Chapter 19

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Temperature And The Behavior Of Gases

Thermodynamics

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Thermodynamics involves situations in which the temperature of a system changes due to energy transfers.

To describe thermal phenomena, careful definitions are needed:

- Temperature
- Heat
- Internal energy

Temperature

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- We associate the concept of temperature with how hot or cold an object feels.
- Our senses provide us with a qualitative indication of temperature.
- Our senses are unreliable for this purpose.

We need a technical definition of temperature.

Thermal Contact and Thermal Equilibrium

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- Two objects are in thermal contact with each other if energy can be exchanged between them.
  - The exchanges we will focus on will be in the form of heat.
- The energy is exchanged due to a temperature difference.

- Thermal equilibrium is a situation in which two objects would not exchange energy by heat if they were placed in thermal contact.

Zeroth Law of Thermodynamics

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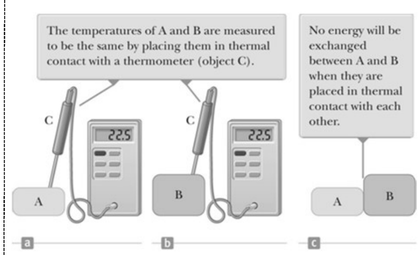
- "If objects **A** and **B** are separately in thermal equilibrium with a third object **C**, then **A** and **B** are in thermal equilibrium with each other."
  - Let object **C** be the thermometer
  - Since they are in thermal equilibrium with each other, there is no energy exchanged among them.



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Temperature – Definition

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- Temperature is the property that determines whether an object is in thermal equilibrium with other objects.
- Two objects in thermal equilibrium with each other are at the same temperature.
- Temperature is something that determines whether or not energy will transfer between two objects in thermal contact.

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Thermometers

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- A thermometer is a device that is used to measure the temperature of a system.
- Thermometers are based on the principle that some physical property of a system changes as the system's temperature changes.
- These properties include:
  - The volume of a liquid
  - The dimensions of a solid
  - The pressure of a gas at a constant volume
  - The volume of a gas at a constant pressure
  - The electric resistance of a conductor
  - The color of an object

Thermometer, Liquid in Glass

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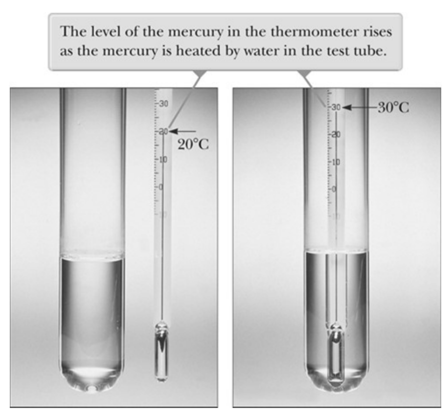
- A common type of thermometer is a liquid-in-glass.
- The material in the capillary tube expands as it is heated.
- The liquid is usually mercury or alcohol.



Calibrating a Thermometer

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- A thermometer can be calibrated by placing it in contact with some natural systems that remain at constant temperature.
- Common systems involve water
  - A mixture of ice and water at atmospheric pressure
    - Called the ice point of water
  - A mixture of water and steam in equilibrium
    - Called the steam point of water
- Once these points are established, the length between them can be divided into a number of segments.

Celsius Scale

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- The ice point of water is defined to be 0^o C.
- The steam point of water is defined to be 100^o C.
- The length of the column between these two points is divided into 100 increments, called degrees.

Fahrenheit Scale

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- A common scale in everyday use in the US
- Temperature of the ice point is 32°F.
- Temperature of the steam point is 212°F.
- There are 180 divisions (degrees) between the two reference points.

