Mathematics and Chemistry

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> No human investigation can be called true science which has not passed through mathematical demonstrations.
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> – Leonardo da Vinci

> The great book of nature is written in the mathematical language, ... without whose help it is impossible to comprehend a single word of it.
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> – Galileo

> I believe that one may ascribe to every study of nature only so much scientific character as it contains mathematics.
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> – Immanuel Kant

The chemistry world encompasses the discovery of molecules to the atoms that occur in nature. There are 92 naturally occurring types of atoms that elements come in, where the atoms differ in their atomic weight. Since the beginnings of chemistry, mathematics was used to create quantitative and qualitative (non-numerical) models for helping to know the world of chemistry by understanding the elements that make up molecules. Numbers have been used to understand the structure of these elements and to classify them into families with similar kinds of chemical properties. This leads to the idea of the periodic table - to try to organize the elements into "clusters" which have similar properties, and then use this information to understand the properties of these elements.

An atom is made up of particles which are known as protons, neutrons, and electrons. The big issue is the measurement of these tiny sub atomic particles. Protons, neutrons, and electrons have mass and they have electrical charge (or are electrically neutral), and mass and charge can be measured. Relationships between the mass and charge of atomic particles helped chemists get

insight into the nature of atoms and the molecules these atoms can form. Mathematics is an essential and integral component of all of the scientific disciplines, and its applications within chemistry are numerous and widespread. Mathematics allows a chemist to understand a range of important concepts, model physical scenarios, and solve problems. Chemists, also follow patterns just like mathematicians do to find a result.

Chemistry is a rich and complex science, exhibiting a diversity of reproducible and precisely describable predictions. Many predictions are quantitative numerical predictions and also many are of a qualitative nature, though both are susceptible to sophisticated mathematical formalization. People have encountered the use of the use of mathematics within chemistry in the early stage of chemistry learning, for example the use of ratios in mixing solutions and making dilutions or the use of logarithms in understanding the pH scale. As moving to higher studies it has been seen that mathematics has increasingly been used to explain chemistry concepts in more sophisticated ways, for example the use of vectors in understanding the structures of crystals, or numerical approximations of ordinary differential equations (ODEs) in kinetics to predict the rates and mechanisms of chemical reactions. The mathematics may be from any of many diverse mathematical areas, and some areas of mathematics such as ordinary differential equations; partial differential equations; group theory Lie algebras; combinatorics; graph theory; the theory of partially ordered sets and lattices; linear algebra and matrix theory; probability theory and statistics; might naturally prove more fruitful for chemistry.

The ability to understand and apply mathematics will be important regardless of the branch of chemistry one is studying, be it the more traditional areas of inorganic, organic and physical chemistry or some of the newer areas of the subject such as biochemistry, analytical and environmental chemistry. The relations of mathematical chemistry to the different fields of chemistry and especially to physical chemistry and chemical physics bear further examination. But these relations have much to do with broad historical trends of development not only in chemistry, but also in physics and in mathematics.

We now look at some of the different ways in which mathematics is used in chemistry.

Balancing

One interaction of mathematics and chemistry that is so familiar now that it is taken for granted, is the way certain quantities are balanced or preserved when a chemical reaction occurs. In a chemical reaction the masses of the inputs to the reaction must be the same as the masses of the products produced by the reaction.

A good example of the complex ways mathematics helps one to understand chemical issues is the recent concern with rising levels of carbon dioxide in the atmosphere, and the pollution that comes from using coal as a source of energy. One way to deal with the issue of the negative aspects of burning coal is to use more natural gas, whenever possible, as a source of energy. One of the major components of natural gas is methane. Methane is an example of a hydrocarbon, a molecule

made up of hydrogen and carbon atoms. Methane when ignited undergoes a chemical reaction that releases energy. The energy is in part stored in the bonds that keep the molecule from separating into the components that make up methane - the hydrogen and carbon atoms.

$$1CH_4 + 2O_2 \longrightarrow 1CO_2 + 2H_2O$$

In the above chemical reaction, if one knows that methane and oxygen mix to produce carbon dioxide and water, the question is how much of each of the "reagents" are involved? Where do the coefficient numbers shown for the chemical reaction above, the $1, 2, 1, 2$ respectively, come from?

