Mathematics for Chemistry with Symbolic Computation

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This interactive electronic book is organised into several separate computer files, each called a *Maple* worksheet; each worksheet contains executable commands and assignments in a sequence, with interspersed text to explain their purposes and effects, but particularly to introduce mathematical concepts and principles and to implement the mathematical operations. These assignments and commands are generally intended to be executed in a linear sequence from the top to the bottom of each section or page, and the user is intended to read the interspersed text to understand the progression of these commands. Each file of this book is a document, comprising a single chapter that contains text, and commands executable on a computer operating software *Maple*^{TM}; this electronic document, a worksheet, is operable entirely interactively: a user reads the text, executes the commands and views the output; according to an experimental approach that is encouraged, a user can freely modify the command to discover the nature of the correspondingly altered output. We recommend that a user retain a separate archival copy of this original document with no output from *Maple*, and that in general a worksheet containing output should not be saved on exit from *Maple* unless such an archival copy of the original document be available; if alterations to any text or command in a worksheet of this electronic book be essential, one should purge the worksheet of output, through use of the command `Remove output` at the bottom of menu `Edit` near the top left corner of this display, and collapse all sections, through use of the bottom command in menu `View` also near the top left of this display.

Within this particular worksheet that includes introductory chapter 0, there are also a preface in a traditional manner, a table of contents and a brief overview of *Maple*. In its separate file, each chapter that treats a traditional area of arithmetic or mathematics comprises in turn groups of sections under a particular title; each section, identifiable on *Maple*'s *classic* interface by a grey square containing a plus sign, +, at the left margin and a heading to the right thereof, is normally collapsed so that content remains hidden until that section is opened according to a mechanism described below. The material is equally accessible with the 'standard' interface in the 'worksheet' mode; use of the classic interface with a *Maple* release after *Maple 2017* is not recommended. To view content of such an indented section with the *classic* interface, set, with a mouse or equivalent device that serves as pointer, the cursor on a chosen square containing such "+" and depress the left lever of the mouse, or equivalent mechanism of activation; to close an open section for compactness, click on "-" in its square. With *Maple*'s *standard* interface, a section is identifiable by a grey triangle at the left margin ">" that points to its right side and its accompanying heading; opening that section by placing the cursor on that triangle and depressing the left lever of a computer mouse, or equivalent mechanism, causes the triangle to point downward, and closing that section involves the same mechanism -- 'clicking' left with the cursor on the arrow. With

such indented material exposed, one can read the text, in generally black letters as in this paragraph, proceeding down the worksheet in various ways; one can execute an input statement on a line of red characters wherever it appears by ensuring that the cursor is located before the end of that line, even at the first colon or semicolon in that line. The output, if any, from any command in *Maple* so presented in red characters appears in blue characters before the next occurrence of text or another *Maple* command. Reversing the mechanism to open that section causes the section to become closed and collapsed so that the content is concealed from view. Interspersed among these sections presenting description of mathematical operations and their implementation in *Maple* are many examples and exercises, also present normally in collapsed or hidden form. Deemed to be an integral component of the learning or discovery, by means of symbolic computation, these examples and exercises of the presented mathematics should be examined and undertaken in a linear temporal order down any worksheet, and each worksheet in increasing order of chapter number; each example bears an identification at the left margin with initial character *x*, and exercises and their solutions are named explicitly. The reader should attempt the solution of the exercise in a separate window, preferably by copying the statement of the exercise into a new section with the solution to follow. The solutions of exercises are available in a separate worksheet.

Using the left lever of a mouse, or equivalent device, to *click* on any word or set of characters displayed both in green letters and underlined activates a hyperlink, which opens a new screen that contains information pertinent to that hyperlink; to return to the former screen after reading that information, one should click on the *lower* x in the upper right corner of the classic display -- that black x with a white or grey background, *not the upper* x in white on a red background or black on a grey background depending on computer, which initiates termination of the *Maple* session. Test this mechanism of hyperlink by clicking on the next word here -- worksheet; so activating a hyperlink is also a general method of quickly altering material displayed on this monitor from one point in a worksheet to either

- a remote point in the same worksheet, or
- another worksheet that is located appropriately or for which an external linking mechanism is arranged, or
- a specific page that provides help on a pertinent topic in relation to usage of *Maple* comprising descriptions of syntax, data types and functions, or
- a pertinent page in a dictionary of mathematical terms within *Maple*, or
- a remote site through an internet browser.

The pages of either `help` or `dictionary` generally contain further hyperlinks to other pages of the same or other type. In worksheets of this book, almost all such hyperlinks in this electronic document invoke pages of `Help` or the dictionary, thus not requiring a connexion to internet. The `Help` pages provided in *Maple* are extensive and generally comprehensive; their frequent use in learning mathematics with *Maple* is recommended and valuable.

For these files we commend use of *Maple* in the standard (Java) interface in its worksheet mode; use of its **standard** interface might be slow if a computer lack sufficient hardware properties such as speed of processor or amount of memory. Within a *Maple* session thus with its standard interface, a triangle at the left margin pointing right, like that just below this paragraph beside a heading **P preface**, indicates an indented section that contains material about a particular topic to which the heading pertains. To view content of such an indented section, set the cursor, with a mouse or equivalent device to serve as pointer, on a chosen triangle and depress the left lever of the mouse or other mechanism of activation; to close an open section for compactness, click on the same triangle pointing downward. With such indented material exposed, one can read the text, and proceed down this worksheet in various ways; one

can execute an input statement on a line of red characters wherever it appears by ensuring that the cursor is located before the end of that line, even to the left of a colon or semicolon in that line. If, for a particular operating system, use of the standard interface in mode *worksheet* can be set through selection of Tools -> Options -> Interface and setting the default format to be `Worksheet`, rather than Document, which one should then `Apply globally` -- to all future sessions -- rather than the session in which this option is set.

P preface

"Every attempt to employ mathematical methods in the study of a chemical question must be considered profoundly irrational and contrary to the Spirit of Chemistry. If Mathematical Analysis were ever to hold a prominent place in chemistry -- an aberration that is happily almost impossible -- it would occasion a rapid and widespread degeneration of that science."

Auguste Comte, *Philosophic Positive* (1830)

Despite that injunction by a wise man of a past era, Comte, which is even inconsistent with his eminent forebear Bacon quoted below, mathematics and methods thereof have become an essential component of the study and practice of chemistry at any level beyond frivolous mixing of chemical ingredients; even at that date, that attitude had recidivistic overtones, because Immanuel Kant, who, with David Hume, was a major influence otherwise on Comte, had asserted in 1786 that the then current chemistry failed to qualify as a natural science because it lacked a sufficiently mathematical structure. Contrary opinions exist.

The more progress the physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility to which it may be summitted to calculation.

Adolphe Quetelet, astronomer, mathematician and sociologist (1828)

According to a foremost philosopher of the twentieth century,

"Physics is mathematical not because we know so much about the world but because we know so little [*that*] *only its mathematical properties we can discover."*

Bertrand Russell

Like other physical sciences, chemistry comprises not only

- *experiment*, according to which one undertakes observations and correlations of chemical and physical phenomena and measures chemical and physical quantities, and
- *theory*, according to which one deduces and applies rules to rationalize these correlations, interprets the results of experiment, and correlates measurements in various sets, but also, and, to an increasing extent,
- *computation*, through the use of either specific programmes for a particular purpose such as a spreadsheet, or for quantum-chemical calculations, or a general mathematical processor such as *Maple* with which this worksheet is being read.

The practice of chemistry must involve measurements of various quantities, which imply numbers and units. To work with those numbers a symbolic processor that can treat both the numbers and units is ideal.

When you can measure what you are speaking about and express it in numbers, you know something about it;

but whenyou cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind;

it may be the beginning of knowledge, but you have scarcely in your thoughts advance to the state of science, whatever the matter may be.

Lord Kelvin

Mathematics is inextricably involved in both the recording of chemical and physical observations with a numerical component and the correlations between those measurements, and must serve as the basis of the computational scheme. Therefore, as Galileo Galilei remarked in *Il Saggiatore*, 1623 -- thus two centuries before Comte,

"The great book of nature is written in the language of mathematics,
without the help of which one can comprehend not a single word of it."

Even before Galileo, Roger Bacon in Oxford wrote in 1267 that

"Mathematics is the gate and key of the sciences. . . .
Neglect of mathematics works injury to all knowledge,
since he who is ignorant of it cannot know the other sciences or the things of this world.
And what is worse, men who are thus ignorant are unable
to perceive their own ignorance and so do not seek a remedy."

and a prominent physical chemist in Oxford conveyed the following advice,

No human inquiry can claim the status of true knowledge without passing
through mathematical demonstration: and if you say that sciences which
begin and end in the mind possess truth, this cannot be allowed, but must be
denied for many reasons: and first of all because experience does not enter
into such mental exercises, and without it there is no certainty.
(*Leonardo da Vinci, as cited by Sir Cyril Hinshelwood*)

whereas E. T. Bell stated that

Mathematics is both the queen and the handmaiden of all science.

and Adolphe Quetelet, French astronomer, mathematician, statistician and sociologist, 1796–1874, wrote in 1828 that

The more progress the physical sciences make, the more they tend to enter the domain of mathematics,
which is a kind of centre to which they all converge. We may even judge the degree of perfection
to which a science has arrived by the facility to which it may be submitted to calculation.

All these statements enunciated before the chemical era are as applicable for contemporary chemistry as for physics or other discipline of natural science. In 1874 Alexander Crum Brown, trained in both chemistry and mathematics and the first to undertake research in mathematical chemistry, presaged that

"Chemistry will become a branch of applied mathematics, but it will not cease
to be an experimental science. Mathematics may enable us retrospectively
to justify results obtained by experiment, may point out useful lines of research
and even sometimes predict entirely novel discoveries. We do not know
when the change will take place, or whether it will be gradual or sudden ..."

Although, well before 1845, Charles Babbage in Cambridge appreciated the feasibility of undertaking calculations of an arithmetical nature with an *analytical engine* or computer, and although his associate Ada Byron Countess Lovelace even understood the practicality of undertaking mathematical operations with a computational engine, the prospective impact of such computation for chemical purposes was not then apparent for chemists, but, before Brown's demise in 1922, major utilization of mathematics had occurred for physico-chemical applications, such as in thermodynamics and chemical kinetics. About the time of Brown's quoted utterance, in Cambridge, 1875, Cayley was occupied with enumerating chemical isomers, and in 1878 Sylvester, who had earlier studied in Cambridge University but was then in USA before returning to Oxford, introduced the term graph into the mathematical literature in connexion with those isomers. Programmes to enable symbolic computation developed in parallel with

software for merely numeric computation, beginning about year 1952.

Mathematics is both the queen and the handmaiden of all science.

E. T. Bell (1937)

Mathematical chemistry provides the framework and broad foundation on which chemical science proceeds.

J. Karle (Nobel, chemistry, 1985)

A mathematical problem, in chemistry or otherwise, might involve at least these techniques:

- numerical algorithms,
- an algorithmic treatment of analytic, algebraic and geometric problems,
- reference to tables and collections of formulae, and
- statistical analysis and graphical representation.

Contemporary programmes for computers can perform all these techniques; a student or practitioner of chemistry should include such a programme in his arsenal of approaches to attack such problems, which nevertheless require of a user the knowledge and understanding of mathematical concepts and principles.

"There is no science that is not developed from knowledge of phenomena, but, to obtain advantage from this knowledge, it is necessary to be a mathematician."

When Daniel Bernoulli (1700 - 1782), one of eight prominent mathematicians in a famous family, asserted thus, he could not in his wildest dreams have imagined that a programme for a common digital electronic device can not only incorporate enormous mathematical knowledge accumulated over five millennia but also undertake mathematical operations with a speed and accuracy that far surpasses a human computer, so that statement has become inaccurate: one need not be a mathematician -- understanding the mathematical concepts and principles, a scientist need only then instruct a computer to implement whatever operations be appropriate for an analysis of an observed phenomenon. That same computer programme provides, moreover, an admirable vehicle for the teaching, learning and understanding of mathematical concepts and principles. As the computer programme generally enables a quick and correct response to any mathematical command that is posed in an acceptable manner, a student and his instructor are able to focus on a conceptual understanding of each and every topic, each of which is readily susceptible to geometric or graphical, numerical and algebraic presentation for the utmost enhancement of understanding.

Apart from an obvious requirement to process numeric data from a laboratory, which typically requires an application of statistical methods, even a balanced chemical equation is a mathematical statement: unlike an algebraic equation that relates symbols, a chemical equation provides either a concise summary of conversion during a chemical reaction or a relation between physical properties. A balanced chemical equation of either kind implies conservation of both mass and charge, generally without transmutation of chemical elements; a chemical equation of both kinds likewise conveys both symbols that represent chemical species or properties and, implicitly, units: units on both sides of a chemical equation must consequently balance, and results obtained from a formula involving chemical or physical properties must be independent of units according to a chosen system. Beyond these uses of equations in chemistry, one must appreciate the principles that underlie a construction of more overtly mathematical models of processes and structures, to develop understanding at a microscopic level and thereby to test predictive powers of such a model, but neither the model nor the medium must become itself the message. The description, understanding and application of all such models in chemistry form the basis of all instructional courses in chemistry, be they qualitative or quantitative; without models chemistry would remain an accumulation of seemingly unrelated facts and observations. One must learn many facts before one can appreciate the power and application of a theoretical model to create a schema with which to expand one's understanding of chemistry. One must equally possess a significant understanding of the nature and domain of a mathematical model, so as not to confound observable

chemical or physical properties with its artefacts. Of three levels of chemical meaning, a macroscopic domain as a direct object of observation in a chemical laboratory or elsewhere is the most immediate; only a reasonably profound appreciation of mathematical principles and properties enables a chemist to distinguish between a microscopic, or atomic -- but still physical, level, and, at a third level, sophisticated models that chemists and physicists have devised and that seem to blur margins between physical reality and mathematical application. The most important and universal attribute of a graduate in a science subject is the development of a critical faculty -- the capability to distinguish the meanings of terms and the appropriateness of their application to a particular observation. In their citation to Sir John A. Pople (1925 -- 2004), whose initial interest in Cambridge was mathematics but whose admirable achievements throughout his long career greatly advanced the possibility of simulating molecular structure and reactions, when (with W. Kohn) he was named Nobel Laureate in chemistry in 1998, the Swedish committee declared, perhaps with hyperbole apt for the occasion,

"We celebrate the fact that mathematics has invaded chemistry, *that*, *by means of theoretical calculations*, *we can predict* [*diverse*] *chemical phenomena."*

Their allusion to calculations of essentially of only a fundamentally arithmetical character implies a third level to which we allude above, but *quantum chemistry* is by no means the only -- or even the most important -- reason to cultivate a strong basis of mathematics for a purpose of understanding fundamental chemical precepts and to undertake myriad chemical applications.

Mathematics has a structure similar to that of chemistry, but is, by its nature, inherently abstract: one can neither observe nor measure an algebraic formula. Mathematical structures are based on assumptions or axioms in given sets, and provide an impetus to seek theorems that enable one to develop tools for use in mathematics in defined areas, such as number theory, calculus, vector spaces, topology, combinatorics, linear programming et cetera: all these, and other, subject areas provide tools to treat a chemical model. Mathematics resembles chemistry in some respects: whereas a chemist might prepare a new chemical compound or material, a mathematician might develop a new area of mathematics. A problem arises that, to construct a model and to solve equations of all sorts, a chemist requires mathematical principles to develop tools, but mathematical subtleties might be overlooked until anomalous results arise. In acknowledging this situation, we discern and appreciate that software for symbolic computation provides a powerful tool and a *tutor* for application of mathematical principles in a chemical context.

"Throughout history, mathematics has been investigated by observation and quasi-experiments."
B. J. Krist

We denounce a formal mathematical logic of theorem, lemma and corollary devised for inner mathematical documentation and communication such as is associated with, or attributed to, an invented mathematician Nikolas Bourbaki that is entirely inappropriate for almost all students of chemistry; we learn best through examples illustrated by algebraic, geometric or graphical and numeric means, for which purpose powerful software for symbolic computation is astonishingly beneficial. These quasi-experiments are also conveniently performed with computer programs for symbolic computation. Some statements of theorems are, however, useful to even a student of chemistry in providing a precise expression of a particular and important result or rigorous observation; each student of chemistry should experience the teaching of mathematics by a mathematician, and of physics by a physicist, so that he or she acquires some intuition of the ways that exponents of these disciplines approach the solution of their problems; objects in the universe comprise not only chemical aspects, and the capability to appreciate various aspects of systems great and small is part and parcel of a chemical education. Advanced mathematical software such as *Maple* contains mathematical knowledge generated during five millennia that is not only applicable to the solution of problems with a mathematical component but also an accessible repository for that knowledge; Einstein's advice,

"*never memorize anything that you can look up*"

might encourage students or practitioners of chemistry to focus on the understanding of the concepts rather than to devote futile effort merely to retain an inevitablly too small collection of mathematical facts.

The importance of graphical constructions in teaching and learning can not be underestimated, although lacking from that formal logic:

"One picture is worth a thousand words."

attributed to Emperor Sung

Not only geometry benefits from graphical constructions that can simulate objects in three spatial dimensions, with rotation to enable multiple perspectives; animation of these objects essentially brings them to life.

