

# Thermodynamics

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## 1 Definition

**Definition 1** (Thermodynamics). The branch of physics that analyzes the relation between heat and work. Often, both occur together.

**Definition 2** (System, Surroundings). The system is the collection of objects on which attention is focused. The surroundings is everything else in the environment.

**Definition 3** (Diathermal and Adiabatic Walls). Walls separate the system from the surroundings. Diathermal walls permit heat to flow through them. Adiabatic walls are perfectly insulating walls that perfectly prevent heat from flowing between the system and the surroundings.

**Definition 4** (State of a System). A complete description of a system at a given time. Specified by variables for pressure, volume, temperature, and entropy for thermodynamics.

**Definition 5** (Thermal Equilibrium). Two systems are in thermal equilibrium if there is no net flow of heat between them when they are brought into thermal contact.

## 2 The Zeroth Law of Thermodynamics

**Definition 6** (The Zeroth Law of Thermodynamics). Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other. The state of the third system is the same when it is in thermal equilibrium with either of the systems.

The third system is often a thermometer; if two objects have the same temperature, then there are in thermal equilibrium. In effect, the zeroeth law establishes temperature as the indicator of thermal equilibrium (same temperature = thermal equilibrium) *and implies that all parts of a system must be in thermal equilibrium if the system is to have one definable temperature.*

## 3 The First Law of Thermodynamics

When an object participates in a process involving energy as work and heat, the internal energy ( $U$ ) of that object can change.

Suppose a system gains heat  $Q$  and no work is done. Consistent with the law of conservation of energy,  $\Delta U = U_f - U_i = Q$ . (By convention, heat  $Q$  is positive when the system *gains* heat, and negative when the system *loses* heat.)

Similarly, suppose a system does work  $W$  on its surroundings with no heat flow. Consistent with the law of conservation of energy,  $\Delta U = U_f - U_i = -W$ . (By convention, work  $W$  is positive when *done by the system* and negative when done *to the system*).

Combine these two for the **first law of thermodynamics**:

**Definition 7** (The First Law of Thermodynamics). The law of conservation of energy applies to heat, work and changes in internal energy. For change in internal energy  $\Delta U$ , heat  $Q$ , and work  $W$  (all expressed in Joules):

$$\Delta U = U_f - U_i = Q - W$$

**Internal energy is a function of state.** (Or conservative, like gravitational potential energy.) The internal energy of a system depends only on the state of the system at that given time, with no regard to how it got there. Similarly, difference of internal energies are functions only of the initial and final states.

From the first law of thermodynamics, it can be observed that heat and work are not functions of state.  $Q = 500\text{J}$  will change the internal energy of a system just as much as  $Q = 750\text{J}$  and  $W = 250\text{J}$ .

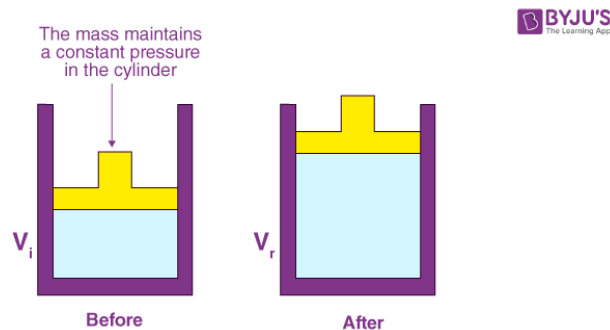


Figure 1: An example of an isobaric system. The gas pushes the mass and piston (surface area  $A$ ) upward when heated.

### 3.1 Thermal Processes

Systems will interact with their environment in several ways. The *thermal processes* described in this section are assumed to be **quasi-static**: changes occur slowly enough such that uniform pressure and temperature exist throughout all regions of the system at all times.

#### 3.1.1 Isobaric Processes

**Isobaric processes are processes that occur at constant pressure.** Consider the piston in Figure 1. Heating the gas causes it to expand from  $V_i$  to  $V_f$ , doing work  $W$  by lifting the piston and mass through displacement  $\vec{s}$ . Because  $W = Fs = (PA)s$ , for all isobaric processes:

$$W = P\Delta V = P(V_f - V_i)$$

#### 3.1.2 Isochoric Processes

**Isochoric processes are processes that occur at constant volume.** While the pressure may increase and exert pressure on the walls of a container, by definition,  $\Delta V = 0$ , and therefore no work is done (via the above equation). From the first law of thermodynamics,  $\Delta U = Q$  for all isochoric processes.

#### 3.1.3 Isothermal Processes

**Isothermal processes are processes that occur at constant temperature.** For ideal gases, assuming constant number of moles,  $P = \frac{nRT}{V}$ .

Because pressure is now a function of volume, work can be solved for using the general form of work discussed below:

$$W = \int_{V_i}^{V_f} \frac{nRT}{V} = nRT \left( \frac{1}{V} \Big|_{V_i}^{V_f} \right) = nRT \ln \left( \frac{V_f}{V_i} \right)$$

Where does the energy for this work originate? Since the internal energy of any ideal gas is proportional to its temperature ( $U = \frac{3}{2}nRT$  for monatomic ideal gases), internal energy remains constant throughout the process. Using the first law of thermodynamics,  $\Delta U = Q - W \rightarrow Q = W$ : the heat from the surroundings is used for work, or vice versa.

### 3.1.4 Adiabatic Processes

**Adiabatic processes are processes where no heat is transferred between the surroundings and the system.** Because  $Q = 0$ ,  $\Delta U = -W$ .

