

CHAPTER 1

The Role of Theory in the Physical Sciences

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1.0 INTRODUCTION

In this chapter we shall consider the role of theory in science and enquire what is meant when we speak of a 'law' in the physical sciences. We shall ask: what are these laws, how do they arise and what is their value or purpose within science? There are two reasons for approaching the subject of the quantum in chemistry in this way. Firstly, these are questions of interest in their own right to which, in my view, insufficient attention is paid in the teaching of science. This can result in a degree of confusion, especially in a subject as inherently complex as quantum theory, where newcomers to the subject are apt to think that if only they knew more mathematics they could derive results which, in fact, cannot be and never were derived. This leads to an undesirable focus of attention upon the mathematical rather than the conceptual aspects of the problem. Thus, the second reason for discussing scientific laws is an attempt to place the laws of quantum theory in a perspective in which their origin, value and meaning can be better appreciated by beginners in the field.

1.1 WHAT IS THE ROLE OF THEORY IN SCIENCE?

It is a matter of historical fact that man has been observing the natural world, and recording his observations, since ancient times. We may safely conclude that the verbal communication of observation is even older, as the times and routes of migrating animals, birds

and fish are of crucial importance to people who live by hunting, while a knowledge of the seasons, of rainfall etc. is essential to food gatherers.¹ The importance of these and other natural phenomena made those whose knowledge of them was most extensive the leaders of their communities and exceptional status was accorded to those who had, or were believed to have, the ability to predict such events.

Historically, prediction has been attempted either through an appeal to the supernatural or by means of a reasoned extrapolation of facts already known. These two approaches to the same problem are not as different as they might appear. If an observed fact, the annual flooding of a river for example, is believed to be under the direct and immediate control of the gods, then it is quite rational to consult those gods about such events. Nor does the involvement of the supernatural necessarily conflict with the making and recording of observations. It has been suggested that a preoccupation with astrology may well account for the fact that the Mesopotamians of the first millennium BC excelled in astronomy.² Thus, the ancient fascination with the prediction of the future led not only to the use of rite and ritual but also to the recording and ordering of observations, a tendency which also received support from the widespread belief that there must be a system or order in the universe. The challenge of finding this system, and of demonstrating that one has found it by predicting the results of observations yet to be made, is the driving force of science and necessitates not only the collection of data but also the arrangement of that data within some conceptual framework that makes it easier to remember, understand and use.

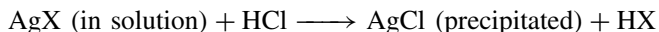
We can distinguish two broad categories of such conceptual frameworks, or models. The first comprises models of an essentially descriptive nature in which the phenomenon in question is likened to objects of our everyday experience. An example of this type of model would be the description of the fundamental constituents of matter given by Lucretius, a Roman of the first century BC. In his view, all substances were composed of indestructible atoms and . . . ‘Things that seem to us to be hard and stiff must be composed of deeply indented and hooked atoms held firmly by their intertangling branches. . . . Liquids, on the other hand, must owe their fluid consistency to component atoms that are hard and round, for poppy seed can be poured as easily as if it were water . . .’³ The molecular models used by modern chemists fall into this category; atoms are represented by coloured spheres and bonds by metal rods.

The second category of model is the mathematical model in which natural phenomena are represented by a set of symbols, the meanings of which have been defined, and which obey some particular rules of mathematical manipulation. A differential equation, for example, may be used to model a chemical reaction by providing a description of the rates of change with time of the concentrations of the reagents involved in the reaction. It is this kind of model to which we refer when we speak of the theoretical structure of the natural sciences. It is the type of model which is most useful to us when we are comparing numerical experimental data with theoretical predictions, i.e. in quantitative work.

A theoretical structure is essential to all the natural sciences. It provides the framework into which the pieces of the jigsaw of experimental data are fitted, thus revealing their inter-relationships and exposing gaps in our knowledge which need to be filled with the results of new experiments. In filling these gaps theory plays a leading role; it not only shows where new measurements are required but also tells the experimentalist what to expect when the experiments in question are performed. This is very important since,

clearly, the apparatus must be designed so that it is capable of measuring the phenomena to be studied and the quantities used must be appropriate to the equipment.

For example, suppose we wish to determine the amount of silver in the waste solution from a photographic processing laboratory by precipitating insoluble silver chloride with hydrochloric acid and weighing it. Our theory is embodied in the chemical equation:



The formula AgCl in this equation provides the information whereby the amount of silver in the precipitated silver chloride can be determined; provided, of course, that we know the relative atomic masses of silver and chlorine. The whole equation allows us to calculate how much silver chloride will be formed for a given amount of silver in the aqueous mixture. This information is required not only to determine the amount of silver, but also to plan the experiment in such a way that the precipitate to be weighed is of a mass appropriate for the chemical balance with which we propose to weigh it. To do this we may need to make a preliminary estimate of the amount of silver in the waste.

