General Processes in Chemical Physics

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By

Paul Blaise, Adina Velcescu
and Olivier Henri-Rousseau

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PREFACE

The book by Profs. Paul Blaise, Adina Velcescu and Olivier Henri-Rousseau entitled “General Processes in Chemical Physics” is a continuation of the book "From Atom to Molecule: How the Principles of Physics Work" published by Cambridge Scholars Publishing in 2022.

The book is composed of three parts entitled: "From gas to liquid", "Experimental laws in solution" and "Thermochemistry". It presents in an illustrative, didactic and attractive way current knowledge in the area of molecular physics at the basic and advanced level for undergraduate science students. The book contains photos of eminent scientists and well-designed figures. Most of chapters end with well-prepared tutorials containing problems to be solved and answers.

This book is a valuable source of knowledge in molecular physics at undergraduate level and is recommended to students in physics, chemistry and molecular science.

Prof. Dr. Hab. Marek J. Wójcik
Jagiellonian University
Krakow, Poland

FOREWORD

This book is a follow-up to the one published in 2022 by Cambridge Scholars Publishing entitled "The Fundamental Principles of Physics, From Atom to Molecule" which treated on structure of matter.

In this continuity, we are now interested in the general processes in chemical physics. This book puts together all the courses for the first two years university students in the field of processes involving the three states of matter.

The book is structured into three parts, as follows.

A first part entitled: "From gas to liquid" focusses on the experimental laws of gases and their extension to liquids.

A second part, "Experimental laws in solution" deals with solutions of gases, liquids and solids in solvents.

A third part "Thermochemistry" talks about the thermodynamic processes related to chemical reactions.

At the end of chapters, some examples of tutorials are given.

FIRST PART
FROM GAS TO LIQUID

This first part is devoted to gases and liquids in general. The reader is guided from definitions and properties to more general laws and other phase equilibria.

CHAPTER I:
GENERALITIES

1. Introduction to physical sciences

Physical sciences, including astronomy, physics, chemistry and Earth sciences, are the systematic study of the inorganic world, as distinct from the study of the organic world, which is the object of biological science. Physics focusses more particularly on the laws that govern the movement of objects and chemistry rather on what characterizes them. But the border is never precise between physics and chemistry. To better understand physical phenomena, it is necessary to know an appropriate vocabulary and use some mathematical methods.

a. Notions of geometry

Geometry is a branch of mathematics concerned with properties of space such as the distance, shape, size and relative positions of figures. Euclidean geometry includes the notions of point, line, plane, distance, angle, surface and curve as fundamental concepts.

b. Notion of kinematics

Kinematics is concerned with the movement of an abstract point. We can always assign a position denoted $\vec{r}$ to a point in space at the condition of defining a frame (O,$\vec{\imath}$,$\vec{\jmath}$,$\vec{k}$), as depicted by Figure I-I-1.

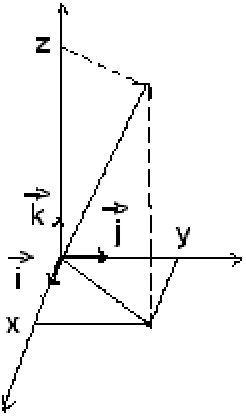


Figure I-I-1. The Cartesian frame

The position vector $\vec{r}$ is expressed within the Cartesian frame as

$$\vec{r} = \vec{\imath}x + \vec{\jmath}y + \vec{k}z$$

To describe a movement, it is necessary in addition to the geometry, to have a measurement of the movement. Time is a measure of movement according to the "before" and the "after". The unit of time is the second. The speed $\vec{v}$ of a material point is defined as the path traveled per unit time:

$$\vec{v} = \vec{\imath}\frac{dx}{dt} + \vec{\jmath}\frac{dy}{dt} + \vec{k}\frac{dz}{dt}$$

The speed can be uniform or variable. The acceleration $\vec{\gamma}$ is defined as the change in speed per unit time.