"*He who understands geometry understands anything in the universe.*"

Galileo Galilei

The overview of each chapter in the present work provides, however, a synopsis of pertinent principles and definitions; at least browsing each such section is recommended before embarking on an implementation of those principles, and regular consultation of an overview is likewise commended during progress through the various sections and groups thereof. In this introductory chapter and after plotting comands are introduced at length in chapter 2 and section group 2.1, copious figures and geometric constructs abound to illustrate every topic within the many sections following the overview of each chapter.

"*I could have done it in a much more complicated way*," said the Red Queen, immensely proud.

"*Whatever is worth doing is worth doing well.*" - Lewis Carroll

Students who arrive at an institution of tertiary educational level to study chemistry and who possess diverse backgrounds and varying knowledge of mathematics might evince astonishment on being confronted with a prospect of undertaking further courses in mathematics concurrently with chemistry.

"He who understands only chemistry does not understand that properly either."

Georg Christoph Lichtenberg 1742 -- 1799

The thus essential content of mathematics in such supportive courses has tended to be traditional, in the sense that, with few notable exceptions, topics covered and a mode of their delivery have been developed with regard to perceived real or imagined needs before the present era of readily accessible and powerful computing hardware and associated mathematical software. Many students of science find mathematical concepts difficult to understand, no matter how carefully and thoroughly they are explained, because mathematical abstraction is an inescapable and impeding element: for instance, in early stages of a course of chemistry students find it difficult to distinguish between variables and parameters in a formula or equation -- with a requirement to maintain a consistent treatment of units as an added complication. We must therefore recognise that mathematics might be difficult for students of chemistry, a significant proportion of whom might lack a capacity to understand mathematics at a level required for use in chemical applications deemed important. In universities of deservedly commendable academic reputation, instructors of service courses in these circumstances emphasize reproducing mathematical recipes to be used by students to solve standard exercises without much understanding. Students who find mathematics indigestible during their introductory courses experience considerable difficulty when exposed to applications within a chemical context because the original mathematical concepts, commonly rooted in familiar variable identifiers x and y, are incompletely understood.

Readily available software for symbolic computation proffers an opportunity to develop the teaching of mathematics to chemists in an alternative way. Such a course, which differs from traditional teaching in both content and development of skills, provides an opportunity for all mathematical processes to be performed using sophisticated software for symbolic computation: availability of this software consequently alters the way that we teach, learn and apply mathematics in a chemical context. Use of symbolic computation increases a level of what can be achieved without a necessity to understand higher

mathematics in fine detail, thereby enabling a student to focus on chemical applications; for example, one can solve differential equations of chemical kinetics without knowledge of the detail of these equations, such as their symmetries, as one merely instructs the software to find a solution. A student can thereby concentrate on the solution of exercises in which, for example, parameters of a chemical problem are varied. Likewise, in treating series one need no longer to remember and to apply an appropriate test of convergence: the software is instead instructed to sum a series; if a result is finite, although oscillating partial sums might not be recognized, convergence is possible. Although these and other applications of mathematical tools serve to challenge the way that we teach and have taught mathematics, we must remain aware of those aspects of chemistry in which a profound understanding of mathematics is essential: in these cases one must develop new courses that emphasize and develop concepts in an appropriate manner, taking care to integrate the application of symbolic computation as a tool to execute calculations.

A paradox has arisen that, during the past half century, chemistry has become formally much more mathematical, with strong emphasis on, or influence of, quantum mechanics and chemometrics within undergraduate curriculum, whereas in major universities the total number of hours of lectures in obligatory formal courses of mathematics for students of chemistry might have greatly decreased, for instance from as much as 400 to less than 120 hours. Here again, symbolic computation provides a means whereby a student of chemistry can acquire both an understanding of concepts and a capability and facility to execute chemical calculations without concern about details of mathematical methods and their tedious implementation; in sparing a student much tedious manual practice to ingrain skills, either the range of topics taught through use of symbolic computation can be much increased within a given duration of lectures, or the total duration can be significantly decreased -- or both! Although typical use of this book is likely as a textbook associated with a lecture course of traditional form but incorporating demonstrations and complemented with supervised practical sessions, the nature of this book and its particular files that operate interactively on a computer on which *Maple* is installed make it peculiarly applicable to self learning, or for distance learning at any location even remote from a campus or human instructor. Depending on the general level of attainment of a student entering a traditional course within an institution for which this book might serve as text, an instructor might cover most material within part I in lectures as few as 40 hours, roughly one group of sections per lecture of nominal duration one hour, but we commend that an equal duration of individual practice on a computer with tutorial supervision be arranged for each student, naturally supplemented by separate practice without tutor as much as each student requires. Lectures and practical classes of total duration 80 hours, during a typical academic year that might be subdivided into semesters or terms, might be thus the minimum formal instruction envisaged to provide a student of chemistry with a capability to undertake all mathematical operations discussed in chapters 1 - 8 that constitute part I herein; when circumstances allow, extension of a course over three terms or semesters might be preferable. Although a student whose learning of mathematics at tertiary educational level proceeds according to this medium might lack capabilities to perform routine manual operations relative to a student taught in a traditional way with formal instruction of the same duration, the former student, given a computer, *Maple* and files corresponding to this book, is likely to be far more successful in solving real chemical problems over a broad range and with a mathematical component -- not merely trivial examples, than the latter student given his or her textbooks and tables, pen and paper: that advantage is our objective, our vision. A student taught to do mathematics on a computer in this way must naturally be assessed on such use analogously with a computer.

"The human mind is never performing its highest function
when it is doing the work of a calculating machine."
Lord Kelvin

With this justification to abandon teaching mathematics in a traditional manner to support chemistry, we take as our objective and purpose to show how to undertake successfully many mathematical

operations encountered during, or beyond, an undergraduate programme of chemical study. In succeeding chapters, we summarize mathematical concepts and principles associated with each topic, and incline the presentation to illustrate the use of *Maple* software to implement appropriate operations, to display plots and to solve mathematical and chemical problems. We recognise that to understand a concept means to assimilate that concept into an appropriate schema, and that an appropriate schema implies taking into account enduring learning, not just an immediate result. Our objective is an enduring understanding of concepts, not merely acquiring a transient skill to manipulate mathematical quantities by means of a computer. The curricular topics that we present are selected for their epistemic and pedagogical, but primarily, pragmatic value. In so proceeding, we eschew any tacit assumption that a student of chemistry has been already exposed to aspects of mathematics in other courses in general mathematics at a tertiary level: assuming only traditional arithmetic, algebra, plane geometry and trigonometry commonly taught in a secondary school, we explain mathematical operations and their implementation on a computer with the use of software to accept the burden of most algebra and analysis. Indeed, we formally recall, in a manner impracticable without powerful algebraic and graphic resources, pertinent arithmetic, algebra and elementary functions in chapter 1, and descriptive geometry and trigonometry in chapter 2. At university entrance, students are typically acquainted with use of a computer for *word processing*, *spreadsheets* and *graphics*; some students might have also written and executed programmes in Basic, Fortran, C, Pascal, Visual Basic or other languages. All technical tasks for which a student of chemistry is likely to consider the use of a computer can be performed with a single piece of software, with which one can execute not only operations of arithmetic with real or complex numbers but also those of a symbolic nature such as algebra, trigonometry, differential and integral calculus, differential and integral equations, group theory, theorems in plane geometry and statistics. A single computer programme developed to encompass this nature contains within itself immense mathematical knowledge accumulated over a few millennia, making obsolete traditional repositories of mathematical information such as tables of values of elementary functions, lists of definite and indefinite integrals, handbooks of special functions et cetera; if such tables be not compiled or verified with symbolic computation, they are likely to contain typographical and other errors. Such software even enables the preparation of comprehensive essays and reports complete with mathematical analysis, tables of data in embedded spreadsheets or other array forms, and illuminating graphs and embedded pictures. We must bear in mind, however, that any mathematical software, like any other product of human ingenuity, is prone at any time to contain its own flaws of design and execution, inconsistencies and peccadilloes roughly analogous to typographical errors in traditional media; an advantage of such software over statically printed material is that one can immediately test answers for correctness, and one might even correct the internal procedures if desired. With such software, an opportunity arises during presentation of each mathematical topic to explore algebraic, descriptive, graphical and numeric aspects of that topic or algebraic input; in particular, our strong emphasis on graphical illustration greatly aids a student to develop his or her geometric intuition about each and every mathematical concept, which is a substantial component of a mathematical understanding.

As a vehicle in our presentation we employ a particular commercial software product *Maple*^{TM}, because

- it is highly developed for mathematical purposes, incorporating algebraic, graphic and numeric aspects, within a teaching environment, and even includes packages of commands intended for instructional purposes,
- it is readily available, has a gradual learning curve and makes only moderate demands on typical contemporary computing hardware, and
- it has licensing arrangements such that student copies might become attractively priced.

Maple originated in a concerted academic endeavour at University of Waterloo in Canada primarily

to assist a student of science and engineering to undertake mathematical operations with software in much the same way that such a student executed arithmetical operations on a pocket calculator, or analogously executed programmed sequences of arithmetical operations in a traditional numeric *language* such as Fortran or Pascal for a digital computer, but has become a product of an industrial company that is part of the global software industry. Books numbering more than 500 titles on *Maple* and its diverse applications have been published, and students and academic staff in their millions in educational institutions around the globe have immediate access to this software. Much information about available *Maple* worksheets and reference materials can be found at the Maple application centre, and on employing a search mechanism of an internet browser program. At the same time, a familiarity with *Maple* and an endeavour to accomplish other than trivial operations make one abundantly aware of its present and inevitable deficiencies, which exist through omission and commission of its commercial developers and their failure to maintain vigilantly an alert and responsive appreciation of genuine and articulate technical criticism. Much, if not all, that we describe in *Maple* can be accomplished with alternative programmes -- that likewise suffer from idiosyncratic deficiencies, but with variations in form of command or syntax, in reliability of results and in speed of computation. Except as otherwise noted, all computer instructions in accompanying files and discussion about *Maple* statements apply directly to *Maple* in its form *release* 2017, to which we refer hereafter as *Maple*; operation in another release is naturally subject to features of design specific to that release, but few commands that we employ according to release 2017 operate differently according to preceding releases back to even *Maple 8*, apart from those few commands that rely on newer packages. We have tested all this material with *Maple*'s release 2017 but have incorporated few innovations of this software since *Maple* 11.

An attractive approach to the teaching of mathematics and to performance of calculations on a computer might seem to be to develop principles of mathematics for students of chemistry in a traditional way, and subsequently to demonstrate how corresponding applications are executed on a computer using a symbolic processor. Such an approach embodies two significant impediments: students who find it difficult to understand mathematics taught in a traditional way find their problems compounded at a subsequent stage involving implementation of mathematics on a computer; secondly, whether inevitably or not, a user must respect the conventions of the chosen software, which at present operates in a logical manner that might differ from that in which a traditional mathematician might think or have been taught. A symbolic processor is, moreover, capable of displaying rotatable objects and animated graphics that transcend traditional static limitations of printed paper or blackboard. For these reasons, we introduce progressively many arithmetical or mathematical operations in *Maple*, although commands for these functions and operators form only a small fraction of the total in *Maple*, and we seek to exploit this graphical capability; our resolve is concurrently to explain the mathematical relevance of these operations illustrated with mathematical and chemical applications. Based on our experience of teaching mathematics with *Maple* in this way, we contend that a student of chemistry can thereby acquire an understanding of mathematics at least as profound as he or she might according to a traditional regime: first learning principles, then practising solution of mathematical problems but without mindless drill, and rapidly undertaking applications in chemistry. Our approach here is based on a premise that, even if a user of this material is already acquainted with mathematical concepts and principles underlying most topics, such as in chapters 1 and 2 in part I of which pupils in schools encounter various aspects before university admission, recollection of a foundation of each topic aids an understanding of the execution of associated commands and operators; we thus recall and propound essential mathematical topics, both principles and practice, whether presenting them afresh to a particular student, and emphasize illustrating how one can execute pertinent mathematical operations with symbolic processor *Maple*. When a mathematical concept is likely to be fresh for a student at tertiary educational level, we provide sufficient explanation beyond that required to enable implementation of the software in a reasonably competent manner. The great extent of the content of

part I of this interactive electronic textbook might seem daunting in advance; far from indicating an unwillingness to distinguish *relevant material* from *minor details*, this bulk enables a user of symbolic computation for chemical purposes to have, in one readily searchable source, nearly all the mathematical armoury that he or she might apply to attack a pertinent mathematical problem.

In this book, viewed whether in printed form or interactively on a computer's monitor, we seek to demonstrate how one can employ symbolic computation to implement not only mathematical operations that are traditionally undertaken manually but also realistic calculations of intrinsic chemical and heuristic interest. Consistent with these objectives, we develop the requisite material in two parts: the chapters in part I are akin to material discussed in traditional textbooks of basic mathematics according to traditional subdivisions algebra, calculus, linear algebra, differential equations and statistics, in which we illustrate the grammar and syntax of *Maple*, but with occasional examples of a chemical nature, where practicable, selected to illustrate application of mathematical methods and operations; the chapters in part II cover selected topics of direct chemical applications in some depth to show advanced or special applications of mathematical methods in a chemical context, for which previous knowledge of topics in part I is essential. By including diverse areas of mathematics and their applications within a single work, we have sought to maintain an holistic view of mathematics rather than to consign topics to separate compartments of knowledge; our emphasis is thus placed on all mathematics rather than particular subsidiary parts such as calculus, linear algebra et cetera, even if individual chapters bear such titles. We hope that students who are taught or who learn in this way appreciate mathematics as a whole tool that is applicable to the solution of chemical problems. Although pedagogical exercises and problems number fewer than in traditional text books collectively covering topics in the same range, the best practice of these mathematical topics involves solution of chemical problems in textbooks of chemistry; in this way those mathematical topics of greatest chemical importance become practised most intensively.

> *A great discovery solves a great problem, but there is a grain of discovery in the solution of any problem. Your problem may be modest, but if it challenges your curiosity and brings into play your inventive faculties, and if you solve it by your own means, you may experience the tension and enjoy the triumph of discovery.*
>
> George Polya

Of the hundreds of exercises that pervade the chapters of Part I, many accompanying solutions contain additional explanation that illuminates the topic; even if a reader directly solves an exercise, consulting the given solution is still meritorious because an alternative method or additional comment conveys enlightenment. In any case there seems little point in stimulating repeated input of the same command in repetitive problems on a particular topic; such drill we consign to the traditional teaching of mathematics. With this book's reasonably broad coverage of mathematical topics of prospective application in chemistry, whenever a reader encounters elsewhere a problem with unfamiliar mathematical connotation, recourse to study of appropriate material in this book is likely to facilitate solution. By not refraining from producing somewhat complicated expressions, which a student would typically never be expected to treat with only manual operation, we reinforce a student's understanding of an algebraic formulation of mathematical concepts, and strengthen his or her ability to undertake meaningful manipulations. With regard to part II, we claim neither to achieve exhaustive coverage nor to treat comprehensively a particular topic; the topics selected reflect the interests and experience of the author and his colleagues, and serve as examples of mathematical approaches amenable to execution with symbolic computation, whilst aiding students to appreciate how mathematics becomes applicable to chemical problems. A reader whose interests lie in other chemical directions can of course employ operations presented in the early chapters, with examples of methods discussed thereafter, to develop his or her own treatment of a desired topic.

During the past half century biochemistry has become a discipline nearly separate from chemistry,

although it retains a strongly chemical outlook and shares the same mathematical basis; the content of part I of this book is consequently just as suitable for students of biochemistry as for chemistry. As the chemical examples and illustrations still occupy only a small portion of part I, this book might equally well serve students of other science and engineering divisions.

In composing this work we have consulted many standard textbooks of mathematics and its various branches, and our colleagues, for further edification of diverse aspects of both mathematics and its implementation with *Maple*. We generally omit historical aspects of mathematics; such information is available at www-groups.dcs.st-and.ac.uk/~history, whereas biographies of mathematicians and origins of mathematical terms are found at jeff560.tripod.com/mathword.html. *Maple* contains inherently a useful mathematical dictionary including some historical and biographical content; a related printed compendium of explanations of mathematical terms is available in *Dictionary of Mathematics*, by E. J. Borowski and J. M. Borwein, published originally by Harper-Collins in 1989 and reprinted in further editions; another useful source of information about mathematical terms is *Words of Mathematics* by S. Schwartzman. We make copious references to *Maple*'s dictionary of mathematical topics through hyperlinks, underscored and appearing in green letters such as is embodied in two such words; within Part I of this work, we typically make such an appropriate hyperlink for a possible term at its first occurrence within each section, so that a reader might find each such section as self contained as is practicable, but it is certainly envisaged to be neither necessary nor desirable for a reader to activate each and every hyperlink encountered in reading the text between *Maple* commands. Moreover, not only do some meanings in this dictionary comprise multiple senses, the most appropriate of which a reader must select for the particular context of the hyperlink, but also some meanings might appear tangential to that context; a reader must simply endeavour to derive the maximum benefit from the available information.

