Theory of Heat and Thermodynamics

In this chapter we will analyze systems composed of many particles, typically on the order of 10^{23} particles (atoms or molecules). These systems will consist mainly of gases, but also of rigid bodies and fluids. Specifically, we will examine the macroscopic properties of these systems and the laws that govern them.

Temperature

In everyday language, we use temperature to express how hot or how cold a body is. In reality, giving a precise definition of what temperature is, is not at all an easy task. We will try to give two definitions in the following way:

Temperature a) In the case of rigid bodies or fluids, temperature is related to the thermal vibration of atoms.

b) In the case of gases, temperature is a measure of the average kinetic energy of the molecules.

The Kelvin scale

In order to be able to measure temperature, using for example a thermometer, we need to define a scale.

The Kelvin scale The Kelvin scale is defined using two reference points: a) Zero on the scale coincides with absolute zero of temperature, that is, the point at which the molecules or atoms are completely at rest. b) The triple point of water corresponds to a temperature of 273.16 on the Kelvin scale.

Pressure

Pressure Pressure is defined as the force exerted perpendicularly on a surface, divided by the surface itself:

$$p = \frac{F}{a} \tag{1}$$

Unit of measurement: In the International System it is the Newton per square metre, which is abbreviated as the *Pascal*:

$$[p] = 1\text{Pa} = 1\text{N}/\text{m}^2 \tag{2}$$

Other units of measurement are *atmospheres* (atm):

$$1\text{atm} = 1.01325 \cdot 10^5\text{Pa} \tag{3}$$

and *bars* (bar):

$$1\text{bar} = 100\text{kPa} \tag{4}$$

Gay-Lussac's Law

Experimentally, it is observed that the volume of a gas at constant pressure is proportional to the temperature:

Gay-Lussac's Law

$$V = C_1 T \quad \text{at constant pressure} \tag{5}$$

Experimentally, we can also observe another relationship of this kind: the pressure of a gas at constant volume is proportional to the temperature.

$$p = C_2 T \quad \text{at constant volume} \tag{6}$$

Ideal gases

Ideal gas We define an ideal gas as a collection of many uncharged atoms or molecules whose interactions and expansion are negligible.

A gas of this kind cannot be brought to the liquid state.

The equation of state of ideal gases

We saw in Chapter 1.3 how temperature is related to pressure and volume.

Experimentally, we can make a further statement:

Boyle-Mariotte's Law

$$pV = cost. \tag{7}$$

By combining all these results, we can construct the equation of state of ideal gases:

Equation of State of Ideal Gases

$$pV = Nk_B T \tag{8}$$

$$pV = \nu RT \tag{9}$$

The two formulations are equivalent.

k_B is the **Boltzmann constant** and has the value $1.381 \cdot 10^{-23}\ J/K$, N is the number of molecules/atoms present in the gas, ν is the number of moles of the gas, and R is the ideal gas constant and has the value $8.314\ J/(mol\ K)$

Thermal energy and heat capacity

When two systems at different temperatures are brought into contact, they exchange heat until, after some time, they reach the same temperature. Specifically, it is the hotter system that gives up heat to the colder system. Initially, before the true nature of heat was understood, the calorie (cal) was introduced as the unit of measurement of heat.

The calorie The calorie is defined as the heat Q required to heat one gram of water at $p = 1$ bar by exactly one degree.

By studying the subject more deeply, it was discovered that a body must give up *energy* in order to change its temperature. Nowadays, therefore, the unit of measurement of heat in the International System is the Joule:

$$1 \text{ cal} = 4.1868 \ J \tag{10}$$

Definition of heat capacity

Different bodies can be distinguished by the amount of energy required to raise their temperature by a certain amount. If we supply a body with a certain quantity of heat ΔQ, its temperature will increase by a certain ΔT.

Heat Capacity Heat capacity of a body is defined as:

$$C = \frac{\Delta Q}{\Delta T} \tag{11}$$

The heat capacity of a substance with respect to its mass is called **specific heat capacity**:

Specific Heat Capacity

$$C_m = \frac{1}{m}\frac{\Delta Q}{\Delta T} \tag{12}$$

where m is the mass of the substance.

The heat capacity of a substance with respect to the amount of matter is called the **molar heat capacity**:

Molar Heat Capacity

$$C_m = \frac{1}{\nu}\frac{\Delta Q}{\Delta T} \tag{13}$$

where ν is the number of moles of the substance.

The heat that must be supplied to a body to increase its temperature from T_a to T_b is given by:

$$Q^{\swarrow} = \int \delta Q^{\swarrow} = \int_{T_a}^{T_b} C(T) dT \tag{14}$$

The arrow indicates that heat is supplied to the body, and the symbol δ denotes an inexact differential, which is not a state function.

Note that, in general, the heat capacity varies with temperature. However, for not too high temperatures we can consider it constant; consequently, we have:

$$Q^{\swarrow} = C(T_b - T_a) = C\Delta T \tag{15}$$

The zeroth law of thermodynamics

The zeroth law of thermodynamics is essentially the existence of temperature.

The Zeroth Law of Thermodynamics Two systems in contact that initially have different temperatures will, after a certain period of time, reach the same temperature; this is said to be when they reach **thermal equilibrium**.

The First Law of Thermodynamics

The definition of internal energy

Internal Energy The internal energy U is a **state function** of the system under consideration. It can depend on various factors:

$$U = U(p, V, T, ...) \tag{16}$$

Thermodynamics describes **thermal processes** in which a body passes from one state of thermal equilibrium to another. During these processes, the internal energy of the body can change.

The change in internal energy does not depend on the intermediate states but only on the initial and final states:

$$\Delta U = (U_f - U_i) \tag{17}$$

The First Law of Thermodynamics 1) When we supply heat Q to a body, its internal energy changes.

2) Similarly, it is possible to supply energy to the body through mechanical work W.

Written in mathematical terms:

$$dU = \delta W^{\swarrow} + \delta Q^{\swarrow} \tag{18}$$

Specific Heat of Ideal Gases

Let us return to ideal gases, distinguishing between two different types of specific heat.

Specific Heat at Constant Volume At constant volume, the following relation holds.

$$\Delta Q = \nu C_V \Delta T \tag{19}$$

where C_V is the specific heat at constant volume. Note that in order to increase the temperature at constant volume, the pressure of the gas must necessarily increase.

Specific Heat at Constant Pressure At constant pressure, the following relation holds:

$$\Delta Q = \nu C_p \Delta T \tag{20}$$

Where C_p is the specific heat at constant pressure. Note that in order to increase the temperature of a gas while keeping the pressure constant, the volume must necessarily increase.

At constant pressure we need a greater amount of heat than at constant volume. We have:

$$C_p = C_V + R \tag{21}$$

This relationship can easily be derived from the first law of thermodynamics. This derivation is left to the reader as an exercise.

Equipartition principle

Equipartition principle The average energy of a molecule with f degrees of freedom is:

$$\langle E \rangle = \frac{f}{2} k_B T \tag{22}$$

For an ideal gas in amount ν, we calculate the internal energy (which is nothing other than the kinetic energy of molecular motion) with the following expression:

$$U = \nu N_A \frac{f}{2} k_B T = \nu \frac{f}{2} RT \tag{23}$$

Where $N_A = 6.022 \cdot 10^{23} mol^{-1}$ is Avogadro's number and $k_B = \frac{R}{N_A} = 1.381 \cdot 10^{-23} J/K$ is the Boltzmann constant.

State changes of ideal gases