mathematics for chemistry and physics

Mathematics for CHEMISTRY AND PHYSICS

GEORGE TURRELL

$$y(x,0) = \sum_{n=1}^{\infty} B_n \sin$$

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GEORGE TURRELL
University of Science and Technology, Lille, France

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Preface

This book has been written in an attempt to provide students with the mathematical basis of chemistry and physics. Many of the subjects chosen are those that I wish that I had known when I was a student. It was just at that time that the no-mans-land between these two domains – chemistry and physics – was established by the "Harvard School", certainly attributable to E. Bright Wilson, Jr., J. H. van Vleck and the others of that epoch. I was most honored to have been a product, at least indirectly, of that group as a graduate student of J. C. Decius. Later, in my post-doc years, I profited from the Harvard–MIT seminars. During this experience I listened to, and tried to understand, the presentations by those most prestigious persons, who played a very important role in my development in chemistry and physics. The essential books at that time were most certainly the many publications by John C. Slater and the "Bible" on mathematical methods, by Margeneau and Murphy. They were my inspirations.

The expression "Chemical Physics" appears to have been coined by Slater. I should like to quote from the preface to his book, "*Introduction to Chemical Physics*" (McGraw-Hill, New York, 1939).

> *It is probably unfortunate that physics and chemistry ever were separated. Chemistry is the science of atoms and of the way in which they combine. Physics deals with the interatomic forces and with the large-scale properties of matter resulting from those forces. So long as chemistry was largely empirical and nonmathematical, and physics had not learned how to treat small-scale atomic forces, the two sciences seemed widely separated. But with statistical mechanics and the kinetic theory on the one hand and physical chemistry on the other, the two sciences began to come together. Now [1939!] that statistical mechanics has led to quantum theory and wave mechanics, with its explanations of atomic interactions, there is really nothing separating them any more . . ..*
> *A wide range of study is common to both subjects. The sooner we realize this the better. For want of a better name, as Physical Chemistry is already preempted, we may call this common field Chemical Physics. It is an overlapping field in which both physicists and chemists should*

be trained. There seems no valid reason why their training in it should differ . . .

In the opinion of the present author, nobody could say it better.

That chemistry and physics are brought together by mathematics is the "raison d'être" of the present volume. The first three chapters are essentially a review of elementary calculus. After that there are three chapters devoted to differential equations and vector analysis. The remainder of the book is at a somewhat higher level. It is a presentation of group theory and some applications, approximation methods in quantum chemistry, integral transforms and numerical methods.

This is not a fundamental mathematics book, nor is it intended to serve a textbook for a specific course, but rather as a reference for students in chemistry and physics at all university levels. Although it is not computer-based, I have made many references to current applications – in particular to try to convince students that they should know more about what goes on behind the screen when they do one of their computer experiments. As an example, most students in the sciences now use a program for the fast Fourier transform. How many of them have any knowledge of the basic mathematics involved?

The lecture notes that I have written over many years in several countries have provided a basis for this book. More recently, I have distributed an early version to students at the third and fourth years at the University of Lille. It has been well received and found to be very useful. I hope that in its present form the book will be equally of value to students throughout their university studies.

The help of Professor Daniel Couturier, the ASA (Association de Solidarité des Anciens de l'Université des Sciences et Technologies de Lille) and the CRI (Centre de Resources Informatiques) in the preparation of this work is gratefully acknowledged. The many useful discussions of this project with Dr A. Idrissi, Dr F. Sokolić, Dr R. Withnall, Prof. M. Walters, Prof. D. W. Robinson and Prof. L. A. Veguillia-Berdicía are much appreciated.

My wife, Irène, and I have nicknamed this book "Mathieu". Throughout its preparation Irène has always provided encouragement – and patience when Mathieu was a bit trying or "Miss Mac" was in her more stubborn moods.

George Turrell
Lille, May 1, 2001

1 Variables and Functions

1.1 INTRODUCTION

The usual whole numbers, integers such as 1, 2, 3, 4 . . . , are usually referred to as Arabic numerals. It seems, however, that the basic decimal counting system was first developed in India, as it was demonstrated in an Indian astronomic calendar which dates from the third century AD. This system, which was composed of nine figures and the zero, was employed by the Arabs in the ninth century. The notation is basically that of the Arabic language and it was the Arabs who introduced the system in Europe at the beginning of the eleventh century.

