University of Washington
Department of Chemistry
Chemistry 452/456
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Lecture 1. 6/23/14
EDR: Ch. 1,2
Devoe: Ch. 2

"The proper study of biology should really *begin* with the theme of energy and its transformations."
Albert L. Lehninger (from *Bioenergetics: The Molecular Basis of Biological Energy Transformations*)

A. Introduction and Basic Principles

- Thermodynamics: The field which describes and quantifies energy transformations. Describes the transfer of work and heat in going from one equilibrium state to another.

- Energy: The capacity to do work.
  Energy assumes many forms: potential, kinetic, thermal, electrical, etc. The transformation of energy from one type into another is of central importance in biology. Energy transformation is an important capability of a living cell. It is a critical feature in man-made engines.

- Advantages of Thermodynamics: Very general tool for describing energy transformations. Can be used to describe transformations of energy in very complicated and perhaps not thoroughly defined systems. Thermodynamics describes energy transformations in the *macroscopic* world.

- Disadvantages: The generality of thermodynamics can be disarming. The formalism of thermodynamics is couched in the calculus of functions of several variables. Detailed, *microscopic* (i.e. detailed mechanical information) information is lost.

- Range of Validity:
  - Thermodynamics can describe *average* properties of large amounts of *ordinary* matter. It can describe the energetics of living things (i.e. bioenergetics).
  - Thermodynamics does NOT describe how long a process takes to convert a system from one equilibrium state to another.
  - Thermodynamics does not describe fluctuations, i.e. brief excursions from equilibrium involving small quantities of matter (e.g. Brownian motion).
  - The validity of thermodynamics at cosmological scales is questionable.

B. Methodology and Basic Assumptions of Thermodynamics

- It is assumed, for the purpose of solving energy transformation problems, that the universe is divided into two parts, the *system* and the *surroundings*.
- The system is divided from the surrounding by a *boundary*. The nature of the boundary must be defined carefully. In particular it must be established what may or may not pass through the boundary.
  - Open system: matter and energy may pass through the boundary between the system and the surroundings.
  - Closed system: matter may not cross the boundary between the system and the surroundings. Energy may be exchanged between the system and the surroundings, however.
  - Isolated system: Neither energy nor matter may cross the boundary.
  - Equilibrium: Consider a complicated system (e.g. a large number of molecules) which undergoes a change from an initial state A to a final state B. This may, for example, involve a chemical reaction where reactant molecules (i,e. the A state) converted to product molecules (the B state).

$$A \underset{R_r}{\overset{R_f}{\rightleftarrows}} B$$

When the rate (R_f) at which reactant molecules are converted to product molecules equals the rate (R_r) at which product molecules are converted back to reactant molecules, (i.e. $R_f=R_r$) a state of equilibrium exists.

  - If there is a *net* conversion of molecules from the A state to the B state (or vice versa), such that the A state (or B state) becomes depleted of molecules, *net transport* is said to have occurred. If net transport occurs, a system is not at equilibrium.
  - A system at equilibrium is described by a set of state variables, which includes pressure (P), temperature (T), volume (V), and composition (described by a set of mole amounts $\{n_i\}$).
  - Assume a single component system (e.g. an ideal gas) with molar amount n. There are four state variables: P, V, T, n. These variables are related by an equation of state. As discussed in Lectures 1-3, the equation of state for an ideal gas is $PV=nRT$. Thus the state variables are not independent quantities. Only three of the four state variables are independent, because once three are measured, the fourth can be calculated from the equation of state.
  - Changes between equilibrium states are quantified by changes in state functions.
  - A state function F is a function of the state variables P, V, T, $\{n_i\}$.
  - A state function is defined when a system reaches equilibrium.
  - Thermodynamics provides means to calculate changes in state variables when a system passes from an initial equilibrium state to a final equilibrium state. That is, thermodynamics enables us to calculate $\Delta F = F(final) - F(initial)$.
  - Unlike mechanics, thermodynamics does not provide a means to calculate F…only ΔF. However, some exceptions exist (see the discussion on the Third Law).

C. Mechanical vs. Thermodynamic Energy

- In mechanical problems involving a single mass, the energy is easily expressed as a sum of explicit forms for the kinetic energy K and the potential energy V:

$$E = K\left(v_x, v_y, v_z\right) + V\left(x, y, z\right) \tag{1.1}$$

- Note the kinetic energy K is a function of the velocities and the potential energy V is a function of the coordinates of the mass.
- In simple mechanical calculations, the energy is obtained by solving an equation of motion. We need a form for K and V. For a mass M vibrating in the x direction on a spring we have $E = \frac{1}{2}mv^2 + \frac{1}{2}\kappa x^2$ where κ is the spring constant. If a mass m is displaced by a distance x from the resting state of the spring, taken to be x=0, the spring exerts a resisting force F=-κx. So the spring constant expresses the "strength" of the springs resistance to extension or compression). The negative sign expresses the tendency of the spring to resist the extension or compression.