It turns out that one can use ideas from the algebra learned in high school (or in a linear algebra class) to use systems of linear equations to "balance" chemical reactions in this spirit. The idea is to introduce letters for the molecules involved and then to use chemical principles for producing these equations. For example, in the equation above we have four molecules CH_4, O_2, CO_2, and H_2O. Suppose we use the letters x, y, z, w for the numbers of these molecules, respectively. We can then deduce relationships between the values of x, y, z and w. Since C (carbon) appears on the left and right of the "equation" we can say that $x = z$. What about O (oxygen)? We have $2y = 2z + w$ because there are two oxygen atoms on the left, and two atoms in the carbon dioxide and one in the water. Finally, for Hydrogen (H), we have $4x = 2w$. Notice here we have more "unknowns" than equations and if there is a way to balance this reaction we will need to use nonnegative integers as the values for x, y and z.

Graph theory in chemistry

The value of graph theory to chemistry started to become apparent in the 19th century. Work by two British mathematicians, Arthur Cayley and James Joseph Sylvester, laid the ground for a long tradition of successful use of graph theoretical ideas in chemistry. It was Sylvester that we have to thank for introducing this second sense of the word "graph".

It is Cayley's work in using what are today called graphs in chemistry that is quite significant in terms of what he accomplished and what it inspired people, who followed him to do. Cayley, pioneer that he was here, had to develop his own terminology. He used the terms plerograms and kenograms for the two kinds of graphs that one might consider when studying hydrocarbons which are trees (graphs in one piece, with no circuits) when drawn as graphs. The plerogram would show all of the atoms of the molecule involved, hydrogen as well as carbon atoms. The kenogram would show only the carbon atoms.

Spectroscopy

Spectroscopic theory with a strong mathematical flavor developed enormously during the 20th century, with foundational work on rotational, vibrational, and electronic spectra, as well as molecular excitonic spectra, electron-spin resonance, and nuclear magnetic resonance. The Nobel prize to G. Herzberg was for (implicitly mathematical) deductions from electronic spectra of features

of electronic potential curves or surfaces. With the availability of suitable high-performance electronics, there has further followed mathematical (and experimental) development of general Fourier-transform, multi-photon, nonlinear, and multi-dimensional spectroscopies (which indeed have garnered a Nobel prize). Further there are different (e.g., mass) spectroscopies based on other than electromagnetic waves. Various important applications of mathematics to chemistry involve spectra. When a molecule transfers from one energy state to another, some "mark" of the molecule can be determined, i.e. different molecules can be identified because the measurements in energy changes are characteristic of specific molecules.

This work involves the idea of eigenvalues of matrices (array or table of numbers) and other topics in linear algebra and operator theory. One goal of this work is to be able to see what molecules are present in different parts of the visible universe. Molecules of different kinds far away from Earth can be determined by a technique called spectroscopy. Mathematics has played a big role in helping with spectroscopy.

Quantum mechanics

Quantum mechanics has proved to be exceedingly successful in understanding the physical world. Chemistry, as much as physics, has benefited from insights from quantum mechanics, and mathematics plays an important role in quantum mechanics.

Thermodynamics

Foundational equilibrium thermodynamics was begun long ago in a mathematical mode, e.g., by A. Avogadro and H.L. Le Chatelier and most especially by R. Clausius, then also by J.H. van 't Hoff, W. Ostwald, S. Arrhenius, J.W. Gibbs, W. Nernst, F. Haber, and G.N. Lewis. This early work received several Nobel prizes.

Statistical mechanics

Equilibrium statistical mechanics was also begun a little over a century ago by Gibbs and many others (often physicists, like Maxwell and Boltzmann), all in a highly mathematical mode. Later (mathematical) developments arise with J. Mayer's and others graphical cluster expansions for statistical-mechanical thermodynamic properties, with E. Montroll's powerful transfer-matrix methodology for the solution of partition functions.

Electrochemistry

In the field of electrochemistry different notable Scientist like H. Davy, M. Faraday and G. Kirchhoff have developed many theories using mathematical ideas. (Especially Kirchoff's work is accepted as mathematical, while the mathematically uneducated Faraday ended up founding 'field theory'.) More recent mathematical contributions are encountered with P. W. Debye and E. Hückel in their theory of ionic solutions (and activity coefficients), or with R. M. Fuoss and L. Onsager and others in the theory of conduction in ionic solutions, or with R. Marcus in his Nobel-Prize winning

work on structure-mediated charge transfer.

