MATHEMATICAL CONCEPTS FOR CHEMISTS

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CONTENTS

Logarithms

A logarithm is an exponent. It is the exponent to which the *base* must be raised to produce a given number.

For example, since

$$2^3 = 8 \qquad 1.1.1$$

3 may be called the logarithm of 8 with base 2.

Thus, $3 = \log_2 8$ 1.1.2

3 is the *exponent* to which 2 must be raised to produce 8.

Thus,

$\log_b x = n$ implies that $b^n = x$. In particular,
$\log_b 1 = 0$ 1.1.3

In any base, the logarithm of the base itself is 1. i.e $\log_a a = 1$

The system of common logarithms has 10 as default base, unless base is specifically implied.

For example, log 100 = 2

One can also find logarithm of a fraction

For example, logarithm of 1/1000 is -3, of 1/100 is -2, of 100 is 2 etc. Logarithm of a number less than 1 is negative. However, logarithm of negative number is not defined, since no power of base (10 for common logarithms) can be negative.

Natural logarithms

The system of natural logarithms has the number called "*e*" as its base. (*e* is named after the 18th century Swiss mathematician, Leonhard Euler.) Base *e* is used in all theoretical work; it the base that is used in calculus.

e is an irrational number, whose decimal value is approximately 2**.**71828182845904.

"ln" is used to denote the natural logarithm.

$\ln(y) = x$ implies $e^x = y$ 1.1.4

Rules of Logarithms

From the above definitions, one can derive the following rules**.**

i). $\log_b (x * y) = \log_b x + \log_b y$ 1.2.1

The logarithm of a product is equal to the sum of the logarithms of each factor.

ii). $\log_b \frac{x}{y} = \log_b x - \log_b y$ 1.2.2

The logarithm of a quotient is equal to the logarithm of the numerator minus the logarithm of the denominator.

iii) $\log_b x^n = n \log_b x$ 1.2.3

The logarithm of a power of x is equal to the exponent of that power times the logarithm of x. These rules are valid for any base.

Factorials

The factorial of a positive integer n is denoted by n! ("n factorial"). By this we mean the product of consecutive numbers 1 through n.

$$n! = 1\cdot 2\cdot 3\cdot \cdot\cdot (n-2)(n-1)n \qquad 2.1.1$$

$$= n(n-1)(n-2)\cdot \cdot\cdot 3\cdot 2\cdot 1 \qquad 2.1.2$$

The order of the factors does not matter, whether backwards or forwards.

0! is defined as 1. The concept of factorial is very useful and is often required in finding permutations and combinations of processes.

We now discuss an important application of factorials in chemistry. The number of valence diagrams for aromatic conjugated systems can be obtained using Wheland's formula.

Valence diagrams $= n!/[(n/2)!((n/2)+1)!] \lim_{x\to 0}$ where n is the number of ***pi*** electrons in conjugated systems. For examples in benzene n=6, thus number of valence diagrams is

$6!/(3!*4!)$ $6!/(3!*4!)$

$= (1*2*3*4*5*6)/(1*2*3)*(1*2*3*4) = (1*2*3*4*5*6)/(1*2*3)*(1*2*3*4)$

$= 5$ $= 5$

For non-integer numbers factorials are obtained using gamma functions.

Permutations

The concept of a permutation expresses the idea that distinguishable objects may be arranged in various different orders. The essential difference between a *permutation* and a set is that the elements of a permutation are arranged in a specified order. In other words, the non-technical definition of permutation is that of a one-to-one correspondence, or bijection, of labeled elements with "positions" or "places" that are arranged in a straight line. In more technical contexts, the elements may not be arranged in a linear order, or indeed in any order at all. There are two fundamental principles of counting:

Addition rule: If an experiment can be performed in 'n' ways and another experiment can be performed in 'm' ways then *either* of the two experiments can be performed in (m+n) ways. This rule can be extended to any finite number of experiments.

Multiplication Rule: If a work can be done in m ways, another work can be done in ‘n’ ways, *both* of the operations can be performed in m x n ways. It can be extended to any finite number of operations.

BY THE PERMUTATIONS of the letters *abc* we mean all of their possible arrangements:

abc acb bac bca cab cba 2.2.1

There are 6 permutations of three different things. As the number of things (letters) increases, their permutations grow astronomically. If something can be chosen, or can happen, in *m* different ways, and, after that has happened, something else can be chosen in *n* different ways, then the total number of ways of choosing both of them is $m \cdot n$.