When, using a more elaborate example, we say that the length of the O–H bond in the water molecule is 95.7×10^{-12} m and the HOH bond angle 104.5° , then these figures have been obtained using a theory, quantum mechanics in fact, which relates the measured absorption by water vapour of electromagnetic radiation in the microwave region (wavelengths of the order of 1–2 cm) to the masses of the nuclei and the molecular geometry. Theory is not simply a substitute for experiment, it is a vital adjunct to it.

But theory is always a suggestion or *hypothesis*, the correctness, or otherwise, of which can only be tested against experimental fact. Therefore, theory must always be subordinate to experiment. If, after thorough checking for errors, the results of an experiment are found to differ from those predicted by theoretical calculations, then the theory must be amended, or perhaps even discarded. Thus, although the theoretical framework of science is an essential aspect which guides our progress towards a deeper understanding, we must always recognise that a current theory may one day prove to be inadequate and require replacement. These points can be illustrated by means of the gas laws.

1.2 THE GAS LAWS OF BOYLE AND GAY-LUSSAC

In 1662 Robert Boyle (1627–1691) published the results of a series of experiments on the compression of air in the closed, short arm of a J-shaped tube. Boyle observed that as the pressure, P , measured by the difference of height of the columns of mercury in the two arms of the tube, increased, the volume, V , of air in the closed end of the tube decreased. Further, he noted that *at constant temperature the volume is inversely proportional to the pressure*, a quantitative result which could be expressed in the simple equation:

$$P \propto 1/V \text{ or } PV = \text{constant} \quad (1.2.1)$$

The words in italics and Equation (1.2.1) are both expressions of what we now know as Boyle's law, and in answer to two of the questions posed above we may say that Boyle's law arose from of a series of experiments and that it expresses the results of those experiments in a convenient and precise mathematical form.

The dependence of the volume of a gas upon temperature, t , at constant pressure was studied by four French scientists, Guillaume Amontons (1663–1705), Jacques Charles

(1746–1823), Joseph Gay-Lussac (1778–1850) and Henri Regnault (1810–1878). The result of their labours is known as the law of Gay-Lussac, which was published in 1847 by Regnault. He refined the earlier experimental methods and expressed the law in the form:

$$V = V_0(1 + t/273) \quad (1.2.2)$$

Where V_0 is the volume of the gas at 0°C . Here again we have a law which has been discovered by experimental measurements and, if we consider it carefully, we find that it says that, at constant pressure, the volume of a gas increases by $1/273$ of its volume at 0°C for every degree rise in temperature. Clearly, Equations (1.2.1) and (1.2.2) are of great practical value. They can, for example, be used to calculate the volumes and pressures of gases at high temperatures. Such calculations are essential in the design of industrial plant for chemical processes, many of which take place at very high temperatures and pressures.

1.3 AN ABSOLUTE ZERO OF TEMPERATURE

But Equation (1.2.2) carries a far more fundamental message, as Amontons had realised. As we decrease the temperature of the gas below 0°C , i.e. when t becomes negative, the volume of the gas decreases. But this process must have a limit, since there is no such thing as a negative volume, and it is clear from Equation (1.2.2) that the limit of zero volume is reached at $t = -273^\circ\text{C}$. Therefore, -273°C must be the lowest temperature which can be achieved. We are forced to a remarkable conclusion; although we can go up in temperature indefinitely, there is a clear lower limit. This surprising result has been substantiated experimentally and a more exact figure for the absolute zero of temperature is -273.15°C , which is the origin of the scale of absolute temperature where temperature, T , is measured in degrees Kelvin or K:

$$T(\text{K}) = t(^{\circ}\text{C}) + 273.15 \quad (1.3.1)$$

It is interesting to note here the importance of the accuracy of experimental data in formulating scientific laws. The mere observation that the volume of a fixed quantity of

