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Thermodynamics

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter.

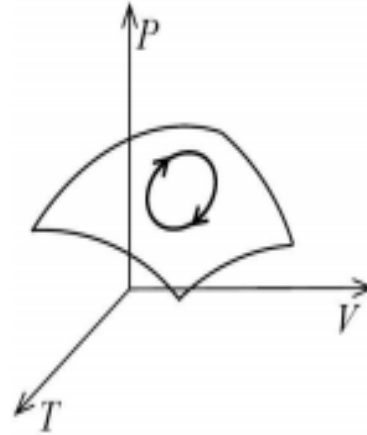
Zeroth Law of Thermodynamics

The **zeroth law of thermodynamics** states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. Accordingly, thermal equilibrium between systems is a transitive relation.

Concept of Work & Heat

Cyclic process. During a *cyclic process* the path in the equation-of-state space is a closed loop; the work done is along a closed cycle on the equation-of-state surface $f(P, V, T) = 0$:

$$W = - \oint P dV.$$

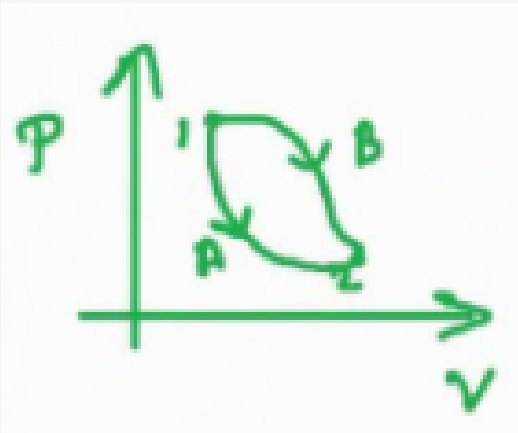


1) Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system through external macroscopic forces.

2) Energy is transferred in a system in the form of heat when no mechanical work is exerted, viz when $\delta W = -P dV$ vanishes. Compare (1). Other forms of energy (magnetic, electric, gravitational, ...) are also considered to be constant

State functions

A property whose value doesn't depend on the path taken to reach that specific value is known to as *state functions* or *point functions*. In contrast, those functions which do depend on the path from two points are known as *path functions*. State functions are the values which depend on the state of the substance like temperature, pressure or the amount or type of the substance. as a matter of fact, state functions do not depend on how the state was reached or established.



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First law of thermodynamics and its differential form

The **first law of thermodynamics** is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called Internal energy.

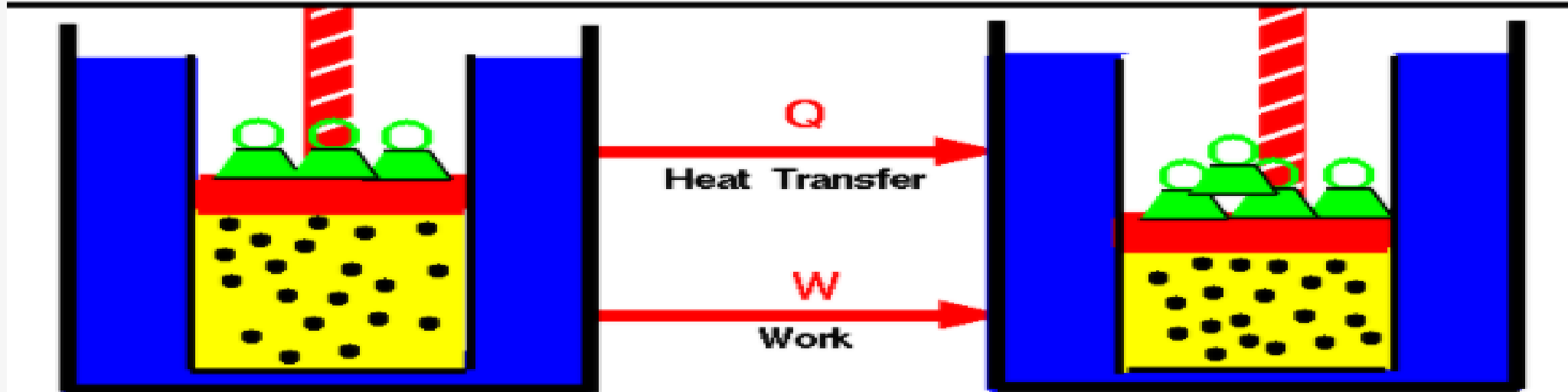
$$dU = \delta Q - \delta W + \mu dN$$

where μ is chemical potential. By convention, the heat flow into the system is taken as positive, whereas work done by a system is considered positive.

