Reese Ch. 13, Part B1
(pp. 599-615)

- Thermal Effects in Gases: Ideal Gas Law
- Calorimetry
- Reservoirs (a.k. a. "Heat Reservoirs")
- Mechanisms for Heat Transfer

Thermal Effects in Gases: Boyle's Law

- In 1660, Robert Boyle discovered that if a sample of dilute gas is kept at a fixed temperature, its pressure and volume are inversely proportional:

$$PV = \text{constant (at fixed temperature)}$$

Other investigators subsequently found that the product PV varies in direct proportion to the absolute temperature and also to the number of molecules in the sample.

Thermal Effects in Gases: The Ideal Gas Law

- These results can be combined into a single equation known as the <u>ideal gas law</u>:

$$\boxed{PV = NkT}$$

- Here
  - T represents the kelvin temperature,
  - N is the number of molecules in the sample, and
  - k (Boltzmann's constant) is independent of the quantity or chemical identity of the gas:

$$k = 1.381 \times 10^{-23}\, J/K$$

The Ideal Gas Law: Mass, Moles, Avogadro's Number and all that

- The mass m of a gas sample is the number of moles n times the <u>molar mass</u> M: $\boxed{m = nM}$
- The molar mass M is Avogadro's number N_A times the <u>mass μ of one molecule</u>: $\boxed{M = N_A \mu}$
- The number of molecules is the number of moles times <u>Avogadro's number</u> : $\boxed{N = n N_A}$
- The ideal gas law can be written as $\boxed{PV = nRT}$ where $R = N_A k = 8.314$ J/(mol-K) is called the <u>universal gas constant.</u>

Calorimetry I

- Calorimetry experiments involve two (or more) thermodynamic systems (A and B) that are placed in thermal contact with one another, but thermally insulated from the "outside world."
- In many such experiments, the principle of the conservation of energy allows us to conclude that the energy lost from one system equals the energy gained by the other: $\boxed{\Delta E_A + \Delta E_B = 0}$

Calorimetry II

- It often happens that the energy transfer through performance of work by one system on the other is negligible. Then (and only then!), the energy lost by one system through heat transfer equals the energy gained by the other through heat transfer. *Very loosely speaking*, we say:

"Heat gained" = "Heat lost"

Calorimetry III

- When a system gains energy through heat transfer, typically either
  - (1) the system's temperature increases, or
  - (2) the system changes its phase.
- Experiments confirm that in case (1) the temperature rise is proportional to the energy δQ received via heat transfer and inversely proportional to the mass of the system. We summarize this by: $\boxed{\delta Q = mcdT}$

c is called the specific heat.

Calorimetry IV

- In the case of a phase change, the amount of matter Δm that changes phase is proportional to the energy received. We write:

$$\boxed{\delta Q = (\Delta m) L_{xform}}$$

- Notes:
  - During a phase change, the temperature of the system remains constant until all of the material has changed phase.
  - L_{xform} is called the latent heat of transformation

Reservoirs

- A <u>thermal reservoir</u> is an (idealized) system for which the product of specific heat and mass (sometimes called the "heat capacity") is practically infinite.
- When a system is placed in contact with a thermal reservoir, the temperature of the reservoir may be assumed to remain constant, when any finite amount of energy transfer occurs to or from the reservoir.

Mechanisms of Heat Transfer: Conduction

- If two systems are placed in physical contact and heat transfer occurs without any macroscopic motion of matter, we say that "heat is being conducted."
- Conductive heat flow (joules/s) is proportional to the area of contact and the local temperature gradient:

$$\boxed{\frac{\delta Q}{dt} = -kA\frac{dT}{dx}}$$

k is called the thermal conductivity; its SI unit is watts/(meter-kelvin).

Steady-state Conduction through Materials in "Series" or "Parallel": I

- In many cases of practical importance (for example, space heating), we can determine steady-state heat flow in a way analogous to the solution of a DC electrical circuit with resistors in series or parallel.
- Important ideas here include:
  - R-value of a layer (R = thickness/k)
  - heat flow is independent of x in steady state

Steady-state Conduction through Materials in "Series" or "Parallel": II

- Heat flow for layers in series: $\boxed{\frac{\delta Q}{dt} = A\left(\frac{T_H - T_C}{R_{total}}\right)}$
  where $R_{total} = \sum_n R_{layer\#n}$
- Heat flow with parallel paths:

$$\boxed{\frac{\delta Q}{dt} = \left[\sum_n \left(\frac{A_n}{R_n}\right)\right](T_H - T_C)}$$

Mechanisms of Heat Transfer: Convection

Convective heat transfer involves the macroscopic motion of fluids (gases, liquids, the Earth's mantle . . .). Much of the energy transfer in the Earth's lower atmosphere is convective. Quantitative analysis of convection is beyond the scope of this introductory survey.

Mechanisms of Heat Transfer: Radiation (I)

- Radiative heat transfer the emission and absorption of electromagnetic waves from materials.
- In 1879, Josef Stefan discovered the rate of emission of radiant energy from the surface of an object is proportional to the 4th power of its (kelvin!) temperature.
- The study of thermal emission was historically very important to the development of quantum mechanics around the beginning of the 20th Century.

