1 Introduction

Our society relies on the use of energy and matter in a plenitude of different forms. They are produced from natural resources by technical processes of energy and matter conversion that have to be designed in an economically and ecologically optimum way. In these processes it is the fluid state of matter that dominates the relevant phenomena. In particular, the properties of fluid systems in equilibrium enter into the fundamental process equations and control the feasibility of the various process steps. Models for fluids in equilibrium are thus a prerequisite for any scientific process analysis. Although fluid models can be constructed entirely within the framework of a macroscopic theory on the basis of experimental data, it is clear that this approach is limited to those few systems for which enough data can be obtained. Typical examples are the working fluids of the standard power generation and refrigeration processes. The vast majority of technically relevant processes are, however, concerned with complex fluid systems that cannot be analyzed experimentally in sufficient detail with a reasonable effort. In such cases one must turn to the microscopic basis of matter and design a theory based on the molecular properties of a fluid that requires only few data or is even fully predictive. In this introductory chapter we present an overview of the challenges of this approach by presenting a review of macroscopic fluid phase behavior in equilibrium, along with the problems associated with obtaining the necessary information from data. We also give a first introduction to the primary concepts of the microscopic world, including a brief glance at the properties of real molecules and the philosophy behind formulating molecular models.

1.1 The Macroscopic World

Energy and matter conversion processes are part of the macroscopic world. They are carried out without taking notice of the underlying microscopic phenomena, much like breathing air and handling materials in every day life. Within the limits of the macroscopic world the properties of the associated fluid

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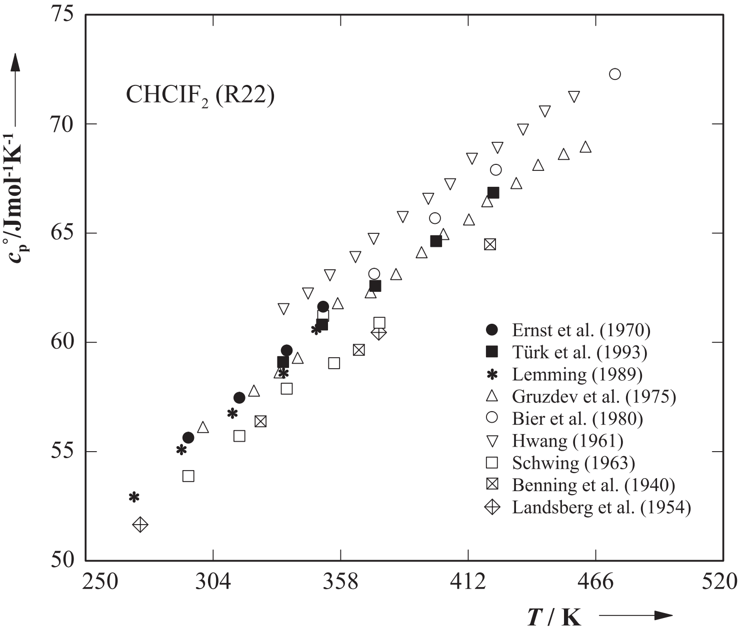

Fig. 1.1. Experimental data for the heat capacity of R22 (references to data given in [1]).

systems must be obtained from experiment. Fluid phase behavior is very plentiful, when studied over a wide range of temperature, pressure, and composition, and there are many fluids of technical interest. A few examples may illustrate this wealth of phenomena and the limitations of the macroscopic approach in providing the property information necessary to design technical processes.

An important property related to the energy conversion of a process is the heat capacity c_p. Fig. 1.1 shows the temperature dependence of the zero-pressure gaseous heat capacity of refrigerant R22 [1]. For calculations of refrigeration processes this property should be known to an accuracy of about 1%. The available experimental data reveal a spectrum of values differing by up to 10%. Little can be said about the reliability of the individual data sources on a purely macroscopic basis because experiments as a rule are not described in enough detail to assess their potential inaccuracies. Frequently, more recent data are given more credit than older data, and data from well-known laboratories are preferred over those from no-name sources, but this may be misleading, as was also found for R22. So, within the macroscopic approach to fluid properties and without an independent theoretical basis for evaluation of accuracy, we have to rely on the measured data as they are. We shall see, however, in Chapter 3 that molecular theory allows an unambiguous decision as to which set of data is correct and even a prediction when no data are available.