However, in reality there are not material points which move but bodies.

c. Notion of dynamics and notion of mass

Dynamics is concerned with real movements. The behavior of material bodies is thus described by two fundamental principles: The principle of inertia and the fundamental principle of dynamics.

The principle of inertia

A material point at rest which is not subjected to any force remains at rest. A moving material point which is not subjected to any force is animated by a uniform rectilinear movement.

The fundamental principle of dynamics

A material point whose movement is accelerated is subjected to a force. Force is the principle of explanation of acceleration. The fundamental principle of dynamics states that there is a relationship between force and acceleration such that

$$\vec{F} = K\vec{\gamma}$$

K is not a fundamental constant because it depends on the body in question. It is the characteristic inertia factor of the body, i.e., its mass.

$$K = m$$

Matter and its three states

Matter is the opposite of vacuum. If we consider the vacuum as that which occupies a certain volume and which has no mass, matter is that which occupies a certain volume and which has a mass. There are mainly three forms of matter: matter can either keep its volume and its shape and we speak about *solid state*; when matter keeps its volume but can change of shape, we speak about *liquid state*; finally, when both volume and shape can change, we speak about *gaseous state*. In each of its three states, matter will be characterized by its *volumetric mass density* or shorter, *density*, which is the mass per unit volume

$$\rho = \frac{m}{V}$$

d. Difference between Physics and Chemistry

Physics and chemistry are interested in matter but not in the same way. The example of Newton's tube given in **Figure I-I-2** is characteristic

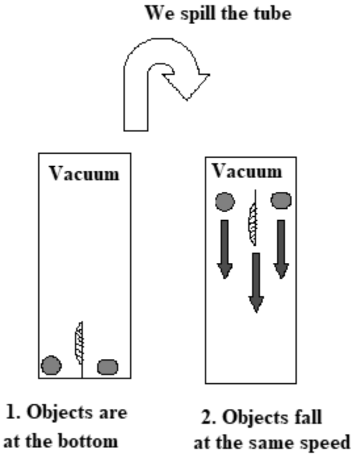


Figure I-I-2. **Newton's tube experiment.**

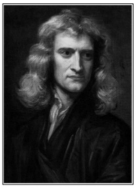
We can conclude from this experiment that all objects fall in a vacuum at the same speed which is the same for all bodies and independent of their nature. However, even though all bodies behave in the same way during their motion, they all differ in their substance. Each substance has its own qualities. They interest the chemist more than the physicist. Moreover, the chemist is interested not only in the nature of substances but also in their transformations.

e. Atmospheric pressure

Atmospheric pressure is the weight exerted by the overhead atmosphere on a unit area of surface

$$P = \frac{F}{S}$$

If the force is expressed in Newton (N) and the surface in square meters (m^2), then the pressure is expressed in Pascal (Pa).



Isaac Newton[1]

Blaise Pascal[2]

Atmospheric pressure can be measured in the following way: A tube filled with mercury is inverted onto a vat of mercury as given in **Figure 1-I-3**

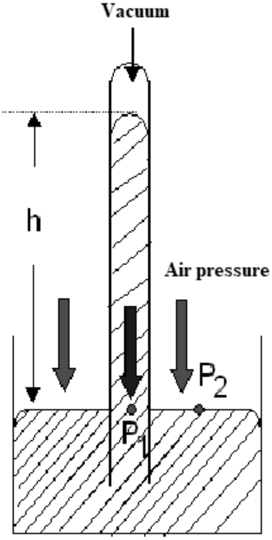


Figure I-I-3. Atmospheric pressure

The mercury sinks into the tube and forms a volume consisting of vacuum. The pressure P_1 exerted by the column of mercury of height h in 1 is the

---

[1] Isaac Newton (1643-1727) English philosopher, mathematician, physicist, alchemist, astronomer and theologian. He is best known for his theory of universal gravitation and the creation, in competition with Leibniz, of infinitesimal calculus.