For the second edition of this part I during 2005 -- 2008, and again for the third editions in years 2010 -- 2011, the fourth edition in year 2013 and the fifth edition in 2016 - 2019, all chapters have been thoroughly revised and extended, resulting in nearly three times as much material as in the first edition 2005; particular emphasis was directed at the strengthening of the content for chapters on linear algebra, differential equations and statistical topics. Although the present coverage in part I largely fulfills the objective of its encompassing almost all material that an instructor of chemistry at an undergraduate level might wish his students to have learned and understood from courses taught by professors of mathematics, there remains scope for improvement and enhancement. Concurrently with this revision and extension of part I, work on part II has yielded much material on topics requiring a strong mathematical foundation, even though these topics are traditionally taught in senior undergraduate or post-graduate courses in chemistry by professors of chemistry as instructors. The titles of several prospective chapters for part II appear in the Table of Contents below as a tentative indication of the scope of that second volume, and a few of those topics have resulted in either full chapters, or introductions that will become expanded to full chapters in subsequent editions; such topics must clearly be selective rather than comprehensive, but have been chosen for their general interest and pedagogical value, naturally reflecting the interests and experience of the author and those colleagues who have kindly contributed material over the past decade or more. For the fifth edition 2016, apart from significant enhancements in part I, Mathematics for Chemistry, there is a major development of chapters 12 quantum mechanics, 13 spectrometry and 14 Fourier transforms in chemistry. Further chapters in part II will appear in future editions.

For this edition of this book that includes no solutions of exercises, that separate worksheet is available on explicit request to the author at ogilvie@cecm.sfu.ca.

We thank many colleagues and friends who have provided valuable information and assistance at various periods during the preparation of this work. In particular, three colleagues have contributed significant material to this work: before retirement from University of York, U.K., and its department of chemistry, Dr. Graham Doggett generated extensive material and comments during a period in which he

worked actively as coauthor, before pressure of other activities required him to withdraw from this project, and he graciously gave permission for the inclusion of this material without his formal coauthorship; at Simon Fraser University in an environment of the *Centre for Experimental and Constructive Mathematics*, G. J. Fee and Professor M. B. Monagan also generously provided advice and information about procedures and commands that have both assisted greatly the correctness and extended the scope of this work, and have greatly encouraged the development of this project throughout its duration. In recognition of those significant contributions, the names of those three men appear under mine at the authorship level, but are not formally assigned coauthorship because they must not be held responsible for any deficiencies of the published work. Among others who have contributed also significant advice and material but to a lesser extent and whose specific contributions are attributed at particular points, I am grateful to Dr. P. Alsholm who contributed his procedure for non-linear regression and other helpful advice, Professor R. Israel who contributed a procedure to balance chemical equations automatically and many helpful hints to solve programming problems, Dr. E. Cheb-Terrab, Dr. A. Wittkopf and Dr. D. Holmgren who provided much helpful advice and information about differential equations, Professor R. Corless about integral equations, and other colleagues and visitors in Centre for Experimental and Constructive Mathematics, at www.cecm.sfu.ca on internet, and the Department of Mathematics, at www.math.sfu.ca, at Simon Fraser University, at www.sfu.ca, Professor V. Arguedas, E. Romero, M. Gutierrez, R. Rodriguez and R. Hidalgo at Universidad de Costa Rica; in a contemporary context, the former *Maple* bulletin board, Maple Primes and current news groups on symbolic computation and on *Maple* in particular have naturally provided a source of advice and inspiration. I am particularly grateful to the late Professor D. P. Craig, F.R.S., who was my host in the Australian National University during which in 1973 occurred my initial acquaintance with computer algebra and the first of about a dozen processors thereof including *Maple*, whose comments and criticism on most aspects of Part I over several years have been most incisive and instructive, and who has also kindly provided some examples. Students in several countries -- Australia, Canada, Costa Rica, Denmark, Poland, USA -- have been exposed to various material in Part I during the years since the inception of the formal construction of this book in 1997, and their response and reaction have proved most helpful in identifying errors and obscurities to be rectified. Errors of both omission and commission, reflecting a necessarily limited knowledge and understanding of any topic, remain the responsibility of this author; I shall naturally welcome all comments on, and constructive criticism of, this work, particularly about errors and omissions and suggestions for extension.

J. F. Ogilvie, 2020 October

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I index of chemical applications in part I

In this textbook designed to teach, and for the learning of, mathematics for chemistry, the collected material naturally includes sections or groups thereof, examples and exercises with a chemical theme or application; this section provides an index to those components, classified as thermodynamics and general, chemical kinetics and structure in a broad sense. Items in the succeeding lists with initial letter *e* pertain to exercises and letter *x* to examples; items lacking either such letter pertain to sections, or a set thereof.

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I Mathematical Operations -- Mathematics for Chemistry

with contributions from G. Doggett, G. J. Fee, M. B. Monagan and others

O overview of *Maple*

Maple is primarily a computer programme, or software, with which one undertakes interactive calculations involving mathematical objects, although in its mature state its capabilities far transcend that quintessential aspect. One can work with *Maple* in more than one way, even on a particular computer and under a particular operating system on that machine. For most purposes involving exploration of mathematical topics and general interactive calculations, a *Maple* worksheet provides a convenient display that includes

- input statements and commands and their output in numeric and symbolic form,
- plotting instructions and their output as figures embedded within a worksheet,
- spreadsheets also embedded within a worksheet although such a spreadsheet is deprecated from *Maple* 2019, and
- associated explanatory text.

For intensive programmed calculations a worksheet is less efficient, or executes less rapidly, than *Maple* used in another form that allows input only as command lines, not by clicking on icons in menu and context bars et cetera.

In a form such as this worksheet, our content is designed to take advantage of a graphic interface for a user: three components --

- an essential kernel that executes mathematical commands,
- libraries of procedures for more or less special purposes, and
- an interface between machine and user

-- combine to constitute an operational version of *Maple*. For purely arithmetical operations, a compiler enables execution of procedures at the full speed of the processor, unlike the typical interpreted code in worksheets. The libraries, some of which are automatically invoked on input of particular commands whereas others require explicit invocation, and the kernel of *Maple* in a particular release are common to computers of almost all types, but a graphic interface is peculiar to each type to the extent that features and operations might vary among those types. A worksheet is a document that can contain descriptive text, like this paragraph printed in black, execution groups with input in red and output in blue, such as

```
> (3*x + 5)*(2*y  + 3);
```

$$6xy + 9x + 10y + 15$$

and embedded graphics and spreadsheets; such a worksheet has a common appearance across various computers and operating systems, and is entirely transferable between computers, provided that they run *Maple* in the same release and, for *Maple* 9 or afterward, that the computer operates the same interface -- either classic or standard. As a result of the graphic interface, operations are undertaken in various ways, such as with explicitly typewritten commands that make no profound use of such an interface, or with control or command keys depressed concurrently with various other keys, or with moving a cursor onto a pictograph near the top or bottom of a display on a monitor and clicking a mouse -- or equivalent mechanism. To initiate a desired action, we generally employ the former mechanism, namely with commands and statements typed explicitly, because an explanation of such a procedure from this printed text is easier that way than otherwise. We assume generally a computer on which this worksheet executes to possess a mouse with two or more levers, and express actions accordingly to effect some result; if a particular computer have an alternative peripheral device, one must undertake the corresponding action.

When one has opened a worksheet within a *Maple* session to read this text, one can generally observe at the top of the display on the monitor three or more horizontal rows of words or pictographs, each of which is called a *bar*. Uppermost, a *title bar* likely indicates at left a version of *Maple* and a name of a

file that is open in the present window; clicking at extreme right ends of this bar is likely to terminate, after confirmation, this *Maple* session. Below this title bar is a menu bar: clicking, with a computer 'mouse' or equivalent device, on any word therein, from `File`, at left, to `Help`, near the centre or extreme right, invokes a menu corresponding to that heading. Three items at top of menu `View` relate to three further bars -- for tool, context and status, which one can thereby make to appear or to disappear according to their status altered on clicking with a mouse. Menu `File` operates in a more or less standard manner according to the underlying operating system of the computer on which *Maple* is running, whereas other menus relate more specifically to operation of *Maple*. That menu `File` contains an item `Preferences` according to which a user may set conditions of operation of *Maple*, for instance to save automatically the file on which a user is working at the end of a particular specified interval, or to activate or to deactivate Balloon Help. If that `Balloon Help` be activated, on clicking left on that name, subsequent motion, by means of a mouse, of the cursor, in the form of an arrow, onto a particular pictograph, or item of a menu, causes display of a short description to advise about a function of that item. Below the menu bar, a tool bar contains pictographs relating to common operations such as copying, printing, reading an existing worksheet or restarting to clear the internal memory. The fourth row down from the top of the display is a context bar, the content of which depends on the nature of a location of the cursor within the visible portion of a worksheet: if that cursor be located within text such as these words, the context menu pertains to properties of text such as font, size of letters, justification at right or left or not at all, et cetera, whereas, if the cursor lie on a command executable with *Maple*, or a graph, or a spreadsheet, a separate context bar that contains pertinent pictographs appears automatically. On activating an icon, containing *!!!*, in the context bar that appears when the cursor is on a *Maple* input or output item, one can even execute automatically all *Maple* commands in an entire worksheet. At the bottom right of the display appears a status bar that indicates the cumulative duration of execution involving the computer processor, size of workspace and available memory.

To effect a particular action, mechanisms alternative to typing commands in an input line might exist, such as use of key *Ctrl* or *Alt* in combination with a key for an alphabetical or numeric character; through consultation of `Help` invoked in a menu at the top of the display, or of printed manuals, or of experienced users of *Maple*, one can become acquainted with these mechanisms. For instance, clicking on `Help` above, or, equivalently, depressing concurrently keys *Alt* and *H* is an alternative to typing ? in an input line to invoke help; depressing function key F1 whilst the cursor is on a *Maple* command, or even a key word within this text -- for *Maple* 11, invokes the Help page for that command or term. In this text we habitually neglect such vital ancillary activities as beginning, suspending and ending a *Maple* session, saving and recalling files, use of a mouse with one, two or three levers or buttons et cetera. Experience with other software on a computer of a particular type is helpful in relation to operation of *Maple* on the same machine, as *Maple* is designed to operate under conventions fairly standard for a machine of that type, but even without such experience one can learn quickly how to undertake mathematical operations by executing commands and statements, as we cursorily sample in section 0.21 of this worksheet. With *Maple* 9.5 or subsequent release, a dictionary of mathematical terms is accessible through menu `Help` or through clicking on a particular hyperlink with a lever on a mouse; explanations and examples of applications of many mathematical terms appear there.

Once this worksheet is open, so that one can read this text, one proceeds by placing the cursor in a line of input to *Maple* displayed in red lettering -- the best location at which to place the cursor is just to the right of a black symbol **>** displayed at the left margin -- and by then depressing key "Return" or a key marked <--' or possibly "Enter", depending on a computer of a particular type; after execution of that input line, the cursor moves automatically to the left edge of the next line of input, which is similarly executed. We expect that, on encountering a particular portion of this content for the first time, one reads the text in black displayed between lines of input in red; therein we recall mathematical

principles and explain how to implement them in practice with this computer programme. According to a convention under which *Maple* is designed, a line of input intended to be executed begins in the classic interface beside a black character **>** and is printed in red letters; if the corresponding output expression, printed in blue, be short, it is centred across the screen or page, otherwise it is printed beginning from the left margin. Unexecutable text such as these words, intended for human not mechanical attention, is printed in black letters. At those locations within text at which we mention *Maple* commands rather than just terms or algebraic quantities, these commands might be printed in **red** letters and a distinctive font, whereas output quoted within the text might be printed in blue letters, but such commands are not there executable.

Just as for any traditional spoken or written language, vocabulary, punctuation and rules to construct a command -- syntax -- are associated with a programming language. Unlike a spoken or written sentence, in which lack of grammatical precision or imprecise spelling or pronunciation might not preclude understanding, with computer programmes almost no deviation from rules is allowed in construction of a statement, corresponding to a succession of operators with precise names and punctuation. There is not just one way to achieve a desired outcome: just as in any spoken language, a command can be posed with words in disparate sequences to achieve a given objective. In programming environments such as *Maple*, economical use of commands is a preferred style. In early chapters of this text we generally endeavour to avoid using too succinct collections of operators, so as to preclude a reader puzzling over programming syntax rather than an underlying logical basis to solve a particular problem.

In all languages punctuation is important: in both computer and written languages, commas separate items in a sequence, list or set; all commands to a computer have a particular terminating character analogous to a full stop, period or point at the end of a printed sentence, whether it be an explicit mark or a generally invisible character to signal the end of a line. In *Maple*, a mathematical sentence or statement in only one form -- a *command* or *instruction* -- invokes action of *Maple*, whereas a *comment* is ignored by this processor and appears solely for information of a reader; anything following **#** on an input line is treated as a comment, such as in this example,

```
> # This is a comment.
```

whereas anything else on an input line or anything before **#** is treated as input and must accordingly obey rules for an error message to be averted.

A semicolon ; is important!

When *Maple* is invoked ready for use according to a classic interface that presents **>** at the left margin as a prompt, to terminate the specification of any input to *Maple* within that line, in the classic worksheet one must type either a *semicolon* **;** or a *colon* **:** and depress key "Enter" or (carriage) "Return" before execution can begin; merely depressing a key for "Enter" without presence of a semicolon or colon is insufficient to initiate execution, but generally elicits a Warning about premature end of input. If a semicolon be used, any output appropriate to an input is displayed, in blue; if a colon be used, a command is executed but no output is displayed. Messages to advise of an error in input or a warning about altered meanings of names of operators appear in magenta or blue. In the worksheet mode with the standard interface, such use of a semicolon is superfluous. To have displayed a result of a calculation we generally terminate an input line with **;** and initiate execution of a statement or instruction by depressing key "<---'" or "Enter"; a few commands produce no output even when terminated with a semicolon, whereas invoking `help` with ? or ?topic, in which topic denotes a name of a command of interest, requires no terminating punctuation.

An alternative mode -- mathematical input -- exists for which a question mark **?** serves as a prompt; under these conditions no colon or semicolon is required to terminate a particular command or statement to initiate execution -- a depression of key "Enter" suffices. To enter this mode involves clicking on the

icon x at the left of the context bar when the context is a line of input.

Details about use of reserved names and arithmetical operators, distinction between parentheses ( ), brackets [ ] and braces { }, and related matters we introduce summarily in section 0.21 below or as required in section 1.118 and elsewhere in chapter 1 and subsequently; on proceeding through exemplary illustrations in chapter 0 here below, one achieves a glimpse of both the nature of contemporary symbolic computation, and the use of *Maple* in particular, concurrently with discovering the immense mathematical capabilities of this processor.

chapter 0 Exemplary illustrations of use of *Maple*

2021 August, edition 6

0.0 overview

Maple is a mathematical programme for electronic digital computers that contains mathematical knowledge accumulated during 5000 years. Here follow five diverse illustrations to demonstrate how powerful and flexible is *Maple* software applied to mathematical aspects of chemical and physical phenomena. First we solve equations of two kinds: in a direct chemical context we treat six linear equations in a set with seven unknowns to balance a chemical equation, deriving thereby a numerical answer; we then solve an equation involving a cubic formula that arises in a problem of physico-chemical interest, seeking a symbolic answer. We exhibit *Maple*'s symbolic capability also with an algebraic operation according to differential calculus on a simple expression, which might be a challenging manual task. To demonstrate a graphic capability we display approximately a unit cell of a crystal in quasi-three-dimensional form. *Maple* is not merely a symbolic and numeric calculator with graphical capabilities but also a repository of much mathematical and scientific knowledge; on 'clicking' to activate an underscored word or phrase, such as *linear equations* above, one views material from a dictionary of definitions of mathematical and statistical terms, whereas *Maple* is a repository also of much information about chemical elements and fundamental physical constants, among other topics. With a spreadsheet in *Maple* one can implement both traditional numeric operations and a novel symbolic capability.

To proceed throught this chapter, or any succeeding chapter, one simply opens a section of which a number and title appear at the left side of this display, reads the text displayed in black letters and executes the commands displayed in red letters, by depressing key "Enter" or equivalent depending on type of computer; the latter generally causes display of output dictated by that command, in blue type for mathematical expressions or as a graph for a plotting command. Sample these sections to acquire a flavour of this powerful software for mathematical applications; explore the menus at the top of this display to discover how to use *Maple* as a text editor and diverse other capabilities.

Following these five sections designed to whet a user's appetite for symbolic computation and associated capabilities in their advanced form in *Maple*, a further section presents a brief introduction to some essential commands and operations that a reader might find directly useful and applicable on the basis of already learned mathematical knowledge; these commands are likely pertinent beyond the mathematical context of these worksheets concurrent with this study of mathematics, and every topic or command in this summary is explained at an appropriate length in succeeding chapters in part I of this book.