Number of permutations of n different things, taken r at a time, is given by $^nP_r = n!/(n-r)!$

Proof: Say we have ‘n’ different things $a_1, a_2 \ldots\ldots, a_n$. There are r number of places to be filled up.

Clearly the first place can be filled up in ‘n’ ways. Number of things left after filling-up the first place is (n-1)

So the second-place can be filled-up in (n-1) ways. Now number of things left after filling-up the first an

second places = n - 2

Now the third place can be filled-up in (n-2) ways.. Thus, Number of ways of

filling-up r places =: n (n-1) (n-2) ------------ (n-r+1)

Hence:

^nP_r = n (n-1)(n-2) --------------(n-r+1)

= [n(n-1)(n-2)----------(n-r+1)] [(n-r)(n-r-1)-----3.2.1.] / [(n-r)(n-r-1)] ----3.2.1

$$^nP_r = n!/(n-r)! \qquad 2.2.2$$

Number of permutations of ‘n’ different things taken all at a time is given by:- $^nP_n = n!$

Corollary to this is the following:

The number of permutations of n different things taken n at a time is n!.

$^nP_n = n! /(n-n)!$

$= n! / 0!$

$= n!/1$

$=n!$

2.2.3

$^{n}P_{n}$ is the number of permutations of n different things taken n at a time -- it is the total number of permutations of n things: n!

By definition **0! = 1**

Number of permutations of n-thing, taken all at a time, in which 'p' are of one type, 'g' of them are of second-type, 'r' of them are of third-type, and rest are all different is given by :-

$n!/p! \bullet q! \bullet r!$

Number of permutations of n-things, taken 'r' at a time when each thing can be repeated r-times is given by $= n^r$.

Proof.

Number of ways of filling-up first –place $= n$

Since repetition is allowed, so number of ways of filling-up second-place is also n.

Hence total number of ways in which first, second ----r th, places can be filled-up

$= n \bullet n \bullet n$ ------------- r factors.

$= n^r$

Restricted Permutations

(a) Number of permutations of 'n' things, taken 'r' at a time, when a particular thing is to be always included in each arrangement $= r\ ^{n-1}P_{r-1}$

(b) Number of permutations of 'n' things, taken 'r' at a time, when a particular thing is fixed: $= {}^{n-1}P_{r-1}$

(c) Number of permutations of 'n' things, taken 'r' at a time, when a particular thing is never taken: $= {}^{n-1}P_{r.}$

(d) Number of permutations of 'n' things, taken 'r' at a time, when 'm' specified things always come together $= m! \bullet (n-m+1)!$

(e) Number of permutations of 'n' things, taken all at a time, when 'm' specified things always come together $= n! - [m! \bullet (n-m+1)!]$

Combinations

A **combination** is an un-ordered selection made from a group of objects. Contrast to this, a **permutation**, on the other hand, is an ordered selection made from a group of objects
In permutations, we count *abc* as different from *bca.* But in combinations we are concerned only that a, b, and c have been selected. abc and bca are the same combination.

${}^{n}C_{k}$ = The number of combinations of n things taken k at a time.

Obviously, there are more permutations than combinations.

${}^{n}C_{k} = n(n-1)(n-2)........k \text{ factors } /k!$
2.3.1

In terms of factorials, the number of selections -- combinations -- of *n* things taken *k* at a time, can be represented as follows:

${}^{n}C_{k} = n! /(n-k)!\, k!$ 2.3.2a

${}^{n}C_{k} = {}^{n}C_{n-k}$ 2.3.2b

Number of Combination of 'n' different things, taken 'r' at a time is given by:-

${}^{n}C_{r} = n! / r! \bullet (n-r)!$
2.3.3

Proof: Each combination consists of 'r' different things, which can be arranged among themselves in r! ways.

For one combination of 'r' different things, number of arrangements = r!