Proceeding to the large area of combustion processes, we need the heat capacities at much higher temperatures, but in particular we need properties related

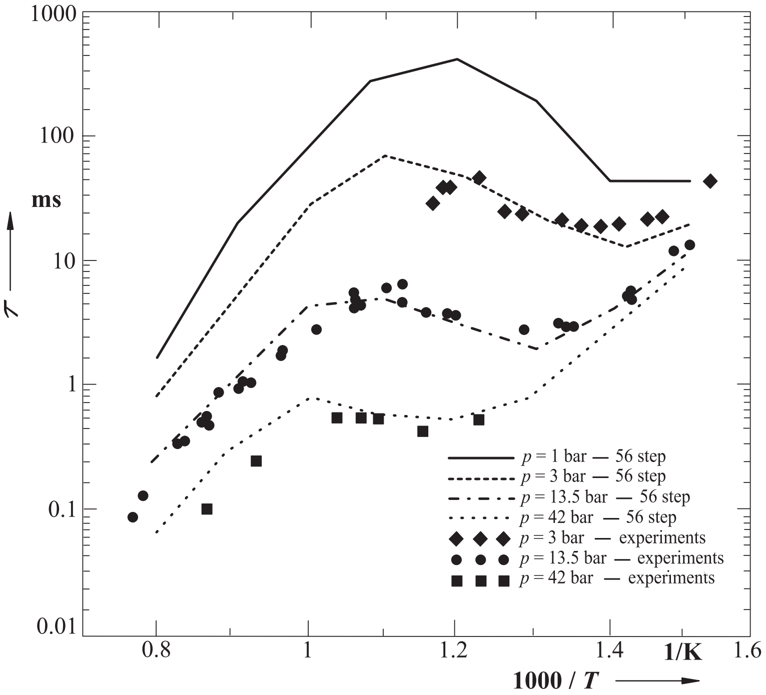

Fig. 1.2. Comparison of experimental ignition delay times with predicted values for heptane [2].

to the reactivity of the gaseous mixtures. An example is the ignition of heptane with stoichiometric air. In Fig. 1.2 we compare experimental ignition delay times for various pressures with model calculations on the basis of a 56-step skeletal reaction mechanism assumed to describe this combustion process [2]. The ignition delay time τ, i.e., the time that elapses until autoignition starts in a premixed fuel–air mixture, is plotted in milliseconds against the temperature of the mixture. Such information is relevant, e.g., in diesel engines. It can be seen that the ignition delay time first increases with decreasing temperature, but then shows the opposite behavior in an intermediate temperature range. To model such a combustion process, thermodynamic enthalpies of formation and standard entropies, as well as heat capacities, are required in the context of the law of mass action connecting forward and backward kinetic coefficients. The data are needed at high temperatures and for all relevant combustion intermediates, frequently radicals. Such data, although not readily obtained from experiment, can be calculated on the basis of the molecular models developed in Chapter 3.

Another example of high-temperature fluid phase behavior is provided in Fig. 1.3, which shows the composition of air at low density and at very high temperatures, including dissociation and ionization effects. The composition is given in terms of the number of particles per atom of air. The usual weight fraction of each constituent i is calculated from this number by multiplication