In Europe the notion of the zero evolved slowly in various forms. Eventually, probably to express debts, it was found necessary to invent negative integers. The requirements of trade and commerce lead to the use of fractions, as ratios of whole numbers. However, it is obviously more convenient to express fractions in the form of decimals. The ensemble of whole numbers and fractions (as ratios of whole numbers) is referred to as rational numbers. The mathematical relation between decimal and rational fractions is of importance, particularly in modern computer applications.

As an example, consider the decimal fraction $x = 0.616161\cdots$. Multiplication by 100 yields the expression $100\,x = 61.6161\cdots = 61 + x$ and thus, $x = 61/99$, is a rational fraction. In general, if a decimal expression contains an infinitely repeating set of digits (61 in this example), it is a rational number. However, most decimal fractions do not contain a repeating set of digits and so are not rational numbers. Examples such as $\sqrt{3} = 1.732051\cdots$ and $\pi = 3.1415926536\cdots$ are irrational numbers.* Furthermore, the logarithms and trigonometric functions of most arguments are irrational numbers.

*A mnemonic for π based on the number of letters in words of the English language is quoted here from "the Green Book", Ian Mills, *et al.* (eds), "Quantities, Units and Symbols in Physical Chemistry", Blackwell Scientific Publications, London (1993):

'How I like a drink, alcoholic of course, after the heavy lectures involving quantum mechanics!'

In practice, in numerical calculations with a computer, both rational and irrational numbers are represented by a finite number of digits. In both cases, then, approximations are made and the errors introduced in the result depend on the number of significant figures carried by the computer – the machine precision.* In the case of irrational numbers such errors cannot be avoided.

The ensemble of rational and irrational numbers are called real numbers. Clearly, the sum, difference and product of two real numbers is real. The division of two real numbers is defined in all cases but one – division by zero. Your computer will spit out an error message if you try to divide by zero!

1.2 FUNCTIONS

If two real variables are related such that, if a value of x is given, a value of y is determined, y is said to be a function of x. Thus, values may be assigned to x, the independent variable, leading to corresponding values of y, the dependent variable.

As an example, consider one mole of a gas at constant temperature. The volume V is a function of the applied pressure P. This relation can be expressed mathematically in the form

$$V = f(P), \tag{1}$$

or, $V = V(P)$. Note that to complete the functional relationship, the nature of the gas, as well as the temperature T, must be specified. A physical chemist should also insist that the system be in thermodynamic equilibrium.

In the case of an ideal gas, the functional relationship of Eq. (1) becomes

$$V = \frac{C(T)}{P}, \tag{2}$$

where $C(T)$ is a positive constant which is proportional to the absolute temperature T. Clearly, the roles of V and P can be reversed leading to the relation

$$P = \frac{C(T)}{V}. \tag{3}$$

The question as to which is the independent variable and which is the dependent one is determined by the way in which the measurements are made and, mathematically, on the presentation of the experimental data.

*Note that the zero is a special case, as its precision is not defined. Normally, the computer automatically uses the precision specified for other numbers.

Suppose that a series of measurements of the volume of a gas is made, as the applied pressure is varied. As an example, the original results obtained by Boyle* are presented as in Table 1.

In this case V is a function of P, but it is not continuous. It is the discrete function represented by the points shown in Fig. 1a. It is only the mathematical function of Eq. (2) that is continuous. If, from the experimental data, it is of interest to calculate values of V at intermediate points, it is necessary to estimate them with the use of, say, linear interpolation, or better, a curve-fitting procedure. In the latter case the continuous function represented by Eq. (2)

Table 1 Volume of a gas as a function of pressure.

V, Volume[a]	P, Pressure (inches Hg)	$1/V$
12	29.125	0.0833
10	35.3125	0.1
8	44.1875	0.125
6	58.8125	0.1667
5	70.6875	0.2
4	87.875	0.25
3	116.5625	0.3333

[a]Measured distance (inches) in a tube of constant diameter.