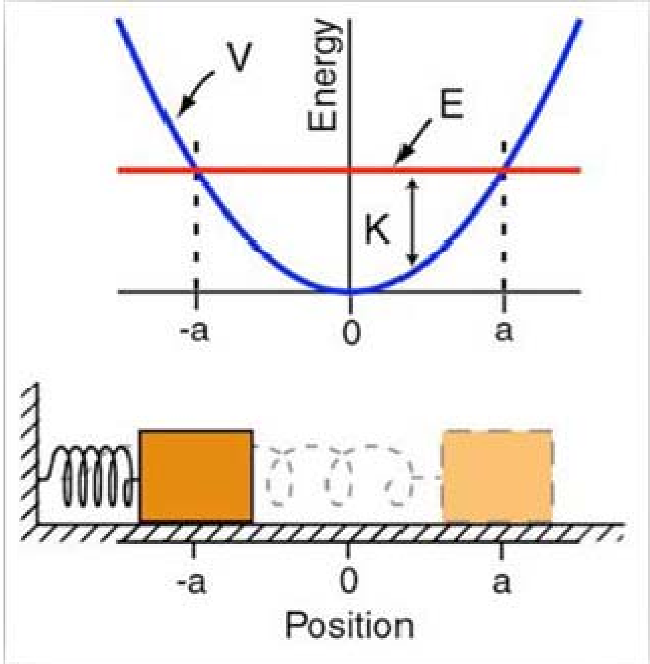

Figure 1: A mass connected to a spring oscillates harmonically between –a and +a

- The energy of the spring is calculated by solving Newton's equation: F=ma. Note because F=-κx and the acceleration $a = \frac{d^2x}{dt^2}$, Newton's equation is

$$-\kappa x = m\frac{d^2x}{dt^2} \tag{1.2}$$

- . Assuming that at t=0, x=+a and v =0, we can solve Newton's equation to get

$$x(t) = a\cos\left(\sqrt{\frac{\kappa}{m}}t\right) \tag{1.3}$$

- . And the velocity is related to x by:

$$v(t) = \frac{dx}{dt} = -a\sqrt{\frac{\kappa}{m}}\sin\left(\sqrt{\frac{\kappa}{m}}t\right) \tag{1.4}$$

.

- Putting equations 1.3 and 1.4 into 1.1 we obtain for the total energy

$$E = \frac{\kappa a^2}{2} \tag{1.5}$$

- Note although the kinetic and potential energies are time dependent, the overall energy is conserved in value.
- In contrast, thermodynamic energies are energies of large numbers of molecules. Thermodynamic energies are often expressed on a per mole basis. The energy per mole in thermodynamics is called the internal energy U. u and e are related by $U = N_A\langle E\rangle$ where $\langle E\rangle$ is the average energy per molecule for the system. U is called the internal energy, because it contains information about all motions internal to a system.
- Note:

$$\frac{U}{N_A} = \langle E\rangle = \langle K\rangle + \langle V\rangle = \tfrac{1}{2}m\langle v^2\rangle + \tfrac{1}{2}\kappa\langle x^2\rangle \tag{1.6}$$

- where $\langle v^2\rangle$ and $\langle x^2\rangle$ are the average velocity squared and the average displacement squared.
- There is a principle of mechanics called the equipartition principle. It states that for every dimension x, y, z , the average of V is $RT/2N_A$. This means that

$$\langle V(x)\rangle = \langle V(y)\rangle = \langle V(z)\rangle = \frac{RT}{2N_A} \tag{1.7}$$

- Similarly for the kinetic energy on average:

$$\langle K(v_x)\rangle = \langle K(v_y)\rangle = \langle K(v_z)\rangle = \frac{RT}{2N_A} \tag{1.8}$$

- Examples:
  - One mole of one dimensional oscillators:

$$U_{vib} = N_A\left(\langle K(v_x) + V(x)\rangle\right) = N_A\left(\frac{RT}{2N_A} + \frac{RT}{2N_A}\right) = RT \tag{1.9}$$

  - Energy is equally partitioned between dimensionas. For a three dimensional oscillator:

$$U_{vib} = U_{vib,X} + U_{vib,Y} + U_{vib,Z} = 3RT \tag{1.10}$$

  - If an ideal gas is confined to a container the mechanical motions involved would be translation in three dimensions:

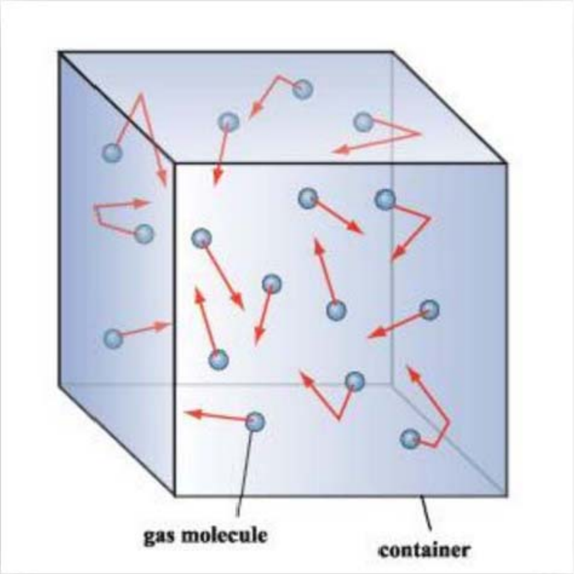

Figure 2: In an ideal monatomic gas, the mechanics is described by translational motion in three dimensions.

- The internal energy for one mole of ideal monatomic gas molecules translating in three dimensions is ;

$$\begin{aligned} U_{trans} &= N_A \langle E \rangle = N_A \left[\langle K(v_x) \rangle + \langle K(v_y) \rangle + \langle K(v_z) \rangle \right] \\ &= N_A \left[\frac{RT}{2N_A} + \frac{RT}{2N_A} + \frac{RT}{2N_A} \right] = \frac{3RT}{2} \end{aligned} \tag{1.11}$$

  - The heat capacity C_V is defined as the change in the internal energy U with unit change in temperature at constant volume. So to get the heat capacity of one mole of a monatomic ideal gas we differentiate 1.11 with respect to T:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3R}{2} \tag{1.12}$$

  - For one mole of three edimensional oscillators the heat capacity is predicted by 1.10 to be

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3R \tag{1.13}$$