[2] Blaise Pascal (1623-1662) French mathematician, physicist, inventor, philosopher, moralist and theologian.

same as that P_2 exerted in 2 by the air. The tube having a section S, the column of mercury therefore has a volume

$$V = S \times h$$

The density of mercury being ρ_{Hg} the mass of mercury in the column is:

$$m = \rho_{Hg} \times S \times h$$

The weight of mercury is the force it exertes at point 1, i.e.

$$p_{Hg} = mg = \rho_{Hg} \times S \times h \times g$$

where g is the acceleration due to gravity. We deduce the pressure P_1

$$P_1 = \frac{p_{Hg}}{S} = \rho_{Hg} \times h \times g$$

As the density of mercury is ρ_{Hg} =135951 kg×m^{-3}, the acceleration of gravity g=9.80665 m×s^{-1} and the atmospheric pressure is 101396 Pa, we deduce that the height of the column of mercury in the tube is

h=0.76 m

or 760 mm of mercury. Normal atmospheric pressure is the pressure balanced by a column of mercury 760 mm high at a temperature of 0°C. Various units are used to express atmospheric pressure: the Pascal but also the mm of mercury (Torr), the atmosphere and the bar.

$$1\,atm = 101325\,Pa = 760\,Torr; 1\,bar = 10^5\,Pa$$

A physical process carried out at constant pressure is said to be *isobaric*.

f. Temperature

A distinction must be made between heat intensity and heat quantity.

Heat intensity and temperature

We can tell of a body by touching it that it is hot or cold. So, if you plunge your hand into two containers, one containing cold water and the other hot water, you can see the difference. However, this feeling is qualitative. To make it quantitative we will use a thermometer which is based on the principle that bodies tend to expand in contact with heat and contract in contact with cold.

Thermal balance

Consider a hot piece of iron and immerse it in a container of cold water. The iron will cool while the water will heat up to a state of equilibrium. The bodies then have a common temperature which is intermediate between the two initial temperatures. We will say that heat has passed from the hotter body to the colder body until equilibrium is reached. The opposite phenomenon has never been observed.

Thermal expansion

When a body is heated it expands. Examples are given in **Figure I-I-4**

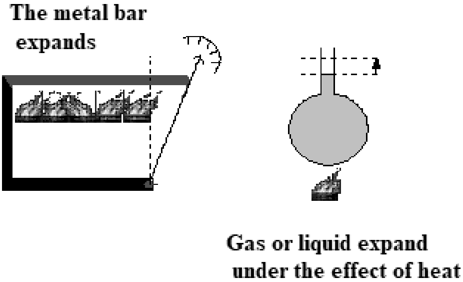


Figure I-I-4. Expansion of objects by heating

Mercury thermometer

This device uses the phenomenon of dilation to evaluate the intensity of the heat received by a body.

A thermometer consists of a mercury reservoir surmounted by a capillary tube. Depending on whether the mercury is hot or cold, it rises or falls in the tube. To assess the thermal intensity, i.e. the temperature, the device must be calibrated as it is done in **Figure I-I-5**.

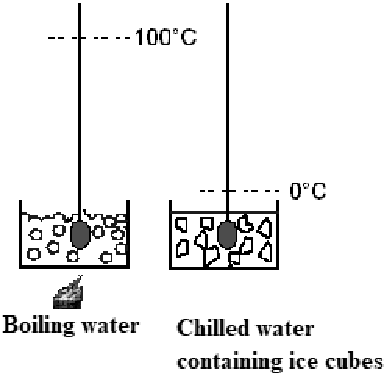
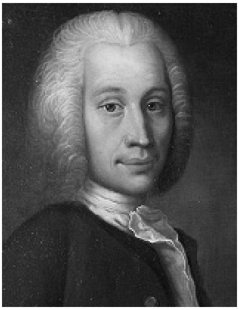


Figure I-I-5. Calibrating a thermometer

The two temperatures are identified, that of boiling water and that of melting ice. The degree Celsius is defined as the hundredth part of the interval between the two conventional temperatures θ=100°C for boiling water and θ=0°C for melting ice.