Absolute Zero

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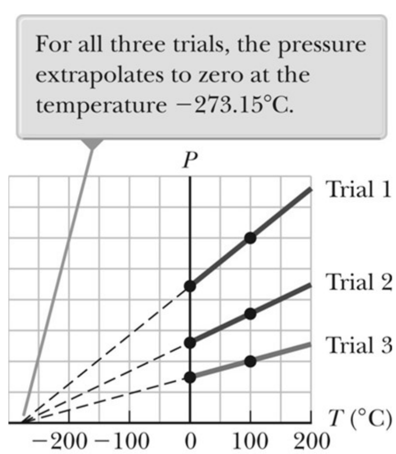
- If the lines for various gases are extended, the pressure is always zero when the temperature is –273.15° C.
- This temperature is called absolute zero.
- Absolute zero is used as the basis of the absolute temperature scale.
- The size of the degree on the absolute scale is the same as the size of the degree on the Celsius scale (100 degrees).



Absolute Temperature Scale

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- The absolute temperature scale is now based on two new fixed points.
  - One point is absolute zero.
  - The other point is the triple point of water.
    - This is the combination of temperature and pressure where ice, water, and steam can all coexist.
  - The triple point of water occurs at 0.01° C and 4.58 mm.Hg.
  - This temperature was set to be 273.16 on the absolute temperature scale.
  - The units of the absolute scale are Kelvins.

Comparison of Scales

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- Celsius and Kelvin have the same size degrees, but different starting points.

$$T_C = T_K - 273.15$$

Celsius and Fahrenheit have different sized degrees and different starting points.

$$T_F = \frac{9}{5} T_C + 32$$

- To compare changes in temperature

$$\Delta T_C = \Delta T_K = \frac{5}{9} \Delta T_F$$

- Ice point temperatures

$$0\,^{\circ}C = 273.15\,K = 32^{\circ}F$$

- Steam point temperatures

$$100\,^{\circ}C = 373.15\,K = 212\,^{\circ}F$$

Comparison of Scales

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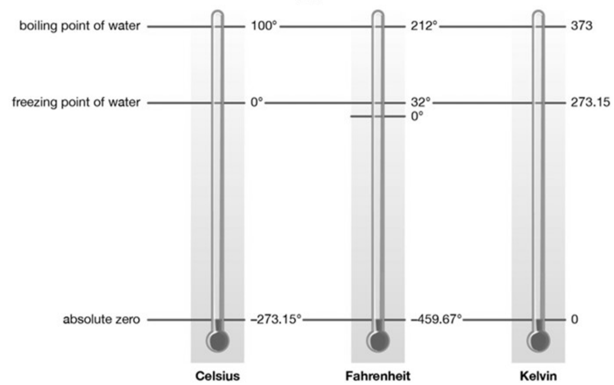

General formula:

- $\frac{T_C - 0}{100} = \frac{T_F - 32}{180} = \frac{T_K - 273.15}{100}$

Internal Energy

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- Internal energy is all the energy of a system that is associated with its microscopic components.
  - These components are its atoms and molecules.

- Internal energy includes kinetic energies due to:
  - Random translational motion
  - Rotational motion
  - Vibrational motion
- Internal energy also includes potential energy between molecules.
- The SI unit is (Joule).

Heat

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- Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.
- The term heat will also be used to represent the amount of energy transferred by this method.
- Heat, internal energy, and temperature are all different quantities.
- The SI unit is (Joule).

Molecular Masses

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- **Monoatomic** gases: their molecules are single atoms, such as: Helium (He) and Argon (Ar).
- **Polyatomic** gases: their molecules contain two or more atoms, such as: Oxygen (O_2), Carbon Dioxide (CO_2) and Ammonia (NH_3).
- An **atomic mass unit (u)** is defined as 1/12 the mass of the carbon-12 isotope. It has been determined that:

$$1\ u = 1.66 \times 10^{-2}\ \ kg$$

- The **molecular mass (m)** of a molecule is defined as the sum of the masses of its constituent atoms in atomic mass unit.

