

## ESSENTIALS OF MATHEMATICS IN TEACHING CHEMISTRY

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**Abstract:** In this paper, mathematical skills necessary for understanding the subject of chemistry are described, which are believed to enhance the pedagogy of chemistry course and build confidence of students in the justifications of the subject matter. The features of some frequently used mathematical applications in chemistry, addressed in this article are: (i) Numbers and Dimensions; the different classes of numbers and relations between physical quantities based on dimensional analysis are described (ii) Variables, Functions and their applications in chemistry are discussed (iii) Differential Calculus and Ordinary Differential Equations and Partial differentiation and their applications in chemistry are described. (iv) The application of integration in chemistry is discussed. (v) Series Expansions of Functions and its applications for the solutions of integrals and linear differential equations are described. (vi) The method of Determinants and Matrices and their utility in chemical applications are illustrated. The choice of material presented in this article has been evolved from teaching a course “Mathematics for chemists” for the last fifteen years to the M.Sc. chemistry students in the University of Peshawar, Pakistan. The emphasis in the paper is on the application of mathematical skills rather than on the proving of theorems. Mathematical techniques are illustrated with chemical examples taken from the referred texts. It has been our experience that the knowledge of mathematical skills in chemistry greatly

enhances the student's learning and understanding of the material in the texts and also increases their research capability i.e. in the analysis and presentation of their experimental data.

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**Introduction:** With the advancement of science and technology, focus of chemical research has changed thereby affecting the topics covered in a modern chemistry course. The interaction between different science subjects has been increased. The need of knowing related subjects has enhanced due to the many fold applications of chemistry. Chemistry is sister to all the subjects of natural science and is also an important subject in medical and in engineering sciences. Due to its widespread applications and complexity of the problems, it has involved mathematics as main partner in achieving its goals. Taking the mathematics as a tool many complicated problems are solved and the results are obtained in a simple but logical way which otherwise would have been very difficult<sup>10</sup>. A report in *Science*<sup>1</sup> concerning a novel use of macromolecules, suggests that we may soon be experiencing a dramatic reversal in the traditional role played by chemistry and mathematics. It further speculates that where as in the past chemists with intractable numerical problems have usually had to defer to those with superior mathematical skills, in the future it seems that just the opposite may be occurring. Mathematicians could be looking to chemists to solve a whole range of problems that even mathematicians themselves admit are exceedingly difficult to solve.

Although chemistry is difficult with mathematics but it is impossible without it. Let us admit that mathematics has seldom been popular among chemists in general. The physical chemistry in particular, that provides theoretical basis for the chemical reactions to occur use mathematics as a tool for description. In my years of teaching chemistry, I have found it helpful to review mathematical topics before using them to explain chemical concepts to students. The students face problems in learning chemistry mostly because they in their undergraduate courses opt chemistry as a major without mathematics in combination. As a result the staff admitted in the postgraduate chemistry department has less than 1% of the students who are acquainted with mathematical skills. An attempt is made in this article to present some mathematical methods, the need for which arise in teaching chemistry, which enhances the students pedagogy, understanding of the subject and in building confidence. Some of the topics of equal importance like Symmetry and Group theory, Coordinates System, Probability and Statistics, which though are not covered in this article, are also extensively applied in chemistry. I may suggest that a course that cover the topics given in this article and also the few mentioned above may be made essential for all those who chose chemistry as their carrier subject and particularly to those who have not opted for mathematics in their undergraduate studies.

**Need of Mathematics for Teaching Chemistry:** Students of chemistry have, in general, a more limited mathematical background than physics or engineering students. Teaching mathematical applications in chemistry at the graduate/undergraduate level enables the students to comprehend the advanced chemistry courses like those of quantum mechanics, statistical mechanics, mechanics of molecules, thermodynamics, chemical kinetics, chemical equilibrium, surface phenomena, electrochemistry, spectroscopy, polymer chemistry, gases, liquids, solid state

chemistry, decay and radiation processes, etc. etc. We admit 120 students in the chemistry department each year in M.Sc. previous class, and equal number in the final M.Sc. final class. Some of these students enroll in the M.Phil/Ph.D program of the department. Both theory and experimental work is extensively involved in chemistry. The theory courses in particular the physical chemistry, analytical chemistry, inorganic chemistry and environmental chemistry use different levels of mathematics for description of the subject matter. The physical chemistry paper in the exam has compulsory questions from applications of mathematical in chemistry.