For monatomic ideal gases,  $\Delta U = \frac{3}{2}nR\Delta T$  as well, so  $W = -\frac{3}{2}nR\Delta T$ .

When an ideal gas expands adiabatically, it does positive work, so  $W$  is positive. Therefore,  $T_i - T_f$  is positive, so the temperature of the gas decreases. Similarly, if a ideal gas compresses adiabatically, it does negative work, so the temperature of the gas increases.

It can be shown that  $P_i V_i^\gamma = P_f V_f^\gamma$ , where  $\gamma = \frac{C_p}{C_v}$ : the ratio specific heat capacities of the gas at constant pressure and constant volume. (See 3.2.1 for a proof of this.)

### 3.1.5 Other Processes

Processes may be complicated enough that they may not be easily identifiable as one of the four processes just discussed. However, correlary to the equation for isobaric processes, the following can be proven, assuming pressure is a function of volume:

$$W = \int_{V_i}^{V_f} P(V) dV$$

## 3.2 Specific Heat Capacity of Gases

Similar to how  $Q = mc\Delta T$  for substances, a similar analog exists for gases:

$$Q = Cn\Delta T$$

$C$  (vs.  $c$ ) refers to the **molar specific heat capacity** (units  $\frac{\text{J}}{\text{mol} \times \text{K}}$ ), and  $n$  analogously refers to the number of moles in the gas. For gases, it

is necessary to differentiate between the molar specific heat capacities for constant volume ( $C_v$ ) and constant pressure ( $C_p$ ).

To determine these heat capacities, we must first calculate  $Q$  needed to raise  $T_i$  to  $T_f$ . According to the first law,  $Q = \Delta U + W$ . For ideal gases,  $\Delta U = \frac{3}{2}nR\Delta T$ . For constant pressure,  $W = P\Delta V$ . According to the ideal gas law (holding pressure constant),  $P\Delta V = nR\Delta T$ , so  $W = nR\Delta T$ . For constant volume,  $W = 0$ . So:

$$Q = \Delta U + W$$

$$Q_{\text{const. p}} = \frac{3}{2}nR\Delta T + nR\Delta T = \frac{5}{2}nR\Delta T$$

$$Q_{\text{const. v}} = \frac{3}{2}nR\Delta T + 0 = \frac{3}{2}nR\Delta T$$

Because  $Q = Cn\Delta T$ ,  $C = \frac{Q}{n\Delta T}$ :

$$C_p = \frac{Q_{\text{const. p}}}{n\Delta T} = \frac{5}{2}R$$

$$C_v = \frac{Q_{\text{const. v}}}{n\Delta T} = \frac{3}{2}R$$

Thus, the ratio  $\gamma$  between them (for monatomic ideal gases):

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

Real monatomic gasses at STP show ratios similar to the theorized  $\gamma = \frac{5}{3}$ .

For diatomic ideal gases, molecules can exhibit translational, rotational, and vibrational motion (vibrational at sufficiently high temperatures). For these gasses, it can be shown that  $C_p = \frac{7}{2}R$ ,  $C_v = \frac{5}{2}R$ , and subsequently,  $\gamma = \frac{7}{5}$ .

It can be shown that for **all** gases:

$$C_p - C_v = R$$

### 3.2.1 Proof of PV Relation for Adiabatic Processes\*

Assume that the gas changes by volume  $\Delta V$  causing subsequent temperature change  $\Delta T$ . From this,  $\Delta W = P\Delta V$ , and by the process being adiabatic,  $\Delta Q = 0$ .

$$\Delta U = C_v n \Delta T$$

From the first law:

$$\Delta U = C_v n \Delta T = \Delta Q - \Delta W = 0 - P \Delta V \rightarrow \Delta T = -\frac{P \Delta V}{C_v n}$$

From the ideal gas law (differential)

$$\Delta(PV) = \Delta(nRT) \rightarrow P \Delta V + V \Delta P = nR \Delta T$$

Rearranging for  $\Delta T$ :

$$\Delta T = \frac{P \Delta V + V \Delta P}{Rn}$$

Setting both equations for  $\Delta T$  equal:

$$\frac{P \Delta V + V \Delta P}{Rn} = -\frac{P \Delta V}{C_v n} \rightarrow C_v (P \Delta V + V \Delta P) + R P \Delta V = 0$$

Dividing by  $PV$ :

$$C_v \left( \frac{\Delta V}{V} + \frac{\Delta P}{P} \right) + \frac{R \Delta V}{V} = 0$$

Using  $C_v = C_p - R$

$$C_v \frac{\Delta P}{P} + (C_p - R) \frac{\Delta V}{V} + \frac{R \Delta V}{V} = C_v \frac{\Delta P}{P} + C_p \frac{\Delta V}{V} = 0$$

$$C_v \frac{\Delta P}{P} + C_p \frac{\Delta V}{V} = \frac{\Delta P}{P} + \gamma \frac{\Delta V}{V} = 0 \quad (\gamma = \frac{C_p}{C_v})$$

Thus, by intergration by parts:

$$\ln(P) + \gamma \ln(V) = \text{const}$$

$$PV^\gamma = \text{const}$$

Because this is true for all such processes, then we get the original relation:

$$P_i V_i^\gamma = P_f V_f^\gamma$$

## 4 The Second Law of Thermodynamics

### 4.1 Carnot Engines

### 4.2 Entropy

## 5 The Third Law of Thermodynamics