Anders Celsius[3]

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[3] Anders Celsius (1701-1744). Swedish scientist, professor of astronomy at the University of Uppsala (founded in 1477). He was at the origin of a relative temperature scale whose unit, the degree Celsius (°C), honors his name.

Concept of quantity of heat

Consider two blocks of iron of different mass which have been brought to the same temperature (see **Figure I-I-6**). Let us immerse each of these blocks in identical containers containing the same quantity of water and whose initial temperatures are equal to but lower than the temperature of the pieces of iron. Once thermal equilibrium has been achieved, we notice that it is the container containing the largest piece of iron that has undergone the greatest rise in temperature.

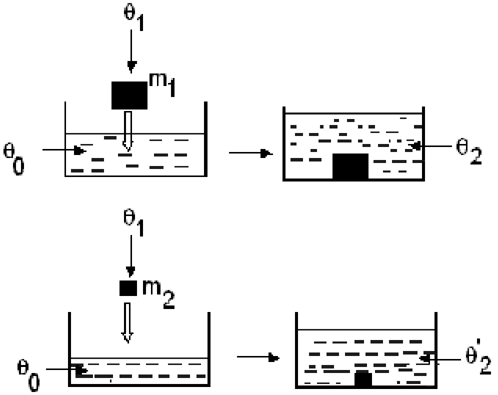


Figure I-I-6. Heat transfers

If we reproduce the same experiment with lead, we still observe the same trend but the temperatures are different. We can conclude that the amount of heat exchanged depends on the nature of the bodies, their mass and the difference in temperature that exist between them.

Heat transfer

We consider a container containing a mass m_{water} of cold water at the temperature θ_{water}. A hot body X of mass m_X is immersed in it, at the temperature θ_X. The final equilibrium temperature of the system is θ_f. The amount of heat emitted by the body is

$$Q_X = m_X \times c_X(\theta_f - \theta_X)$$

where c_X is the specific heat or heat capacity of body X The heat received by the water is

$$Q_{water} = m_{water} \times c_{water}(\theta_f - \theta_{water})$$

where c_{water} is the *specific heat* or *heat capacity* of water. The specific heats are expressed in joules·kg^{-1}·degree^{-1}. We must have

$$Q_X + Q_{water} = 0$$

The unit of quantity of heat is the joule. We sometimes use the calorie which is the quantity of heat necessary to raise the temperature of 1 g of water by 1 degree. We have 1cal=4.18 joules.

Water equivalent of a calorimeter

Heat exchanges are generally carried out in a device called a calorimeter. It is a thermally insulated system (Dewar vase for example in **Figure I-I-7**), heat exchanges hardly occurring with the outside.

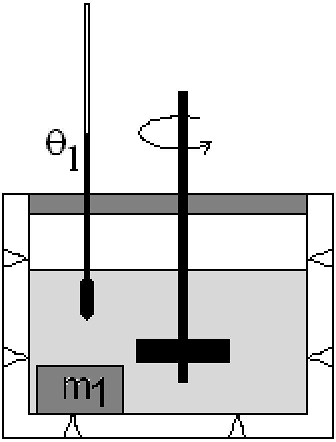


Figure I-I-7. A calorimeter

Suppose that a solid of mass m_1 at temperature θ_1 is immersed in a mass m_{water} of water whose temperature is θ_1. The heat exchanges for the whole (calorimeter + water + solid) lead to a thermal equilibrium at the temperature θ_f. The energy balance relating to this set is written

$$Q_{metal} + Q_{water} + Q_{calorimeter} = 0$$

where $Q_{calorimeter}$ is the heat exchanged by the calorimeter itself and which is considered equal to a mass $m_{water,cal}$ of water at the temperature θ_o. This is the water equivalence of the calorimeter and its accessories (stirrers, thermometer). So, we have the equation

$$m_1 c_{metal}(\theta_f - \theta_1) + c_{water}(M + m)(\theta_f - \theta_0) = 0$$

and the quantity

$$c_{calo} = m c_{water}$$

is the heat capacity of the calorimeter.

