

# Thermodynamics (Chapters 17–20)

## Temperature and Kinetic Gas Theory (Chapter 17)

The temperature of an object is a measure of its average internal molecular kinetic energy. A consistent temperature scale can be defined in terms of properties of gases at low densities.

### Thermal Equilibrium and Temperature:

Our sense of touch tells us if an object is hot or cold. A physical property that changes with temperature is called **thermometric property**.

If we place a warm and a cold object into **thermal contact**, the cold object warms and the warm object cools. Eventually, this process stops and the two objects are said to be in **thermal equilibrium** and the two objects are then defined to have the **same temperature**.

### The zeroth law of thermodynamics:

If two objects are in thermal equilibrium with a third, then they are also in thermal equilibrium with one another.

# The Celsius and the Fahrenheit Temperature Scales

Any thermometric property can be used to establish a temperature scale. The common **mercury thermometer** consists of a glass bulb and tube containing a fixed amount of mercury. When the thermometer is put in contact with a warmer body, the mercury expands, increasing the length of the mercury column (the glass expands by a negligible amount).

The **ice point temperature** or **normal freezing point** of water is the freezing point of water at a pressure of 1 atm. The **steam-point temperature** or **normal boiling point** of water is the the boiling point of water at a pressure of 1 atm.

**Units of pressure:** Pascal (Pa):  $1 \text{ Pa} = 1 \text{ N/m}^2$ , atmosphere (atm):  $1 \text{ atm} = 101.325 \text{ kPa} = 14.70 \text{ lb/in}^2$ , millimeters of mercury (mmHg) in a U-tube barometer (Figures 13-6 and 13-7 of Tipler-Mosca), a unit called torr:  $1 \text{ atm} = 760 \text{ mmHg}$  .

The **Celsius temperature scale** defines the ice-point temperature as zero degree Celsius,  $0^\circ\text{C}$ , and the steam-point temperature as  $100^\circ\text{C}$ . The space between  $0^\circ\text{C}$  and  $100^\circ\text{C}$  marks is divided into one hundred equal intervals (degrees) on the mercury scale.

Degree markings are extended below and above these points by the equation

$$t_C = \frac{L_t - L_0}{L_{100} - L_0} \times 100^\circ\text{C}$$

where  $t_C$  is the temperature on the Celsius scale and  $L_t$  the length of the mercury column at the temperature indicated by the subscript.

The **Fahrenheit temperature scale** defines the ice-point as  $32^\circ\text{F}$  and the steam-point as  $212^\circ\text{F}$ .

$$t_C = \frac{100}{212 - 32} (t_F \text{ C/F} - 32^\circ\text{C}) = \frac{5}{9} (t_F \text{ C/F} - 32^\circ\text{C}) .$$

Originally Fahrenheit designed his scale so that  $0^\circ\text{F}$  was the coldest temperature he could create in his laboratory and  $96^\circ\text{F}$  for the temperature of the human body. The upper scale was later slightly modified.

## Gas Thermometers and the Absolute Temperature

When different thermometers are calibrated at the ice-point and steam-point temperatures, they give slightly different readings at the points between. Discrepancies increase markedly above and below this range. Exceptions are the **constant-volume gas thermometers**, for which the measured temperatures agree closely even far from the calibration points. In these thermometers the volume is kept constant and the change in gas pressure is used to measure the temperature (Figure 17-4 of Tipler-Mosca). For the Celsius scale:

$$t_C = \frac{P_t - P_0}{P_{100} - P_0} \times 100^\circ\text{C} .$$

The agreement between different gas thermometers is best at low gas densities.

Figure 17-6 of Tipler-Mosca shows a plot of measured temperature versus pressure for a constant-volume gas thermometer at very low density. When we extrapolate the straight line towards zero pressure, the temperature approaches the **absolute zero at**

$$T_0 = -273.15^\circ\text{C} .$$

A reference point that is more precisely reproducible than either the ice or the steam points is the **triple point of water**. This is the unique temperature and pressure at which water, water vapor and ice coexist in equilibrium, namely at  $0.01^{\circ}\text{C}$  and  $P_3 = 4.58 \text{ mmHg}$ . The **Kelvin or ideal gas temperature scale** is defined so that the triple point is at  $273.16 \text{ K}$  and the absolute zero temperature is at  $0 \text{ K}$ :

$$T = \frac{273.16 \text{ K}}{P_3} P$$

where  $P$  is the observed pressure of the gas thermometer. The lowest temperature that can be measured with a gas thermometer is about  $1 \text{ K}$ , and requires helium. Below this temperature helium liquefies and all other gases liquefy at higher temperatures. Later, we use the second law of thermodynamics to define the absolute temperature scale without reference to the properties of a particular substance. Temperatures as low as  $10^{-6} \text{ K}$  have been measured this way. To convert from Celsius to Kelvin one merely adjusts the absolute zero temperature:

$$T = t_{\text{C}} \text{ K/C} + 273.15 \text{ K} .$$

The absolute (Kelvin) temperature scale is most convenient for scientific purposes.

