**University of Washington**
**Department of Chemistry**
**Chemistry 452/456**
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Lecture 3 6/30/14
EDR 2.1-2.4
DeVoe: 3.1

## A. The First Law of Thermodynamics

- The First law of thermodynamics identifies the way in which a state variable, the internal energy can change, then makes a statement about how the internal energy of the universe can change.
- Assume a gas is in a closed system. Then we have shown that for such a system:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (3.1)$$

- Let us specify carefully that dU is the internal energy change of a system, and that this energy changes as a result of a change in T and/or V.
- The First Law asserts that to effect such changes in T or V which result in an increase or decrease in the system's energy, energy must cross the boundary and thus enter or leave the system. The change in the systems energy dU must be exactly accounted for either by the flow of heat q in or out of the system or the performance of work w on or by the system.
- In differential form the First Law of Thermodynamics is

$$dU_{sys} = \delta q + \delta w \qquad (3.2)$$

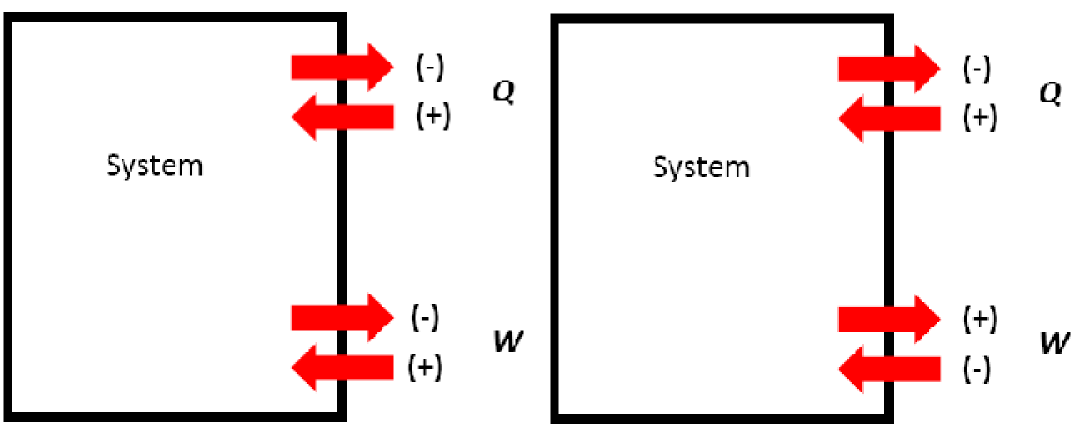
where the δ notation indicates δq and δw are inexact differentials.
- The implication of 3.2 is that δq and δw are NOT state functions and are not properties associated with a system at equilibrium. Heat is that form of energy that is transferred between two bodies that differ in energy. When two bodies at different temperatures come into thermal contact, they exchange heat. After a while thermal equilibrium is reached at which point their temperatures equalize and heat flow between them ceases. This statement is sometimes called the zeroth law of thermodynamics. The zeroth law basically relates the concepts of temperature, heat flow, and equilibrium.
- Work similarly is not a state function. Both heat and work are sometimes called path functions, to reflect their dependence on the path being followed.
- Upon integration…

$$\Delta U_{sys} = q + w \qquad (3.3a)$$

- Note that upon integration $q = \int \delta q \quad and \quad w = \int \delta w$. We never write $\Delta q = \int \delta q \quad or \quad \Delta w = \int \delta w$ because Δq and Δw imply the integral is independent of path.
- Chemistry/Biochemistry Sign Conventions: It is important to keep track of whether heat/work enter or leave the system. This is done with sign conventions. In the fields of chemistry and biochemistry, if heat q flows from the system into the surroundings or if the system does work w on the surroundings, then $q<0$ and $w<0$. Thus according to equation 3.3a, if heat leaves the system or work is done by the system, the internal energy is diminished. If on the other hand work is done on the system or heat flows into the system, then $q>0$ and/or $w>0$ and the internal energy increases.
- Physics/Engineering Sign Convention: In Physics and Engineering thermodynamics texts , the work sign convention is reversed. Work done by the system is positive $w>0$. The sign convention for heat remains the same. However, when work is done by the system, the system's internal energy must still decrease. Therefore using the physics/engineering sign convention for work, the first law must be written as:

$$\Delta U_{sys} = q - w \tag{3.3b}$$

- These sign conventions are summarized in Figure 1 below. ONLY equation 3.3a will be used in this course.




Chemistry Convention:

$$\Delta U_{sys} = q + w$$

Physics/Engineering Convention:

$$\Delta U_{sys} = q - w$$

Figure 1: The heat work sign conventions used in Chemistry/Biochemistry versus Physics/Engineering. The work sign conventions are reversed in the two systems which impacts the form of the First Law of Thermodynamics.

- In addition to specifying how changes in the system's internal energy come about as a result of work and heat flow, the First Law also requires conservation of energy in the sense that energy changes in a system be balanced exactly by energy changes in the surroundings such that the total energy of the universe is invariant. This is sometimes called the Invariance Principle.

