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## 1 System and Surroundings

#### Definitions:

- System: A system is a portion of the universe that has been chosen for study. Put simply, it is a set of objects to be analyzed. Conversely, the universe is a system that is made up of sub-systems within it.
  - A closed system is one that does not exchange matter with its surroundings.
     I.e. the quantity of matter in the system is constant.
  - 2. An **isolated system** has even stricter requirements it is one where **neither** matter nor energy can be exchanged with the surroundings.
- In contrast, the **surroundings** are everything external to the system that may also interact with it.

## 2 First Law of Thermodynamics

#### Law. 1

$$\Delta U = Q - W \tag{1}$$

- $\Delta U$  is the change in internal energy of the system.
- Q is the energy supplied to the system.
- W is the work done by the system.

#### By the Clausius sign convention:

- 1. Q > 0 when energy is transferred to the system, and vice versa.
- 2.  $\Delta U > 0$  when the internal energy of the system increases, and vice versa.
- 3. W > 0 when work is done by the system **on the surroundings**, and vice versa.

This is a result of energy conservation. The internal energy of a system changes when:

- 1. The system does work, or work has been done on the system.
- 2. Energy is transferred to or from the system when there are temperature differences between the system and the surroundings.

An example of a measure of the internal energy of a system is the temperature of an ideal gas.

### 2.1 Piston – Common Scenario Analysis

The three quantities in Equation (1) in this particular system are

- $\Delta U$ : The **change in temperature**, and this can be converted using the temperature equation under section 4.3 (ideal gas kinetic model) in B3.
- Q: Any thermal energy supplied to the gas, or inversely, the thermal energy lost by the gas.
- W: The work done by the gas on the piston (e.g. when the gas expands to push the piston), or the work done on the gas by the piston (e.g. when the gas is compressed).

## 3 Pressure-Volume Graphs

Consider the following situation

- The system consists of an **ideal gas** in a cylinder with a movable piston.
- We assume, for the sake of simplicity, that the gas is kept at a **constant pressure**. This of course requires energy to be somehow transferred from the surroundings to the gas. Analogously, there is a positive Q.

As the gas expands, the following occurs:

- 1. The volume of the gas increases.
- 2. The expansion pushes the piston upwards, doing work on the surroundings. Thus, there is a positive W.

This work done is given as

$$W = P\Delta V > 0 \tag{2}$$

*Proof.* Let  $\Delta x$  be the distance moved by the piston. Then, the work done is given as  $F\Delta x$ . Since F=PA, where A is the area of the piston, we have  $W=PA\Delta x$ . Notice that  $A\Delta x=\Delta V$ , so  $W=P\Delta V$ .

## 3.1 Graphical Interpretation

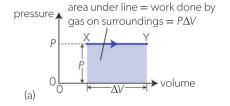
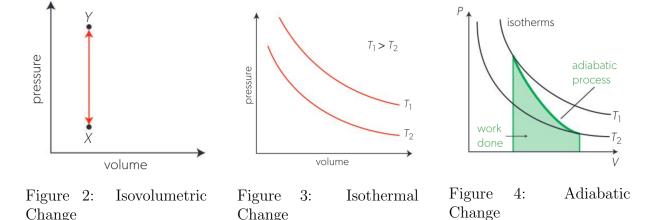


Figure 1: Pressure-Volume Graph

- The area under the graph represents the work done by the gas.
- The work done is positive when the gas expands, and negative when the gas is compressed. Use the arrow to verify this.
- Make sure that the axes start at 0; otherwise, in the case of a false origin, add in the missing bit.

#### Types of Changes in a Gas 4

"Iso" is a word of greek origin that means "same".



#### Isobaric Change 4.1

Change

A change in a gas carried out at constant pressure throughout.

The gas law that applies in this case, is the **Charle's Law**, i.e.  $\frac{V}{T} = \text{constant}$ .

On a P-V graph, this is represented by a horizontal line (see Figure 1).

Change

Note also, that Equation (1) can be rewritten as

$$\Delta U = Q - P\Delta V$$

### 4.2 Isovolumetric Change

A change in gas carried out at constant volume throughout.

The gas law that applies is **Gay-Lussac's Law**, i.e.  $\frac{P}{T} = \text{constant}$ .

On a P-V graph, this is represented by a vertical line (see Figure 2).

In this case, the first law is rewritten as

$$\Delta U = Q - P\Delta V = Q - 0P = Q$$
 
$$\Delta U = Q$$

### 4.3 Isothermal Change

A change in gas carried out at constant temperature (and hence constant internal energy) throughout.

The gas law that applies is **Boyle's Law**, i.e. PV = constant.

On a P-V graph, this is represented by an **isothermal curve**. Each temperature has a different curve (see Figure 3). Each curve is referred to as an isotherm.