## The Ideal-Gas Law

Experimental results by Robert Boyle (1627-1691), Jacques Charles (1746-1823) and Gay-Lussac (1778-1850) for a fixed amount of gas combine to the equation

$$PV = CT$$

where  $P$  is the pressure,  $V$  is the volume,  $T$  is the absolute temperature and  $C$  is a proportionality constant. We see that  $C$  is proportional to the volume by doubling the amount of gas, while holding the pressure and temperature constant. Therefore, we write  $C = kN$ , where  $k$  is a constant and  $N$  the number of molecules in the gas. Then, we have

$$PV = NkT .$$

The constant  $k$  is called **Boltzmann constant** and found experimentally to be

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

An amount of gas is often expressed in moles. A **mole** (mol) is the amount of a substance that contains **Avogadro's number**  $N_A$  of molecule, defined as the number of carbon atoms in 12 g of  $^{12}\text{C}$ :

$$N_A = 6.022 \times 10^{23} .$$

If we have  $n$  moles of a substance, the number of molecules is then  $N = n N_A$ .  
The constant

$$R = N_A k = 8.314 \text{ J/mol} \cdot \text{K} = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$$

is called **universal gas constant**. The pressure, volume, and temperature of an **ideal gas** are related by

$$P V = n N_A k T = n R T .$$

The variables  $P$ ,  $V$ , and  $T$  describe the **macroscopic state** of a gas. The **microscopic state** would be described by giving the position and velocity of each molecule of the gas. An equation which relates the macroscopic state variables is called an **equation of state**.

At higher densities corrections must be made to the ideal gas law. The van der Waals equation, discussed in Chapter 20 of Tipler-Mosca, includes such corrections.

The temperature of 0°C (273 K) and the pressure of 1 atm are often referred to as **standard conditions**. Under standard conditions 1 mol of an ideal gas occupies a volume of 22.4 L.

Figure 17-9 of Tipler-Mosca shows plots of  $P$  versus  $V$  for several constant temperatures. These curves are called **isotherms**. For a fixed amount of gas we have

$$\frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1} = n R$$

where the subscripts label two different macroscopic states.



# The Kinetic Theory of Gases

The description of the macroscopic state of a gas can be related to simple averages of microscopic quantities such as the mass and speed of the molecules in the gas. From the point of view of kinetic theory, a gas consists of a large number of molecules making elastic collisions with each other and with the walls of the container. In the absence of external forces (gravity may be neglected as it leads only to a slight increase of pressure at the bottom of the container), there is no preferred position for a molecule in the container and no preferred direction of its velocity vector.

## The Pressure Exerted by a Gas:

We consider a rectangular container of volume  $V$  containing  $N$  molecules, each of mass  $m$  moving with a speed  $v$ . Let us calculate the force exerted by the molecules on the right wall of area  $A$  (Figure 17-10 of Tipler-Mosca). The molecules hitting this wall in a time interval  $\Delta t$  are those which are within distance  $v_x \Delta t$  of the wall. This number of molecules is

Molecules that hit the wall in  $\Delta t = \frac{1}{2} \frac{N}{V} v_x \Delta t A$

where the factor  $1/2$  comes because, on the average, only half the molecules move to the right. The magnitude of the total change of momentum  $\Delta p$  of these molecules during the time interval  $\Delta t$  is

$$\Delta p = (2m v_x) \left( \frac{1}{2} \frac{N}{V} v_x \Delta t A \right) = \frac{N}{V} m v_x^2 \Delta t A$$

The force exerted on the wall is  $\Delta p / \Delta t$ . The pressure is the force divided by the area:

$$P = \frac{F}{A} = \frac{1}{A} \frac{\Delta p}{\Delta t} = \frac{N}{V} m v_x^2 \quad \text{or} \quad P V = N m v_x^2 .$$

To allow for the fact that the molecules in the container have different speeds, we replace  $v_x^2$  with its average  $(v_x^2)_{\text{av}}$ . Using the average for the kinetic energy, we have

$$P V = N k T = 2N (m v_x^2 / 2)_{\text{av}} .$$

The Molecular Interpretation of Temperature: Dividing the number of molecules out, we have

$$(m v_x^2/2)_{\text{av}} = k T / 2 .$$

Using  $(v^2)_{\text{av}} = (v_x^2)_{\text{av}} + (v_y^2)_{\text{av}} + (v_z^2)_{\text{av}} = 3 (v_x^2)_{\text{av}}$  we have

$$K_{\text{av}} = \left( \frac{1}{2} m v^2 \right)_{\text{av}} = \frac{3}{2} k T .$$

The last equation relates the average translational kinetic energy of the molecules to the absolute temperature. We can use this result to estimate the order of magnitude of the speeds of the molecules of the gas:

$$(v^2)_{\text{av}} = \frac{3kT}{m} = \frac{3RT}{M}$$

where  $M = N_A m$  is the molar mass. The root mean square (rms) speed becomes:

$$v_{\text{rms}} = \sqrt{v_{\text{av}}^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} .$$

This is similar to the equation for the speed of sound in a gas

$$v_{\text{sound}} = \sqrt{\gamma RT/M} .$$

This is not surprising since pressure fluctuations are propagated by collisions between molecules.

Examples at 300 K:

$$v_{\text{rms}}(O_2) = 483 \text{ m/s} , \quad v_{\text{rms}}(H_2) = 1.93 \text{ km/s} .$$

For  $H_2$  the order of magnitude is such that the escape velocity of earth is slightly exceeded, while Jupiter retains  $H_2$  easily.