2. State changes and purity criteria

a. Pure body behavior

Let's place a container containing ice on a stove and note the evolution of the temperature as a function of time as given in **Figure I-I-8:**

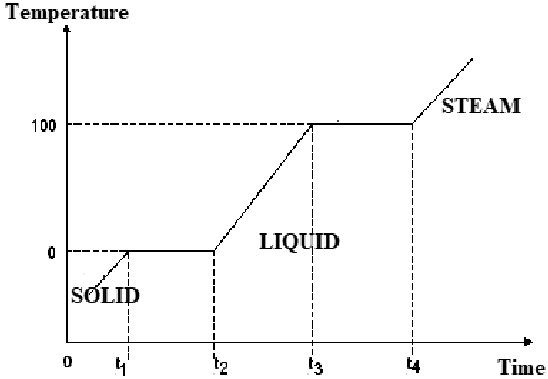


Figure I-I-8. State changes for a pure body

The curve has 5 phases:

The first phase corresponds on the graph to the time interval 0 to t_1. Ice, which is solid, undergoes an increase in its temperature from the initial temperature θ_i. to its melting temperature which is 0°C. The heat exchanged is given by the relation:

$$Q_1 = m_{ice}c_{ice}(\theta - \theta_i)$$

where c_{ice} is the specific heat of the ice and θ the temperature of the ice at a given instant.

The second phase corresponds to the melting of the last parcel of ice. As long as there is ice, the temperature does not increase. The curve therefore has a plateau. The heat exchanged between times t_1 and t_2 obeys the relationship:

$$Q_2 = m_{ice}C_{L,ice}$$

where $C_{L,ice}$ is the latent heat of the fusion of the ice.

The passage of a pure substance from one physical state to another always takes place at a temperature which remains fixed for the duration of the transformation.

The third phase corresponds to the rise in temperature of the water formed by the complete melting of the ice. The relationship to use is:

$$Q_3 = m_{water}c_{water}(\theta - \theta_{iL})$$

where c_{water} is the specific heat of the water and where θ_{iL} is the initial temperature of water in the liquid phase.

The fourth phase corresponds to the vaporization of water. As long as there is a parcel of liquid, the temperature remains constant and equal to the boiling temperature. The relationship to use to calculate the heat exchange is

$$Q_4 = m_{water}C_{L,water}$$

where $C_{L,water}$ is the latent heat of the vaporization of water.

Finally, the fifth phase corresponds to the rise in temperature of the steam. All water is in vapor form and the following relationship applies

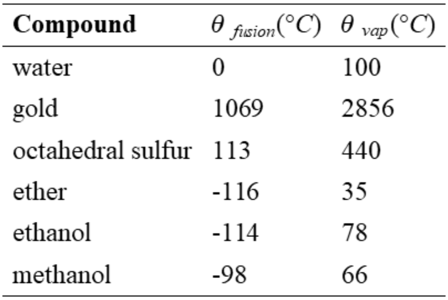
$$Q_5 = m_{water} c_{steam} (\theta - \theta_{iV})$$

where c_{steam} is the specific heat of the steam and where θ_{iV} et θ are the temperatures of water in vapor phase at two different instants.

Under isobaric conditions, the change of state of a pure substance is an isothermal process. In the following **Table I-I-1** are given the melting and vaporization temperatures of various compounds.