For ${}^{n}C_{r}$ combination number of arrangements: r ${}^{n}C_{r}$

Total number of permutations = r! ${}^{n}C_{r}$

But number of permutation of 'n' different things, taken 'r' at a time= ${}^{n}P_{r}$

${}^{n}P_{r} = r!\ .\ {}^{n}C_{r}$
2.3.4

or $n!/(n-r)! = r!\ .\ {}^{n}C_{r}$

or ${}^{n}C_{r} = n!/r! \bullet (n-r)!$

Note: ${}^{n}C_{r} = {}^{n}C_{n-r}$

or ${}^{n}C_{r} = n!/r! \bullet (n-r)!$ and ${}^{n}C_{n-r} = n!/(n-r)! \bullet (n-(n-r))!$

$= n!/(n-r)! \bullet r!$ 2.3.5

Restricted Combinations

(a) Number of combinations of 'n' different things taken 'r' at a time, when 'p' particular things are always included = ${}^{n-p}C_{r-p}$.

(b) Number of combination of 'n' different things, taken 'r' at a time, when 'p' particular things are always to be excluded = ${}^{n-p}C_r$

EXAMPLE: In how many ways can a cricket team of 11 players be chosen out of 16 players? if

(i) A particular player is always chosen,

(ii) A particular is never chosen.

Ans:

(i) A particular player is always chosen, it means that 10 players are selected out of the remaining 15 players.

=. Required number of ways = ${}^{15}C_{10} = {}^{15}C_5$

= 15!/(5!x10!)

(ii) A particular players is never chosen, it means that 11 players are selected out of 15 players.

=> Required number of ways = ${}^{15}C_{11}$

= 15!/(11!x4!)

(iii) Number of ways of selecting zero or more things from 'n' different things is given by:- 2^n-1

Proof: Number of ways of selecting one thing, out of n-things = ${}^{n}C_1$

Number of selecting two things, out of n-things =${}^{n}C_2$

Number of ways of selecting three things, out of n-things =${}^{n}C_3$

Number of ways of selecting 'n' things out of 'n' things = ${}^{n}C_n$

=>Total number of ways of selecting one or more things out of n different things

$= {}^nC_1 + {}^nC_2 + {}^nC_3 + \text{-------------} + {}^nC_n$

$= ({}^nC_0 + {}^nC_1 + \text{-----------------}{}^nC_n) - {}^nC_0$

$= 2^n - 1$ [${}^nC_0=1$]

Example

How many alphabets need to be there in a language if one were to make 1 million distinct 3 digit initials using the alphabets of the language?

Sol:: 1 million distinct 3 digit initials are needed.

Let the number of required alphabets in the language be ‘n’.

Therefore, using ‘n’ alphabets we can form $n * n * n = n^3$ distinct 3 digit initials.

Note distinct initials is different from initials where the digits are different.
For instance, AAA and BBB are acceptable combinations in the case of distinct initials while they are not permitted when the digits of the initials need to be different.

This n^3 different initials = 1 million

i.e. $n^3 = 10^6$ (1 million = 10^6)
$\Rightarrow n^3 = (10^2)^3 \Rightarrow n = 10^2 = 100$

Hence, the language needs to have a minimum of 100 alphabets to achieve the objective.

Limits

Limit of a function:

Limit of a function is an extremely important concept in calculus. Function f(x) is said to have a limit $\lim_{x \to a} f(x) = c$ if, for all $\varepsilon \succ 0$, there exists a $\partial \succ 0$ such that $|f(x) - c| \prec \varepsilon$ whenever $0 \prec |x - a| \prec \partial$. Limits may be taken from below , $x \to a_{-}$ or from above , $x \to a_{+}$, if the two are equal, then "the" limit is said to exist.

Continuity of function:

A **continuous function** is a function for which, intuitively, small changes in the input result in small changes in the output. Otherwise, a function is said to be **discontinuous**

To be more precise, we say that the function *f* is continuous at some point c when the following two requirements are satisfied.

F(c) must be defined (i.e *c* must be an element of the domain of *f*)

The limit of *f(x)* , as x approaches *c*, must exist and be equal to *f(c)*. (If the point *c* in the domain of *f* is not an accumulation point of the domain, then this condition is vacuously true, since x cannot approach *c*. Thus, for example, every fuction whose domain is the set of all integers is continuous, merely for lack of approtunity to be otherwise. However, one does not usually talk about continuous functions in this setting.)

We call the function **every where continuous**, or simply **continuous**, it it is continuous at every point of its domain, More generally, we say that a function is continuous on some subset of its domain, it it is continuous at eery point of that subset. It we simply say that a function is continuous, we usually mean that it is continuous for all real numbers.