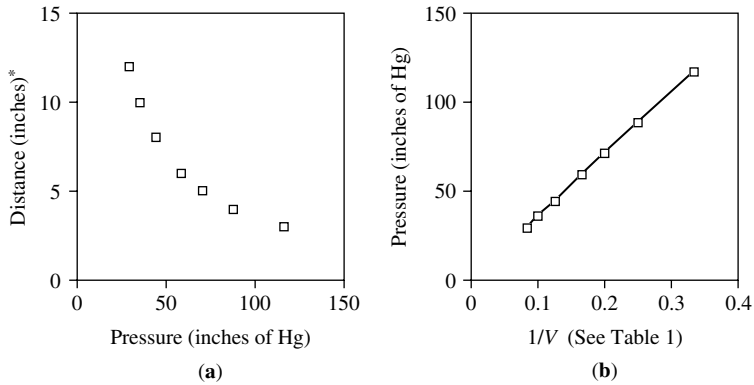

Fig. 1 Volume of a gas (expressed as distance in a tube of constant diameter) *versus* pressure (**a**). Pressure as a function of reciprocal volume (**b**).

*Robert Boyle, Irish physical chemist (1627–1691)

would normally be employed. These questions, which concern the numerical treatment of data, will be considered in Chapter 13.

In Boyle's work the pressure was subsequently plotted as a function of the reciprocal of the volume, as calculated here in the third column of Table 1. The graph of P *vs.* $1/V$ is shown in Fig. 1b. This result provided convincing evidence of the relation given by Eq. (3), the mathematical statement of Boyle's law. Clearly, the slope of the straight line given in Fig. 1b yields a value of $C(T)$ at the temperature of the measurements [Eq. (3)] and hence a value of the gas constant R. However, the significance of the temperature was not understood at the time of Boyle's observations.

In many cases a series of experimental results are not associated with a known mathematical function. In the following example Miss X weighed herself each morning beginning on the first of February. These data are presented graphically as shown in Fig. 2. Here interpolated points are of no significance, nor is extrapolation. By extrapolation Miss X would weigh nearly nothing in a year-and-a-half or so. However, as the data do exhibit a trend over a relatively short time, it is useful to employ a curve-fitting procedure. In this example Miss X might be happy to conclude that on the average she lost 0.83 kg per week during this period, as indicated by the slope of the straight line in Fig. 2.

Now reconsider the function given by Eq. (3). It has the form of a hyperbola, as shown in Fig. 3. Different values of $C(T)$ lead to other members of the family of curves shown. It should be noted that this function is antisymmetric with respect to the inversion operation $V \rightarrow -V$ (see Chapter 8). Thus, P is said to be an odd function of V, as $P(V) = -P(-V)$.

It should be evident that the negative branches of P *vs.* V shown in Fig. 3 can be excluded. These branches of the function are correct mathematically,

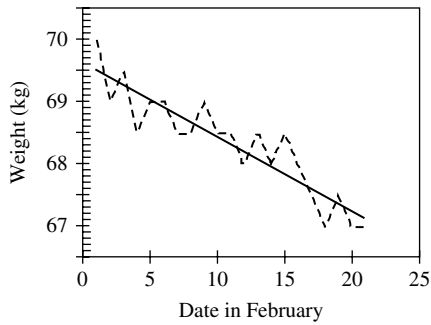

Fig. 2 Miss X's weight as a function of the date in February. The straight line is obtained by a least-squares fit to the experimental data (see Chapter 13).

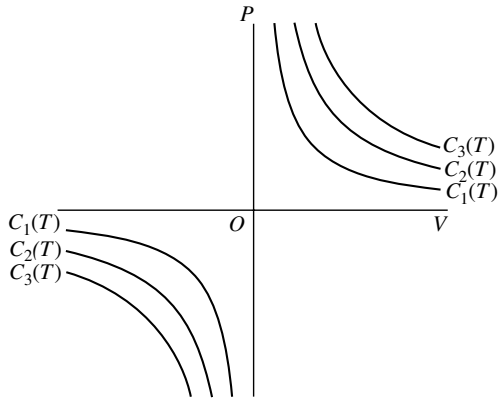

Fig. 3 Pressure *versus* volume [Eq. (3)], with $C_3(T) > C_2(T) > C_1(T)$.

but are of no physical significance for this problem. This example illustrates the fact that functions may often be limited to a certain domain of acceptability. Finally, it should be noted that the function $P(V)$ presented in Fig. 3 is not continuous at the origin ($V = 0$). Therefore, from a physical point of view the function is only significant in the region $0 < V < \infty$. Furthermore, physical chemists know that Eqs. (2) and (3) do not apply at high pressures because the gas is no longer ideal.