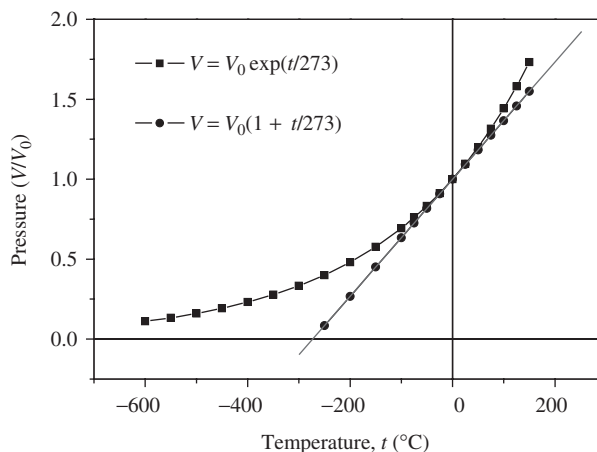


Figure 1.1 Exponential and linear temperature-volume relationships for a gas

gas decreased when the temperature was lowered might not have led to the concept of an absolute zero of temperature, much less to a value for it. Changes in physical quantities are frequently described by an exponential function and in Figure 1.1 it is shown that the equation:

$$V = V_0 \exp(t/273) \quad (1.3.2)$$

gives a temperature–volume relationship which is very similar to that given by Equation (1.2.2) in the region of temperature readily accessible to early researchers, i.e. -20 to $+100^\circ\text{C}$. But according to Equation (1.3.2), the volume of the gas never reaches zero, no matter how low the temperature. So it was vitally important that the accuracy of Regnault’s experimental measurements showed clearly that the relationship between the temperature and the volume of a gas was a linear rather than an exponential one.

1.4 THE GAS EQUATION OF VAN DER WAALS

Attempts to study Gay-Lussac’s law down to very low temperatures failed because the gases all liquefied long before the absolute zero was reached. And, indeed, many gases were found to show marked deviations from the pressure–volume–temperature (*PVT*) behaviour described by Boyle and Gay-Lussac for what became known as ideal gases which obeyed the combined equation:

$$PV = nRT \quad (1.4.1)$$

where R is the ideal gas constant which has a value of $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ and n is the number of moles of gas in the sample (1 mole of gas contains 6.022×10^{23} molecules). These deviations of the *PVT* behaviour of real gases from the ideal could be represented by more complex gas laws such as that proposed by Johannes Diderik Van der Waals (1837–1923) in 1873:

$$(P + a/V^2)(V - b) = nRT \quad (1.4.2)$$

in which a and b respectively are parameters that allow for the attraction between the molecules and for the finite volumes of the molecules themselves. They have different values for different gases which are found by comparing the experimentally determined *PVT* behaviour of the gas with the Equation (1.4.2).

But to describe Van der Waals’ equation in detail would deviate too far from the central theme of this book and we therefore turn to a summary of the answers to the questions about physical laws posed in Section 1.0.

1.5 PHYSICAL LAWS

A physical law expresses, either in words or in algebraic form, the result which is to be expected of a particular experiment. Thus, Equation (1.2.2) tells us what volume of gas we would have at any temperature, t , if its volume at 0°C is V_0 . From Equation (1.2.1) we can calculate either pressure or volume, though we must first perform an experiment to determine the value of the constant for the particular gas. If it is an ideal gas then the constant is nRT , where n is the number of moles of gas in the sample (Equation (1.4.1)).

Laws arise, are discovered or deduced as a result of experimental observations. They are not derived by pure mathematical reasoning though they may be, and indeed very frequently are, expressed in an algebraic form. It follows from this that since laws are found as a result of experimentation they must also stand or fall by the results of any other experiments to which they relate. Thus the ideal gas law (Equation (1.4.1)) failed the test of application to all gases, especially in the region of low temperatures and/or high pressures. The law is therefore of limited applicability. But it is not useless and there are many circumstances in which it can provide valuable results.

A group of one or more laws normally underlies a theoretical model of some aspect of the real world as it is seen by science. Thus, the three laws of thermodynamics are the foundation stones, discovered by experiment, which allow us to describe quantitatively the inter-conversion of the various forms of energy; of heat into mechanical work for example. Together they form a mathematical model of all such processes. Newton's three laws perform the same function for mechanics, the study of motion; in the next chapter we shall examine them in more detail.

The value of laws to science and technology applies at various levels. At the most simple, but highly significant in applied science, there is the practical use of a law to predict a quantity which cannot be readily measured; the gas pressure in a novel chemical plant which is still at the planning stage, for example. A law also establishes the framework into which experimental results may be fitted as they become available. This not only provides the means of interpreting the results but also alerts the experimentalist when a new result cannot be reconciled with the current structure of the theory. This may mean that an experimental error has been made or that the law is flawed. At a deeper level, laws reveal new concepts which were not suspected at the time when the measurements which gave rise to the law were made. We may safely assume that the concept of an absolute zero of temperature was not the idea which stimulated the first experiments of Amontons; but it arose directly from them. Here lies the great importance of laws for the development of the natural sciences. As the full significance of the quantities related in a law is appreciated, scientists are led to a deeper understanding of their subject and to the formulation of new experiments to test the law at the more fundamental level. If the law fails, such a test it must be regarded as flawed and of limited use, but not necessarily totally useless. The important point is that experiment is the only test of the validity of a law. Laws summarise the results of a wealth of experimental data and present them in a condensed form suitable for application or for further study. But they are always subordinate to experiment.