Here are some properties of limits, for continuous functions *f*(*x*) and *g*(*x*):

$\lim\limits_{x \to c}\left[f(x)+g(x)\right]$	=	$\frac{dy}{dx}=\frac{dy}{du}*\frac{du}{dx}\ \lim\limits_{x \to c}\left[f(x)\right]+\lim\limits_{x \to c}\left[g(x)\right]$
$\lim\limits_{x \to c}\left[f(x)-g(x)\right]$	=	$\lim\limits_{x \to c}\left[f(x)\right]-\lim\limits_{x \to c}\left[g(x)\right]$
$\lim\limits_{x \to c}\left[f(x)*g(x)\right]$	=	$\lim\limits_{x \to c}\left[f(x)\right]*\lim\limits_{x \to c}\left[g(x)\right]$
$\lim\limits_{x \to c}\left[k*f(x)\right]$	=	$k*\lim\limits_{x \to c}\left[f(x)\right]$
$\lim\limits_{x \to c}\left[f(x)\big/g(x)\right]$	=	$\lim\limits_{x \to c}\left[f(x)\right]/\lim\limits_{x \to c}\left[g(x)\right]$ assuming $\lim\limits_{x \to c}\left[g(x)\right]\neq 0$

Derivatives

Derivatives of a function

The derivative of a function represents an infinitesimal change in the function with respect to one of its variables. The "simple" derivative of a function f with respect to a variable x is denoted as either $f'(x)$ or $\frac{df}{dx}$ often written in-line as df/dx. When derivatives are taken with respect to time, they are often denoted using Newton's overdot notation for fluxions, $\frac{dx}{dt}=\dot{x}$. This also gives the slope of the curve.

When a derivative is taken n times, the notation $f^{(n)}(x)$ or $\frac{d^n f}{dx^n}$ is used,

When a function $f(x, y, \ldots)$ depends on more than one variable, a <u>partial derivative</u>

$$\frac{\partial f}{\partial x}, \frac{\partial^2 f}{\partial x \partial y} \text{ etc}$$

can be used to specify the derivative with respect to one or more variables. The derivative of a function f(x) with respect to the variable x is defined as

$$f^{'}(x) = \lim_{h \to 0} \frac{f(x+h) - f(x)}{h} \qquad 4.1.1$$

but may also be calculated more symmetrically as

$$f^{'}(x) = \lim_{h \to 0} \frac{f(x+h) - f(x-h)}{2h} \qquad 4.1.2$$

provided the derivative is known to exist. If the first derivative exists, the second derivative may be defined as

$$f^{''}(x) = \lim_{h \to 0} \frac{f^{'}(x+h) - f^{'}(x)}{h} \qquad 4.1.3$$

and calculated more symmetrically as

$$f^{''}(x) = \lim_{h \to 0} \frac{f(x+2h) - 2f(x+h) + f(x)}{h^2} \qquad 4.1.4$$

again provided the second derivative is known to exist.

Note that in order for the limit to exist, both $\lim_{h \to 0+}$ and $\lim_{h \to 0-}$ must exist and be equal, so the function must be continuous. However, continuity is a necessary but *not* sufficient condition for differentiability.

If f is differentiable at x_0, it is continuous at at $x_{0.}$ Differentiability at x_0 implies

$$x_o \lim_{x \to x_o} \frac{f(x) - f(x_o)}{x - x_o} = f^{'}(x_o) \qquad 4.1.5$$

We have,

$$\lim_{x \to x_o} \left[f(x) - f(x_o) \right] = \lim_{x \to x_0} (x - x_o) \frac{f(x) - f(x_o)}{x - x_o}$$

$$= \left[\lim_{x \to x_0} (x - x_o) \right] \left[\lim_{x \to x_o} \frac{f(x) - f(x_o)}{x - x_o} \right]$$

$$= 0 \; . \; f^{'}(x_o)$$

$$= 0 \qquad 4.1.6$$

$\lim_{x \to x_o} f(x) = f(x_o)$ which means f is continuous at x_o

Properties of derivatives

a) A constant function

Take f(x) = c.