Experimental work/research, need preparation of standard solutions, solution speciation, instrumentation, data collection, plotting of the data and graphs according to certain equation related to the study. Often slope and intercept are obtained from the linear graph which are then used to calculate other parameters related to the study. For example rate constant of a kinetic reaction obtained from the slope are then used in the Arrhenius equation to evaluate the activation energy, the value of which is then used for computing enthalpy, entropy and Gibb's free energy of the reaction. Similarly data of an equilibrium reaction can be manipulated.

Students need to learn mathematics as a tool for the completion of both theoretical and experimental work. In a situation when less than 1% of the students with mathematics background can learn and understand the subject matter and for the rest it is hard to patch with, the need of teaching mathematics become evident. Some times the students do not have the idea of imaginary numbers, complex numbers or complex conjugates and they are almost ignorant of rules of differentiation and integration. They know that  $\ln x = 2.303 \log x$ , but they do not give satisfactory answer for why multiply with 2.303 for the conversion. Let us consider another simple example of the evaluation of thermal energies of a mole of gas molecules, in order to understand the need of mathematics in teaching chemistry. The derived equation for thermal energy is  $E - E_0 = \frac{RT}{q} \times \frac{dq}{dt}$ , where  $q$  is called partition function which is by definition the

summation in the denominator of the Boltzmann distribution equation and is given by

$q = \prod_i g_i e^{-(\epsilon_i - \epsilon_0)/kT}$ . The equations of  $q$  and  $dq/dt$  for translation, rotation and vibration types of energies are needed to be inserted in the thermal energy expression. Following table shows the expressions and indicates the operations needed to get the result. Differentiation and integration both are used.

Table-1. Calculation of thermal energy of gas molecules.

Energy type	Partition function	Thermal energy
$\epsilon_{trans} = \frac{n^2 h^2}{8ma^2}$	$q_x = \int_0^a e^{-\frac{n_x^2 h^2}{8ma^2 kT}} dn_x = \sqrt{\frac{2\pi ma^2 kT}{h^2}}$	$(E - E_0)_{trans} = \frac{3}{2} RT$
$\epsilon_{rot} = J(J+1) \frac{h^2}{8p^2 I}$	$q_{rot} = 2 \int_0^\infty J e^{-\frac{J^2 h^2}{8p^2 I kT}} dJ = \frac{8p^2 I kT}{h^2}$	$(E - E_0)_{rot} = RT$
$\epsilon_{vib} = (v + \frac{1}{2}) h\nu$	$q_{vib} = \sum_{v=0}^\infty e^{-\frac{[(v+\frac{1}{2})h\nu - \frac{1}{2}h\nu]}{kT}}$ $= 1 + e^{-\frac{h\nu}{kT}} + e^{-\frac{2h\nu}{kT}} + \dots = \frac{1}{1 - e^{-\frac{h\nu}{kT}}}$	$(E - E_0)_{vib} = \frac{RT (\frac{h\nu}{kT})}{e^{\frac{h\nu}{kT}} - 1}$

**Numbers and Dimensions:** A young child learns and grasps early the concept of numbers that we call positive integers and zero. In the elementary school he learns addition, subtraction and division of integers. Then he learns fractions like  $n/m$ . The collection of all the numbers that can be written as  $n/m$ , where  $n$  and  $m$  are integers (excluding  $m = 0$ ), is called the **rational number system** since it is based on the ratio of whole numbers. The rationales include both fractions and whole numbers. Later in the student's early teens, **irrational numbers** are learned. These numbers come from two sources: algebraic equations with exponents, for example, the quadratic  $x^2 = 2$ ; and geometry, like the ratio of the circumference to the diameter of a circle,  $\pi$ . For  $x^2 = 2$ ,