The Mole

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- **The mole** is the amount of substance of a system whose mass in grams is numerically equal to the molecular mass in atomic mass unit.
- **Avogadro's number (N_A):** the number of molecules in 1 mole:

$$N_A = 6.022 \times 10^{-23}\ mol^{-1}$$

- The **molar mass (M):** is the product of the mass (*m*) of one molecule and the number of molecules in 1 mol:

$$M = mN_A$$

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The Mole

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- The **number of moles (n)** contained in a sample of any substance is equal to the ratio of the number of molecules (N) in the sample to the number of molecules N_A in 1 mol:

$$n = \frac{N}{N_A}$$

- **Also**, we can find the number of moles (n) in a sample from the mass (M_{sample}) of the sample and the molar mass (M) :

$$n = \frac{M_{sample}}{M} = \frac{M_{sample}}{mN_A}$$

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Moles, cont

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The number of moles can be determined from the mass of the substance, or from the number of molecules:

$$n = \frac{M_{sample}}{M} = \frac{N}{N_A}$$

- n: is the number of moles.
- M_{sample}: is the mass of the sample (in g).
- M: is the molar mass of the substance.
  - Can be obtained from the periodic table
  - Is the atomic mass expressed in grams/mole
  - Example: (He) has mass of 4.00 u so M = 4.00 g/mol
- N: is the number of molecules
- N_A: Avogadro's number:
$$N_A = 6.022 \times 10^{-23}\ mol^{-1}$$
- u: is the atomic mass unit:
$$u = 1.67 \times 10^{-2}\ \ kg$$

Pressure

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- Pressure is the ratio of the magnitude of the normal force applied divided by the surface area:
$$P = \frac{F}{A}$$
- Pressure is a scalar quantity, and the SI unit is the Pascal (Pa):
$$1Pa = 1\,N/m^2$$
- The **atmospheric pressure** (atm) is:
$$1\ atm. = 1.013 \times 10^5\ \ N/m^2 = 760\ mmHg$$

An Ideal Gas Law

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- For gases, the interatomic forces within the gas are very weak.

For a gas, no "standard" volume at a given temperature.

- For a gas, the volume depends on the size of the container.
- It is useful to know how the volume, pressure, and temperature of the gas of mass m are related.
- The ideal gas can be defined as any gas that its pressure (p), its temperature (t) and its volume (v) can be related at low pressure.
- The equation that interrelates these quantities is called the ideal gas law.

Ideal Gas Experiment

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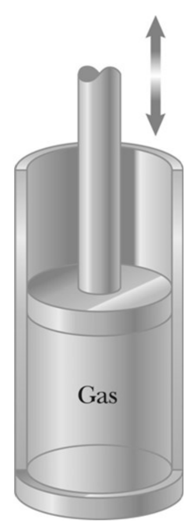
- Suppose an ideal gas is confined to cylindrical container.
- The volume can be varied by means of a movable piston.
- Experiments determine a great deal of information about the gas.



Gas Laws

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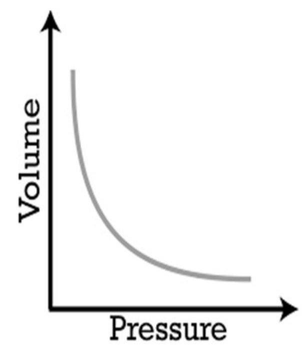
- Boyle's law:
- When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume.

- $PV = constant$



Gas Laws

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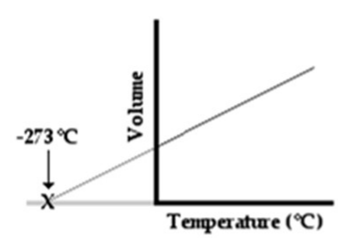
- Charles law:
- When a gas is kept at a constant pressure, its volume is directly proportional to its temperature.

- $\frac{V}{T} = constant$



Gas Laws

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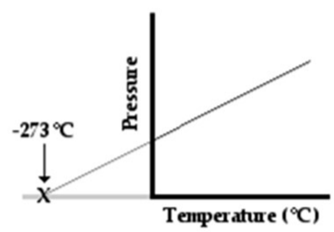
- Guy-Lussac's law:
- When the volume of the gas is kept constant, the pressure is directly proportional to the temperature.

- $\frac{P}{T} = constant$



Ideal Gas Law

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- The equation of state for an ideal gas combines and summarizes the other gas laws:

$$PV = nRT$$

- This is known as the ideal gas law.
  - n: number of moles
  - T: temperature in (K)
  - P: pressure
  - V: volume
  - R: is the Universal Gas Constant.

