
Thermo - The First Law

P Chem

Ron Robertson

I. Basic Concepts

A. Energy - property of a system that allows for work to be done. In non-nuclear transformations it is conserved.

B. System - the part of the world in which we have an interest

open - matter and energy can be transferred with the surrounding

- **closed – matter cannot be transferred with the surroundings but energy can**
- **isolated - neither matter nor energy can be transferred**
- **adiabatic - energy cannot be transferred by heat (insulated)**

C. Energy transfer in closed systems

- **work - Force (distance)**
: a transfer of energy that achieves or utilizes uniform motion in the surroundings
- **heat - energy transfer as a result of a temp difference**
: a transfer of energy that achieves or utilizes chaotic motion in the surroundings

II. First law of Thermo

A. Internal Energy

- The total energy of a system.
- It is the sum of all KE and PE terms of the particle.
- It is a state property (state function) because it only depends on the current state and is independent of how that state was determined.
- It is also an extensive property.
- Like all energy units it is measured by the Joule (J) as is heat and work. An older unit of the calorie (1 calorie = 4.18 J) is also used.

B. The First Law

**The internal energy of an isolated system is a constant.
In all other systems it can be changed by heat or
work.**

$$DU = q + w$$

w = work done on the system

q = heat gained by the system

**Positive values for w and q mean an increase in
internal energy.**

D. Hess's Law

It is possible to combine several equations to get a final new equation for a reaction. The DH for the sum of the reactions is equal to the sum of the individual reaction DH's.

V. Kirchhoff's Law

Variation of Enthalpy with Temperature

Suppose we know the enthalpy change at one temp and we wish to know what it is at another temp. Kirchhoff's Law allows us to compute this.

$$\Delta H_{T_2}^{\circ} = \Delta H_{T_1}^{\circ} + \Delta C_p \Delta T$$

ΔC_p is the change in heat capacity between reactant and products. In actual practice ΔC_p is usually very small and a good approximation in most problems is to assume that ΔC_p is independent of temperature.