the unknown  $x$  is neither a whole number nor a fraction, but is a decimal expression 1.41421356... up to infinite decimal places<sup>2</sup>, the digits do not display a repetitive pattern. The rationales are thus supplemented by Irrational numbers, i.e. the numbers that are represented by infinite non repeating decimals. The totality of these two kinds of numbers is known as the **real number system**. The student faces a new complication when he comes to solution of the equation of the form  $x^2 = -2$ , or  $x^2 = -1$ . He knows that no real number times itself will yield a negative real number. To cope with the dilemma, a larger system of numbers the **complex number system** - which has both real and imaginary parts, is usually presented in high school. The solution of the problem that he gets is  $x = \sqrt{-2} = 2\sqrt{-1}$ ,  $x = \sqrt{-1}$ . The result that obtained is not real number so obviously we call it an **imaginary number**. The number  $\sqrt{-1}$  is represented by,  $i$  (iota). Now a number  $z = a + ib$  has ' $a$ ' and ' $b$ ' which represent real numbers and  $i = \sqrt{-1}$  is imaginary. We say that the number ' $z$ ' has a real part ' $a$ ' and imaginary part ' $b$ '. Note that both the real and imaginary parts of complex number have real numbers. Two complex numbers are said to be equal if, and only if, the real part of one equals the real part of the other and the imaginary part of one equals the imaginary part of the other. That is, if  $z = a + ib$ ,  $w = c + id$  and  $z = w$ , then  $a = c$ ,  $b = d$ . A pair of complex numbers are said to be conjugate of each other if they have identical real parts and identical imaginary parts except the imaginary part being opposite in sign. Thus if  $z = a + ib$  then  $z^* = a - ib$ . and it is important to note that  $zz^* = a^2 + b^2$ , which is always a positive number. The quantity  $|z| = \sqrt{zz^*}$  is known as absolute value of  $z$ , which is always positive and real. In quantum chemistry the probability of finding a particle in an area of space is given by  $\psi\psi^*$  where  $\psi$  is wave function and  $\psi^*$  is its complex conjugate. The

$|\psi|$ , is both positive and real. The wave function  $\psi$  is thus called a “well behaved function” in quantum chemistry. For considering electron motion around nucleus we need polar coordinates. A useful relation called Euler formula provides a link between exponential and trigonometric function;  $e^{i\theta} = \cos\theta + i\sin\theta$ , which is used in finding probability of electron around nucleus.

Measurement is the essence of science. Without exact quantitative measurements no fact or law can be established in science. Every quantity has a magnitude and a scale or unit of measurement. Since 1960 an international system of units “**SI**” units has been adopted which uses decimals for measuring physical quantities. This is also called **MKS system**, which represents length in meters, mass in kilogram and time in seconds having symbols as ‘m’, ‘kg’, and ‘s’ respectively. These fundamental units are used to define the **derived units** in chemistry. As the unit of length is meter (m), so the unit of volume will be  $V = m \times m \times m = m^3$  (cubic meters). Density is  $\rho = \text{mass/volume} = \text{kg/m}^3 = \text{kg} \cdot \text{m}^{-3}$ , concentration = number of moles/volume =  $\text{mol/l} = \text{mol/dm}^3 = \text{mol dm}^{-3}$ . Dimensional analysis is a method of checking and predicting relations between physical quantities and is based simply on the principle that the dimensions must balance in an equation. Take for example the units of ideal gas constant R, defined by the relation  $R = PV/nT$ . If pressure is in atmosphere (atm.), volume in  $\text{dm}^3$  (or liters) and temperature in Kelvin (K) and n in moles (mol), then  $R = 0.0825 \text{ liter atm mol}^{-1} \text{ K}^{-1}$ . If we need to use SI units instead then we make use of the conversion factors:  $1 \text{ atm} = 101325 \text{ Nm}^{-2}$ ,  $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$ ,  $1 \text{ J} = 1 \text{ Nm}$ , so R in the derived units will be  $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$  which is expressed in the energy units.

Numbers, dimensions and units are needed to every chemistry student for understanding and learning of general chemistry and in the quantitative chemical analysis. The topics of fundamental interest may include, measurement of temperature in different scales, weight, length, area, volume, density, gas laws calculations, molecular weights determination (from: formula, gram molecular weight, lowering of freezing point, elevation of boiling point, osmotic pressure), law of combining weights, determination of atomic weights (from: chemical analysis, equivalent weight), percentage composition, calculation of formula, calculations based on chemical equations, calculations involved in preparation of standard solutions (normality and molarity), law of mass action, ionic product of water, solubility product, specific heat, heat of fusion and vaporization, heat of reaction and Faraday's laws of electrolysis, etc. It is observed that if the concept of students regarding numbers, units of dimensions and the significant figures are clear then they feel confident in learning and understanding the subject matter in the texts and similarly in performing the laboratory work.