School of Basic and Applied Science

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State 1

E = Internal Energy

State 2

$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

Internal Energy

The **internal energy** of a thermodynamic system is a measure of the energy within it, excluding the kinetic energy of motion of the system as a whole, and the potential energy of the system as a whole due to external force fields. It keeps account of the gains and losses of energy of the system that are due to changes in its internal state.^{[1][2]} The internal energy is measured as a difference from a reference zero defined by a standard state. The difference is determined by thermodynamic processes that carry the system between the reference state and the current state of interest.

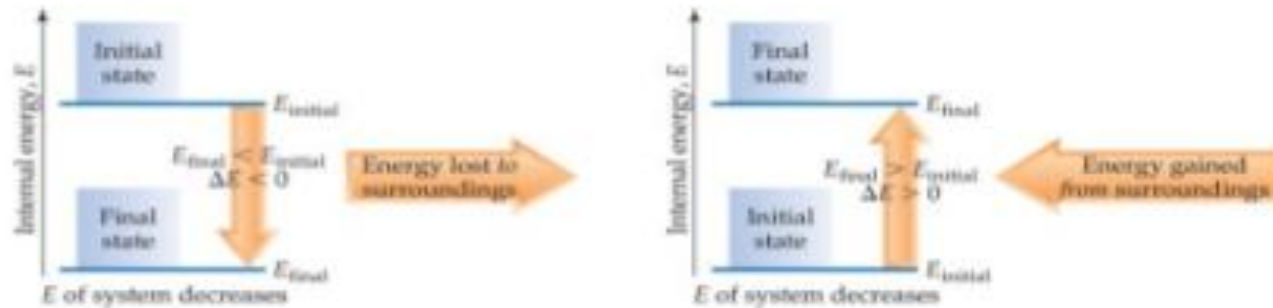
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$$\Delta U = \sum_i E_i$$

Internal Energy

By definition, the change in internal energy, ΔE , is the final energy of the system minus the initial energy of the system:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$



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Applications of first law of thermodynamics

The first law of thermodynamics has been successfully applied to diverse physical and chemical processes. In a sense, this law is universal and explains large scale phenomena occurring in nature as well as the microscopic processes that can be observed in a laboratory. For instance, the drop in temperature as we move upward in the outer atmosphere is explained rather well using the first law. We can also explain the pressure oscillations in a sound wave. Its applications to flow processes and chemical reactions leads to very interesting results. We begin by considering the heat capacities, which give us information about variation of internal energy of a substance with volume.

General Relation between C_p and C_v



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



$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_v dT + \left\{ p + \left(\frac{\partial U}{\partial V}\right)_T \right\} dV$$



$$C_v = \left(\frac{\delta Q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$



$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\left(\frac{\partial U}{\partial V}\right)_T + p \right) \left(\frac{\partial V}{\partial T}\right)_p$$



$$C_p - C_v = \left(\left(\frac{\partial U}{\partial V}\right)_T + p \right) \left(\frac{\partial V}{\partial T}\right)_p$$

Work Done during Isothermal and Adiabatic Processes

Isothermal process • P, V may change but temperature is constant. • The cylinder must have conducting walls. • It must happen very slowly so that heat produced during compression is absorbed by surroundings and heat lost during compression is supplied by surroundings.

Adiabatic process • In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero. • Since there is no heat exchange with the surroundings, • When expansion happens temperature falls • When gas is compressed, temperature rises.

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