Ideal Gas Law

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If:
- Pressure in N/m^2
- Volume in m^3

Then:
- $R = 8.314\ J/mol.K$

If:
- Pressure in atmospheric
- Volume in liter

Then:
- $R = 0.08207\ L.atm/mol.K$

Ideal Gas Law

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Conversions:
- $1\ m^3 = 10^3 liter$
- $1\ atm = 1.013 \times 10^5\ N/m^2 = 760\ mmHg$

Ideal Gas Law

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•The ideal gas law is often expressed in terms of the total number of molecules, *N*, present in the sample.

$$PV = Nk_BT$$

k_B : is Boltzmann's constant

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}\ J/K$$

Gas Mixtures

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- How do we deal with gases composed of a mixture of two or more different substances? The answer is known as **Dalton's Law** of Partial Pressures which has these two equivalent statements:
- **(1)** Each gas in a mixture of gases exerts a pressure, known as its partial pressure, that is equal to the pressure the gas would exert if it were the only gas present.
- **(2)** The total pressure of the mixture is the sum of the partial pressures of all the gases present.

Gas Mixtures

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- Suppose there are $n(O_2)$ moles of Oxygen and $n(N)$ moles of Nitrogen in a volume (V) of air at a temperature (T), the partial pressure of Oxygen and Nitrogen will each satisfy the ideal gas law:

$$P_{(O_2)}V = n_{(O_2)}RT$$
$$P_{(N_2)}V = n_{(N_2)}RT$$

- The total pressure (P) (ignoring the small amount of other gases present) of the air is the sum:

$$P = P_{(O_2)} + P_{(N_2)}$$

- And the number of moles is:

$$n = n_{(O_2)} + n_{(N_2)}$$

Temperature and Molecular Energies

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- The ideal gas law, $PV = nRT$, was originally obtained from several types of **experiments**. However, it is also possible to construct a **theoretical model** of a gas that yields the ideal gas law. A byproduct of this model is **the direct identification of the average kinetic energy of the gas molecules with the Kelvin temperature**.
-
- In the ideal gas model, we regard the molecules as particles that **never collide with each other but that do collide with the container walls**. These collisions are assumed to be **elastic**, so the molecules lose no energy, but they do change direction. The change in direction involves a change in momentum of the molecules, and this means that there is a force on the container walls. The average force per unit area exerted by the molecules on the walls is the pressure of the gas.

Temperature and Molecular Energies

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- Calculations based on classical mechanics and statistical analysis show that **the product of the pressure and volume is related to the average kinetic energy** (K_{avg}) **of the molecules by**:

$$PV = \frac{2}{3} nN_A (K_{avg})$$

- Where n is the number of moles, N_A is Avogadro's number and

$$K_{avg} = \frac{1}{2} m (v^2)_{avg}$$

- Where m is the mass of a molecule and $(v^2)_{avg}$ is called the **mean square speed**, and represents the average value of v^2.

Temperature and Molecular Energies

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- Comparing this result with $PV = nRT$, yields:

$$K_{avg} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T$$

- This equation tells us that **the average translational kinetic energy of molecules in random motion in an ideal gas is directly proportional to the absolute temperature of the gas**. And, by knowing the temperature, it gives us a direct measure of the energy available for initiating physical, chemical and biological processes.
- Also we can use the previous equation to calculate how fast molecules are moving on the average, or what is called the **root mean square speed** (v_{rms}), since we are taking the square root of the mean of the square of the speed:

$$v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{2K_{avg}}{m}} = \sqrt{\frac{3k_B T}{m}}$$

Diffusion

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- In a diffusion process, molecules move from a region where their concentration is high to a region where their concentration is lower.
- An equation for the mean squared displacement can be written as:

$$x_{rms}^2 = 2Dt$$

- Where:
  - D is called the diffusion constant.
  - Similar equations hold for y_{rms}^2 and z_{rms}^2.
  - The value of D depends on:
  - the nature of the diffusing atom or molecule
  - the choice of the solvent or medium.