**Variables, Functions and their Graphs:** Experiments in chemistry deal with variable parameters. Some fundamental constants<sup>(3)</sup> involved in calculations are always available in the chemistry texts. When one variable "x" changes (independent variable) producing a change in another variable "y"(dependent variable) during the experiment then we say that "y" is a function of "x", represented mathematically as  $y = f(x)$ . A chemist then looks at the best way to express the relationship between these parameters. He has a choice of several types of different functions both **algebraic** and **transcendental**, for expressing results in the form of an equation. The equation is then plotted on a graph paper to show the trends of variation in the data. The simplest function that gives a linear graph is called

**linear function.** From the graph of the linear function, the intercept i.e. the value of  $y$  when  $x = 0$ , and the slope of the line is obtained. Slope =  $\frac{dy}{dx}$ , is equal to tangent of the angle  $\theta$  between the graph line and the  $x$ -axis. Values of slope and intercept are then interpreted to get quantitative predictions about the chemical process. Whenever an agreement between experimental data and theoretical values are tested a straight-line graph is preferred. Many equations, which are not, originally in the form of straight line are manipulated in to straight-line equation before scaling the graph. For instance the Freundlich adsorption isotherm is expressed as:  $\frac{x}{m} = kp^{\frac{1}{n}}$ , where  $\frac{x}{m}$  is the amount of gas adsorbed per unit mass of adsorbent  $p$  is the equilibrium pressure of the gas and  $k$  and  $n$  are arbitrary constants. Plot of this equation will not give straight line but the logarithmic form of it i.e,  $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$ , give a straight line graph, with slope =  $\frac{x}{m}$  and intercept =  $\log k$ . Let us take another example, the kinetic expression for first order reaction is given by  $k = \frac{2.303}{t} \log \frac{a}{a-x}$  which is not in the form of straight line and is difficult to plot. It may be rearranged as  $\log \frac{a}{a-x} = \frac{kt}{2.303}$  or  $\log(a-x) = -\frac{kt}{2.303} + \log a$ . The plot of  $\log(a-x)$  vs  $t$  will give a straight line with a slope =  $\frac{k}{2.303}$  and intercept =  $\log a$ . Thus we find from the slope the value of rate constant 'k' and from intercept the initial concentration  $a$ . Besides linear functions other algebraic functions important in chemistry are: (i) *Quadratic function*; equation of the form  $y = ax^2 + bx + c$  is called quadratic function. If there are real values of  $x$  for which  $ax^2 + bx + c = 0$ , the curve will intersect the  $x$  axis at the value of  $x$  given by the formula  $x = -b \pm \frac{\sqrt{b^2 - 4ac}}{2a}$ . For example the equilibrium constant for the dissociation of a salt is given by the formula  $\frac{K}{c} = \frac{\alpha^2}{(1-\alpha)}$ .

On rearranging it gives  $\alpha^2 + \frac{K\alpha}{c} - \frac{K}{c} = 0$ , which is in the form of quadratic equation where

$a = 1$ ,  $b = \frac{K}{c}$  and  $c = -\frac{K}{c}$ . So  $\alpha = \frac{K}{c} \pm \sqrt{\frac{K^2 + 4K}{c^2}}$ . (ii) *Single-valued function*; like wave

functions ( $\psi$ ) in quantum mechanics which are *eigen* functions having single values. (iii)

*Many-valued function*, like  $y^2 = x$ , where there are two values of  $y$ , i.e.

$+\sqrt{x}$  and  $-\sqrt{x}$  or  $\pm\sqrt{x}$  for each value of  $x$ . (iii) *Functions of many variables*; a function

that depend on more than one variable is said to be of many variables, for example for the

Ideal gas  $P = \frac{nRT}{V}$ , where pressure depends on three variables  $V$ ,  $T$  and  $n$  for a gas,

i.e.  $P = f(T, V, n)$ . There are some other important algebraic functions used in chemistry

such as polynomial functions, odd functions, implicit and explicit functions. All the non-

algebraic functions are called *transcendental functions*. They include (i) *logarithmic*

*functions*, (ii) *exponential functions*, (iii) *trigonometric functions*, (iv) *inverse*

*trigonometric functions*, (v) *hyperbolic functions* and (v i) *inverse hyperbolic functions*.

