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CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 2: Thermodynamic Variables, Systems, Processes & the First Law

References

1. Levine, *Physical Chemistry*, Sections 1.2, 2.1–2.4

Key Concepts

- Thermodynamic variables can be categorized based on how they change when the system size is changed. *Intensive* quantities, such as pressure and temperature, are independent of system size. *Extensive* variables, such as volume, mass, surface area, depend on the size of the system.
- Thermodynamic variables exist in *conjugate pairs*. The product of the units of these pairs is always energy. They always consist of one intensive variable (a force), for example pressure (P), and one extensive variable (displacement), like volume (V). They appear paired in work terms like $-PdV$, γdA, etc.
- Thermodynamic systems can be described by determining what can pass through the boundary between system and surroundings (isolated, closed, adiabatic, open). Processes can be described in a similar way by looking at parameters or variables that are constant (adiabatic, isochoric, to name a few).
- Processes can also be described based on their reversibility.
  - A *reversible* process is an idealized processes that is always in equilibrium and has no dissipative processes. A reversible processes can occur forward and backward.
  - An *irreversible* process occurs in one direction spontaneously. Most real processes are irreversible.
- The **First Law of Thermodynamics** is a way of expressing the principle of conservation of energy. In the framework of classical thermodynamics, the energy of interest is the *internal energy* (U). The internal energy accounts for energy stored within a material in bonds, vibrations, etc.
- The mathematical form of the first law is:

$$dU = \delta q + \delta w$$

  where δq is the heat flow into ($\delta q > 0$) or out of ($\delta q < 0$) the system and δw is the work done on ($\delta w > 0$) or by ($\delta w < 0$)the system. The d indicates an exact differential, namely that the change in internal energy is path independent. The δ's indicate inexact differentials that are path dependent.
- Work: from physics is defined as the force (F) used to move an object through some displacement (dl). We will be dealing with other kinds of work, but they will always have the same general form, a force or intensive variable, multiplied by a displacement in the conjugate extensive variable: $-PdV$, γdA, or in general YdX, where Y is an intensive variable and X is it's conjugate extensive variable.
- Heat: the "workless" transfer of energy. The quantity of energy that flows across a boundary because of a temperature difference.
- It is important to note that (1) heat an work only refer to **energy transfer** and (2) heat and work are not conserved quantities, they are path dependent.

Related Exercises in Levine

Exercises 1.2, 2.2, 2.4