1.6 LAWS, POSTULATES, HYPOTHESES, ETC.

The waters of the present discussion are sometimes muddied by the variety of terms used to describe the same thing. We speak, for example, of the gas *laws*, Planck's quantum *hypothesis*, the Pauli *principle* and the *postulates* of quantum mechanics. Each term highlighted in italics has essentially the same meaning; it is a statement, which we have here called a law, or a set of such statements, that summarises the results of experimental measurements. The different words express different aspects of the meaning of that statement. The terms *law* and *principle* emphasise the power and immutability; *postulate* and *hypothesis* the fact that this is a suggestion or a proposal which may later require

modification. But in this book we shall regard all such expressions, and some others, as meaning laws.

1.7 THEORY AT THE END OF THE 19TH CENTURY

As the 19th century drew to a close the theoretical basis of the physical sciences appeared to be very mature and powerful. In particular, the three great structures of Maxwell's equations, which describe the behaviour of electromagnetic radiation, thermodynamics and mechanics, were remarkably successful in interpreting the experimental facts then known. Three examples show the range and power of these laws.

The laws of mechanics had been formulated by Isaac Newton (1643–1727) to model the motions of the planets and described these motions with remarkable accuracy. During the 1860s James Clerk Maxwell (1831–1879) and Ludwig Edward Boltzmann (1844–1906) used Newtonian mechanics to describe the motion of molecules in a gas, developing what we now call the kinetic theory of gases. The theory is in excellent agreement with the extensive experimental data encapsulated in the gas laws of Boyle and Gay-Lussac. The many deviations from the experimentally observed behaviour of real gases are due to the failure of other assumptions in the theory; that there is no attractive force between the molecules for example. Newtonian mechanics was thus shown to be applicable to bodies ranging in mass between 10^{-25} and 10^{+25} kg.

In the area of thermodynamics, the frequency of the chirping of the tree cricket, *Oecanthus*, has been found to depend upon the absolute temperature in strict conformity with the equation first put forward by Svante August Arrhenius (1859–1927).⁴ The logarithm of the frequency of chirping is inversely proportional to the absolute temperature, showing that the tree cricket's chirping is quite involuntary and is controlled by its body chemistry which, in turn, is subject to the laws of thermodynamics. The same is true of the autonomous functions of the higher mammals; the human heart beat for example, though the temperature range available to the experimentalist is rather small in this case.

Our final example concerns electricity, magnetism and light. Michael Faraday (1791–1867) had shown that an electric current flowing in a coil produces a magnet and that when polarised light passes through a glass plate surrounded by the magnetic coil the plane of polarisation of the light is rotated. Thus, electricity, magnetism and light are related. An electric current can be measured by determining the magnetism it produces; the units of this measurement are called electromagnetic units, emu. An electric current can also be measured in terms of the flow of charge; the units of this type of measurement are electrostatic units, esu. In 1857, Gustav Kirchoff (1824–1887) showed experimentally that the ratio of the emu to the esu was equal to the velocity of light. These relationships between electricity, magnetism and light and between the emu and the esu were brilliantly and quantitatively interpreted by Maxwell with his mathematical model of electromagnetic radiation published in 1873. Maxwell's model, which is always referred to as *Maxwell's equations*, though they might equally well be called Maxwell's laws, showed that light and all wavelengths of electromagnetic radiation could be described in terms of a magnetic and an electric field that are orientated at right-angles to each other and oscillate with the frequency of the radiation. This led to the prediction that an oscillating electric spark would generate electromagnetic radiation, a prediction which was beautifully confirmed by Heinrich Hertz (1857–1894) in a series of experiments reported in 1886–1888. We shall

explore Maxwell's description of electromagnetic radiation and the properties of polarised light further in Chapter 8.

With successes like these to its credit it seems scarcely surprising that some physicists apparently thought that there was little more to do in the field of theory other than to dot some i's and cross a few t's. Nevertheless, there were a small number of experiments the results of which defied interpretation in terms of the theories, i.e. laws, then available. It was the search for solutions to these problems which led to the revolutionary ideas of Max Planck (1858–1947) and Albert Einstein (1879–1955), and to quantum mechanics. In the next chapter we shall follow the history of mechanics to illustrate further the role which theory plays in science and to see how, early in the 20th century, some of the foundations of the structure of theoretical physics were found to be by no means as secure as they had once appeared.

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