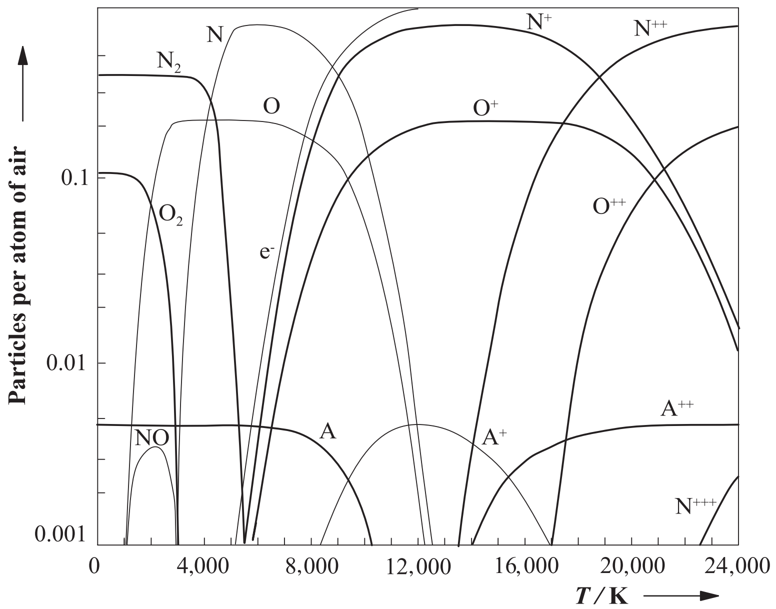

Fig. 1.3. Equilibrium composition of air at low density ($\varrho/\varrho_0 = 10^{-6}$; $\varrho_0 = 1.2927$ kg/m^3) [3].

by $1.991 M_i/M$, where M_i is the molar mass of i and M the molar mass of air. The availability of such data is relevant in aerospace engineering and other high-temperature applications. Because measurements are prohibitively costly, if possible at all, a molecular model is needed to provide insight into the physicochemical behavior of such systems as a basis of their prediction; cf. Chapter 3.

In chemical engineering applications we are frequently interested in fluid phase behavior at normal temperatures and pressures, controlled by mixing effects in liquids. An example is the heat effect that arises when two pure liquids are mixed. This effect is described in terms of the so-called excess enthalpy h^{E}. Fig. 1.4 presents experimental data on the excess enthalpy for the system benzene–hexane at 50°C, along with some predictions from a macroscopic model based on data. The technical interpretation of these data is that on mixing equal amounts of pure benzene and pure hexane, both liquid at 50°C, one has to withdraw a heat of about 800 J/mol if the mixture is to remain at the temperature of 50°C. It turns out, and will be formally derived in Section 2.1, that this aspect of fluid system behavior is related to the temperature dependence of the vapor–liquid equilibrium of the system. So one would expect to be able to predict h^{E} from data on the vapor–liquid equilibrium as a function of temperature. Fig. 1.4 shows that in practice this is not so with sufficient accuracy. Errors on the order of 25% are found when vapor–liquid equilibrium data on the system benzene–hexane are used to obtain the excess enthalpy of this system. Unavoidable uncertainties in the data and an inaccurate mathematical representation of them combine to produce these relatively large errors. Because such inaccuracy is not acceptable in process design, a direct experimental investigation appears necessary. Such experiments are costly, in particular in

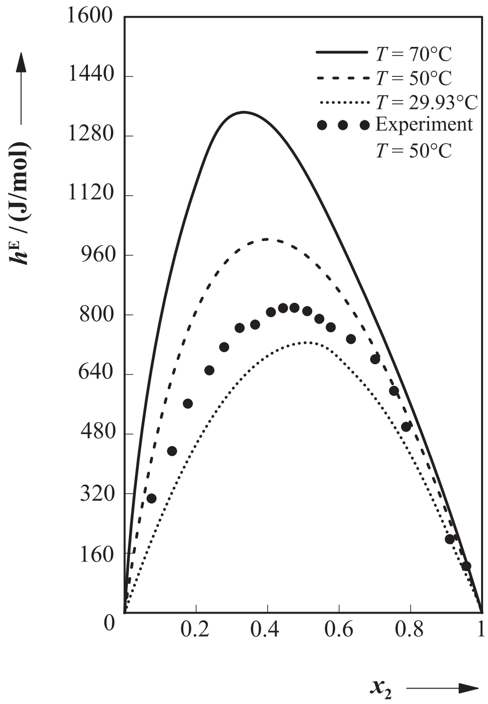

Fig. 1.4. Prediction of excess enthalpy h^E from data on the vapor–liquid equilibrium of the system benzene–hexane in the temperature range from 29.93 to 70°C. Data from [4–6].

multicomponent mixtures. It will be shown in Chapters 4 and 5, however, that an adequate molecular model, even in the absence of data, can give satisfactory results for the excess enthalpy, far more reliable than those obtained by formal management of the vapor–liquid equilibrium data.

