물리화학Ⅰ

Atkins' Physical Chemistry 11th Edition
Part 1. Equilibrium (Thermodynamics)

- 1. The Properties of Gases
- 2. The First Law
- 3. The Second Law
- 4. Physical Transformations of Pure Substances
- 5. Simple Mixtures
- 6. Phase Diagrams
- 7. Chemical Equilibrium
The First Law

Internal Energy

For the purposes of thermodynamics, the universe is divided into two parts, System vs. Surroundings

System: Part of the world of interest.
Surrounding: the region outside system.

Open: Matter can be transferred between system and surroundings
Closed: Matter cannot be transferred but energy can be transferred.
Isolated: Matter and energy cannot be transferred.
The First Law

Work, Heat, and Energy

Work: done to achieve motion against an opposing force

Energy: its capacity to do work

Heat: Energy transferred as a result of a temperature difference.

Exothermic process:
A process that releases energy as heat.

Endothermic process:
A process in which energy is acquired as heat.
The First Law

Molecular interpretation of heat and work

**Thermal motion:**
The disorderly motion of molecules

**Work:**
The transfer of energy that makes use of organized motion in the surroundings

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**Figure 2A.3** When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

**Figure 2A.4** When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.
The First Law

Definition of Internal Energy

Internal Energy \((U)\)
The total energy of a system.

\[ \Delta U = U_f - U_i \]

The internal energy is State Function.

State Function:

A property with a value that depends only on the current state of the system and is independent of how that state has been prepared.
The First Law

Definition of Internal Energy

Molecular interpretation of internal energy

*Internal energy of a perfect gas is independent of the volume it occupies.*

\[ E_{\text{tans}} = \frac{1}{2} mv^2_x + \frac{1}{2} mv^2_y + \frac{1}{2} mv^2_z \]

*Heat and work are equivalent ways of changing the internal energy of a system.*

\[ \Delta U = q + w \]
The First Law

Expansion work

\[ dU = dq + dw \]

The general expression for work

\[ dw = -lFldz \]

\[ dw = - p_{\text{ex}} dV \]

Varieties of work

Expansion, Surface expansion, Extension, Electrical, and so on.
The First Law

Expansion against constant pressure

\[ w = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex}(V_f - V_i) \]

\[ w = -p_{ex}\Delta V \]

Figure 2A.6 The work done by a gas when it expands against a constant external pressure, \( p_{ex} \), is equal to the shaded area in this example of an indicator diagram.
The First Law

Reversible expansion

A change that can be reversed by an infinitesimal modification.

\[ w = -p_{ex} \Delta V = p \Delta V \]

\[ w = - \int_{V_i}^{V_f} p \, dV \]

\[ w = -nRT \int_{V_i}^{V_f} \frac{1}{V} \, dV = -nRT \ln \frac{V_f}{V_i} \]
The First Law

Heat Capacity

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_v \]

Molar Heat Capacity

\[ C_{v,m} = \frac{\partial}{\partial T} \left\{ \frac{3}{2}RT \right\} = \frac{3}{2}R \]

!! \( C_{v,m} = \frac{C_v}{n} \)

\[ dU = C_v \,dT \]

\[ \Delta U = \int_{T_1}^{T_2} C_v \,dT = C_v \int_{T_1}^{T_2} \,dT = C_v(T_2 - T_1) \]