The mathematics dealing with both algebraic and transcendental is important not only for

plotting the graphs but for understanding and learning the derivation of numerous

equations and calculations spread in chemistry texts. In teaching the topics that involve

such equations most of the lecture time is taken by explaining these functions otherwise

the chemistry therein is simple.

**Logarithm** is important in chemistry in many ways. Relations between variables

involved in chemical process are expressed in the form of logarithmic equations. This

makes equation simple and easy to plot on a graph. The concentration and activities of

ionic species in solution are usually expressed in p-scale, which is  $-\log$  of the molar

concentration or activity of the species. pH scale is more familiar to students which is –

$\log [H^+]$ . Both the common logarithm ( $\log_{10}$ ) and natural logarithm ( $\log_e$  or  $\ln$ ) are important. The 'e' represents an irrational number having value 2.71828.... Inter conversion of logarithm is easily done, and it follows the equation;  $\log_{10} x = \frac{\ln x}{\ln 10} = 0.4343 \ln x$ . Logarithms whether natural or common are part of many equations in chemical sciences. Examples that appear in freshman chemistry texts include the equation for pH, the integrated rate equation for the first-order reaction, the relation between standard free energy change and equilibrium constant, the Clausius-Clapeyron equation, Arrhenius equation, and the Nernst equation. With the exception of the equation for pH these examples employ natural logarithms in their derivations. Typically in the last step a conversion to common logarithm is performed. Log. and p-scales are important in all the branches of chemistry, the solution chemist can not work without the tool of these scales. For example the Debye-Huckel equation for the activity coefficient determination and the solution speciation use these scales. For complicated systems commercial speciation software are available for use with computer.

**Differential Calculus and Ordinary Differential Equations:** Transformation of matter and energy are associated with physical and chemical changes. The quantitative relationship between the changes and the rate of change are of concern to chemist. The change is usually represented in science by symbol  $\Delta$  (capital delta), thus  $\Delta x$  means a change in  $x$ . But in chemistry we are concerned with molecular level changes, which are infinitesimal, and such changes are represented by another symbol  $\delta$  (small delta), thus  $\delta x$  means very small change in  $x$ . The chemistry texts also use  $dx$  similar to calculus for small change in  $x$ , which is read as "differential of  $x$ ". When one function 'y' changes with respect to another 'x', then their ratio  $\frac{dy}{dx}$  is called derivative of  $y$  with respect to  $x$ .

Differential calculus uses methods to find  $\frac{dy}{dx}$  in an equation of variable functions. Let us consider two functions  $u$  and  $v$  along with  $y$  being functions of  $x$  and present the simple rules of differentiation applied to the different forms of equations (Table-2). In this table,  $u$  and  $v$  are functions of  $x$  and the values  $n$ ,  $c$  and  $e$  are constants.  $n$  can assume any value except zero,  $c$  can have any value including zero, and  $e$  is equal to 2.71828.... Applications of the rules of differentiation in chemistry, collected from chemistry texts are described by Sayyar<sup>4</sup>. For finding differentiation of function of a function, *Chain Rule* is used.

Table-2: Derivatives of algebraic and trigonometric functions.

EQUATION	DERIVATIVE
$y = c$	$\frac{dy}{dx} = 0$
$y = cu$	$\frac{dy}{dx} = c \frac{du}{dx}$
$y = cu^n$	$\frac{dy}{dx} = cnu^{n-1} \frac{du}{dx}$
$y = u \pm v$	$\frac{dy}{dx} = \frac{du}{dx} \pm \frac{dv}{dx}$
$y = uv$	$\frac{dy}{dx} = u \frac{dv}{dx} + v \frac{du}{dx}$
$y = \frac{u}{v}$	$\frac{dy}{dx} = \frac{v \frac{du}{dx} - u \frac{dv}{dx}}{v^2}$
$y = \sin(u)$	$\frac{dy}{dx} = \cos(u) \frac{du}{dx} = \frac{1}{\sec(u)} \frac{du}{dx}$
$y = \cos(u)$	$\frac{dy}{dx} = -\sin(u) \frac{du}{dx} = -\frac{1}{\csc(u)} \frac{du}{dx}$
$y = \tan(u) = \frac{\sin(u)}{\cos(u)}$	$\frac{dy}{dx} = \frac{1}{\cos^2(u)} \frac{du}{dx} = \sec^2(u) \frac{du}{dx}$
$y = \log_e u$	$\frac{dy}{dx} = \frac{1}{u} \frac{du}{dx}$
$y = \log_a x$	$\frac{dy}{dx} = \frac{1}{u} \log_a e \frac{du}{dx}$
$y = e^u$	$\frac{dy}{dx} = e^u \frac{du}{dx}$
$y = c^u$	$\frac{dy}{dx} = c^u (\log_e c) \frac{du}{dx}$
$y = u^v$	$\frac{dy}{dx} = vu^{v-1} \frac{du}{dx} + u^v \log_e u \frac{dv}{dx}$