0.1 examples of calculations

0.11 solution of equations

```
> restart:
```

Here is a common symbolic description of a prospective chemical reaction, specifically to dissolve solid copper(I) sulfide with aqueous nitric acid,

$$Cu_2S + HNO_3 \text{ --> } Cu^{2+} + NO + S_8 + H_2O$$

in which copper(II) ions in solution, gaseous nitrogen oxide and elemental sulfur are significant products. We seek to convert this qualitative description into a balanced chemical equation in accordance with a conventional conservation of both mass, in the form of each chemical element assumed immutable, and net electric charge, when formal anions and cations are involved. Solution of this particular problem is perhaps an exercise that we performed in school when we first learned about chemical oxidation and reduction, or when we investigated the separation of aqueous ions of metallic elements in their groups; we might then have used various methods to solve this problem, such as trial and error -- inefficient and slow, or oxidation numbers, or electrochemical half-cells, or other approach. What is fundamentally involved from a mathematical point of view is a simultaneous solution of several linear equations based on conservation of mass and charge; combining a mathematical method and physical laws, we hence solve a problem of chemical stoichiometry. To employ symbolic computation for this purpose, we express this chemical equation in a form acceptable for working with *Maple*, as follows. We assign to a quantity named eqn, signifying equation, an equality: to the left of the equality sign appear symbols for the reactants, and to the right for the chemical products. To each symbol denoting a chemical species we prepend, as a multiplicative factor, a letter a, b, ... g to denote a quantity called a stoichiometric coefficient; in a conventional manner we employ multiplication signs ***** between factors within each term for a particular chemical species, and addition signs **+** between such terms. Use of brackets **[ ]** and apostrophes **` `** in input ensures that the output, after we execute this assignment, appears in a natural form with truly descending subscripts and raised superscripts according to traditional chemical practice.

```
> eqn := a*Cu[2]*S + b*H^`+` + c*NO[3]^`-`
       = d*Cu^`2+` + e*NO + f*S[8] + g*H[2]*O ;
```

$$eqn := a\,Cu_2S + b\,H^{+} + c\,NO_3^{-} = d\,Cu^{2+} + e\,NO + f\,S_8 + g\,H_2O \qquad (6.1)$$

To evaluate the stoichiometric coefficient of each term, we apply to each element within the chemical equation the conservation of mass and absence of elemental transmutation, and write an algebraic relation for each of five chemical elements to express this condition as an equation that we assign to a subscripted name; a comment follows on the first line.

```
>eq[Cu] := 2 * a = d;
      # This equation represents a condition of stoichiometry and
 conservation of mass.
```

$$eq_{Cu} := 2\,a = d \qquad (6.2)$$

```
> eq[S] := a = 8 * f;
```

$$eq_S := a = 8\,f \qquad (6.3)$$

```
> eq[H] := b = 2 * g;
```

$$eq_H := b = 2\,g \qquad (6.4)$$

```
> eq[N] := c = e;
```

$$\qquad (6.5)$$

$$eq_N := c = e \tag{6.5}$$

```
> eq[O] := 3 * c = e + g;
```

$$eq_O := 3\,c = e + g \tag{6.6}$$

A further relation expresses the conservation of electric charge: we identify net charge on each side of an equality sign in the chemical equation and assign a condition to a name $eq_{net\,charge}$.

```
> eq[`net charge`] := b - c = 2 * d;
```

$$eq_{net\,charge} := b - c = 2\,d \tag{6.7}$$

For a unique specification of the stoichiometry, the number of these conditions must equal the number of unknown stoichiometric coefficients. Even though this condition is unsatisfied because seven unknown quantities, a ... g, outnumber six conditions, we proceed with solution by presenting the six relations in a *set*, signified by enclosure within braces **{}** and in no particular order. We use operator **isolve** to find integer solutions.

```
> answer := isolve({eq[Cu], eq[S], eq[H], eq[N], eq[O], eq[`net
  charge`]}, n);
```

$$answer := \{a = 24\,n, b = 128\,n, c = 32\,n, d = 48\,n, e = 32\,n, f = 3\,n, g = 64\,n\} \tag{6.8}$$

This parametric solution of six simultaneous linear equations with seven unknown quantities a, b, ... g is not unique, as an undefined parameter n, which appears in that answer because that letter was specified for this purpose at the end of the input command, can acceptably assume any finite positive value; solutions hence exist in uncountable sets: with the same multiple of values of stoichiometric coefficients a, b, c, d... in any *set*, the specified chemical, physical and mathematical conditions are equally satisfied. For instance, in a simple case arising on mixing aqueous solutions of two soluble salts to produce a precipitate, the equation

$$n\ \text{NaCl (aq)} \ + \ n\ \text{AgF (aq)} \ \text{--> } \ n\ \text{AgCl (s)} \ + \ n\ \text{NaF (aq)}$$

is formally, from an arithmetical point of view, an adequate way to balance a chemical equation for n taking any consistent value, but chemists generally prefer the values of stoichiometric coefficients to be the smallest natural numbers; we thus prefer $n = 1$ in this case. For the same purpose in acidic dissolution of CuS according to the above chemical equation, we evaluate that answer with unity assigned to formal parameter n, and we assign those explicit values to stoichiometric coefficients.

```
> assign(eval(answer, n=1));
```

Having made that assignment, for which no explicit response appears characteristically for that command, we simply command, by invoking its name eqn, the original chemical equation to make it become displayed again; letters that denote stoichiometric coefficients in the original equation become replaced with their numerical values obtained on *Maple*'s solution of simultaneous linear equations.

```
> eqn;
```

$$24\,Cu_2S + 128\,H^{`+`} + 32\,NO_3^{`-`} = 48\,Cu^{2+} + 32\,NO + 3\,S_8 + 64\,H_2O \tag{6.9}$$

Maple can solve equations not only linear. As a further instance we allude to an empirical equation of state, proposed by J. D. van der Waals in 1873, supposed to apply to a real gas in thermodynamic equilibrium,

$$\left(P + \frac{a}{V^2}\right)(V - b) = R\,T$$

in which appear symbols P for pressure, V for molar volume of gas, T for absolute temperature, R for gas constant, a for a parameter supposed to pertain to intermolecular forces and b for a parameter supposed to pertain to molecular volume; as this equation is not only lacking in theoretical basis but also a crude approximation that with typically tabulated values of parameters in some ordinary instances yields results worse than those from a simple equation $P\,V = R\,T$ for an ideal gas, it retains only historical but no pedagogic interest and lacks practical value. Redlich and Kwong proposed an alternative empirical equation of state that might be expressed in a simplified form as

$$\left(P + \frac{a}{\sqrt{T}\,V}\right)(V - b) = R\,T$$

that pragmatically represents properties of a non-ideal gas somewhat better than that equation of van der Waals, and in which symbols for variables and parameters have interpretations similar to those described above, even though a theoretical basis of this equation is equally lacking; the principal effect is that temperature appears in the term for the attraction between molecules . After clearing the internal memory with restart, we assign this equation to a name, and solve for each thermodynamic variable in turn.

```
> restart:
> RKeq := (P + a/(T^(1/2)*V))*(V - b) = R*T;
```

$$RKeq := \left(P + \frac{a}{\sqrt{T}\,V}\right)(V - b) = R\,T \tag{6.10}$$

Solution for pressure P is easy, but we embellish the command for solving with two further terms to produce an answer in a perhaps elegant form.

```
> P = collect(normal(solve(RKeq, P)), [T, a]);
```

$$P = \frac{R\,T}{V - b} + \frac{(-V + b)\,a}{V\,(V - b)\,\sqrt{T}} \tag{6.11}$$

Solution for molar volume V in terms of other quantities yields two expressions in a set, between braces {..} and separated with a comma,

```
> V = expand({solve(RKeq, V)});
```

$$V = \left\{ \frac{T\,R}{2\,P} + \frac{b}{2} - \frac{a}{2\,\sqrt{T}\,P} - \frac{\sqrt{T^3\,R^2 + 2\,T^2\,P\,R\,b + T\,P^2\,b^2 - 2\,T^{3/2}\,R\,a + 2\,\sqrt{T}\,P\,a\,b + a^2}}{2\,\sqrt{T}\,P}, \frac{T\,R}{2\,P} + \frac{b}{2} - \frac{a}{2\,\sqrt{T}\,P} + \frac{\sqrt{T^3\,R^2 + 2\,T^2\,P\,R\,b + T\,P^2\,b^2 - 2\,T^{3/2}\,R\,a + 2\,\sqrt{T}\,P\,a\,b + a^2}}{2\,\sqrt{T}\,P} \right\} \tag{6.12}$$

that we recognize to be two conjugate roots of a quadratic equation; which root is more meaningful in a given condition remains to be ascertained. In this expanded form we recognize that a term $\frac{R\,T}{P}$, which pertains to the limit of an ideal gas in which a and b are both zero, arises half from a term before the surd and half from a contribution inside the surd.

Solution for temperature T in terms of other quantities quickly yields an algebraic, even if extensive, expression for a real root.

```
> T = solve(RKeq, T)[1];
```

$$T = \left(\frac{\left((12\,V - 12\,b) \left(9\,a + \sqrt{-\frac{3\left(4\,P^3\,V^3 - 4\,P^3\,V^2\,b - 27\,a^2\,R\right)}{R}} \right) R^2\,V^2 \right)^{1/3}}{6\,R\,V} + \frac{2\,P\,(V-b)\,V}{\left((12\,V - 12\,b) \left(9\,a + \sqrt{-\frac{3\left(4\,P^3\,V^3 - 4\,P^3\,V^2\,b - 27\,a^2\,R\right)}{R}} \right) R^2\,V^2 \right)^{1/3}} \right)^2 \tag{6.13}$$

Two further roots of the original equation, effectively cubic in T, have little direct physical interest because they are complex quantities -- containing real and explicitly imaginary parts. To evaluate T for conditions of P, V, a and b of particular interest, we substitute their numerical values, with that of R in consistent units, into the algebraic formula above. Apart from exceptional cases, algebraic solution of polynomial equations beyond quadratic produces results in a form likely too complicated to be useful for purpose of visual inspection. In any case, these solutions of a somewhat complicated equation demonstrate *Maple*'s strong capability for such tasks that prove tedious for human manipulation.

Numeric and symbolic solution of equations with *Maple* is discussed in sections 1.208 and 1.209.

0.12 a difficult derivative

```
> restart:
```

Consider a simple expression consisting of exponentiation of a variable with itself to two levels, x^{x^x}.

```
> x^(x^x);
```

$$x^{x^x} \tag{7.1}$$

One displays elegantly both the derivative of such an expression, with respect to the variable, and its evaluation with this command.

```
> Diff(%, x) = diff(%, x);
```

$$\frac{d}{dx}\left(x^{x^x}\right) = x^{x^x}\left(x^x\,(\ln(x)+1)\,\ln(x) + \frac{x^x}{x}\right) \tag{7.2}$$

Commands **`Diff(%, x)`** and **`diff(%, x)`** both signify an operation -- differentiation with respect to x. **`Diff(%, x)`** merely displays, in the output at the left, a formal derivative in a symbolic or inert manner, whereas **`diff(%, x)`** is an active command that invokes execution of the specified operation, to yield the result at the right side; **`%`** signifies ditto to indicate that this operation is applied to a quantity corresponding to a result of a directly temporally preceding command that can produce output. Such usage of `%` is deprecated; far preferable is to specify a name for each expression, such as y, and then to

insert that name into the command instead of %. The computer executes this command as a result of interaction with you as user of this computer programme: the output expression that you see displayed in blue is not preformed and stored within this worksheet, but is created before your eyes as a direct result of execution of this command that invokes a calculation with *Maple* according to the rules of mathematics. Altering the input expression from x^{x^x} to another algebraic expression in x would implement a calculation of the corresponding derivative. An operation inverse of differentiation is integration; in this case we produce an antiderivative as an indefinite integral with this command,

```
> Int(rhs(%), x) = int(rhs(%), x);
```

$$\int x^{x^x}\left(x^x\left(\ln(x)+1\right)\ln(x)+\frac{x^x}{x}\right)\,dx = x^{x^x} \qquad \textbf{(7.3)}$$

in which Int and int denote operators for formal and executable indefinite integration, respectively, of a specified integrand, here rhs(%) implying the right side of the preceding output, with respect to a specified variable, here x. The solution of that integration is formally correct for any value of an additive constant, such as c, in the output, but by default *Maple* omits such a constant for such an integral; in the corresponding solution of a differential equation, in contrast *Maple* specifies a formal constant, cf chapter 7. Although finding a derivative of a well behaved algebraic expression or transcendental function is in principle invariably practicable, finding an antiderivative or indefinite integral is known to be impracticable for many functions. For almost all practicable integrals, *Maple* generates an answer that is more likely to be correct than results printed in tables of integrals. Finding a derivative with *Maple* and other topics in differential calculus are discussed at length in chapter 3, and integral calculus is introduced in chapter 4.

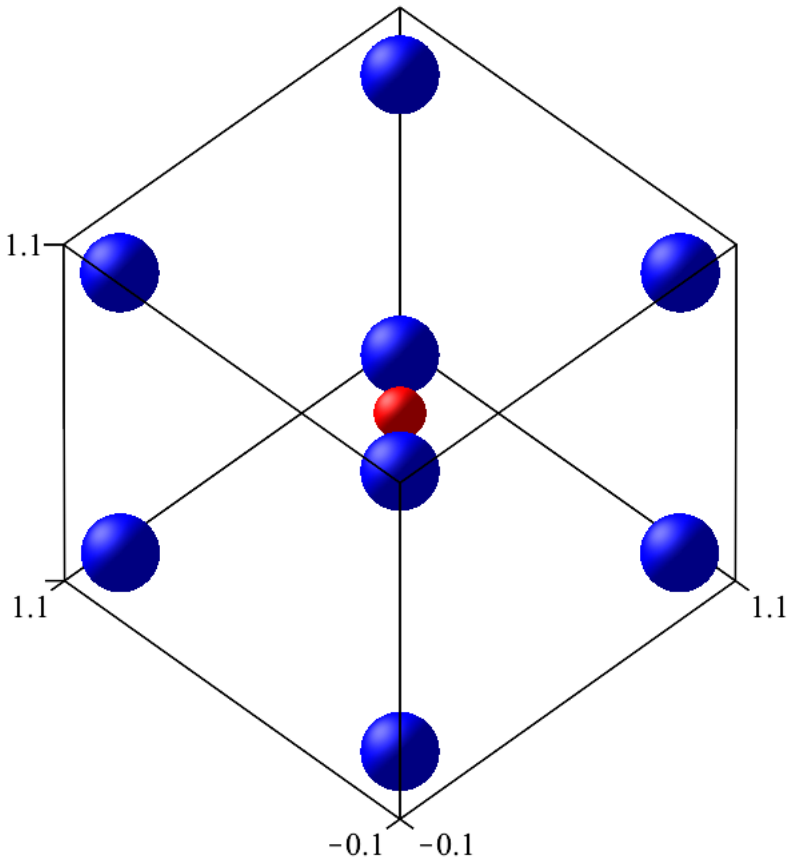
0.13 plot of unit cell of crystalline caesium iodide CsI

```
> restart:
```

A major ancillary capacity of much contemporary software for symbolic computation is graphical depiction of data in many forms, far beyond a simple plot of a line or curve relative to axes for cartesian coordinates in two spatial dimensions; although such plots provide an essential means to grasp the significance of both concepts, through a geometric interpretation, and data, showing their inter-relation, much expanded application of graphical constructs is available to portray objects in three spatial dimensions, to enable scrutiny of those objects from varied points of view through rotation of images, and to elicit features of plots through direct reading of coordinates or setting of angles. Many instances of these applications of such plots for heuristic and illustrative purposes pervade this book, beginning with a systematic, if not comprehensive, survey of plotting facilities in section group 2.1 in chapter 2 after a brief introduction in section 0.21. As a mere hint of the flavour of the versatile graphical capabilities of *Maple* for chemical applications, here is a simple diagram to represent a unit cell of a crystal of caesium iodide assumed to be composed of spherical atomic ions; a red sphere represents an anion $I^{`-`}$ and a blue sphere represents a cation $Cs^{`+`}$.

```
> with(plottools):  with(plots):
  rI := 1/15: rCs := 1/10:  cond := rCs, colour=blue:
  sI := sphere([1/2,1/2,1/2], rI, colour=red):
  sCs1 := sphere([0,0,0], cond):
  sCs2 := sphere([0,0,1], cond):
  sCs3 := sphere([0,1,0], cond):
  sCs4 := sphere([1,0,0], cond):
```

```
sCs5 := sphere([0,1,1], cond):
sCs6 := sphere([1,0,1], cond):
sCs7 := sphere([1,1,0], cond):
sCs8 := sphere([1,1,1], cond):
display([sI,seq(sCs||j, j=1..8)], axes = normal,
   scaling = constrained, view = [-0.1..1.1,-0.1..1.1,-0.1..1.1],
   style = patchnogrid, axes = boxed, tickmarks = [2,2,2],
   title="unit cell of CsI, Cs blue, I red",
   titlefont=[TIMES,BOLD,14], orientation=[-135,45]);
```

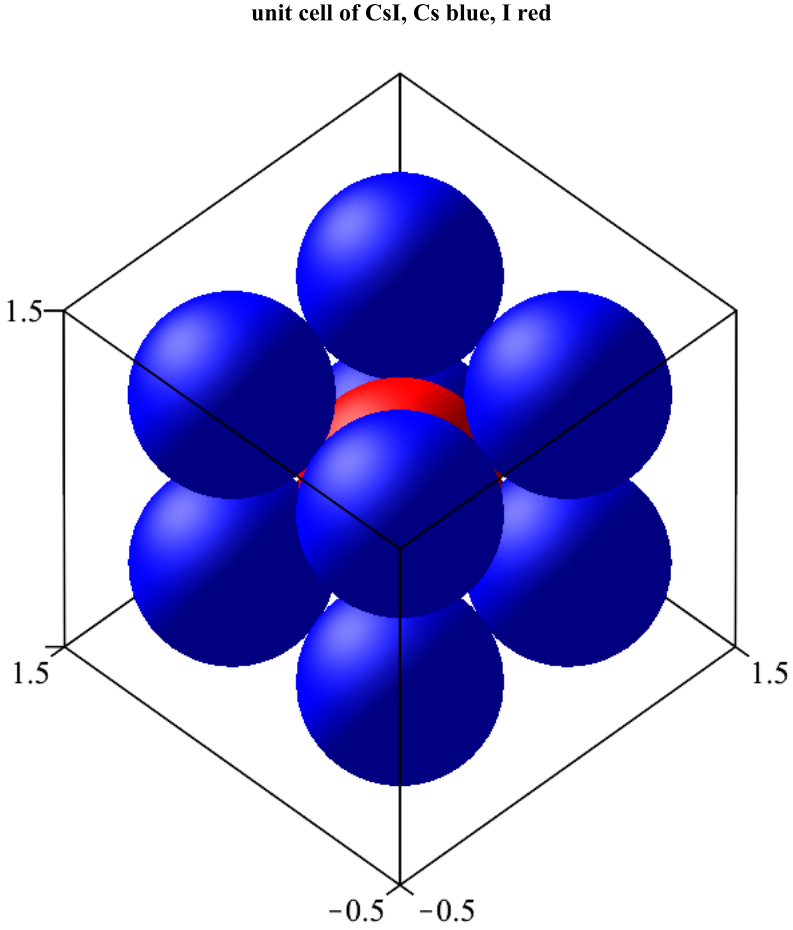


In this plot the range of each axis somewhat exceeds the length of a unit cell; if the range of each axis be only 0..1, only one eighth of each hollow blue sphere would be visible.