Since the internal energy goes through no change, we have  $\Delta U = 0$ . Thus, the first law is rewritten as

$$Q = W$$

- 1. The implication is that **all** the energy supplied to the gas is used to do work.
- 2. If Q, W > 0, then, the gas is expanding, and energy is supplied to the gas, and the gas does work on the surroundings.
- 3. If Q, W < 0, then, the gas is compressed, and energy is lost by the gas, and work is done on the gas by the surroundings.

Practically, isothermal changes are not possible:

- 1. Perfect isothermal changes would theoretically require infinite time, here's why
  - (a) This requires the pressure change to be **quasi-static** (meaning it happens in such small, incremental steps that the system remains in thermal equilibrium throughout).
  - (b) Each tiny change in volume must be **instantaneously counterbalanced** by an appropriate heat transfer to prevent a temperature drop.
  - (c) This will then require each  $\Delta V$  to be infinitely small, which would take infinite time for the entire process to take place.
- 2. A slow enough change can be considered near-isothermal.

### 4.4 Adiabatic Change

A change in gas carried out with no energy transfer between the system and the surroundings. I.e the system is **thermally isolated**. This is done through insulating the system.

In this case, Q = 0, and so  $\Delta U = -W$ . This actually encapsulates two physical situations. It's straightforward that the two quantities have matching magnitudes; let us see why they have opposite signs.

- Gas compression: The surrounding is doing work on the gas, and so W < 0. The gas is increasing in energy, and thus  $\Delta U > 0$ .
- Gas expansion: The gas is doing work on the surroundings, and so W > 0. The gas is losing energy, and thus  $\Delta U < 0$ .

We introduce a new equation that has not been seen before. This is specific to adiabatic changes:

$$PV^{\frac{5}{3}} = \text{constant} \quad \text{and} \quad TV^{\frac{5}{3}} = \text{constant}$$
 (3)

Note that the latter requires constant pressure in addition to the adiabatic condition.

Note that perfect adiabatic changes are also not practically feasible.

- 1. The system must be perfectly insulated, which is impossible.
- 2. Another important reason is that a perfect adiabatic change would allow no time for change to take place.
  - (a) The duration of the change must be **infinitely short** to prevent any heat loss through the boundaries of the system to the surroundings.
  - (b) Thus, for a perfect adiabatic change to take place, the time taken must be 0.
- 3. Again, rapid enough changes can approximate adiabatic changes.

### 4.5 Combining Different Types of Changes

There are many different ways in which the different types of changes can be combined.

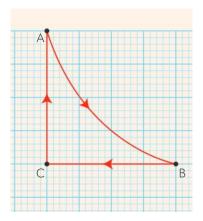


Figure 5: Isobaric, isovolumetric, isothermal

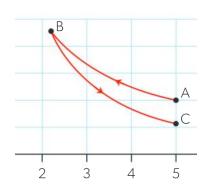


Figure 6: Isothermal, adiabatic

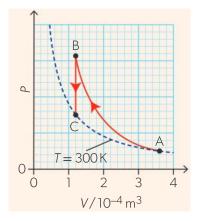


Figure 7: Adiabatic, isovolumetric

A general strategy is to

- 1. For each change, recognize the type.
- 2. Then, consider what is changing and what is constant based on the type of change.

  Considering the area can help.
- 3. Where necessary, invoke the associated gas laws.

## The table below summarizes the changes

Shape	Type	Constant	Possible Variable	Gas Laws
Horizontal line	Isobaric	Pressure	Volume	Charles'
Vertical line	Isovolumetric	Volume	Temperature	Gay-Lussac's
Isothermal curve	Isothermal	Temperature	Pressure	Boyle's
Skipping between	Adiabatic	Internal energy	Pressure, volume,	Equation (3)
two isotherms			temperature	

## 5 Heat Cycle and Engines

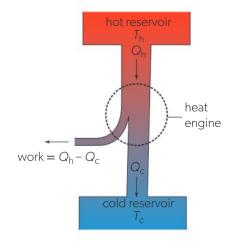


Figure 8: Heat Engine

A heat engine is a device that converts thermal energy into mechanical work. It takes in heat from a high-temperature source, does work, and releases some wasteful heat to a low-temperature sink.

Simplified explanation of the mechanism:

- 1. The engine absorbs  $Q_1$  energy from the hotter reservoir.
- 2. In the process of doing work, the engine releases  $Q_2$  energy to the colder reservoir. This is because it is never 100% efficient.
- 3. The useful work produced by the engine is  $W = Q_1 Q_2$ .

The efficiency of this process  $\eta$  is given by

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{4}$$

- 5.1 The Carnot Cycle
- 5.2 Refrigerators and Heat Pumps

# 6 The Second Law of Thermodynamics

# 7 Entropy

- 7.1 A Macroscopic Interpretation
- 7.2 A Microscopic Interpretation