*Ordinary differential equations* contain only one independent variable and as a consequence, total derivatives. They represent a relation between dependent variable ( $y$ ), its various derivatives and functions of the independent variable ( $x$ ). The *order* of a differential equation is the order of its highest derivative. If the highest derivative  $\frac{d^n y}{dx^n}$ , occurs in the equation, then the order of equation is  $n$ . The *degree* of the differential equation is the power of the derivative of the highest order in the equation after fractional

powers of all the derivatives have been removed. The derivative  $\left(\frac{dy}{dx}\right)^2$  would be of second degree but first order. Thus the equation  $\frac{d^2y}{dx^2} + \left(\frac{dy}{dx}\right)^2 + xy = 0$  is of the second order and first degree, while  $\frac{d^2y}{dx^2} + \left(\frac{dy}{dx}\right)^{\frac{1}{2}} + xy = 0$  is of second order and second degree. If the dependent variable and all its derivatives occur in the first degree and not multiplying each other, the equation is said to be *linear*. Solution of equation of  $n$ th order involves  $n$  integrations. Since, each integration introduces one arbitrary constant, the final solution for independent variable will contain  $n$  arbitrary constants. However a solution in which one or more of these constants are given specific values, for instance the value zero, will also satisfy the differential equation. In view of this consideration two types of solutions of an ordinary differential equation of  $n$ th order may be distinguished: (i) the *complete* or *general* solution which contains its all of  $n$  independent arbitrary constants; (ii) *particular* solutions, obtainable from the general one, by fixing one or more of the constants. In any chemical problem we generally use the given conditions to determine the arbitrary constants. Since differential equations contain derivatives, their solution essentially involves integration. Calculation of vibrational frequencies and energies of molecules, electron energy states in atoms and wave equation for electron motion involve differential equations. Teaching the differential calculus and methods of solution of differential equations, is important for understanding the logical basis of the results given in the chemistry literature.

**Partial Differentiation:** Partial differentiation and partial differential equations are common in chemistry. When there are more than one independent variables in an experiment and the change in the dependent variable  $y$  is determined simultaneously by

all the variables, then the method of partial differentiation is used to find  $dy$ . In other words it is the method of differentiation of function of several independent variables. The science of thermodynamics is the study of the laws that govern transformation of energy during physical and chemical changes. The quantitative physical variables that characterize the thermodynamic system include pressure, volume, temperature, internal energy and entropy. It is not always possible to vary such quantities at will, but specification of some, results in definite values for others. The method of partial differentiation then becomes appropriate<sup>5</sup>. Consider a function  $u$  of two independent variables  $x$  and  $y$ . The functional notation is  $u = f(x, y)$ . The partial derivative of the variable  $u$  with respect to  $x$  keeping  $y$  constant is  $\left(\frac{\partial u}{\partial x}\right)_y$  and similarly the partial derivative of  $u$  with respect to  $y$  keeping  $x$  constant is  $\left(\frac{\partial u}{\partial y}\right)_x$ . The total differential of  $u$  given by the fundamental theorem of partial differentiation is  $du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy$ .

The partial molal quantity of a thermodynamic system is given by  $G = f(T, P, n_A, n_B, \dots)$ .

Its total derivative is given as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_A, n_B, \dots} dt + \left(\frac{\partial G}{\partial P}\right)_{T, n_A, n_B, \dots} dP + \left(\frac{\partial G}{\partial n_A}\right)_{T, P, n_B, \dots} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, P, n_A, \dots} dn_B + \dots$$

Looking through various chemistry texts (6, 7) it is obvious that students are asked to solve problems that involve partial derivatives early in the course.