Among the most important aspects of fluid phase behavior in chemical engineering applications is vapor–liquid equilibrium. It is the basis of many separation processes in the chemical industry. Fig. 1.5 shows data for the vapor–liquid equilibrium of three systems containing 1-chlorobutane at $T = 293.15$ K. Although the second component is quite similar in all three systems, we find rather different phase behavior. The system with 1,4-cyclohexadiene is quite nonspecific and can be represented by an almost ideal interpolation between the pure fluid vapor pressures. A change to cyclohexene induces a strong positive deviation from ideality and a further change to cyclohexane even leads to a strong azeotrope. Because simple estimation from the available pure fluid data thus appears hopeless in the general case, experimental data must be taken. This is costly and so there is definitely a need for prediction methods for such unexpected phase behavior. Such methods can indeed be designed on the basis of molecular theory, as seen in Chapters 4 and 5.

Although the estimation of vapor–liquid equilibria in mixtures from pure component data on a simple mean-value basis frequently gives at least a rough estimate, an even stronger challenge is the prediction of the gas solubility in a solvent. There is no simple correlation between gas solubility and pure

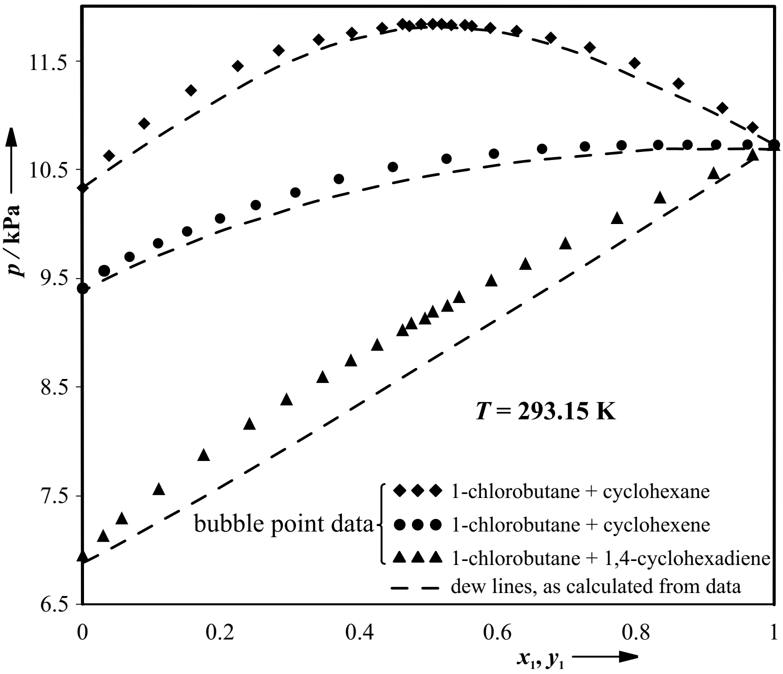

Fig. 1.5. Vapor–liquid equilibrium of three systems containing 1-chlorobutane. Data from [7].