By using a mouse to place the cursor within the area of a plot and clicking, one can rotate axes, according to angles specified in the context bar at left, or merely by dragging the cursor within the area of the plot, as to view the unit cell from those varied angles; by clicking on small black squares in the frame of the plot, one can alter the size of the figure, for instance to increase the area so that a plot might fill the screen. By this means one can deduce certain properties of symmetry of a given plotted object, for instance axes of four fold perpendicular to a face of this cube, axes of three fold along a body diagonal of this cube, axes of two fold bisecting an edge of this cube and parallel to an adjacent edge, or one of several planes of symmetry: such properties of symmetry have an important role in many chemical calculations, and emerge prominently in chemical applications of the theory of groups in chapter 10.

To indicate the relative positions of atomic centres in a plot above, we design radii of ions to be much smaller than the length of a unit cell. Specifying more realistic relative radii so that the spheres tend to fill space, we redraw this figure.

```
> rI := 3/7:  rCs := (sqrt(3) - 2*rI)/2:
  cond := rCs, colour=blue:
  sI := sphere([1/2,1/2,1/2], rI, colour=red):
  sCs1 := sphere([0,0,0], cond):
  sCs2 := sphere([0,0,1], cond):
  sCs3 := sphere([0,1,0], cond):
  sCs4 := sphere([1,0,0], cond):
  sCs5 := sphere([0,1,1], cond):
  sCs6 := sphere([1,0,1], cond):
  sCs7 := sphere([1,1,0], cond):
  sCs8 := sphere([1,1,1], cond):
  display([sI, seq(sCs||j, j=1..8)], axes = normal,
     scaling = constrained, view = [-0.5..1.5,-0.5..1.5,-0.5..1.5],
     style = patchnogrid, axes = boxed, tickmarks = [2,2,2],
     title="unit cell of CsI, Cs blue, I red",
     titlefont=[TIMES,BOLD,14], orientation=[-135,45]);
```



On altering `j = 1..8` to read `j = 1..7` in a line in the latter command beginning with `display`, we eliminate one ion at a corner; we thus reveal a spherical cation to be in contact with an anion along every body diagonal, whereas no two cations are in contact with one another.

Formation of plots with *Maple* we discuss in chapter 2, and many examples and applications appear in subsequent chapters.

0.14 chemical and physical data in *Maple*

```
> restart:
```

Within its internal libraries, *Maple* contains many scientific data, namely values of fundamental constants of physics and much information about chemical elements and properties of nuclides; a library package Scientific Constants contains these commands and operators; the values of the constants are from the CODATA recommended values, 2014 .

```
> with(ScientificConstants);
```

[*AddConstant*, *AddElement*, *AddProperty*, *Constant*, *Element*, *GetConstant*, *GetConstants*, *GetElement*, *GetElements*, *GetError*, *GetIsotopes*, *GetProperties*, *GetProperty*, *GetUnit*, *GetValue*, *HasConstant*, *HasElement*, *HasProperty*, *ModifyConstant*, *ModifyElement*] **(9.1)**

Having invoked that package so that its content is accessible with the indicated direct commands, we ask for information about Avogadro's constant, which we call by name,

```
> GetConstant(Avogadro_constant);
```

$$Avogadro\_constant,\ symbol = N_A,\ derive = \frac{A[r](e)\,M_u}{m_e} \qquad \textbf{(9.2)}$$

or by symbol;

```
> GetConstant(N[A]);
```

$$Avogadro\_constant,\ symbol = N_A,\ derive = \frac{A[r](e)\,M_u}{m_e} \qquad \textbf{(9.3)}$$

for either its name or its symbol, in this particular case the value of N_A is stored not as a number but rather in terms of other constants. To retrieve that numerical value, its uncertainty and its unit, we enter these commands to receive information about value, units and uncertainty.

```
> GetValue(Constant(N[A]));
```

$$6.022140856 \times 10^{23} \qquad \textbf{(9.4)}$$

```
> GetUnit(Constant(N[A]));
```

$$\frac{1}{\mathrm{mol}} \qquad \textbf{(9.5)}$$

```
> GetError(Constant(N[A]));
```

$$7.366533527 \times 10^{15} \qquad \textbf{(9.6)}$$

For which chemical and physical constants is such information available?

```
> GetConstants();
```

A[r](alpha), *A[r](d)*, *A[r](e)*, *A[r](h)*, *A[r](n)*, *A[r](p)*, E_h, F, G, G_0, K_J, M_{Earth}, M_{Sun}, M_u, N_A, Φ_0, R, **(9.7)**

R_{Earth}, R_K, R_∞, V_m, Z_0, a_0, a_e, a_μ, α, b, c, $c_{1,L}$, c_1, c_2, e, ϵ_0, g, g_e, g_μ, g_n, g_p, γ_e, γ_n, γ_p,

$gamma\_prime_h$, $gamma\_prime_p$, h, $\hbar$, k, l_P, $\lambda_{C,\mu}$, $\lambda_{C,n}$, $\lambda_{C,p}$, $\lambda_{C,\tau}$, λ_C, m_P, m_α, m_d, m_e,

$m[e]/m[mu]$, m_h, m_μ, m_n, m_p, m_τ, $m[tau]c^2$, m_u, μ_0, μ_B, μ_N, μ_d, $mu[d]/mu[e]$, μ_e, $mu[e]/mu[p]$,

$mu[e]/mu\_prime[p]$, μ_μ, μ_n, $mu[n]/mu\_prime[p]$, μ_p, mu_prime_h, $mu\_prime[h]/mu\_prime[p]$,

mu_prime_p, n_0, r_e, σ, σ_e, $sigma\_prime_p$, t_P

How many number these constants?

```
> nops({%});
```

85 **(9.8)**

Of these 85 constants the need for several arises commonly in calculations of atomic and molecular properties.

What information is available for a particular chemical element, such as mercury?

```
> GetElement(mercury);
```

$80, symbol = Hg, name = mercury, names = \{mercury\}, boilingpoint = [value = 629.88, uncertainty = undefined, units = K], ionizationenergy = [value = 10.4375, uncertainty = undefined, units = eV], density = \left[value = 13.5336, uncertainty = undefined, units = \frac{g}{cm^3}\right], electronegativity = [value = 2, uncertainty = undefined, units = 1], atomicweight = [value = 200.59, uncertainty = 0.02, units = amu], meltingpoint = [value = 234.32, uncertainty = undefined, units = K]$ **(9.9)**

Information displayed includes atomic number Z, symbol, name, ionization energy with its unit and uncertainty, melting and boiling points with their units but no uncertainty, the density of liquid mercury at an unspecified temperature with its unit but no uncertainty, and atomic mass in unified atomic mass unit with symbol u:

$$1\ \mathrm{u} = \frac{1}{N_A}\ \mathrm{kg}.$$

although 'electronegativity' (on an unspecified scale) is found within that information, this quantity is nonsensical and should be disregarded.

A nuclide is a particular species of atomic nucleus characterized by its number Z of protons, or atomic number, and its number N of neutrons; their sum $A = Z + N$ is the mass number of that nuclidic species, which is hence an integer, but the actual atomic mass of a particular nuclidic species in unified atomic-mass unit, u, varies slightly from that integer value. How many nuclidic species are known in total, whether in nature or artificially produced, according to information stored in *Maple*?

```
> nucl := map( i -> [i[2] - i[1], i[1]],
              {GetIsotopes(output=atomicnumbers )} ):
  nops(nucl);
```

2957 **(9.10)**

Of those numerous nuclidic species, how many are stable, or have a great lifetime before prospective

decomposition into other species?

```
> nucl_stable := map(i -> [i[2] - i[1], i[1]],
            {GetIsotopes(abundance, output=atomicnumbers)}):
  nops(nucl_stable);
```

288 **(9.11)**

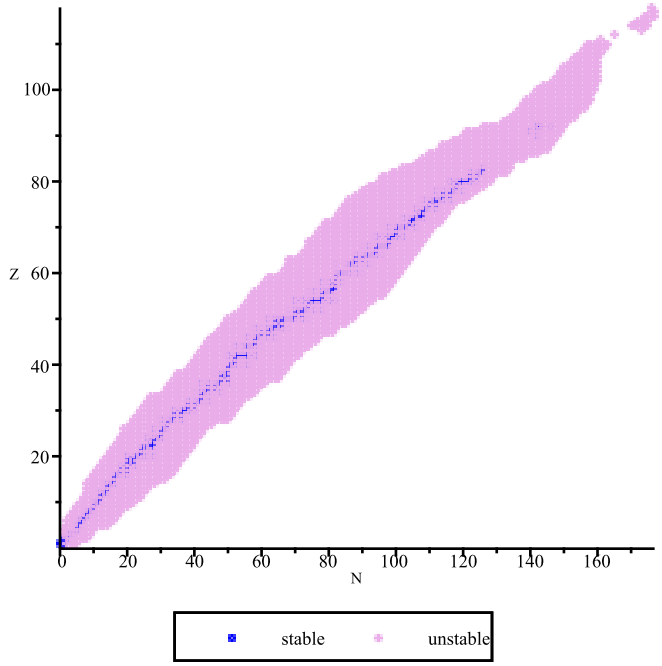
Information available in this package indicates that the half life of a particular unstable nuclidic species varies from as little as 10^{-6} seconds to as much as 10^{24} years = 10^{31} s; the latter period is much greater than the estimated age of our universe, ~1.3 10^{13} years or 4.1 10^{20} s. The number of known unstable nuclidic species equals the total number of nuclidic species minus the number of stable nuclidic species. How many unstable nuclides have been characterised to some extent?

```
> nucl_unstable := nucl minus nucl_stable:
  nops(nucl_unstable);
```

2669 **(9.12)**

We plot a distribution of nuclidic species both stable, depicted with blue circles, and unstable, depicted with pink diamonds, as a function of their numbers Z of protons and N of neutrons. Expand this plot laterally to improve its view.

```
> p_nu_st := plots[pointplot](nucl_stable, colour=blue,
                legend="stable", symbol=circle):
  p_nu_unst := plots[pointplot](nucl_unstable, colour=plum,
                legend="unstable", symbol=diamond):
  plots[display]( [p_nu_st, p_nu_unst], labels=["N", "Z"]);
```



The five blue circles near N ~140 and Z ~91 mark nuclides of which, although they are radioactive such as ^{238}U, their half lives are so great that they exist in natural abundance in our terrestrial environment or as a daughter product of such an enduring radioactive nuclide.

The next plot illustrates the periodicity of atomic first ionization energies, presented in SI unit joule; this energy applies to a process A -> A^{+} + e^{-} for any atom A.

```
> IonEn := map(an -> [an, evalf(Element(an,ionizationenergy))],
                [GetElements(ionizationenergy,output=atomicnumbers)])
  ;
```

$$IonEn := [[1, 2.178703856 \times 10^{-18}], [2, 3.939335745 \times 10^{-18}], [3, 8.638455687 \times 10^{-19}], [4, 1.493661198 \times 10^{-18}], [5, 1.329486160 \times 10^{-18}], [6, 1.804098941 \times 10^{-18}], [7, 2.328619523 \times 10^{-18}], [8, 2.181860144 \times 10^{-18}], [9, 2.791440283 \times 10^{-18}], [10, 3.455029796 \times 10^{-18}], [11, 8.233745873 \times 10^{-19}], [12, 1.225056288 \times 10^{-18}], [13, 9.590308818 \times 10^{-19}], [14, 1.306046316 \times 10^{-18}], [15, 1.680154557 \times 10^{-18}], [16, 1.659854979 \times 10^{-18}], [17, 2.077638555 \times 10^{-18}], [18, 2.524966268 \times 10^{-18}], [19, 6.954568059 \times 10^{-19}], [20, 9.794426119 \times 10^{-19}], [21, 1.051268190 \times 10^{-18}], [22, 1.093982219 \times 10^{-18}], [23, 1.080860392 \times 10^{-18}], [24, 1.084112811 \times 10^{-18}], [25, 1.191058100 \times 10^{-18}], [26, 1.266104053 \times 10^{-18}], [27, 1.262675395 \times 10^{-18}], [28, 1.224030895 \times 10^{-18}], [29, 1.237905744 \times 10^{-18}], [30, 1.505116761 \times 10^{-18}], [31, 9.611938202 \times 10^{-19}], [32, 1.265623400 \times 10^{-18}], [33, 1.568306607 \times 10^{-18}], [34, 1.562506728 \times 10^{-18}], [35, 1.892779417 \times 10^{-18}], [36, 2.242983182 \times 10^{-18}], [37, 6.692451964 \times 10^{-19}], [38, 9.124235639 \times 10^{-19}], [39, 9.960892270 \times 10^{-19}], [40, 1.062867949 \times 10^{-18}], [41, 1.082895156 \times 10^{-18}], [42, 1.136327747 \times 10^{-18}], [43, 1.166384580 \times 10^{-18}], [44, 1.179282102 \times 10^{-18}], [45, 1.195047520 \times 10^{-18}], [46, 1.335718627 \times 10^{-18}], [47, 1.213841052 \times 10^{-18}], [48, 1.440965609 \times 10^{-18}], [49, 9.270834800 \times 10^{-19}], [50, 1.176622489 \times 10^{-18}], [51, 1.379217722 \times 10^{-18}], [52, 1.443497048 \times 10^{-18}], [53, 1.674482852 \times 10^{-18}], [54, 1.943408198 \times 10^{-18}], [55, 6.238715545 \times 10^{-19}], [56, 8.350063896 \times 10^{-19}], [57, 8.935178798 \times 10^{-19}], [58, 8.873975651 \times 10^{-19}], [59, 8.768712647 \times 10^{-19}], [60, 8.852025831 \times 10^{-19}], [61, 8.943349898 \times 10^{-19}], [62, 9.042043978 \times 10^{-19}], [63, 9.084982312 \times 10^{-19}], [64, 9.853546437 \times 10^{-19}], [65, 9.394843270 \times 10^{-19}], [66, 9.515166734 \times 10^{-19}], [67, 9.647506523 \times 10^{-19}], [68, 9.785614148 \times 10^{-19}], [69, 9.908340877 \times 10^{-19}], [70, 1.002033302 \times 10^{-18}], [71, 8.693250128 \times 10^{-19}], [72, 1.093501566 \times 10^{-18}], [73, 1.209579262 \times 10^{-18}], [74, 1.259951695 \times 10^{-18}], [75, 1.255065056 \times 10^{-18}], [76, 1.351948676 \times 10^{-18}], [77, 1.436671776 \times 10^{-18}], [78, 1.435341969 \times 10^{-18}], [79, 1.478088042 \times 10^{-18}], [80, 1.672271848 \times 10^{-18}], [81, 9.786415236 \times 10^{-19}], [82, 1.188286334 \times 10^{-18}], [83, 1.167281799 \times 10^{-18}], [84, 1.348552062 \times 10^{-18}], [86, 1.722099541 \times 10^{-18}], [87, 6.525184724 \times 10^{-19}], [88, 8.456929076 \times 10^{-19}], [89,$$ **(9.13)**

$8.283253131 \times 10^{-19}$], [90, $1.010444730 \times 10^{-18}$], [91, $9.436820298 \times 10^{-19}$], [92, $9.924042208 \times 10^{-19}$], [93, $1.003875805 \times 10^{-18}$], [94, $9.655036753 \times 10^{-19}$], [95, $9.571082699 \times 10^{-19}$], [96, $9.599441225 \times 10^{-19}$], [97, $9.930130479 \times 10^{-19}$], [98, $1.006439288 \times 10^{-18}$], [99, $1.028597391 \times 10^{-18}$], [100, $1.041414804 \times 10^{-18}$], [101, $1.054232217 \times 10^{-18}$], [102, $1.065447453 \times 10^{-18}$], [103, $7.850665443 \times 10^{-19}$], [104, $9.613059726 \times 10^{-19}$]]

As these ionisation energies appear with unit J, we convert them to unit eV.