Crystallography

Mathematical crystallography developed classically with the identification of the Bravais lattices and crystal classes, followed by the seminal identification of crystallographic space groups by Schoenflies and Fedorov. An especially nice (and extremely useful) pure mathematical development is that of J. Karle and P. Hauptmann (who shared a Nobel prize for their joint work on the inversion of x-ray scattering data to crystal structures.

Diffractive methods include both electron and x-ray diffraction methodologies, and in application to crystals has much overlap with mathematical crystallography. There is mathematical work on molecular excitons, on Burdett's characterizations of band structure, and on yet other notable aspects of solid-state theory.

The main fundamental mathematical equation of X-ray crystallography is the Bragg's equation

$$2d \sin \theta = n\lambda,$$

where n is an integer determined by the order given, λ is the wavelength of x-rays, and moving electrons, protons and neutrons, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of scattering angle. Applying Bragg's law, each dot (or reflection) in the diffraction pattern above forms from the constructive interference of X-rays passing through a crystal. The data can be used to determine the crystal's atomic structure.

Stereochemistry

The stereochemistry area includes Pauling's fundamental molecular geometric hybridization rules, informative analyses of inversions or internal rotations or pseudorotations (as in cyclopentane), and Lipscomb's Nobel-prize winning work as well as that of others treating boranes (as a prototypical case manifesting the effects of non-classical bonding) and related novel structures. Also, there is continuing work with isomers, with molecular geometry characterization, with the Ruch-Schönhofer chirality characterization, with degrees of achirality and asymmetry, with extensions of chirality characterizations, with molecular shape, and with molecular knottedness.

Polymer statistics

Polymer statistics concerns the conformation-mediated and structure mediated properties of polymers (especially high polymers), with foundational mathematical chemical (Nobel-prize-winning) work both by P. J. Flory and by P. G. DeGennes, particularly as to the manner of polymer size-scaling as a function of their length, and other control parameters. Monte-Carlo methods have been developed and have proved useful. But there are many further mathematical approaches. Also,

the field has further blossomed with the development of dendrimers, supramolecular structures, and other large-scale morphological characterizations.

Nanotechnology

Recently, chemical nanotechnology has emerged as an interesting and greatly promising separate field, following the development of carbon nanotubes and focused on organic syntheses of novel interconnected nanostructures; there being notable theoretical work and different mathematically oriented articles, some concerning general theory. As examples for particular nanostructures, there are considerations of nanoknots, nano-links, nanotubes, their caps, nano-tori, nano-cones, nanobelts, Möbius nano-strips, and various negatively curved structures, and yet further there are more elaborate molecular devices, such as molecular motors. Most recently there is incredible activity (with reviews) concerning graphene (including a Nobel prize).

The application mathematics in the field of chemistry is broad with a long and incredibly rich history of over a century of developments. It is emphasized that mathematics is an integral part of fundamental science in general, and chemistry in particular, so that a subdiscipline such as mathematical chemistry is naturally anticipated – or perhaps even demanded. Reflecting chemistry as a whole, it is not surprising that the field is rich and diverse. Mathematical and theoretical chemistry are seen to be at the foundation of the science of chemistry A substantial part of mathematical chemistry has been embedded in physical chemistry (where the connection to physics rather than mathematics has been emphasized), and other substantial portions of mathematical chemistry have been embedded in chemical structure, notation, and concepts – where often the nonnumerical and non-geometrical nature of the relevant mathematics has led many to view such ideas as non-mathematical. Mathematical chemistry is seen to contact all 'classical' chemical fields: inorganic, organic, analytical, biochemical, and physical. Evidently some areas of mathematical chemistry have much contact with chemical physics, physics, mathematical physics, or even with biology or mathematical biology. Indeed, the appearance of mathematical chemistry in different chemical fields, the general relevance of mathematical chemistry is well recognized in terms of the numerous examples of associated Nobel prizes awarded. Those who contribute to chemistry have training in chemistry, they can still put to use the mathematics they learn in support of their research into chemistry. However, it is also true that people who start as mathematics majors can become very distinguished research chemists. One dramatic example is the career of Herbert Hauptman, who started out as a mathematics major (at City College in New York) but eventually went on to win the Nobel Prize in Chemistry.