As $C(T)$ is a positive quantity, Eq. (3) can be written in the form

$$ln\ P = ln\ C - ln\ V. \tag{4}$$

Clearly a plot of $ln\ P$ *vs.* $ln\ V$ at a given (constant) temperature yields a straight line with an intercept equal to $ln\ C$. This analysis provides a convenient graphical method of determining the constant C.

It is often useful to shift the origin of a given graph. Thus, for the example given above consider that the axes of V and P are displaced by the amounts v and p, respectively. Then, Eq. (3) becomes

$$P - p = \frac{C(T)}{V - v}, \tag{5}$$

and the result is as plotted in Fig. 4. The general hyperbolic form of the curves has not been changed, although the resulting function $P(V)$ is no longer odd – nor is it even.

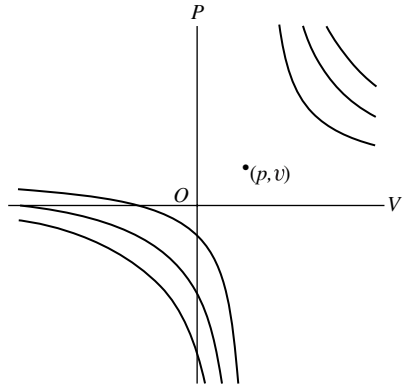

Fig. 4 Plots of Eq. (5) for given values of v and p.

1.3 CLASSIFICATION AND PROPERTIES OF FUNCTIONS

Functions can be classified as either algebraic or transcendental. Algebraic functions are rational integral functions or polynomials, rational fractions or quotients of polynomials, and irrational functions. Some of the simplest in the last category are those formed from rational functions by the extraction of roots. The more elementary transcendental functions are exponentials, logarithms, trigonometric and inverse trigonometric functions. Examples of these functions will be discussed in the following sections.

When the relation $y = f(x)$ is such that there is only one value of y for each acceptable value of x, $f(x)$ is said to be a single-valued function of x. Thus, if the function is defined for, say, $x = x_1$, the vertical line $x = x_1$ intercepts the curve at one and only one point, as shown in Fig. 5. However, in many cases a given value of x determines two or more distinct values of y.

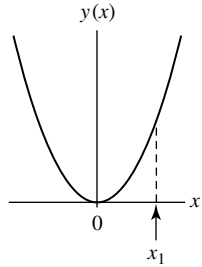

Fig. 5 Plot of $y = x^2$.

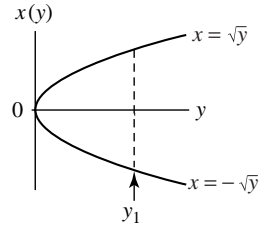

Fig. 6 Plot of $x = \pm\sqrt{y}$.

The curve shown in Fig. 5 can be represented by

$$y = x^2, \tag{6}$$

where y has the form of the potential function for a harmonic oscillator (see Chapter 5). This function is an even function of x, as $y(x) = y(-x)$. Clearly, y is a single-valued function of x. Now, if Eq. (6) is rewritten in the equivalent form

$$x^2 = y, \quad y \geq 0 \tag{7}$$

it defines a double-valued function whose branches are given by $x = \sqrt{y}$ and $x = -\sqrt{y}$. These branches are the upper and lower halves of the parabola shown in Fig. 6. It should be evident from this example that to obtain a given value of x, it is essential to specify the particular branch of the (in general) multiple-valued function involved. This problem is particularly important in numerical applications, as carried out on a computer (Don't let the computer choose the wrong branch!).

1.4 EXPONENTIAL AND LOGARITHMIC FUNCTIONS

If $y = f(x)$ is given by

$$y = a^x \tag{8}$$

$y = f(x)$ is an exponential function. The independent variable x is said to be the argument of f. The inverse relation, the logarithm, can then be defined by

$$x = log_a\, y \tag{9}$$

and a is called the base of the logarithm. It is clear, then, that $log_a\, a = 1$ and $log_a\, 1 = 0$. The logarithm is a function that can take on different values