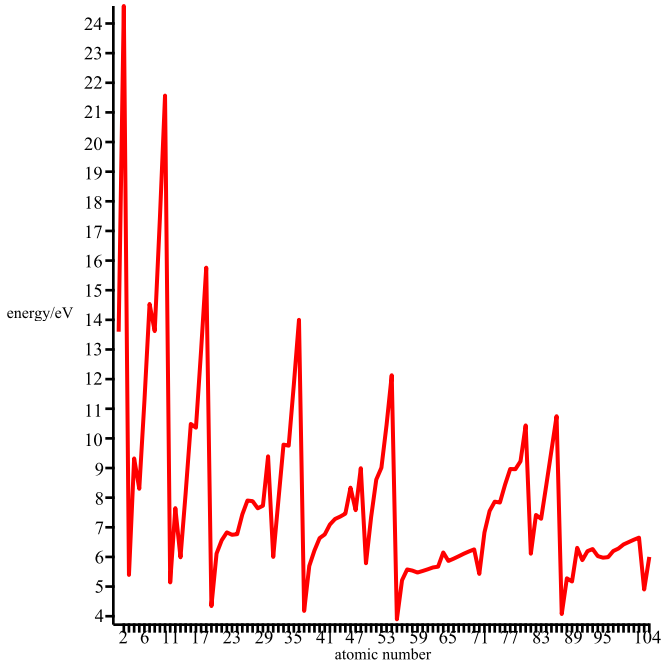
```
> IonEn := map(x -> [x[1],x[2]/1.602e-19], IonEn);
```

$$IonEn := [[1, 13.59989923], [2, 24.59011077], [3, 5.392294436], [4, 9.323727827], [5, 8.298914856], [6, 11.26154145], [7, 14.53570239], [8, 13.61960140], [9, 17.42472087], [10, 21.56697750], [11, 5.139666587], [12, 7.647042996], [13, 5.986459936], [14, 8.152598726], [15, 10.48785616], [16, 10.36114219], [17, 12.96902968], [18, 15.76133750], [19, 4.341178563], [20, 6.113873981], [21, 6.562223408], [22, 6.828852802], [23, 6.746943770], [24, 6.767246011], [25, 7.434819600], [26, 7.903271242], [27, 7.881868882], [28, 7.640642290], [29, 7.727251835], [30, 9.395235711], [31, 5.999961424], [32, 7.900270911], [33, 9.789679194], [34, 9.753475205], [35, 11.81510248], [36, 14.00114346], [37, 4.177560527], [38, 5.695527864], [39, 6.217785437], [40, 6.634631392], [41, 6.759645168], [42, 7.093181941], [43, 7.280802621], [44, 7.361311498], [45, 7.459722347], [46, 8.337819144], [47, 7.577035280], [48, 8.994791566], [49, 5.787037952], [50, 7.344709669], [51, 8.609349076], [52, 9.010593308], [53, 10.45245226], [54, 12.13113732], [55, 3.894329304], [56, 5.212274591], [57, 5.577514855], [58, 5.539310643], [59, 5.473603400], [60, 5.525609133], [61, 5.582615417], [62, 5.644222208], [63, 5.671025163], [64, 6.150778050], [65, 5.864446485], [66, 5.939554765], [67, 6.022163872], [68, 6.108373375], [69, 6.184981820], [70, 6.254889525], [71, 5.426498207], [72, 6.825852471], [73, 7.550432347], [74, 7.864867009], [75, 7.834363645], [76, 8.439130312], [77, 8.967988614], [78, 8.959687696], [79, 9.226517115], [80, 10.43865074], [81, 6.108873430], [82, 7.417517690], [83, 7.286403239], [84, 8.417927977], [86, 10.74968502], [87, 4.073149016], [88, 5.278981945], [89, 5.170569994], [90, 6.307395318], [91, 5.890649374], [92, 6.194782901], [93, 6.266390792], [94, 6.026864390], [95, 5.974458613], [96, 5.992160565], [97, 6.198583320], [98, 6.282392559], [99, 6.420707809], [100, 6.500716629], [101, 6.580725449], [102, 6.650733164], [103,$$ **(9.14)**

4.900540226], [104, 6.000661501]]

and plot them.

```
> plots[pointplot](IonEn, style=line, labels=["atomic number",
              "energy/eV"], colour=red, tickmarks=[spacing(1),
  spacing(1)]);
```



Using the mouse to point to a particular feature, such as a maximum or minimum in the curve constructed by joining consecutive points with a line, prompts a box at upper left of the display that indicates the atomic number of the element; because of limitations of that display the corresponding ionization energy appears as an approximate value with two digits after the decimal point.

Within its internal libraries, *Maple* from release 2018 contains many scientific data also on thermophysical data, namely thermochemical, thermodynamic and thermophysical properties of more than 2000 chemical species.

0.15 spreadsheet

table of chemical elements

```
> restart:
```

As of *Maple* 2019, the spreadsheet feature of *Maple* has become deprecated, but the capabilitity remains. Although what appears just below might resemble simply a table of data, it is actually a spreadsheet, the content of which we can readily insert, extract and manipulate not only manually, in a manner similar to that practicable with other spreadsheets, but also through commands within the worksheet in which the spreadsheet is embedded. In four columns A, B, C and D, this table of chemical elements includes atomic number Z, name, chemical symbol and average mass/unified atomic mass unit, respectively, of chemical elements with atomic numbers in a range [1, 96]; column E contains numbers derived from other columns as described below. Besides being a useful compendium of particular elemental information, we employ these data to illustrate chemical applications in succeeding chapters. These data of atomic number, name, symbol, mean atomic mass and other properties of each element are

available on recall from *Maple*'s package **ScientificConstants**, as introduced briefly in section 0.14 above and described further in section 1.110.

SpreadSheet001

	A	B	C	D	E	F
1	Z	*element*	*symbol*	$\frac{mass}{u}$	$\frac{mass - Z}{Z}$	
2	1	*hydrogen*	*H*	1.00794	0.00794	
3	2	*helium*	*He*	4.002602	1.001301000	
4	3	*lithium*	Li	6.941	1.313666667	
5	4	*beryllium*	*Be*	9.01218	1.253045000	
6	5	*boron*	*B*	10.811	1.162200000	
7	6	*carbon*	*C*	12.011	1.001833333	
8	7	*nitrogen*	*N*	14.00674	1.000962857	
9	8	*oxygen*	O	15.9994	0.999925000	
10	9	*fluorine*	*F*	18.9984032	1.110933689	
11	10	*neon*	*Ne*	20.1797	1.017970000	
12	11	*sodium*	*Na*	22.989768	1.089978909	

This table demonstrates that *Maple* possesses an intrinsic facility of a spreadsheet to display information in an orderly manner; according to columns A, B, C and D, this content is merely a table that one can find in a typical chemical textbook. To employ those data for a calculation of some property of chemical interest, we consider the nature of atomic nuclei: like chemical elements of which the relative abundance varies greatly within a terrestrial context, and likewise also from one astronomical body to another, a nuclidic species, defined according to a particular combination of atomic number Z and mass number A, of each chemical element can have a somewhat variable abundance on this planet, and greater variability elsewhere. A value of atomic mass in this spreadsheet implies a weighted mean, over stable nuclides, of masses of atoms of terrestrial elements in natural abundance, relative to the atomic mass of ^{12}C that is defined to be 12 u. The mass number A of a particular nuclide indicates the number of nucleons within a nucleus of that species: for chemical purposes we might consider an atomic nucleus of a particular nuclide to comprise Z protons and $A - Z$ neutrons.

A ratio of average number of neutrons to protons can vary from one chemical element to another. We employ a numeric capability of *Maple*'s spreadsheet to discover whether any trend in this variability exists: in column E we calculate a ratio

$$\frac{\frac{mass}{u} - Z}{Z} ,$$

in which an average atomic mass, according to a conventional list, divided by its unit is an average mass

number. The difference between this average mass number and an atomic number of the same chemical element indicates an average number of neutrons in nuclides of that element; a quotient of this difference with atomic number yields a mean ratio of number of neutrons to number of protons. After we make this calculation explicitly for element hydrogen in cell E2, we fill column E with corresponding values for other elements, according to a common facility of a spreadsheet as we explain in section group 6.6. For those radioactive chemical elements that lack a conventional atomic mass, we delete manually a value -1 of this ratio for each element for which no value of atomic mass appears in column D. The resulting values of this ratio in column E show considerable scatter, best depicted graphically; for this purpose we extract (here by copying and pasting but an alternative mechanism involving a particular command operable on a spreadsheet is practicable) the content of column E into an expression sequence.

```
> listp := MATRIX([[.794e-2], [1.00], [1.31], [1.25], [1.16],
  [1.00], [1.00], [1.00], [1.11], [1.02], [1.09], [1.03], [1.08],
  [1.01], [1.06], [1.00], [1.09], [1.22], [1.06], [1.00], [1.14],
  [1.18], [1.21], [1.17], [1.20], [1.15], [1.18], [1.10], [1.19],
  [1.18], [1.25], [1.27], [1.27], [1.32], [1.28], [1.33], [1.31],
  [1.31], [1.28], [1.28], [1.27], [1.28], [0], [1.30], [1.29],
  [1.31], [1.30], [1.34], [1.34], [1.37], [1.39], [1.45], [1.39],
  [1.43], [1.42], [1.45], [1.44], [1.42], [1.39], [1.40], [0],
  [1.43], [1.41], [1.46], [1.45], [1.46], [1.46], [1.46], [1.45],
  [1.47], [1.46], [1.48], [1.48], [1.48], [1.48], [1.50], [1.50],
  [1.50], [1.49], [1.51], [1.52], [1.53], [1.52]]):
```

After treatment to remove superfluous brackets,

```
> listp := map(op, op(subs(MATRIX=``, listp)));
```

$$listp := [0.00794, 1.00, 1.31, 1.25, 1.16, 1.00, 1.00, 1.00, 1.11, 1.02, 1.09, 1.03, 1.08, 1.01, 1.06, \quad \textbf{(10.1)}$$

$$1.00, 1.09, 1.22, 1.06, 1.00, 1.14, 1.18, 1.21, 1.17, 1.20, 1.15, 1.18, 1.10, 1.19, 1.18, 1.25,$$

$$1.27, 1.27, 1.32, 1.28, 1.33, 1.31, 1.31, 1.28, 1.28, 1.27, 1.28, 0, 1.30, 1.29, 1.31, 1.30, 1.34,$$

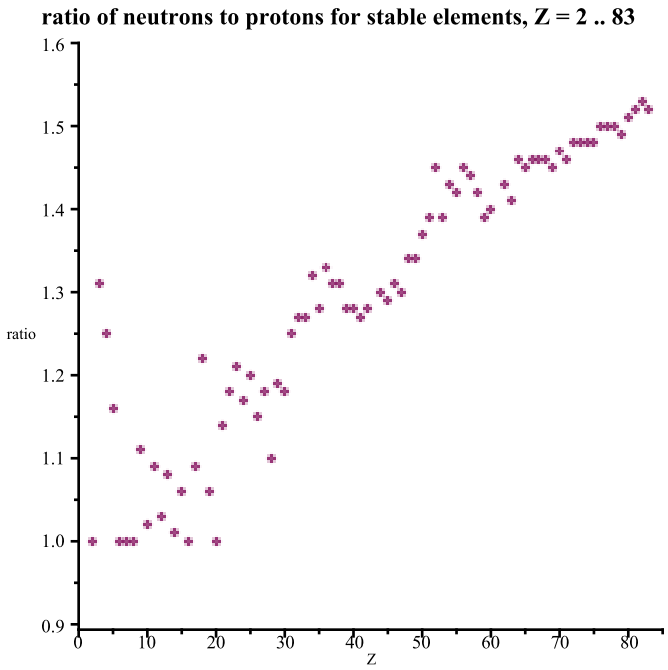
$$1.34, 1.37, 1.39, 1.45, 1.39, 1.43, 1.42, 1.45, 1.44, 1.42, 1.39, 1.40, 0, 1.43, 1.41, 1.46, 1.45,$$

$$1.46, 1.46, 1.46, 1.45, 1.47, 1.46, 1.48, 1.48, 1.48, 1.48, 1.50, 1.50, 1.50, 1.49, 1.51, 1.52,$$

$$1.53, 1.52]$$

we plot this list; by dragging to the right the small square on the right side of the frame after clicking on the plot, expand laterally this plot to improve viewing.

```
> plots[listplot](listp, style=point, view=[0..85, 0.9..1.6], title=
      "ratio of neutrons to protons for stable elements, Z = 2 ..
  83",
      colour=maroon, titlefont=[TIMES,BOLD,14], labels=["Z",
  "ratio"]);
```



On either browsing down column E or glancing at the above plot, we discern a generally increasing trend of ratio of neutrons to protons in atomic nuclei with increasing atomic number, from values typically near unity for small Z to >1.5 for $Z \sim 80$. Apart from a few large values of this ratio for small Z, we perceive in particular an anomalously large ratio of a point at $Z = 18$; we obtain that number by placing the cursor on that point at viewing its coordinates in the context bar at top left. Which element has this atomic number? This command elicits not only a name of that element but also information about its properties.

```
> ScientificConstants[GetElement](18);
```

18, *symbol* = *Ar*, *name* = *argon*, *names* = {*argon*}, *boilingpoint* = [*value* = 87.30, *uncertainty* = *undefined*, *units* = *K*], *electronegativity* = [*value* = 0, *uncertainty* = *undefined*, *units* = 1], *atomicweight* = [*value* = 39.948, *uncertainty* = 0.001, *units* = *amu*], *density* = [*value* = **proc**( )

...

end proc, *uncertainty* = *undefined*, *units* = $\frac{kg}{L}$], *meltingpoint* = [*value* = 83.80, *uncertainty* = *undefined*, *units* = *K*], *ionizationenergy* = [*value* = 15.7596, *uncertainty* = *undefined*, *units* = *eV*] **(10.2)**

These simple operations to manipulate numerical data within a spreadsheet, to transfer those data between a spreadsheet and a worksheet within which that spreadsheet is embedded and to plot these data in a highly illuminating form illustrate the power of symbolic computation in *Maple* and its related facilities. What this table in its form above fails to demonstrate is that with *Maple*, unlike merely numeric spreadsheets in other commercial software, one can employ and operate on purely symbolic quantities that need never possess a particular numerical value, as we show in a following spreadsheet.

table of cosine functions

In this spreadsheet below, row 1 at the top serves merely to present headings, but is not directly used in further calculations. In column A we form integers, from 1 to 5, in a list. In column B we form a cosine function of a quantity θ multiplied by the adjacent integer, designated *n*, in column A, and in column C we expand algebraically the cosine function of the corresponding multiple angle θ, 2 θ, 3 θ .. . In column D we integrate this expanded expression with respect to θ, as in $\int \cos(\theta)\, d\theta$, to produce the antiderivative; these expressions are entirely general and algebraic, applicable to any value of θ.

SpreadSheet002

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	*n*	cos(*n* θ)	*expanded*	*antiderivativ*									
2	1												
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15													

Use of a spreadsheet in *Maple* is discussed in section group 6.6, and its applications pervade succeeding chapters.

0.2 cursory tour

0.21 essential commands and operations

Here we present, in a sequence with minimal explanation and almost no hyperlink, some useful commands for common operations that a reader might wish to employ for applications outside the context of this programme of study of mathematics, for instance in concurrent courses in chemistry or physics, essentially using this hardware and software as an alternative to an advanced calculator.