- The First Law's Invariance Principle: The amount of energy in the universe is a constant. Therefore $\Delta U_{universe}=\Delta U_{system}+\Delta U_{surroundings}=0$.
- As a result of the Invariance Principle, a device whose net effect is to produce work without an accompanying exchange of heat with the surroundings (also called a perpetual motion machine of the first kind), cannot exist.
- We consider in the following sections how to calculate work and heat transfers.

## B. The Work Integral:

- In thermodynamics, work refers to mechanical and/or electrical contact between a system and the surroundings. Work is a form of energy. In the mechanical sense, work is defined as the product of the external force F applied to a mass times the distance d that the mass is compelled to move by the force F. Mathematically this is expressed as

$$w = \int_{start}^{finish} \vec{F} \cdot d\vec{\ell} \qquad (3.4)$$

- Work is calculated for complicated pathways by evaluating the work integral, which is calculated as follows.
  - F is the force displacing the mass along a path. The integral means the path is divided into very small, linear displacements dl (see Figure 2).
  - F and dl are both vectors. Work is a scalar, the inner product of F and dl for the work involved in moving the mass m by a small amount dl.
  - The work along a complicated path is calculated by summing (integrating) the inner products $\vec{F} \cdot d\vec{\ell}$ from the start of the path to the finish:

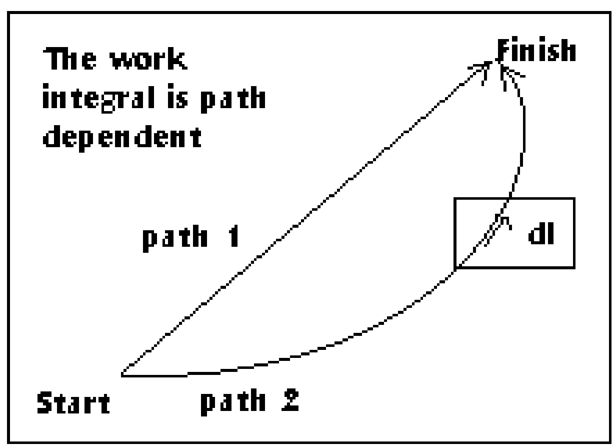



Figure 2: Work is not a state function, it is a path function. The work done in moving a mass from start to finish depends on the specifics of the path followed, not just where the work started and where it ended.

  - Examples of Mechanical Work

Example 1 “Lifting a weight” : A person lifts a weight of mass m=70.0 kg a vertical distance h=1.00 m. Calculate the work done by this person.

Solution:

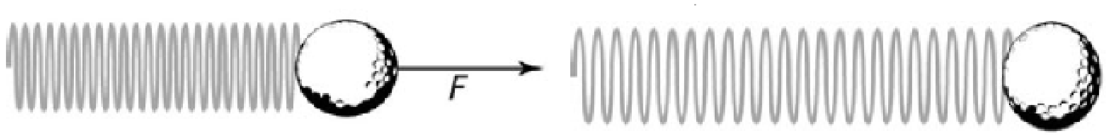
To use equation 3.4 it is important to determine a coordinate system for the purposes of identifying directions of forces. There is no correct or incorrect way to do this but one has to be consistent once one makes the choice. . Assume the vertical upwards direction is +z and so the gravitational force pulls the weight downwards (-z) so that $f_{gravity} = -mg$ where the gravitational constant g=9.81 $ms^{-2}$.

To lift the weight, a displacement force slightly greater than the gravitational force must be applied so that $f_{disp} \approx -(-mg) = mg$ . Then

$$w = \int_0^h f_{disp} dz = \int_0^h mgdz = mg\int_0^h dz = mgh$$

$$\therefore w = mgh = (70.0kg)(9.81ms^{-2})(1.00m) = 687.kgm^2s^{-2} = 687.J$$

Example 2 “Stretching a Spring”: How much work is done if a spring with a mass attached to a wall on the left end and on the right end to a moveable mass is stretched (i.e. to the right) by 1.000x$10^{-2}$ m, as shown below? Assume a spring constant $\kappa = 4900.Nm^{-1}$




Solution: Again determine the coordinate system. It makes sense to identify the +x direction as toward the right in the direction of the stretch. According to Hooke’s Law the force exerted by the spring on the mass tends to pull the mass to the left and toward the wall , which is the –x direction. Therefore the spring force that we must overcome to stretch the spring is according to Hooke’s Law: $f_{spring} = -\kappa x$ . Therefore to displace the mass to the right and thus stretch the spring the displacement force must roughly match this spring foce but to directed to the right. Therefore $f_{disp} \approx -f_{spring} = -(-\kappa x) = \kappa x$ . The work integral is

$$w = \int_0^\ell f_{disp} dx = \int_0^\ell \kappa xdx = \kappa\int_0^\ell xdx = \frac{\kappa\ell^2}{2}$$

$$\therefore w = \frac{\kappa\ell^2}{2} = \frac{1}{2}(4900.Nm^{-1})(1.000\times10^{-2}m)^2 = 0.2450Nm = 0.2450J$$

- Notice in the prior two examples that the work calculated is positive. This means work was done on the system (i.e. the weight or spring) to effecting the displacement.