# 1 The Internal Energy and the First Law of Thermodynamics

Thermodynamics is sometimes defined as the study of the relation of **temperature** of the macroscopic properties of the system. The laws of thermodynamics consists of the following:

1. Energy is *conserved*.
2. The *entropy* of an isolated system always *increases*.
3. The *entropy* of any pure *perfect crystal* can be chosen as equal to zero at 0 K.

**Energy** is the capacity to supply heat or do work. The units of energy consists of any of the following:

- 1 J = 1 kg $m^2/s^2$
- 1 cal = 4.181 J
- 1 dietary = 1000 cal

When energy is transferred from one object to another, it appears as work and heat.

$$\Delta U = q + W \tag{1}$$

## 1.1 The Law of Conservation of Energy

Energy cannot be created or destroyed, it can only be converted from one form to another, or transferred from one object to another. In thermodynamics, we are interested in the flow of energy, particularly in the forms of heat and work. Heat and work describe the energy transfer.

$$E = K + U \tag{2}$$

where $E$ is the total energy, $K$ is the kinetic energy, and $U$ is the potential energy.

How can a material store energy? On a molecular scale, we think in terms of:

- Thermal Energy: Kinetic energy of molecular motion (translational, rotational, and vibrational) which is measured by finding the temperature.
- Chemical Bond Energy: Potential energy stored in molecular bonds.

Since energy cannot be created or destroyed, and that it can be converted from one form to another, another way to put it is that *the total energy of the universe is* ***constant***.

$$\Delta E_{uni} = \Delta E_{sys} + \Delta E_{sur} = 0 \tag{3}$$

or

$$\Delta E_{sys} = -\Delta E_{sur} \tag{4}$$

In general,

$$\Delta E = E_2 - E_1 \tag{5}$$

## 1.2 The First Law of Thermodynamics

Let $E = K + U + u$ be the total energy of the system, where $K$ is the kinetic energy, $U$ is the potential energy, and $u$ is the internal energy, which consists of translational, vibrational, electronic, nuclear energies, and energy of intermolecular interactions.

For the system *at rest* and *with no external fields*:

$$E_{sys} = U \tag{6}$$

and

$$\Delta U = \Delta U_{sys} + \Delta U_{sur} \tag{7}$$

## 1.3 Internal Energy

Internal energy is a *state function* (path independence), so we are only interested in the final $U_2$ and the initial $U_1$ states.

$$\Delta U = U_2 - U_1 \tag{7}$$

where $\Delta$ refers to the change that occurs as a result of an arbitrary process. In the simplest processes, only one of $P$, $V$, or $T$ changes.

The First Law of Thermodynamics states that

$$\Delta U = q + W \tag{8}$$

We note three different processes that occur in the First Law,

- Isothermal: constant $T$ process, or $\Delta T_{sys} = 0$
- Isobaric: constant $P$ process, $\Delta P_{sys} = 0$
- Isochoric: constant $V$ process, or $\Delta V = 0$.
- Adiabatic: no heat transferred, or $q = 0$.

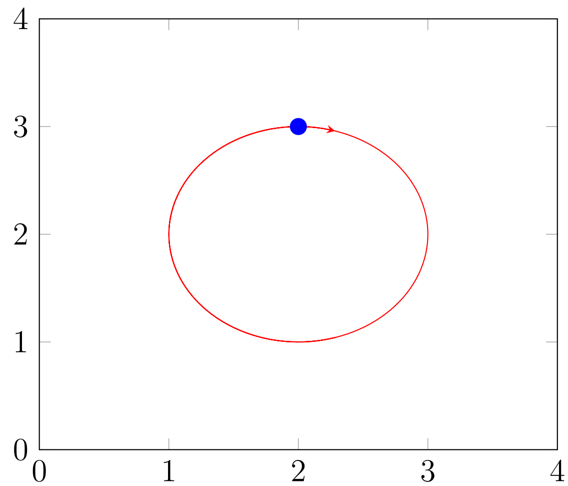
The reaction between hydrogen and oxygen occurs, but the output resulting from the change in internal energy is different. Consider

$$H_2 + \frac{1}{2}O_2 \to H_2O$$

Then we say that $\Delta_r U < 0$, since in general

$$\Delta_r U = U_p - U_r$$

Consider the path that is defined by a circle below, oriented once in the clockwise direction that represents a $PV$-graph.




Since any initial point and the final point in any simple closed curve is going to be the same, then in calculus terms,

$$\int_a^b f'(x)dx = \int_a^a f'(x)dx = f(a) - f(a) = 0$$

# 2 Work

Work in classical mechanics is the product of a *force* times the *distance*. Assume that the vectors of $F$ and $d$ are anti-parallel.

$$W = -F \cdot d = -mad = mg(h_2 - h_1) = -mg\Delta h$$

where $m$ is the units of kg, $h$ is in meters, $W$ is in J, and $g = 9.8$ m/s$^2$.

Work in thermodynamics is defined as a quantity of energy that flows across the boundary between the system and surroundings that can be used to change the height of a mass in the surroundings.

Work is NOT a state function, as it depends on the path taken. In other words, it is an irreversible expansion versus a reversible expansion.

The sign of work may vary depending on the convention.

- Work done ON the system is going to lead to a POSITIVE quantity.
- Work done BY the system is going to lead to a NEGATIVE quantity.

## 2.1 Expansion of Work

$P_{ext}$ is the external force per unit area:

$$P_{ext} = \frac{F_{ext}}{A}$$

Then the infinitesimal volume change $dV = Adh$. Then if

$$dW = -F_{ext}dh = -\frac{F_{ext}}{A} \times Adh = -P_{ext}dV$$

We can integrate both sides with respect to $V$ so that

$$W = \int_{V_1}^{V_2} P_{ext}dV$$

In an adiabatic system (no heat exchange), how can energy be transferred to surroundings, in thw form of work?

$$W = -P\Delta V \Rightarrow W = -\Delta nRT$$

Where $\Delta n = n_p - n_r$.