Table I-I-1

Fusion and vaporization temperatures of some compounds



Compound	$\theta_{fusion} (°C)$	$\theta_{vap} (°C)$
water	0	100
gold	1069	2856
octahedral sulfur	113	440
ether	-116	35
ethanol	-114	78
methanol	-98	66

The vaporization (or boiling) temperature varies with the pressure as shown in the following **Figure I-I-9**:

θ	100	90	80	70	60	50	40	30	20	0
P	760	620	386	234	149	72	46	17	11	6

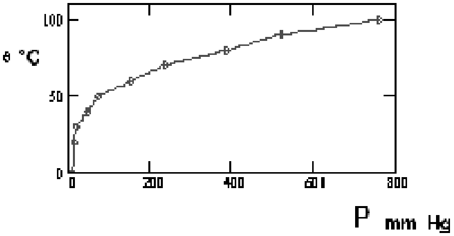


Figure I-I-9. Boiling temperature versus pressure

The different changes of state that a pure body undergoes are summarized in the following **Figure I-I-10.**

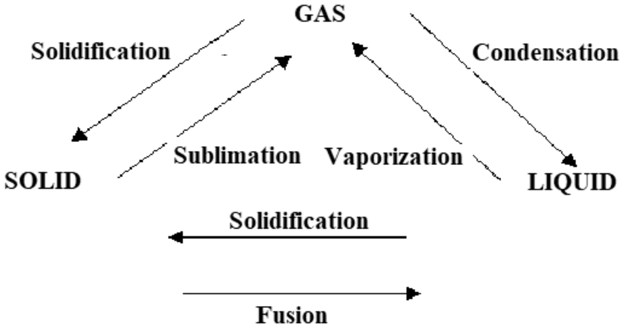


Figure I-I-10. The different changes of state

In this chapter generalities have been given on matter, on matter phase changes, as well as on the notion of temperature. A more detailed study can now be approached with the study of experimental gas laws.

CHAPTER II:
EXPERIMENTAL GAS LAWS

1. Introduction

Pure bodies, whether simple or compound, appear at first sight to be homogeneous when observed in liquid or gaseous state. One can first of all wonder if the mass of a pure body is modified during a physical transformation or a change of physical state.

a. Lavoisier's first law

The mass of an isolated system remains constant whatever the physicochemical transformations of which it is the seat It's the famous expression "*Nothing is lost, nothing is created, everything is transformed*".

Antoine de Lavoisier[4]

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[4] Antoine Laurent de Lavoisier (1743-1794). French chemist, philosopher and economist. He stated the first version of the law of conservation of matter, identified and baptized oxygen (1778), dismissed the phlogiston theory, and participated in the reform of chemical nomenclature. Lavoisier is often referred to as the father of modern chemistry. As he was a powerful member of number of aristocratic councils, and an administrator of the Ferme Générale, he was guillotined during the French

b. Lavoisier's Second Law

The nature and the mass of the various elements which one can extract from a material system formed of several bodies are invariable whatever the physical or chemical transformations it undergoes. In other words, not only the mass is conserved but also the masses of the various elements.

2. Manifestation of mobile and discontinuous properties of matter

a. The spontaneous formation of mixtures

Consider a double bulb one part filled with bromine which is orange and the other part filled with carbon dioxide which is colorless (See **Figure I-II-1**). When the two parts of the bulb are made to communicate, it is observed that the color and consequently the composition of the gas in the bulb become uniform.

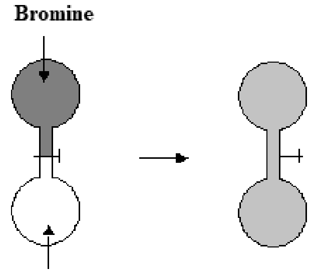


Figure I-II-1. Mobile and discontinuous properties of matter

Now consider a container filled with water (See **Figure I-II-2**). A layer of ink is superimposed. It is observed that gradually the water is colored. Reciprocal dissolution occurs through mutual diffusion of the two substances.