To ensure that there is no memory by the system of preceding calculations, we first clear, with restart, the internal memory and the system nearly to conditions that arise on initially activating *Maple*; this restart; must occur in a separate input command. We terminate this, and almost every other, line of input with a semicolon **;**, so that any output from this statement appears directly below the input line, but in the worksheet mode within the Java interface that punctuation is not optional; not all commands generate output, for instance this one.

```
> restart;
```

i) essential operations

We enter symbolic expressions according to the following examples:

a sum of quantities, $x + y - z$,

```
> x+y - z;
```

$$x + y - z \tag{11.1}$$

a product of quantities, $3\,x^2\,y$,

```
> 3*x^2*y;
```

$$3\,x^2\,y \tag{11.2}$$

a quotient or ratio of quantities, $\frac{x}{y}$,

```
> x/y;
```

$$\frac{x}{y} \tag{11.3}$$

a reciprocal quantity, x^{-1}, in two ways,

```
> x^(-1);
```

$$\frac{1}{x} \tag{11.4}$$

```
> 1/x;
```

$$\frac{1}{x} \tag{11.5}$$

a square root, $\sqrt{x}$, in two ways,

```
> x^(1/2);
```

$$\sqrt{x} \tag{11.6}$$

```
> sqrt(x);
```

$$\sqrt{x} \tag{11.7}$$

a more complicated expression including two divisors, $\frac{3}{(1+x)\,y}$, in two ways, both involving parentheses,

```
> 3/(1+x)/y;
```

$$\frac{3}{(1+x)\,y} \tag{11.8}$$

```
> 3/((1+x)*y);
```

$$\frac{3}{(1+x)\,y} \tag{11.9}$$

and another complicated expression, showing the precedence of operations; the lack of parentheses about $\frac{1}{3}$ as the exponent in the second expression causes that expression to be interpreted without exponent $\frac{1}{3}$. To enhance readability, we can include spaces, ad libitum, between items such as numbers or names, and separate expressions with a comma, but no space is permissible within a number

or name.

```
> 3*x/z+y*z^(1/3), 3*x/z+y*z^1/3;
```

$$\frac{3\,x}{z} + y\,z^{1/3},\ \frac{3\,x}{z} + \frac{y\,z}{3} \tag{11.10}$$

We enter these four constants as follows, first the ratio π of circumference to diameter of a circle,

```
> Pi;
```

$$\pi \tag{11.11}$$

the base e of natural or naperian logarithms,

```
> exp(1);
```

$$e \tag{11.12}$$

the imaginary unit $i = \sqrt{-1}$, in two ways,

```
> I;
```

$$I \tag{11.13}$$

```
> sqrt(-1);
```

$$I \tag{11.14}$$

and infinity, ∞. *Maple* is aware of some properties of π,e and i represented as I, and even might apply these properties in simplification of expressions in which these quantities occur. *infinity* is a name in *Maple* that has several special properties.

```
> infinity;
```

$$\infty \tag{11.15}$$

Here are some formulae that illustrate the input and output of these expressions, first $\sqrt[n]{x}$ as the n'th root of x,

```
> x^(1/n);
```

$$x^{\frac{1}{n}} \tag{11.16}$$

with the canonical exponential function, e^x, which must be input in this form -- in contrast with e^x input as $exp(x)$, the notation e^x is merely some symbol e raised to power x, not the canonical exponential function,

```
> exp(x);
```

$$e^x \tag{11.17}$$

with the natural or naperian logarithm, ln x,

```
> ln(x);
```

$$\ln(x) \tag{11.18}$$

with the common or briggsian logarithm, $\log_{10}(x)$,

```
> log10(x);
```

$$\frac{\ln(x)}{\ln(10)} \tag{11.19}$$

with a logarithm to a general base b, $\log_b(x)$,

```
> log[b](x);
```

$$\frac{\ln(x)}{\ln(b)} \tag{11.20}$$

with some trigonometric expressions, $\sin x$,

```
> sin(x);
```

$$\sin(x) \tag{11.21}$$

$\cos x$,

```
> cos(x);
```

$$\cos(x) \tag{11.22}$$

$\tan x$,

```
> tan(x);
```

$$\tan(x) \tag{11.23}$$

and with their inverse functions, $\sin^{-1} x$,

```
> arcsin(x);
```

$$\arcsin(x) \tag{11.24}$$

with this property,

```
> sin(arcsin(x));
```

$$x \tag{11.25}$$

$\cos^{-1} x$

```
> arccos(x);
```

$$\arccos(x) \tag{11.26}$$

$\tan^{-1} x$,

```
> arctan(x);
```

$$\arctan(x) \tag{11.27}$$

One can readily convert any trigonometric function to an exponential or logarithmic form.

```
> convert(tan(x), exp);
```

$$\frac{-I\left(e^{Ix} - e^{-Ix}\right)}{e^{Ix} + e^{-Ix}} \tag{11.28}$$

```
> convert(arctan(x), ln);
```

$$\frac{I}{2}\left(\ln(1 - Ix) - \ln(1 + Ix)\right) \tag{11.29}$$

Maple provides greek letters, which might be input according to their English names.

```
> sin(theta);
```

$$\sin(\theta) \tag{11.30}$$

Exponential, logarithmic functions are discussed in chapter 1 and trigonometric and other functions in

chapter 2. For other operations involving numbers, such as the absolute value of x or $|x|$,

```
> abs(x);
```

$$|x| \tag{11.31}$$

the lesser of two numbers (extensible to multiple numerical items), such as 2,3,

```
> min(2,3);
```

$$2 \tag{11.32}$$

the greater of two numbers (extensible to multiple numerical items),

```
> max(2,3);
```

$$3 \tag{11.33}$$

a factorial, $n!$,

```
> n!;
```

$$n! \tag{11.34}$$

a binomial coefficient $(n, k) = \frac{n!}{k!\ (n-k)!}$, for instance (5, 2); these operators are introduced in section 1.116 in chapter 1.

```
> binomial(5,2) = 5!/(2! * (5-2)!);
```

$$10 = 10 \tag{11.35}$$

For a piecewise definition such that for $x < 0$ the quantity is nil, for $x < 1$ the quantity is $x^2\ (1+x)^2$, and unity otherwise, this operator is discussed in section 2.410.

```
> piecewise(x<0,0, x<1,x^2*(1+x)^2, 1);
```

$$\begin{cases} 0 & x < 0 \\ x^2\ (1+x)^2 & x < 1 \\ 1 & otherwise \end{cases} \tag{11.36}$$

Discussed in section group 1.1 in chapter 1, here are some commands to operate on numbers, first to evaluate to 10 decimal digits that corresponds to the default setting of numerical precision, such as to evaluate π to 10 decimal digits,

```
> evalf(Pi);
```

$$3.141592654 \tag{11.37}$$

to evaluate to n decimal digits with n a positive integer, such as to evaluate π to 15 decimal digits,

```
> evalf(Pi,15);
```

$$3.14159265358979 \tag{11.38}$$

to test whether an integer n be prime, such as $n = 17$,

```
> isprime(17);
```

$$true \tag{11.39}$$

to factor an integer n, such as $n = 360$,

```
> ifactor(360);
```

$$(2)^3\ (3)^2\ (5) \tag{11.40}$$

to evaluate the sign of a real number, such as $n = -3.5$, $n = 0$ and $n = 7$,

```
> signum(-3.5), signum(0), signum(7);
```

$$-1, 0, 1 \qquad \textbf{(11.41)}$$

to extract the real part of a complex number z or $\Re(z)$, for instance for $z = 3 + 2\,I$, in which I denotes $\sqrt{-1}$,

```
> Re(3 + 2*I);
```

$$3 \qquad \textbf{(11.42)}$$

to extract the imaginary part of a complex number z or $\Im(z)$,

```
> Im(3 + 2*I);
```

$$2 \qquad \textbf{(11.43)}$$

to form the complex conjugate of a complex number z, or $\overline{z}$.

```
> conjugate(3 + 2*I);
```

$$3 - 2\,I \qquad \textbf{(11.44)}$$

ii) equations

Here follow some commands applicable to an equation $y = x$, first to extract the left side of that equality,

```
> lhs(y=x);
```

$$y \qquad \textbf{(11.45)}$$

to extract the right side of that equality;

```
> rhs(y=x);
```

$$x \qquad \textbf{(11.46)}$$

to solve an equation $f(w) = 0$ for w, in which case $f(w)$ must be an explicit expression in terms of w,

```
> solve(f(w)=0, w);
```

$$RootOf(f(\_Z)) \qquad \textbf{(11.47)}$$

and to solve an equation $f(x) = 0$ as a real decimal number, in which case $f(x)$ must be some formula or expression containing only x as a symbolic, i.e. non-numeric, quantity.

```
> fsolve(f(x)=0, x);
```

$$fsolve(f(x) = 0, x) \qquad \textbf{(11.48)}$$

For the solution of an equation $f(x) = 0$ as a real decimal number with a as an initial estimate of the solution, $f(x)$ must be again some formula or expression in which x is the only symbolic quantity.

```
> fsolve(f(x), x=a);  # For this command to work, 'a' must be a
  number.
```

$$fsolve(f(x), x = a) \qquad \textbf{(11.49)}$$

In the latter three examples either a merely formal solution or no solution appears on execution of these commands, because we here specify no explicit formula or expression for $f(x)$, such as $f(x) = x\sin(x) + 3\,x^2 - 4$.

```
> fsolve(x*sin(x) + 3*x^2 - 4 = 0, x);
```

$$1.021284945 \qquad \textbf{(11.50)}$$

iii) algebraic operations

Common algebraic operations on expressions involving a single independent variable include expansion and factoring; substitution of that variable for another variable is a typical application of a processor for symbolic computation, illustrated as follows. Simplification is applicable to both numerical and algebraic expressions, but in some cases a resulting expression might appear more complicated or extensive than the original.

```
> z := expand( (x + 1)^3 );
```

$$z := x^3 + 3\,x^2 + 3\,x + 1 \tag{11.51}$$

```
> z := subs(x = y+2, z);
```

$$z := (y + 2)^3 + 3\,(y + 2)^2 + 3\,y + 7 \tag{11.52}$$

```
> z := simplify(z);
```

$$z := (y + 3)^3 \tag{11.53}$$

```
> z := factor(z);
```

$$z := (y + 3)^3 \tag{11.54}$$

Such common algebraic operations are discussed in sections 1.201 -- 1.204.

To solve an equation or a set thereof is a valuable facility of a processor for symbolic computation; as an example we assign a general quadratic expression in one variable -- x -- and three parameters -- a, b, c -- to a name **eq1**.

```
> eq1 := a*x^2 + b*x = -c;
```

$$eq1 := a\,x^2 + b\,x = -c \tag{11.55}$$

We solve that equation for a specified quantity, which might be x or a or b or c, depending on which quantity we might consider to be of interest, here x.

```
> solve(eq1, x);
```

$$\frac{-b + \sqrt{-4\,a\,c + b^2}}{2\,a}, \; -\frac{b + \sqrt{-4\,a\,c + b^2}}{2\,a} \tag{11.56}$$

This solution is general, but might be invalid for a particular case, for instance with $a = 0$; this processor *Maple* makes generally no test of, or comment about, such validity.

iv) forming a plot

A common occurrence involving numerical data in a chemical laboratory is the acquisition of values of independent and dependent variables that one might seek to plot. For example, we suppose the following table to have been generated as a result of experimental measurements with x as independent and y as dependent variables.

x	y
2	5.1
3	6.9
4	9.1
5	10.9
6	13.0

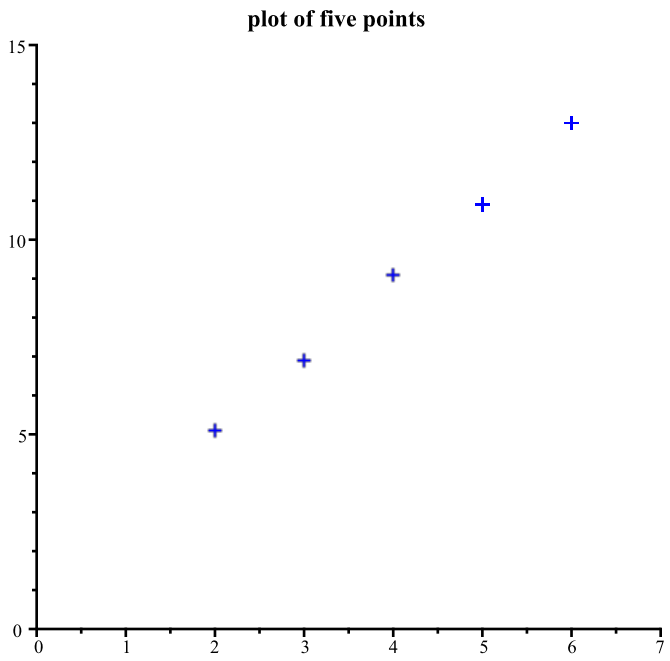
To make a simple plot in two dimensions, we form a list of lists of these points in the following manner. In *Maple* a list is enclosed by brackets, as in "[ ]"; each couple of coordinates, such as 2, 5.1, becomes the content of an inner list, such as **[2, 5.1]**, and these five inner lists then become the content of another and outer list, **[[2, 5.1], [...], ...]**. If we type this line directly, we execute the command on depressing the key " Enter ", or an equivalent key depending on the particular computer, after typing the semicolon; if the line be already typed, as here below, we have merely to place the cursor on the line and then to depress that same key "Enter" to initiate action by the computer. With assignment operator **:=** , we assign this list of lists, with spaces interspersed to improve readability, to a variable named **ldata**, appropriate to a list of data.

```
> ldata := [[2,5.1], [3,6.9], [4,9.1], [5,10.9], [6,13.0]];
```

$$ldata := [[2, 5.1], [3, 6.9], [4, 9.1], [5, 10.9], [6, 13.0]] \qquad \textbf{(11.57)}$$

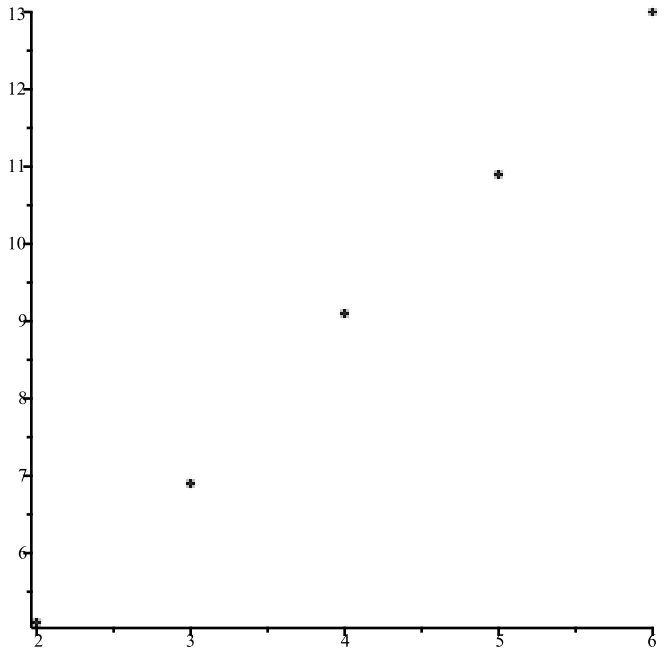
To plot these points, for instance each as a cross of a specified size, we type the following command: as this operation requires a command **pointplot** that must be explicitly called from library **plots**, the first part of this command implements that action, according to the indicated form. Almost any computer operation involving textual input must conform exactly to rules of the particular software employed -- generally no variation in spelling is permissible. Within parentheses **( )** after the name of the command, there follow in a sequence seven items separated by commas **,** that serve as arguments of that particular command: the first item specifies the data to be plotted, as a name of a variable to which these data have been assigned in an appropriate form -- in this case, a list of lists, named **ldata** ; the second item specifies, within a list, first the domain along the abscissal axis, **0..7**, here conventionally used for variable *x* in the table above, and second the range along the ordinate axis, 0..14, here conventionally used for variable *y* in the same table; the third item specifies the type of symbol, here a **cross**, to represent values in each couple that become the coordinates of a point on the plot; the fourth item specifies the size of that symbol, here **12** units; the fifth item specifies the colour of these symbols, here **blue**; the sixth item specifies a title for the plot, here **plot of five points**, and the final item specifies the font and size of characters in that title. Notice that neither the first nor the second line of this command is filled to the right margin; when typing an input line in this way, when we reach the point at which we seek to proceed to a further line, we depress together keys "Shift" and "Enter"; so doing prevents execution of an incomplete command, and thus generating an error message. When we complete the input, merely depressing key "Enter" suffices to initiate execution of the entire command.

```
> plots[pointplot](ldata, view=[0..7, 0..15], symbol=cross,
      symbolsize=12, colour=blue, title="plot of five points",
      titlefont=[TIMES,BOLD,14]);
```



Only the first item -- the name of the variable to which the points to be plotted has been assigned -- is obligatory in the above command; instead of that name of a previously defined list of lists, one might simply type that list of lists directly. If the other items in the list be omitted, either default values are set by the software or no pertinent action is taken. To discover the result of omitting the optional items in the preceding command, we specify explicitly the coordinates of the five points, we delete the optional items and repeat the execution.

```
> plots[pointplot]([[2,5.1], [3,6.9], [4,9.1], [5,10.9], [6,13.0]])
  ;
```



In terms of the superior effect produced, the additional effort to include those optional items in the

preceding plot is considered worth while.