Mechanisms of Heat Transfer: Radiation (II)

- Rate of emission of radiation by an object:

$$\boxed{\left(\frac{\delta Q}{dt}\right)_{radiated} = -eA\sigma T_{obj}^{\,4}}$$

  where *e* is the (average) <u>emissivity.</u>
- Rate of absorption of radiation from (uniformly warm surroundings):

  a is mean <u>absorptivity</u> $\boxed{\left(\frac{\delta Q}{dt}\right)_{absorbed} = aA\sigma T_{surr}^{\,4}}$

Mechanisms of Heat Transfer: Radiation (III)

- Here's an equation that is true at any one wavelength, but is not necessarily true when the average is taken of all wavelengths (Typically, *e* and *a* depend on wavelength.):

absorptivity = emissivity

"Good absorbers are good radiators."

Reese Ch. 13, Part B2
(pp. 615-626)

- Thermodynamic Processes
- The Conservation of Energy
  and the First Law of Thermodynamics
- Work done by a Gas on its Surroundings
- Applying the First Law of Thermodynamics
  when there's a change of state

Thermodynamic Processes

- A thermodynamic process is any way that a system changes from one state of thermodynamic equilibrium to another.
  - Reversible versus irreversible processes. A reversible process is one that can occur in the opposite direction, with all parts of the universe returning to their original conditions.
  - Quasi-static processes are processes that proceed through a sequence of equilibrium states. Many (but not all) quasi-static processes are reversible.

Four special thermodynamic processes

- Isothermal process: T = constant
- Isobaric process: P = constant
- Isochoric process: V = constant
- Adiabatic process: zero heat transfer
  - An adiabatic process that is also quasi-static is often called an isentropic process.
- NOTE: These descriptions can be applied to subsystems.

Energy Conservation and the First Law of Thermodynamics: I

- The total energy of a system includes both:
  - macroscopic or mechanical energy E (= KE +PE) , and
  - microscopic or internal energy U
- Notice carefully that in thermodynamics, U is not used to refer to macroscopic potential energy but rather to microscopic energy (both kinetic and potential).

Energy Conservation and the First Law of Thermodynamics: II

- Notice that when work is done on a system by external agents and there is also heat transfer from the surroundings, the conservation of energy requires that:

$$Q + W_{allx} = \Delta U + \Delta(KE)$$

Energy Conservation and the First Law of Thermodynamics: III

- But the work done by external agents is the sum of the work done by conservative forces and that done by nonconservative forces:

$$\boxed{W_{allx} = W_c + W_{nc}}$$

- The work done by conservative forces is minus the change in macroscopic potential energy: $\boxed{W_c = -\Delta(PE)}$

Energy Conservation and the First Law of Thermodynamics: IV

- Gathering these results, we find that:

$$\boxed{Q + W_{nc} = \Delta U + [\Delta(KE) + \Delta(PE)] = \Delta U + \Delta E}$$

- <u>In cases where there is no change in the macroscopic mechanical energy E</u>, this reads:

$$\boxed{Q + W_{nc} = \Delta U}$$

Energy Conservation and the First Law of Thermodynamics: V

- Typically the subscript "nc" is dropped, with the understanding that the work being referred to here is the work done on the system to increase the internal microscopic energy U. (Reese calls it W' – see p. 618.) $\boxed{Q + W_{on} = \Delta U \Rightarrow \Delta U = Q + W_{on}}$
- Reese writes the first law of thermodynamics as $\boxed{\Delta U = Q - W_{by}}$ because he uses W in the thermodynamics chapters to mean the work done by the system on its surroundings.

Work done by a Gas on its Surroundings: I

- If a gas of pressure P expands slightly against its surroundings, the work done by the gas on the outside world is

$$\boxed{\delta W_{by} = PdV}$$

- This expression can be integrated to give the work done by the gas in a finite change represented by a curve in a V vs. P graph (a "PV diagram").

Work done by a Gas on its Surroundings: II

- For any path in the PV plane, the work done by the gas is:

$$\boxed{W_{by} = \int_{V_i}^{V_f} P(V)dV}$$

Work done by a Gas on its Surroundings: III

Special results:

- Isobaric process: $W_{by} = P_i \times (V_f - V_i) = P_i \Delta V$
- Isochoric process: $W_{by} = 0$
- Isothermal process: $W_{by} = nRT \ln\left(V_f / V_i \right)$ (for a perfect gas)

Work done by a Gas on its Surroundings: IV

- For a <u>cyclic change</u>, in which the final state of the gas is the same as its initial state, the work done is not necessarily zero:

$$\boxed{W_{by} = \oint_{i \to f} P(V)dV}$$

This is the area enclosed inside the curve in the PV plane. (+ if the boundary proceeds clockwise; - if the boundary proceeds counterclockwise)

Using the First Law when there are changes of state

- The various expressions for the work done by a gas can also be used for changes involving fluids and even many solids.
- When water is vaporized at constant temperature and pressure, some of the inward heat transfer is needed to allow for the work necessary to push back the surroundings. The internal energy change is given by: $\boxed{\Delta U = mL_{vap} - P(V_{vap} - V_{liq})}$