component properties of either the solvent or the solute, while at the same time the solubility of different gases in the same solvent may vary over orders of magnitude. Fig. 1.6 illustrates this for the solubility of some simple gases in water over a range of temperatures, as described by the Henry coefficients [8]; cf. Section 2.1. The mole fraction of the gas dissolved in the liquid is roughly inversely proportional to the Henry coefficient. So pure oxygen will be roughly twice as solvable in water at room temperature as pure nitrogen, and pure carbon dioxide about 50 times as solvable. Clearly, such large differences have important consequences for the technical processes associated with gas solubility and reliable models to predict it are highly desirable. Such models can be formulated on the basis of molecular theory, as shown in Chapters 4 and 5. The problem of predicting the solution behavior of gases in liquids becomes even more challenging in electrolyte solutions. Whereas solubilities in simple systems can frequently be modeled on the basis of ideal dilute solution behavior, thus leading to an inverse linear relationship between solute concentration in the gas and in the liquid, controlled by the Henry coefficient, this is usually not so when electrolytes are involved. Nonidealities thus become noticeable even at rather small concentrations of the solute in the liquid. Experimental determination of Henry coefficients from solubilities in the ideally dilute region is then no longer sufficient, but rather data over the full range of partial pressures of the solute in the gas phase must be taken. For any new component

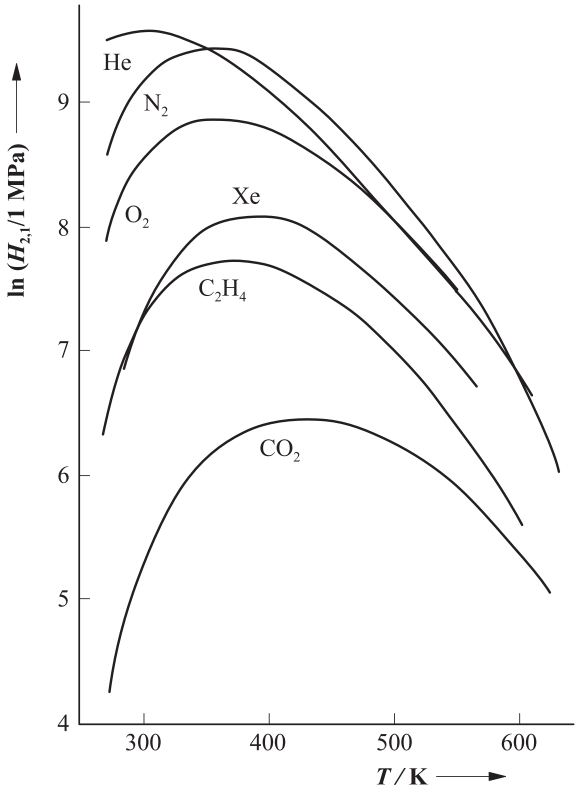

Fig. 1.6. Solubility for several gases in water as a function of temperature [8].

in the system a corresponding new series of measurements is required. Fig. 1.7 demonstrates this type of solution behavior for sulfur dioxide in the system $H_2SO_4 + H_2O$ [9]. Predictions from simple macroscopic concepts are bound to fail, but become possible on the basis of molecular models, as briefly touched on in Section 2.4.

Finally, another type of phase equilibrium that is important in technical applications is liquid–liquid equilibrium, i.e., the equilibrium between two liquid phases. Fig. 1.8 shows as an example this phase behavior for two systems containing ethanenitrile. Although in both systems the second component is rather similar, i.e., two isomers of octane, we find significant differences in the quantitative miscibility gaps. So, whereas the two liquids enthanenitrile and 2,4,4-trimethyl-1-pentene are completely miscible at $T = 320$ K, there is a heterogeneous two-liquid region at this temperature between about $x_1 = 0.25$ and $x_1 = 0.85$ when the second component is 2,4,4-trimethyl-2-pentene. Evidently, the detailed structures of the molecules have a significant influence on fluid systems' phase behavior. Many rather different types of liquid–liquid equilibria are known experimentally. The prediction of such phase behavior is a strong challenge for any fluid model. We shall readdress this problem within the context of molecular theory in Chapters 4 and 5.

