Introduction

Thermodynamics is neither engineering, nor physics, nor chemistry, nor biology.
It is a tool used by all above and taken by all science and engineering students.
Thermodynamics occupies the same place in sciences as logic in humanities.

The origin

- **The term "thermodynamics" was introduced by Lord Kelvin himself to direct attention to the dynamic nature of heat and to contrast this perspective with previous conceptions of heat as a type of Fluid.**
- **When taken literally, thermodynamics implies a field concerned with the mechanical action produced by heat.**

the Science of Heat

In ancient west, Earth, Water, Air and Fire are the generally known and often quoted ancient elements of nature (Aristotle added Aether as the 5^{th}, the quintessence)

- In China, we have 土木火水金.
- By the end of the 18th century, French rich aristocrat chemist Lavoisier advocated a theory explaining that the phenomena involving the transfer of heat are the result of a weightless fluid substance, he called "caloric."

- **This "caloric," as Lavoisier assumed, permeated the gaps between atoms of a solid causing thermal expansion and whose loss through the surface could explain Newtonian cooling.**
- **Count (伯爵) Rumford found that heat can be produced by the boring of cannons and one can generate "unlimited amount" of heat simply by keeping boring the cannon—mechanical to heat**
- **Count Rumford's opinion eventually prevailed, but not after Lavoisier being severed by a Guillotine.**

the “arrow of time”

Why we interested in the second law ?

It is vividly recognized by consciousness

It is equally insisted on by our reasoning faculty (capability to reason)

Increase in randomness in the study of organization a number of individuals

Hamilton’s Equation

For a single particle

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}$$

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}$$

$$H = T + V$$

$$= \frac{1}{2m}\mathbf{p}^2 + \mathrm{V}(\mathbf{r})$$

$$H = \sum_{i=1}^{3} \frac{p_i^2}{2m} + V(q_1,\ q_2,\ q_3)$$

Hamilton's Equations

Energy is a constant of the motion

$$\frac{dH(p_i,\ q_i)}{dt} = \sum_i \left(\frac{\partial H}{\partial p_i} \frac{dp_i}{dt} + \frac{\partial H}{\partial q_i} \frac{dq_i}{dt} \right)$$

$$\frac{dH}{dt} = \sum_i \left(-\frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} + \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} \right)$$

$$\frac{dH}{dt} = 0$$

At microscopic level no sense of "arrow of time", events can equally unfold forward or backward.

It seams increase in randomness can equally be possible forward or backward.

This lead us to the big band.

At the beginning of the time, everything is highly ordered, with the expansion, randomness set in.

Before the "final" state of equilibrium, randomness increases with time.

- **With the big ban theory, Friedmann-Lemaitre-Robertson-Walker (FLRW) metric, we may introduce the Hubble parameter,**

$$\mathscr{H}(t) = \frac{\frac{da(t)}{dt}}{a(t)}$$

where *a* is a time dependent dimensionless scale factor.

- **Using pseudo-Newtonian representation**

$$\frac{d\underline{p}}{dt} = -\frac{\partial U(\underline{q})}{\partial \underline{q}} + \frac{\frac{d^2 a}{dt^2}}{a} \cdot \underline{q}$$

- **where U(x) is the potential energy**

- **The i-th component of the observed velocities is then,**

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} + \frac{\frac{da}{dt}}{a} \cdot q_i = \frac{p_i}{m_i} + \mathscr{H} \cdot q_i$$

- **Obviously the last term breaks the time symmetry, when (t→-t),**

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} - \mathscr{H} \cdot q_i$$

- **We will leave the discussion of the change of entropy in later lectures.**

Objectives

- **The main objective of chemical thermodynamics is the analysis of spontaneity and equilibrium,**
- **The energy changes that accompany a physical or chemical transformation;**
- **Ideal and nonideal solution;**
- **The study of phase equilibria.**

Limitations

- Classic thermodynamics deals only with measurable properties of matter in bulk (pressure, temperature, volume, etc.)
- It is an empirical and phenomenological science, and in this sense, it resembles classic mechanics.
- Statistical mechanics (or statistical thermodynamics) is the science that relates the properties of individual molecules and their interactions to the empirical results of classical thermodynamics.

- **Thermodynamics can formulate necessary conditions but not sufficient conditions.**
  - **It may rule out a given chemical reaction by indicating that such a transformation cannot proceed spontaneously under any set of available conditions.**
  - **However, if the analysis indicates that a reaction may proceed spontaneously, no statement can be made from classical thermodynamics alone indicating that it will do so in any finite time.**