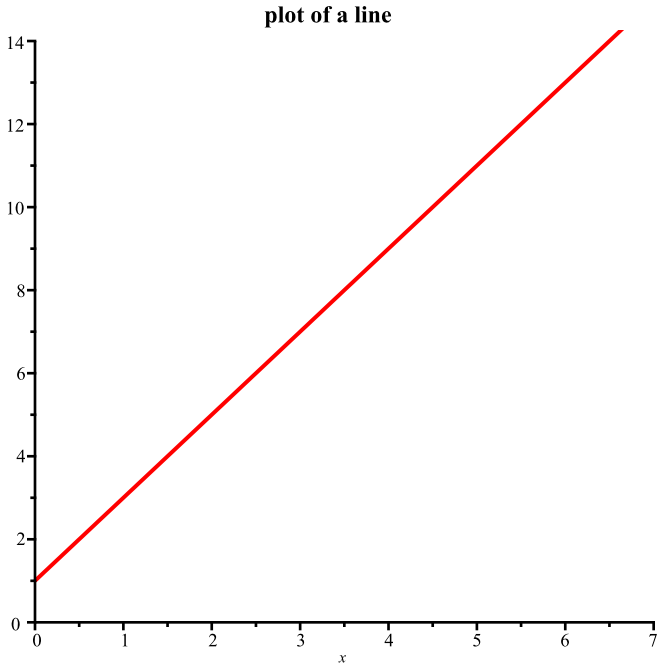
We proceed by supposing that we have a line that we either fit, somehow, to those points, or apply as the result of a theoretical model; the equation of the line has this form: $y = 2\,x + 1$. To plot this line, we input lines in a manner analogous to those above, first defining the line through the dependent variable y, to which we assign as value the expression $2\,x + 1$. The arithmetic operators * for multiplication and + for addition must both be typed explicitly; although symbolic quantities -- symbols used as names of variables or parameters -- are acceptable within any expression for algebraic purposes with *Maple*, for the purpose of plotting, only the independent and dependent variables must lack numerical values at the time of plotting. Arithmetical operations on integers, real and complex numbers are explained in sections 1.101 -- 1.115.

```
> y := 2*x + 1;
```

$$y := 2\,x + 1 \qquad \textbf{(11.58)}$$

As plotting a line or curve in two dimensions is a common operation, the corresponding command **plot** is available without invoking an additional library of commands. In this case the items within parentheses following the name of the command are first the name of the dependent variable **y** to which an expression to define the line is previously assigned, second the name of the independent variable **x** and the intended domain along the abscissal axis belonging to that variable, in the form of an equation ***x*=0..7** with a range **0..7** as the right side of an equality, and third the corresponding range **0..14** of the dependent variable for the ordinate axis; the remaining three items in this sequence correspond exactly to those in the first plot command above.

```
> plot(y, x=0..7, 0..14, colour=red, title="plot of a line",
      titlefont=[TIMES,BOLD,14]);
```



If we seek to plot both points and line in the same figure, we must adopt a slightly variant strategy, which involves forming two separate plots as plot structures and combining them as follows. We form a plot structure of the points, which is just the same as the plot command above, and assign it to a name, here **pdata**. In this case, because we refrain from exhibiting the output from this plot structure, we terminate this input line with a colon **:** instead of a semicolon **;**; otherwise we cause the output of the plot structure that is generally uninteresting. We require no title, with its title font, as part of this plot

structure, because we make a title for the subsequent combined plot within an ensuing command.

```
> pdata := plots[pointplot](ldata, symbol=cross, symbolsize=12,
  colour=blue):
```

We form another plot structure of the line and likewise assign it to a name, here **pline**; use of a colon **:** to terminate the input line again suppresses unwanted output. We must specify the domain within which the line must appear, but apart from the specification of the data and that domain other options are superfluous; we indicate only the desired colour.

```
> pline := plot(y, x=1..7, colour=red):
```

We combine these two plot structures in a command **display**, which we must invoke from its separate library just as for **pointplot**. The first item in the sequence of arguments of this command is a list of names of the plot structures; successive items specify the regions along the abscissal and ordinate axes, the title and its font.

```
> plots[display]([pdata, pline], view=[0..7, 0..14],
    title="plot of a line and five points", titlefont=[TIMES,BOLD,
  14]);
```

Instead of a line, a curve might be specified according to an appropriate expression involving a variable and arithmetic operators; functions, such as sine or logarithm, supplied within *Maple* or as already defined by a user are also usable in plot statements. Much further information about constructing diverse plots in two and three dimensions appears in section group 2.1.

Just as we might solve a single equation according to commands above, we can likewise solve simultaneous equations, generally if they be linear, but even in suitable conditions if they be nonlinear. After restarting to avoid interference from preceding operations, we specify each of two equations and assign each to an evocative name.

```
> restart:
> eq1 := 2*x + 3*y = 7 ;
  eq2 := 5*x - y = 3 ;
```

$$eq1 := 2x + 3y = 7$$

$$eq2 := 5\,x - y = 3 \qquad \textbf{(11.59)}$$

Here we apply **solve** by specifying two linear simultaneous equations within a set, thus enclosed with braces { }, and specifying the two unknowns, likewise within a set, for which to solve. To see the solution as decimal numbers rather than exact rational fractions, we evaluate as floating-point numbers, through application of command **evalf**, as mentioned above.

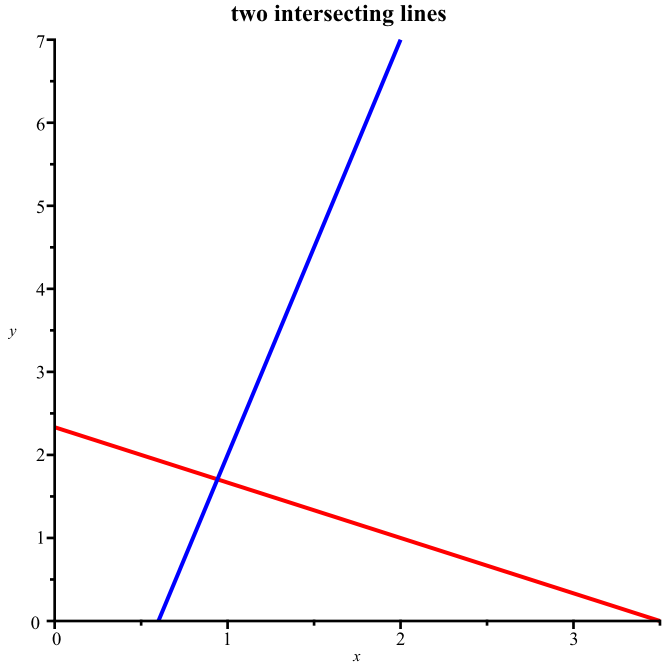
```
> evalf(solve({eq1, eq2}, {x,y}));
```

$$\{x = 0.9411764706,\ y = 1.705882353\} \qquad \textbf{(11.60)}$$

The solutions appear with ten decimal digits, by default.

We proceed to plot these two equations. Because we assign these two linear simultaneous equations each to a name, we must apply **implicitplot**, invoked from library **plots**, rather than the simpler command **plot** as above.

```
> plots[implicitplot]([eq1, eq2], x=0..5, y=0..7, colour=[red,
  blue],
      title="two intersecting lines", titlefont=[TIMES,BOLD,14]);
```



If we place the cursor anywhere on the area of the plot, and click with the left lever of the mouse -- or equivalent operation, the plot becomes surrounded by a frame; the context menu, directly above the working area in this display, alters to that pertinent to a plot. If we place the point of the arrow, constituting the cursor when it is within the plot frame, at the point of the intersection of the two lines, we can read the coordinates of this point, with only two places after the decimal point, at the left side of that context bar.

An alternative approach to solve linear equations is based on a quantity called matrix, which is a rectangular arrangement of numbers or their algebraic symbols in rows and columns and which serves as a collection of those numbers or their symbols but has no numerical value; if a matrix be square it has an associated determinant, which is just a single number or an equivalent algebraic expression. For the coefficients of x and y in the two equations above,

$$eq1 := 2\,x + 3\,y = 7$$
$$eq2 := 5\,x - y = 3$$

we form a square matrix with the coefficients of x in the first column and the coefficients of y in a second column,

```
> M := <<2 | 3>, <5 | -1>>;
```

$$M := \begin{bmatrix} 2 & 3 \\ 5 & -1 \end{bmatrix} \tag{11.61}$$

of which its determinant is just a number, calculated as

```
> DM := LinearAlgebra:-Determinant(M);
```

$$DM := -17 \tag{11.62}$$

The solutions for x and y from those two simultaneous linear equations are obtained, according to Cramer's rule, on dividing a determinant obtained on replacing one or other column of the matrix of coefficients, above, by the right sides of the two equations by the determinant of the matrix of coefficients, just calculated. Replacing 2 and 5 in the first column by 7 and 3, respectively, yields a matrix of which the determinant becomes divided by the above determinant,

```
> LinearAlgebra:-Determinant(<<7 | 3>, <3 | -1>>)/DM;
```

$$\frac{16}{17} \tag{11.63}$$

whereas replacing 3 and -1 in the second column by 5 and 3, respectively, yields another matrix of which the determinant becomes in turn divided by the above determinant.

```
> LinearAlgebra:-Determinant(<<2 | 7>, <5 | 3>>)/DM;
```

$$\frac{29}{17} \tag{11.64}$$

When we apply command **evalf** to the latter two results,

```
> evalf([%, %%]);
```

$$[1.705882353, 0.9411764706] \tag{11.65}$$

we find exactly the same values of y and x that we see above. Although this method is simple, it is inefficient under various conditions, but it generates here an acquaintance with a matrix and a determinant that are discussed at length in chapter 6 on linear algebra. Solution of equations is discussed, with several examples, in sections 1.208 and 1.209.

v) derivatives and integrals

Two common operations in algebraic calculus are differentiation, to produce a derivative of a dependent variable with respect to one or more independent variables, and integration, to produce an indefinite or definite integral with respect to one or more independent variables, as sampled in section 0.12; here we simply preview these operations in the most succinct manner. For explicit differentiation of an expression, either stated directly within the operator's arguments or assigned previously to a name, with respect to a symbolic quantity within that expression, such as x, *Maple* provides an operator **diff(... , *x*)**, in which the ellipsis marks **...** before the comma indicate the position of either an expression or its name, according to the following usage. As expression $\sqrt{x} + 2\,a\,x + \frac{3\,x^{\frac{3}{2}}}{2}$ contains one term as a square root, equivalent to power $\frac{1}{2}$, and another term to power $\frac{3}{2}$, its appearance below indicates an acceptable manner of formulating input containing functions of these types. The results of the first and

third commands hereunder are the derivatives of the indicated expression with respect to the stipulated variable. For illustrative purposes *Maple* provides an inert operator **Diff(..., *x*)** that shows the intended operation in a mathematical notation but undertakes no execution of that operation; it is appropriate to show these two operations, inert and active, across an equality sign; such a usage implies no assignment or even a relation.

```
> restart:
> Diff(sqrt(x) + 2*a*x + 3/2*x^(3/2), x) = diff(sqrt(x) + 2*a*x +
  3/2*x^(3/2), x);
```

$$\frac{\partial}{\partial x}\left(\sqrt{x}+2\,a\,x+\frac{3\,x^{3\,|\,2}}{2}\right)=\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4} \qquad \textbf{(11.66)}$$

```
> y := sqrt(x) + 2*a*x + 3/2*x^(3/2);
```

$$y:=\sqrt{x}+2\,a\,x+\frac{3\,x^{3\,|\,2}}{2} \qquad \textbf{(11.67)}$$

```
> Diff(y, x) = diff(y, x);
```

$$\frac{\partial}{\partial x}\left(\sqrt{x}+2\,a\,x+\frac{3\,x^{3\,|\,2}}{2}\right)=\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4} \qquad \textbf{(11.68)}$$

Operator **int(..., *x*)** implements the inverse operation, an indefinite integral or antiderivative, and its inert form is **Int(..., *x*)**; here the integrands -- expressions to be integrated -- are exactly the result of differentiation above.

```
> Int(1/(2*x^(1/2))+2*a+9/4*x^(1/2), x) = int(1/(2*x^(1/2))+2*a+9/4*
  x^(1/2), x);
```

$$\int\left(\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4}\right)dx=\sqrt{x}+2\,a\,x+\frac{3\,x^{3\,|\,2}}{2} \qquad \textbf{(11.69)}$$

```
> yp := 1/(2*x^(1/2))+2*a+9/4*x^(1/2);
```

$$yp:=\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4} \qquad \textbf{(11.70)}$$

```
> Int(yp, x) = int(yp, x);
```

$$\int\left(\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4}\right)dx=\sqrt{x}+2\,a\,x+\frac{3\,x^{3\,|\,2}}{2} \qquad \textbf{(11.71)}$$

As integrating the result of the former differentiation yields the original expression, apart from a possible constant of integration that is not presented in *Maple* output of such an indefinite integration, these operations have proceeded correctly. For a definite integral between limits 3 and *b*, these values are provided as a range **3 .. b** to integration variable ***x***, as follows.

```
> Int(yp, x=3..b) = int(yp, x=3..b);
```

$$\int_3^b\left(\frac{1}{2\sqrt{x}}+2\,a+\frac{9\sqrt{x}}{4}\right)dx=-6\,a-\frac{11\sqrt{3}}{2}+2\,a\,b+\sqrt{b}+\frac{3\,b^{3\,|\,2}}{2} \qquad \textbf{(11.72)}$$

A second derivative of an expression involves a first differentiation of that expression and then a second

differentiation, of the derivative resulting from the preceding differentiation, accomplished by repeating the name of the differentiation variable. As the next command applies differentiation, twice, to the result, assigned to name y, of the first differentiation above, the following result

```
> Diff(yp, x, x) = diff(yp, x, x);
```

$$\frac{\partial^2}{\partial x^2}\left(\frac{1}{2\sqrt{x}}+2a+\frac{9\sqrt{x}}{4}\right)=\frac{3}{8x^{5/2}}-\frac{9}{16x^{3/2}} \tag{11.73}$$

corresponds to a third derivative of the original expression, as we here verify by evaluating the third derivative of the original expression for comparison with the result above.

```
> Diff(sqrt(x) + 2*a*x + 3/2*x^(3/2), x, x, x) = diff(sqrt(x) + 2*a*
  x + 3/2*x^(3/2), x, x, x);
```

$$\frac{\partial^3}{\partial x^3}\left(\sqrt{x}+2ax+\frac{3x^{3/2}}{2}\right)=\frac{3}{8x^{5/2}}-\frac{9}{16x^{3/2}} \tag{11.74}$$

The variable of name *yp* retains the value of the first derivative of the original expression,

$$yp := \frac{1}{2x^{\frac{1}{2}}}+2a+\frac{9x^{\frac{1}{2}}}{4},$$

which is therefore equal to $\frac{\partial}{\partial x}y$.

$$\frac{\partial}{\partial x}y = \frac{1}{2x^{\frac{1}{2}}}+2a+\frac{9x^{\frac{1}{2}}}{4}$$

This equality has the form of a differential equation, for the solution of which *Maple* provides a particular operator **dsolve(yq(*x*), *x*)**, but that operator expects the dependence of the dependent variable on the independent variable to be stated explicitly, in this case as $yq(x)$ so that this name has no preceding value; for this reason we rewrite that differential equation accordingly.

$$\frac{d}{dx}yq(x) = \frac{1}{2x^{\frac{1}{2}}}+2a+\frac{9x^{\frac{1}{2}}}{4}$$

We assign that differential equation to a name **deq**.

```
> deq := diff(yq(x),x) = 1/(2*x^(1/2)) + 2*a + 9/4*x^(1/2);
```

$$deq := \frac{d}{dx}yq(x)=\frac{1}{2\sqrt{x}}+2a+\frac{9\sqrt{x}}{4} \tag{11.75}$$

We expand this differential equation after solution,

```
> expand(dsolve(deq, yq(x)));
```

$$yq(x)=\frac{3x^{3/2}}{2}+\sqrt{x}+2ax+\_C1 \tag{11.76}$$

to ensure that it has the same form as the original expression; we notice, however, that there exists an

additional term, *_C1*, which serves as the constant of integration for the corresponding integral. *Maple* refrains from specifying such a constant of integration in output from an indefinite integral, despite its appropriateness in such a location, but, for a differential equation, presents that quantity equivalent to a constant of integration unless a condition is provided that allows its evaluation.

Much description and explanation of differential infinitesimal calculus of a single variable appears in chapter 3, of the corresponding integral infinitesimal calculus in chapter 4, of both differential and integral calculus of functions of multiple variables in chaper 5, and of differential and integral equations in chapter 7. We include here no sample of operations of linear algebra, treated at length in chapter 6 on matrix, vector, eigenvector and eigenvalue, spreadsheet and related topics, but, for somebody who might have great haste to apply the corresponding commands, there is no particular impediment in proceeding from chapter 2 to chapter 6 if sufficient concentration be applied, or even -- with even greater resolve -- from this terse summary directly to chapter 6.

Before those chapters be reached in a systematic and orderly progression through this electronic textbook, part I, the common commands here summarized might be useful for applications beyond this course of mathematics, but we caution the user that there is a distinct possibility that the results of such operations might be those neither intended nor sought, because the user, at this stage, might lack both the knowledge of the mathematics and the experience to apply the software in a reliable manner.

summary of chapter 0

After these few samples of what software for symbolic computation and associated operations can accomplish, we proceed, in eight succeeding chapters within part I, to introduce systematically both the important mathematical concepts and principles and the corresponding commands and operations in *Maple* that we require to undertake significant chemical applications, such as those for which we deploy mathematical methods in part II. The mere sample of some common commands and operations in section 0.21 that concludes this chapter is intended not to guide a user to undertake confidently those operations but only to demonstrate the possibilities; a user should avoid implementing those, or any other, commands without either consulting menu `Help` on the properties of each particular item and option or progressing through the ensuing text to the appropriate explanation provided therein.

After six decades of intensive development, software for symbolic computation has achieved an astonishing performance and power, matching the enormous development of the hardware on which it operates; though not lacking in minor deficiencies, *Maple* in particular offers incomparable resources to solve problems of a mathematical, or mathematically expressible, nature to enhance the capability of a chemist, or of a scientist and engineer in general, to accomplish practically all technical aspects of his or her professional tasks. Even the content of the next eight chapters is far from a comprehensive survey of the total extent of commands and operators that *Maple* offers, but anybody who has achieved a reasonably firm knowledge of these chapters is likely to find that he or she possesses a capability to develop effective solutions to almost all mathematically expressible problems for which formal, algebraic, numeric and graphical methods might be applicable separately or in combination. A prime objective of the use of software for symbolic computation is to enable a user to concentrate on formulating the mathematical problem, rather than to be concerned with tedious details of its solution according to a well defined formulation: a substantial knowledge of both the mathematical principles and their implementation with software is a requisite for this purpose.