A Brief History of Thermodynamics

- The driving force for the development of thermodynamics was the invention of the steam engine at about 1700
- From 1700 to 1900, thermodynamic theory was slowly and painfully developed
- By 1900, “classical” thermodynamics was essentially complete
- In time, various special branches of thermodynamics developed

Thermodynamics at UC Berkeley

Mechanical thermo: Energy Conversion; air conditioning; power cycles (ME 105)

Chem. Engin thermo: Solutions; interphase equilibrium; chemical equilibrium (ChE 141)

Chemical thermodynamics: same as above, but no engineering applications (Chem 120B)

Biothermodynamics: Thermodynamics of living organisms and the ecosystem (BioEng C105B)

Statistical thermodynamics: Microscopic basis of thermodynamics (Phys 112)

Geothermodynamics: thermodynamics at high pressures (Earth & Planetary Sci. 131)

Engineering Thermo: 1st and 2nd laws; reversibility, equilibrium,Materials and Chemical thermo (E115)

The Concept of Temperature

- Without realizing its significance, Galileo (ca 1630); Fahrenheit (1715); measured “T” by expansion of a fluid (gas or mercury)
- Celsius (1742) defined 0^oC as the melting point of ice; 100^oC as the boiling point of water; with a scale in between linear with expansion of fluid – why?
- With the realization that matter is composed of discrete atoms and molecules, Lavoisier (1780), Dalton (1808), temperature was an seen as a measure of the particles’ speed (gas) or vibration (solid)

- Kelvin (ca 1885) introduced the notion of the *absolute zero temperature,* where all atomic motion stops: T(K) = T(^{o}C) + 273; absolute zero temperature is 0 K or –273^{o}C

- International Committee (1954): defines the unique state *of* water: the *triple point* (where ice, water, and water vapor coexist) as 0.01^{o}C at 611 Pa (0.00611 atm)

Heat

- Since the 18th Cent., heat was viewed as a “fluid” (caloric) that moves from a body at high temperature to one at low temperature
- Rumford disproved the caloric theory by his investigation of canon boring
- During the 19th Cent., the correct view of heat was uncovered: Heat is *energy in motion* from a hot system to cold surroundings (or vice versa)
- Some effects of heat :
  - increasing the temperature of a body
  - melting a body
  - vaporizing a liquid
  - producing mechanical work

Work

- Known from mechanics since Newton (1687) as *force x distance.*
- Heat and Work are two aspects of energy in motion; work is completely convertible to heat (Rumford, Joule (1840))
- Forms of Work:

  - expansion/contraction (like a balloon)

  - rotating equipment (a steam or gas turbine)

  - electrical work (electric cars)

  - mechanical: (moving levers, lifting weights, etc.)

Energy and the First Law

- Energy comes in many interconvertible forms:
  - internal (atomic vibrations);
  - electrical
  - chemical (in chemical bonds)
  - kinetic and potential
- energy cannot be created or destroyed:
  (**conservation of energy**) Mayer (1842)
- energy is related to heat and work by the
  (Helmholz, Clausius, ca 1850)

1st Law of Thermodynamics

- Energy is a property of a body; heat and work are not

Joule (ca 1850) – the first thermodynamic experimentalist –measured:

The Mechanical Equivalent of Heat –

heat in *calories* (to raise the temp. of water 1°C)

work in *Joules* (exerting a force of 1 Newton over 1 meter)

Joules per calorie: 4.184

- With energy, heat and work in the same units, the 1st Law could be written:

$$\Delta U = Q - W$$

Q = heat added to the syem

W = work done by the system

Entropy and the Second Law

- Development of steam engines (Watt 1778) showed that heat is not completely convertible to work
- Carnot (1824) showed theoretically why this is so
- Clausius and Kelvin developed the concept of *reversible* and *irreversible* processes
- By analyzing many experiments and processes involving transfer of heat, Clausius (ca 1850) uncovers a new thermodynamic property, which he names entropy, denoted by **S**
- Changes in this property during a *reversible process* are related to the heat exchanged between system and surroundings by:

$$\Delta S = Q/T$$

The 2nd Law (con't)

- Qualitative statements of the 2nd Law:

Kelvin – Planck: "It is impossible for any any engine to transfer heat from a cold source to a hot source without work being done"

Clausius: "It is impossible to convert heat completely to work"

- With a high-temp. *heat source* and a low-temp. *heat sink,* practical *cycles* for producing work are developed (Rankine, Otto, Brayton) 19th Cent.

Chemical/Materials Thermodynamics

- This branch deals with:
  - multiple components, multiple phases
  - chemically reacting mixtures
  - equilibrium at conditions of fixed p and T
- Developed by Willard Gibbs (Yale Univ. 1890)
- Gibbs introduces the ***chemical potential*** – the driving force for:
  - Chemical reactions
  - Exchange of a species between phases
  - Diffusion of a species in a single phase
- At equilibrium, these processes STOP

Statistical Thermodynamics

- Links atomic motions to thermodynamic properties

Boltzmann (ca 1885) discovers the formula for the absolute entropy: **$S = k\ln W$**

Planck (~ 1900) quantization of energy states

Einstein, Debye (1905) – quantum mechanical explanation of specific heats of solids

Fermi, Dirac, Bose – quantum statistical thermodynamics

Giauque (1930, UCB)- the 3rd Law: *The entropy of a body is zero at 0 K*