system and invoke changes
- Imagine the energy required to lift a book – that work changes the potential energy of the book, but is not related to heat...

Internal Energy, *U*

- Changes in U, dU or DU, are + if energy of a system increases:
  - Energy here as heat → heat added = +
  - Work done on the system → +
  - Sometimes it has been formulated that work done BY a system is + in energy change → not how we have it formulated above, difference in perspective..Be careful when reading other sources, this sign change confusion propogates through the rest of thermodynamics…

Mechanical work

- Work = force required to move a body x distance that body is moved

$$w = \int_{x_0}^{x} F dx$$

- Because F=PA, force= pressure per unit area

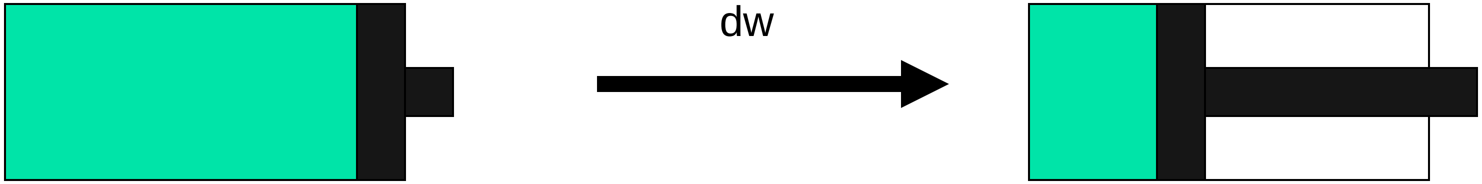
$$w = \int_{x_0}^{x} F dx = -(PA)(x - x_0) = -PdV$$

1st Law

- Aka the Law of conservation of energy, Gibbs in 1873 stated energy cannot be created or destroyed, only transferred by any process
- The net change in energy is equal to the heat that flows across a boundary minus the work done by the system
    - $\Delta U = q + w$
  - Where q is heat and w is work
  - Some heat flowing into a system is converted to work and therefore does not augment the internal energy

Work and the 1^{st} Law

- We can think about work as a function of pressure and volume
  - $dw = PdV$
- Where PdV is the incremental small change in volume at pressure associated with force x distance (dimensions of work)
- Restate the first law as:
  - $\mathbf{dU = dq - PdV}$



Internal Energy change

- Taking $dU = dq - PdV$ from state 1 to state 2:

$$\int_1^2 dU = \int_1^2 dq - P\int_1^2 dV$$

- Yields: $U_2 - U_1 = (q_2 - q_1) - P(V_2 - V_1)$
- Make $q_p = q_2 - q_1$, multiply PV terms and rearrange:
- $q_p = (E_2 + PV_2) - (E_1 - PV_1)$
- q_p is MEASURABLE – by measuring temperature changes resulting from energy changes (i.e. from a chemical reaction)

Enthalpy (H)

- $H = U + PV$
- Total differential for Enthalpy is:

$$dH = dU + PdV + VdP$$

- For our integrated change in state previous:
- $H_1=U_1-PV_1$ and $H_2=U_2-PV_2$

$$DH = H_2-H_1 = q_p \quad \text{(AT constant P, V)}$$

- Recall that energy is not known, only the change is meaningful
- Therefore change is measured from a reference state → pure elements, 25ºC, 1 bar pressure have an enthalpy of zero → H^0_f

2nd Law

- 2nd Law introduces entropy, S

$$dS = \frac{dq}{T}$$

(reversible)

$$dS > \frac{dq}{T}$$

(irreversible)

- Some of the enthalpy in a system is not convertible into work (PdV work for instance) because it is consumed by an increase in entropy
- Which could be restated that is requires some amount of work to increase entropy

SECOND LAW

- The First Law of Thermodynamics tells us that during any process, energy must be conserved.
- However, the First Law tells us nothing about in which direction a process will proceed spontaneously.
- However, experience tells us that certain processes only run spontaneously in one direction or the other. This allows us to deduce the Second Law.

THE SECOND LAW

- The Kelvin formulation - It is impossible to construct an engine that, working in cycles, shall produce no effect other than the extraction of heat from a reservoir and the production of work.
- The Clausius formulation - It is impossible to construct an engine that, working in cycles, shall produce no effect other than the transfer of heat from a colder to a hotter body.

Directionality of Entropy

- Entropy is central to the second law of thermodynamics, which states that the entropy of an isolated system left to spontaneous evolution cannot decrease with time For any spontaneous irreversible process, entropy is always increasing

$$dS > \frac{dq}{T}$$

- As a result, isolated systems evolve toward thermodynamic equilibrium, where the entropy is highest. A consequence of the second law of thermodynamics is that almost all natural processes are irreversible.

ENTROPY

- Entropy is a measure of the disorder (randomness) of a system. The higher the entropy of the system, the more disordered it is.
- The second law states that the universe always becomes more disordered in any real process.
- The entropy (order) of a system can decrease, but in order for this to happen, the entropy (disorder) of the surroundings must increase to a greater extent, so that the total entropy of the universe always increases.

Entropy

- "There is a great difference between energy and availability of energy...The availability of energy is always decreasing. This is... what is called the entropy law, which says the entropy is always increasing." – Richard Feynman

- "The thermodynamic sense of order decrease that is enshrined in the second law is at first sight in conflict with many of the complicated things that we see going on around us. We see complexity and order increasing with time in many situations: when we tidy up our office,... the evolution of complex life-forms from the simpler ones...

  "In many of these cases, we must be careful to pay attention to all the order and disorder that is present in the problem. Thus the process of tidying the office requires physical effort on someone's part. This causes ordered biochemical energy stored in starches and sugars to be degraded into heat. If one counts this into the entropy budget, then the decrease in entropy or disorder associated with the tidied desk is more than compensated for by the other increases."
  Barrow (1990)

Equilibrium

- Combining the 1st and 2nd Laws of Thermodynamics:

$$dU = dq_{rev} + dw = TdS - PdV$$

- If a process is at constant volume, V, and entropy, S → dU = 0 → nothing happens, energy does not change in the system
- This is EQUILIBRIUM:
  - dU>0 → spontaneous rxn products to reactants
  - dU<0 → spontaneous rxn reactants to products