Revolution, despite appeals to spare his life in recognition of his contributions to science.

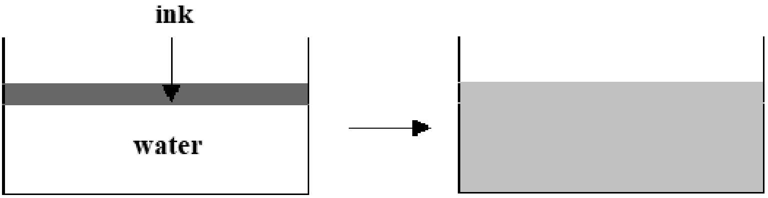


Figure I-II-2. Spontaneous diffusion of substances

This spontaneous diffusion of the substances supposes that there are movements of very small parts of the two substances which mix even if this movement is invisible to the naked eye.

The phenomenon of the mixture of pure bodies is the visible manifestation of an invisible phenomenon.

b. Brownian motions

These movements can be demonstrated by examining a particle of cigarette smoke under a microscope, for example. If we follow the evolution of the trajectory of a carbon particle in a smoke over time, we observe the erratic movement given in **Figure I-II-3.**

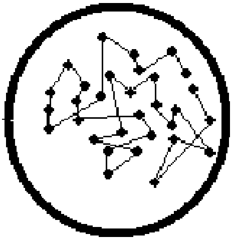
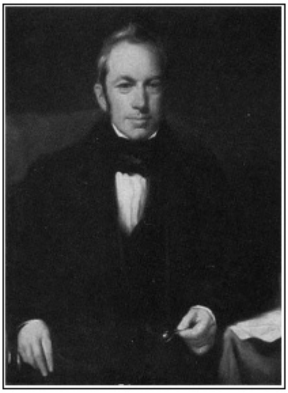


Figure I-II-3: Brownian motions

This particle, far from remaining motionless, constantly moves in all directions, in the absence of a current of air, without ever manifesting itself in it the slightest tendency to rest. The changes of direction of this particle seem to be due to chance. We then speak of Brownian motions. These are random movements.

c. Explanation of Brownian motions



R. Brown[5]

The movements of the smoke particles can only be explained if we consider incessant collisions with invisible particles animated by random movements.

3. The experimental laws of ideal gases

The study of gases shows that their behavior can be explained very well if we consider that they are formed by very small mobile particles.

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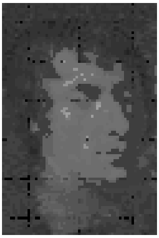
[5] Robert Brown (1773-1858). Scottish botanist. He is paradoxically known for a non-botanical discovery: Brownian motion.

a. Boyle's law (Mariotte's law)

Robert Boyle[6]



Abbé Edmé Mariotte[7]

Let us consider a certain mass m_{gas} of gas located in a vertical cylinder provided with a mobile wall on which one can place weights (see Figure I-II-4).

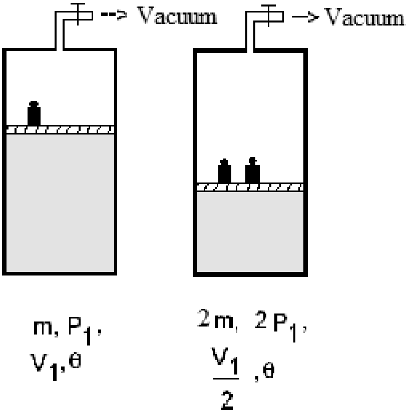


Figure I-II-4: **Boyle or Mariotte's law illustration**

First, a weight of mass m is placed on the wall. The volume of the gas is then V_1 and its pressure P_1. In a second step, a second identical weight is

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[6] Robert Boyle (1627-1691). Irish physicist and chemist.

[7] Abbé Edmé Mariotte (1620-1684). French physicist and botanist.