Partial differential equations frequently occur in chemistry texts. In the study of structure of atoms and in spectroscopic studies, one uses the wave equations like the Schrödinger equation or the equation for vibrating string, which are the partial differential equations. Making use of the method of separation of variables such equations are solved. In teaching quantum chemistry and chemical thermodynamics, the lecture material mostly is

partial differentiation and the solution of partial differential equations. The importance of it is thus evident, for learning the chemistry in these subjects and understanding the basis of the relationships in the texts.

**Integration:** Integration is a method of summing or adding a sequence of small changes or small parts. It is the reverse of differentiation. Indefinite and definite integral are the two types we find in chemistry texts. When the variable has given limits it is called definite integral and integral without limits is known as indefinite integral. The solutions are simple and some basic rules of integration are given in Table-3.

Table-3. Basic antiderivatives.

$\int dx = x + c$
$\int x^n dx = \frac{1}{n+1} x^{n+1} + c$
$\int x^{-1} dx = \ln x + c$
$\int e^x dx = e^x + c$
$\int e^{ax} dx = \frac{1}{a} e^{ax} + c$
$\int a^x dx = \frac{a^x}{\ln a}$
$\int \ln x dx = x \ln x - x + c$
$\int \log_a x dx = \log_a e(x)(\ln x - 1)$
$\int \cos x dx = \sin x + c$
$\int \sin x dx = -\cos x + c$
$\int \sec^2 x dx = \tan x + c$

In Table-3,  $c$  is the constant of integration, which cancels out in the case of definite integrals,  $\int_a^b y dx = f(b) - f(a)$  and is not written. Examples of application of the methods of integration found in elementary texts are: relation for entropy from its changes in an ideal gas, free energy of ideal gas, integration of Clausius-Clapeyron equation for the calculation of enthalpy change, enthalpy change from variation of the equilibrium constant, calculation of free energy using the Arrhenius equation, solutions of the rate expressions etc. Definite integral is widely used in thermodynamic and kinetic studies of the chemical reactions.

For finding integrals of simple problems, just the rules of integration given in Table-2 are applied, but the complex problems are first brought in a form fit for the application of the rules. Depending upon the nature of the equation the methods used are: algebraic simplification, substitution, integration by parts and integration by partial fractions. These methods provide tools to solve complicated integral equation, found in the chemical kinetics, chemical thermodynamics, quantum chemistry, electrochemistry, surface chemistry, statistical thermodynamics, analytical chemistry, etc. texts. The mechanism of a chemical reaction for example, is determined from the kinetic study of the reaction. Where the rate of reaction, rate constant and the order of reaction are important. Methods of integration are used in the derivation of kinetic expression and for treatment of the experimental data for determining mechanism of the chemical reactions, thus its teaching is important, without which the students will not be able to investigate the reaction and understand its mechanism.

**Mathematical series:** A sum of terms is known as series. If finite terms are present then the series is named as finite series and if infinite terms then it is called infinite series. A

series having increasing powers of a variable is called geometric series. If in the geometric series each of the successive higher power of the variable has a multiplied coefficient then it is a power series. The power series may be finite or infinite depending upon the number of added terms. Power series are used to obtain numerical approximations for the value of an integral that cannot be evaluated in terms of standard

functions. For example given the problem of determining  $\int_0^{0.2} \frac{(e^x-1)}{x} dx$ , the student might first seek, in the tables of integrals, the antiderivatives of  $\frac{(e^x-1)}{x}$ . None will be found.

However an approximate evaluation of the integral can be had by replacing  $e^x$  in the integrand by perhaps the first three terms of the infinite series

$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$ . Having done so, we see that solution of  $\int_0^{0.2} \frac{(e^x-1)}{x} dx$ , is as

easy matter. Power series are also used in the solution of **linear differential equations** in cases where it is possible to express the function by means of a power series. A power

series may be written as  $f(x) = \sum_{n=0}^{\infty} c_n (x-x_0)^n = c_0 + c_1(x-x_0) + c_2(x-x_0)^2 + \dots$ . Here  $c_0$ ,

$c_1$ , etc. are called the coefficients of expansion. As an example of the series application

in solution of linear differential equation we can take the case of finding the possible values of the energy and shape of the corresponding wave functions in the case of Harmonic oscillator, where the method is used for solution of the differential equation<sup>(8)</sup>

$\frac{d^2 H}{d\xi^2} - \frac{2\xi dH}{d\xi} + [(\frac{\alpha}{\beta}) - 1]H = 0$ . Power series method is also needed in solution of differential

equation for finding possible energy and wave functions of electron in hydrogen atom.