The slope of the tangent line at any point is 0. So, $\frac{d}{dx} c = 0$ 4.2.1

b). f(x) = x

The slope of the tangent line in point p of the function x is 1. So, $\frac{d}{dx} x = 1$ 4.2.2

c). The sum f(x) + g(x) Rule

If the functions f(x) and g(x) are differentiable then

$$\frac{d}{dx}(f(x) + g(x)) = \lim_{h \to 0} \frac{(f(x+h) + g(x+h)) - (f(x) + g(x))}{h}$$

$$= \lim_{h \to 0} \frac{f(x+h) - f(x)}{h} + \lim_{h \to 0} \frac{g(x+h) - g(x)}{h}$$

$$= \frac{d}{dx} f(x) + \frac{d}{dx} g(x)$$

4.2.3

This property is extendable to the sum of n differentiable functions.

d). The product f(x).g(x)

If the functions f(x) and g(x) are differentiable then

$$\frac{d}{dx}(f(x)/g(x)) = \lim_{h\to 0}\frac{f(x+h)/g(x+h) - f(x)/g(x)}{h}$$

$$= \lim_{h\to 0}\frac{f(x+h)*g(x+h) - f(x+h)*g(x) + f(x+h)*g(x) - f(x)*g(x)}{h}$$

$$= \lim_{h\to 0}\frac{f(x+h)(g(x+h) - g(x)) + g(x)*(f(x+h) - f(x))}{h}$$

$$= f(x)*g^{'}(x) + f^{'}(x)*g(x) \qquad 4.2.4$$

thus, for u=f(x) and c is a constant $\frac{d}{dx}(cu) = cu^{'}$ 4.2.5

e). Power of f(x)

If u=f(x) is differentiable $\frac{d}{dx}(u^{n}) = n(u^{n-1})u^{'}$ 4.2.6

The quotient f(x)/g(x)

If the functions f(x) and g(x) are differentiable then

$$\frac{d}{dx}(f(x)/g(x)) = \lim_{h\to 0}\frac{f(x+h)/g(x+h) - f(x)/g(x)}{h}$$

$$= \lim_{h\to 0}\frac{f(x+h).g(x) - f(x)g(x) + f(x)g(x) - f(x).g(x+h)}{h.g(x).g(x+h)}$$

$$= \lim_{h\to 0}\frac{g(x) . (f(x+h)-f(x))/h - f(x) . (g(x+h)-g(x))/h}{g(x).g(x+h)}$$

$$= \frac{g(x).f'(x) - f(x).g'(x)}{g(x).g(x)}$$

$$(u/v)' = \frac{(v u' - u v')}{v^2} \qquad 4.2.7$$

Partial Derivatives

Definition of partial derivatives

So far we discussed functions of single variables. When we have functions of **many variables** ***partial differentiation*** is used. A **partial derivative** of a function of several variables is its derivative with respect to one of those variables with the others held constant (as opposed to the total derivative, in which all variables are allowed to vary). Suppose we have a function *f* such that it depends on several independent variables, say x, y and z. Consider, for a moment, in such function *f(x,y,z)* y and z as constant, then *f(x,y,z)* only depends on the variable x. Then, we can calculate the derivative with respect to x. We note this derivative as $f_x'(x,y,z)$. Similarly we can calculate , $f_y'(x,y,z)$ and $f_z'(x,y,z)$. The partial-derivative symbol ∂ is a rounded letter, distinguished from the straight *d* of total-derivative notation. The notation was introduced by **Legendre** and gained general acceptance after its reintroduction by **Jacobi**.

For the following examples, let *f* be a function in *x*, *y* and *z*.

First-order partial derivatives:

$$\partial f / \partial x = f_x$$

$$\partial f / \partial x = \lim_{\partial x \to 0} f(x + \partial x, y) - f(x, y) / \partial x$$

Second-order partial derivatives:

$$\partial^2 f / \partial^2 x = f_{xx}$$

Second-order mixed derivatives:

$$\partial^2 f / \partial x \partial y = f_{xy}$$

This matrix of second-order partial derivatives of *f* is called the **Hessian matrix** of *f*. The entries in it off the main diagonal are the **mixed derivatives**; that is, successive partial derivatives with respect to different variables. In most normal circumstances the Hessian matrix is indeed symmetric. However, in some cases it is not true like in example below

Consider the function

$$f(x, y) = xy(x^2 - y^2)/(x^2 + y^2)$$

with *f*(0,0) = 0. Then the mixed partial derivatives of *f* exist, and are continuous everywhere except at (0,0). However,

$$\frac{\delta}{\delta x}\left(\frac{\delta f}{\delta y}\right) \neq \frac{\delta}{\delta y}\left(\frac{\delta f}{\delta x}\right)$$

at (0,0).

In chemistry we need partial derivatives more often than the total derivatives.