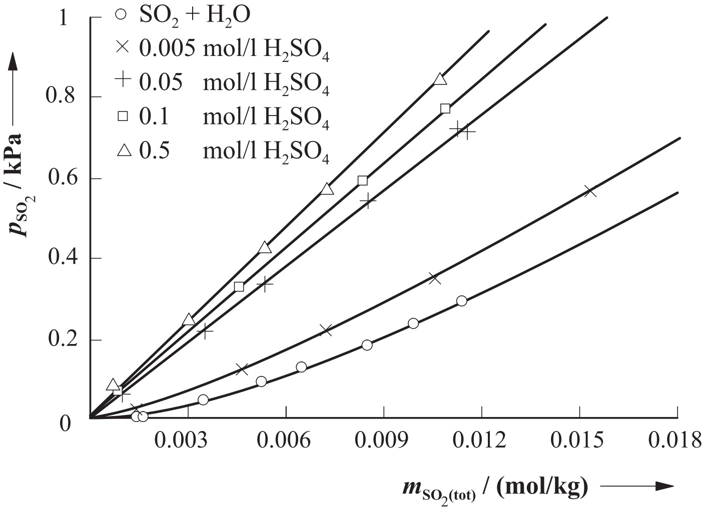

Fig. 1.7. Solubility of SO_2 in a H_2O-H_2SO_4 mixture at 298 K [9].

Even on the basis of the few examples discussed above we realize that fluid phase behavior manifests itself in a plenitude of different phenomena with applications in various different technologies. With an increasing number of components the phenomena become more complex. To design and operate technical processes we need quantitative knowledge of the relevant fluid phase properties. Experimental studies can only be done for a few systems

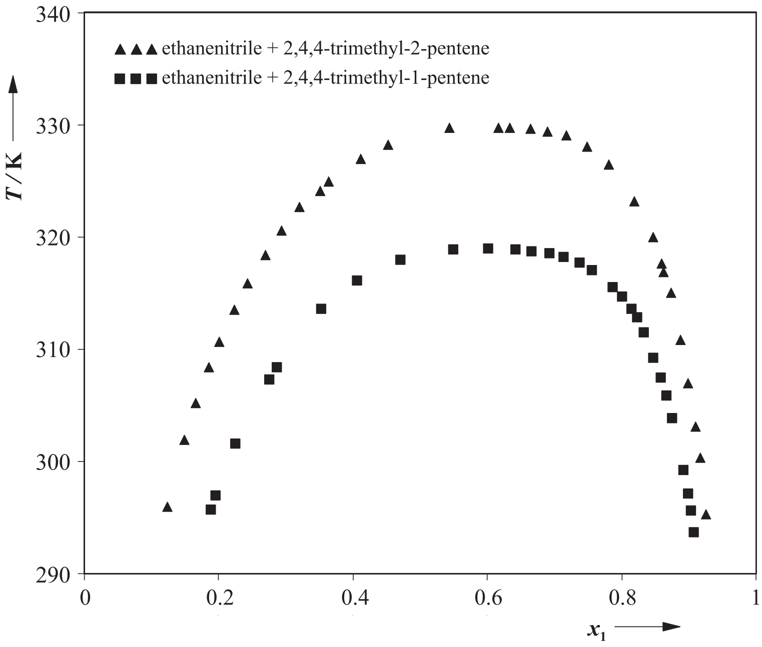

Fig. 1.8. Liquid-liquid equilibrium for two systems containing ethanenitrile [7].

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of particular relevance. Generally, information on fluid phase behavior must therefore be obtained from a theory based on the molecular properties of the fluids under consideration.

1.2 The Microscopic World

Fluid systems, like all types of matter, consist of atoms and molecules. The existence of molecules had been inferred long before it could be proven experimentally. Today there are a variety of experimental techniques to make molecules visible. From such data we learn that molecules are generally rather complicated charge clouds and geometrical structures. Further, experiment tells us that a fluid owes its particular behavior not only to the properties of the single molecules but in most cases much more to the energetic interactions between them. Related to the interactions between the molecules and the resulting molecular motions we can differentiate between three states of matter, the gaseous, the solid, and the liquid. The state of a gas, i.e., at low density, is characterized by molecules moving about freely, hitting each other and the walls of the container only after having traveled relatively long distances without being disturbed by the presence of other molecules in the system. In a solid, on the other hand, molecules are packed close together and their motion is restricted to small vibrations about space-fixed positions. Thus a solid is a highly structured molecular system whereas a gas is essentially without order, i.e., chaotic. The molecular motion in liquids lies in between that of gases and that of solids. Neutron scattering experiments on liquids reveal that there is order at short distances from a selected molecule which, however, dies off rapidly with the distance increasing to more than a few molecular diameters.

