CEN 202 Thermodynamics

Introduction to Chemical Engineering Thermodynamics

CHAPTER 2

The First Law and Other Basic Concepts

Joule's Experiments

James P. Joule conducted experiments on the nature of heat and work. These exeriments demonstrated the existence of a quantitative relationship between work and heat. The experiments showed that heat is a form of energy.

It was determined from the experiments that a constant amount of work is required to increase the temperature of the unit amount of water by mixing with each degree (1 °C). James P. Joule concluded that energy transformed from one form to another. This transformation is defined as INTERNAL ENERGY.

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INTERNAL ENERGY: It is called all energy (vibration + rotation + translation + electronic + attraction) that the smallest structure units such as atoms, ions, and molecules make up a system. The absolute value of internal energy is not known (In fact this is not necessary), we only need **internal energy changes.**

The Energy of a System:

It consists of “microscopic level (internal energy) + macroscopic level (kinetic + potential)”.

The First Law of Thermodynamics

First law: Although energy assumes many forms, the total quantity of energy is constant, when energy disappears in one form it appears simultaneously in other forms.

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The first law applies to the system and its surroundings, not to the system alone. For any process, the first law requires

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0$$

"Δ" signifies finite changes

The energy of the system shows finite quantities (internal energy, potential energy or kinetic energy). Since we are concerned with the system, we are not concerned with the energy changes of the surroundings.

Energy Balance For Closed System

Work and heat show energy, quantity that passes through the boundaries of the system and its surroundings. Such energies (heat and work) are not stored and contained in the system. Energy is stored as potential, kinetic and internal energy (with matter).

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Energy Balance For Closed System

Closed system is a system that there is no mass transfer between the system and its surroundings. Its mass is necessarily constant. However, there is energy transfer. All energy exchange (between the system and the environment) is heat and work. The total energy change of the surroundings equals to the net energy transferred to or from it as work and heat. So instead of the second term in the equation above,

$$\Delta(\text{Energy of surroundings}) = \pm Q \pm W$$

Heat Q and work W always refer to the system. The sign of Q and W depends on the direction of energy transfer (flow). The first term in equation includes different forms of energy such as internal energy, kinetic energy and potential energy changes.

$$\Delta(\text{Energy of system}) = \Delta U^t + \Delta E_K + \Delta E_P$$

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Energy Balance For Closed System

$$\Delta U^t + \Delta E_K + \Delta E_P = \pm Q \pm W$$

Since there is no change in external kinetic and potential energies in closed systems,

$$\Delta U^t = Q + W$$

For differential changes

$$dU^t = dQ + dW$$

Equilibrium and the Thermodynamic State

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any tendency toward change on a macroscopic scale.

Thermodynamic state: It is the state that shows the changes in the molecular or microscopic level, that is, the internal state of the system

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In summary:
The internal state of the system indicates "thermodynamic state". Thermodynamic state is expressed with features such as T, P, V, ρ.

State Functions: Changes are not dependent on the path (depending on initial and final states of the system).

Path Functions: Changes depend on the path.

The differential of a state function represents an **infinitesimal change** in its value.
The differentials of heat and work are not changes, but are **infinitesimal amounts.** When integrated, these differentials give note finite changes, but finite amounts. Thus,

$$\int dQ = Q \ \ and \ \ \int dW = W$$