Maximum and minimum values

Relative maximum

We say that a function f(x) has a relative maximum for x = t, if and only if there is a strictly positive real number e such that f(x) =< f(t) for all x in [t-e,t+e] .Often the word 'relative' is omitted.

Relative minimum

We say that a function f(x) has a relative minimum for x = t if and only if there is a strictly positive real number e such that f(x) >= f(t) for all x in [t-e,t+e] .

Roots of f'(x)

If f'(x) exists in an open interval that contains the value x = t, and suppose that f reaches a maximum for x = t. Then, f'(t) = 0.

Rolle's theorem

If

- f is continuous in [a,b]
- f is differentiable in]a,b[
- f(a) = f(b)

Then, there is a c-value in [a,b] such that f'(c) = 0.

Proof:
If f is constant in [a,b], then the proof is trivial. Now, suppose f is not constant in [a,b]. Then there is a number d in]a,b[such that f(d) is different from f(a) and f(b).

Suppose first that f(d) > f(a). Since f is continuous in [a,b], f attains, according to <u>Weierstrass</u>, a greatest image.

Thus, there is a c-value in]a,b[such that f© is maximum and since f is differentiable in]a,b[, f’© = 0.

In the same way, you can prove the theorem for f(d) < f(a).

Concavity

Concave upward

If, in an interval, f''(x) > 0 , then f'(x) is increasing. Then the slope of the tangent line is increasing with x. We say that f(x) is concave upward in that interval

Concave downward

If, in an interval, f''(x) < 0 , then f'(x) is decreasing. Then the slope of the tangent line is decreasing with x. We say that f(x) is concave downward in that interval. If, in an interval, f''(x) < 0 then f(x) is concave downward in that interval.

L'Hospitals rule and special limits

Theorem 1

If $\lim_{x\to a} f(x) = 0$ $\lim_{x\to a} g(x) = 0$ so that $\frac{f(x)}{g(x)} = \frac{0}{0}$ or $\frac{f(x)}{g(x)} = \frac{\infty}{\infty}$

L'Hospital's rule allow us to determine $\lim_{x\to a} \frac{f(x)}{g(x)}$.

L'Hospitals rule says that

$\lim_{x\to a} \frac{f(x)}{g(x)} = \lim_{x\to a} \frac{df(x)}{dg(x)}$**,** provided that the right hand limit either exists or is equal to plus or minus infinity.

Application of Maxima and Minima

Rate of change:: The derivative of a function *y=f(x)* is the rate of change of y with respect to change in x. It can be used to get radioactive decay, the amount of substance left at time t is given by $a = e^{-kt}$ $a = e^{-kt}$ where a is the initial amount and k the radioactive constant. The Rate of decay is given by $\frac{dx}{dt} = -kae^{-kt} \qquad = -kx$

Another important application of maxima and minima is in minimizing energy of a system in quantum mechanics/chemistry.

Example : If y = x^2 + 8, find the minimum in y .
dy/ dx = 2x . It is 0, when x=0

d^2y/ dx^2 at x=0 is +2, hence at x=0, y is minimum and the **value of the minimum is 8**

Maxima and Minima of Functions of Two Variables

Condition for maximum or minimum of a function *f(x,y)* is $f_x(a,b) = 0 \qquad f_y(a,b) = 0$.

Working rule to find the maximum and minimum values of *f(x,y)*

1. Find $\int \psi^* \mu_x \psi dx = TM$ and $\frac{\delta f}{\delta y}$ and equate each of them to zero. Solve these equations simultaneously in x and y .

2. Calculate the values if $r = \frac{\delta^2 f}{\delta x^2}$, $s = \frac{\delta^2 f}{\delta x \partial y}$ and $t = \frac{\delta^2 f}{\partial y^2}$ for each pair of values.

3.

i) If $rt - s^2$>0 and r<0 at (a,b), f(a,b) is a maximum value.

ii) If $rt - s^2$>0 and r>0 at (a,b) ,f(a,b) is a minimum vale.

iii) If $rt - s^2$<0 at (a,b), f(a,b) is not an extreme value, i.e. it is a saddle point.

iv) If $rt - s^2$=0 at (a,b) , the case needs further investigation.