The overwhelming plenitude of the macroscopic world consists of no more than about 100 elements. The applications addressed in this book even refer to molecules containing only a few of them, notably hydrogen, carbon, oxygen, nitrogen, fluorine, chlorine, and sulfur. Still, as will be seen, the majority of practically interesting fluids are covered by this small basis of atoms. This is a first indication of the potential of going to the atomic level when prediction methods for fluid phase behavior are to be set up.

Molecules are specific groupings of atoms. Rules that have their origin in the properties of the electrons underlie their formation. A covalent bond between two atoms results when they share a common pair of electrons. The two electrons thus serve as a kind of electrostatic glue. The number of bonds that one atom can form with other atoms depends on the number of electrons it can share with its neighbors, and is, for example, one for hydrogen, four for carbon, two for oxygen and three for nitrogen. Besides single bonds there are also double and triple bonds. The bond structure of a molecule can be visualized as shown in Fig. 1.9, where the molecule fumaric acid ($C_4H_4O_4$) is

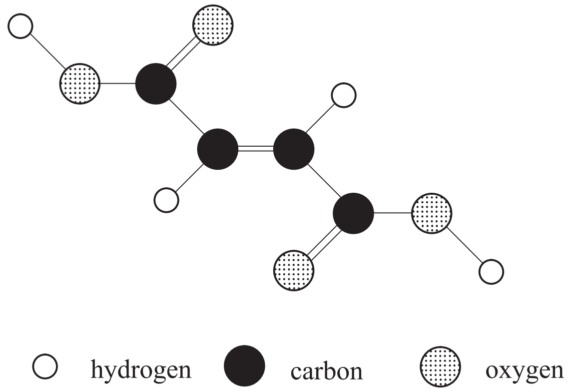

Fig. 1.9. Molecular structure of fumaric acid.

shown.[1] There are single bonds between a hydrogen atom and an oxygen atom or a carbon atom, as visualized by a simple bar. Double bonds are shown by double bars, and here appear at several locations between two carbon atoms and a carbon and an oxygen atom. Counting the bars reproduces the numbers of bonds associated with a particular atom. Whereas single bonds permit free internal rotation and folding, double and triple bonds are rather stiff and prevent internal rotation. Those electron pairs that do not take part in covalent bonds are called lone electron pairs and have an influence on the charge distribution of the molecule.

The arrangement of atoms or groups of atoms in a molecule, i.e., the molecular structure, is described by the terms configuration and conformation. The two notions are not identical. The configuration of a molecule represents the positions of the atoms as a well-defined geometrical structure. It is peculiar to a molecule. Molecules with identical sum formulae may display different configurations of their atoms and then are referred to as isomers. So octane (C_8H_{18}) can exist as *n*-octane and one of several isooctanes, with two isomer configurations as shown in Fig. 1.10. The atoms are bonded together differently in the two isomers, with the outside of the chain location of the carbon atom making isooctane stiffer than *n*-octane. The two molecules have different physicochemical properties, and there are various other isomers of octane depending on the particular arrangements of the atoms. Further, there may be different arrangements of molecular groups associated with discrete torsional angles around a stiff double bond, such as fumaric acid of Fig. 1.9 in comparison to maleic acid of Fig. 1.11, which both have the same sum formula. These are again two different molecules referred to as isomers, where fumaric acid represents the so-called *trans*-configuration and maleic acid the so-called *cis*-configuration. Again, the two isomers show quite different physicochemical

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[1] The radius of a carbon atom is about 15 nm. Representing it by a circle of order of magnitude 1 cm in diameter thus means an increase by a factor of about 10^7.