This mathematical method is thus also important to be known to chemistry students for

overcoming the difficulties involved in theoretical derivations of some very important expressions.

**Determinants and Matrices:** A *determinant* is an arrangement of quantities or elements  $a_{ij}$  in rows and columns in which the number of rows is equal to the number of columns.

$$\det A = |A| = \begin{vmatrix} a_{11} & a_{12} & a_{13} & \text{L} & a_{1n} \\ a_{21} & a_{22} & a_{23} & \text{L} & a_{2n} \\ a_{31} & a_{32} & a_{33} & \text{L} & a_{3n} \\ \text{M} & \text{M} & \text{M} & & \text{M} \\ a_{n1} & a_{n2} & a_{n3} & \text{L} & a_{nn} \end{vmatrix}$$

The determinant has  $n$  rows and  $n$  columns, and thus  $n$  is the *order* of the determinant. In chemistry applications, the elements of the determinant are numbers or functions (real or complex), the determinant itself will also be a number or function whose value or form is determined by certain combination of its elements. Whenever a determinant such as  $\det A = 0$ , we say the matrix  $A$  is *singular*; otherwise,  $A$  is called *nonsingular*. Students of chemistry should be familiar with the use of determinants in the solution of  $n$  linearly independent equations with  $n$  unknowns.

A *matrix* may be defined as a two-dimensional array of elements that obey a certain set of rules called matrix algebra. The elements may be real or complex, are arranged in rows and columns. Unlike determinants, matrices may be square or rectangular and also a matrix does not have a value. An example of an arbitrary matrix  $A$  is the following.

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \text{L} & a_{1n} \\ a_{21} & a_{22} & a_{23} & \text{L} & a_{2n} \\ a_{31} & a_{32} & a_{33} & \text{L} & a_{3n} \\ \text{M} & \text{M} & \text{M} & & \text{M} \\ a_{n1} & a_{n2} & a_{n3} & \text{L} & a_{nn} \end{bmatrix}$$

Matrix A is said to be an  $m \times n$  matrix, since it has  $m$  rows and  $n$  columns. The general *element* of matrix A is written  $a_{ij}$  where the subscript  $i$  identifies the row and  $j$  identifies the column. When  $n$  and  $m$  are equal then A is called *square* matrix; when  $n = 1$  and  $m > 1$  then A is a *column* matrix.; when  $n > 1$  and  $m = 1$  then A is called a *row* matrix. When the matrix has  $m \neq n \neq 1$ , then the matrix is called rectangular matrix.

Introduction to the concept of a matrix and matrix algebra enables the students to find solution of simultaneous equations in a more systematic way and to express the result more compactly. Matrices are also used to describe transformations from one coordinate system to another. Familiarity with the matrix method is essential for the application of the symmetry and group theoretical methods, to the molecular problems.

#### References:

- 1 ADLEMAN, L. M., (1994). *Science*, 266: 1021; GIFFORD, D.K., (1994). *Science*, 266, 993.
- 2 BOYER, C. B. (1985). A history of mathematics. Princeton University Press, Princeton, Chapter 25.
3. J. Phys. Chem. Ref. Data, (1973), 2(4): 741; PILAR, F. L.(1990). Elementary quantum chemistry. 2<sup>nd</sup> ed., McGraw-Hill Pub. Co. New York.
4. SAYYAR MOHAMMAD., (1999). Application of mathematics in chemistry, M.Sc thesis, University of Peshawar.
5. BLINDER, S. M., (1966), Mathematical methods in elementary thermodynamics. *Journal of Chemical Education*, 43 (2): 85-92

6. ATKINS, P.W.,(1994) Physical chemistry, 5<sup>th</sup> ed., W.H. Freeman. New York.
7. KAUZMANN, W., (1957). Quantum Chemistry. Academic Press, New York. Pp. 203-304.
8. MARGENAU, H., MURPHY, G. M., (1956). The Mathematics of physics and chemistry. D. Van Nostrand Co. New York.
9. MCQUARRI, D. A., SIMON, J.D., (1999) Physical chemistry, a molecular approach. Viva Books Pvt. Ltd. New Delhi.
10. KLEIN. D. J., RANDIC. M. eds., (1990). Mathematical chemistry. Proceedings of the 3<sup>rd</sup> International conference on mathematical chemistry. Galveston, TX (USA). March 1989.