Curve Sketching

Important points for sketching of curve

i). **X-intercepts**. These can be found by putting y=0 and solve for x.
ii). **Y-intercepts**. These can be found by putting x=0 and solve for y.
iii). **Stationary points**. Found by calculating the derivative of the function, set it to zero and solve for x.
iv). **Asymptotes**. Lines on the plane that the curve tends towards, but does not cut. Can be vertical, horizontal or oblique. Found by letting x or y tend to infinity and check if the function approaches a certain value.
v). **Gradient**. Is the gradient positive or negative for the relevant portions of the graphs. It can be deduced from the derivative. These techniques can be used for any graph, especially if you do not know the general shape of the graph.

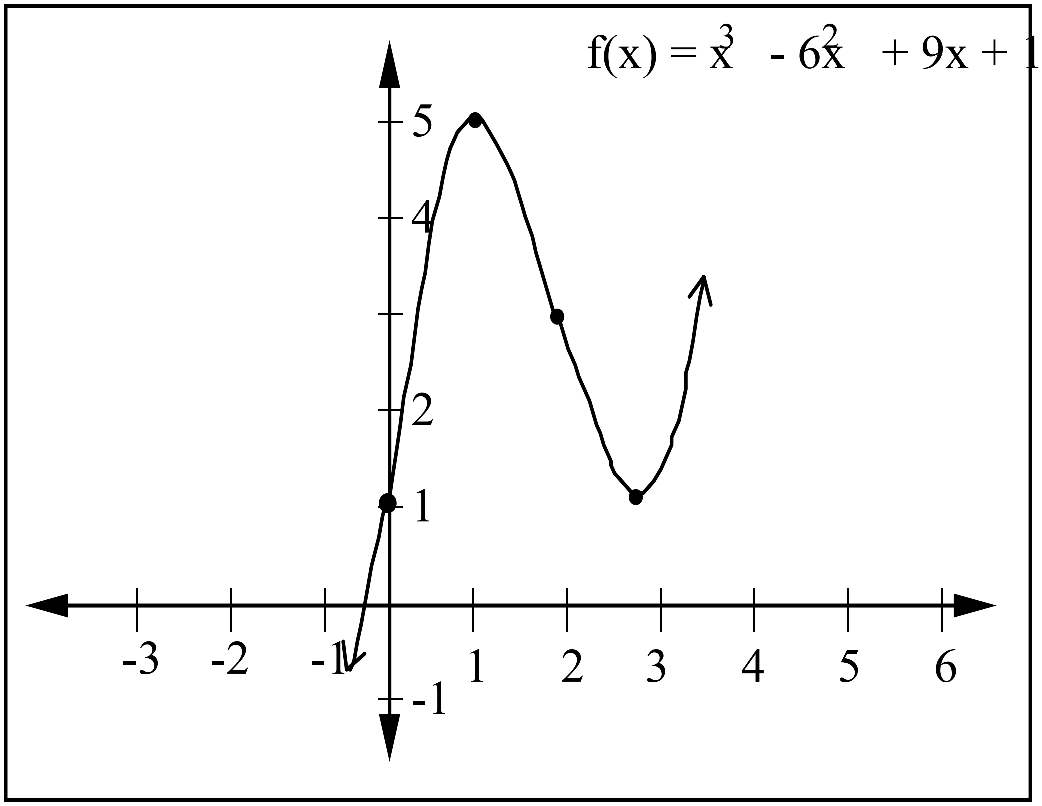
Example *: sketch the graph for* $y = x^3 - 6x^2 + 9x + 1$

a. Find y-intercept.
When x = 0, y = 1
b. Find x-intercepts.
skip
c. Find stationary points.
$dy/dx = 3(x^2-x+3) = 0$
$(x-3)*(x-1)=0$
x=3 and x=1
d. Asymptotes: none

e. Gradient.

x	F'(x)	F(x)
-1	24	-15
0	9	1
1	0	5
2	-3	3
3	0	1
4	9	5

Mark these points on a set of axes and draw a smooth curve through them.



Example

Sketch the graph of $y = \frac{1 + x}{1 - x}$

1) Asymptotes: When $x = 1$, we end up dividing by zero so there will be an asymptote at $x = 1$.

Also think about what happens when $y = -1$.

$$-1 = \frac{1 + x}{1 - x}$$

$-1(1 - x) = 1 + x$

$-1 + x = 1 + x$

$-1 = 1$.

This cannot happen, since $-1 \neq 1$, so the graph cannot be defined for $y = -1$. This is therefore another asymptote.

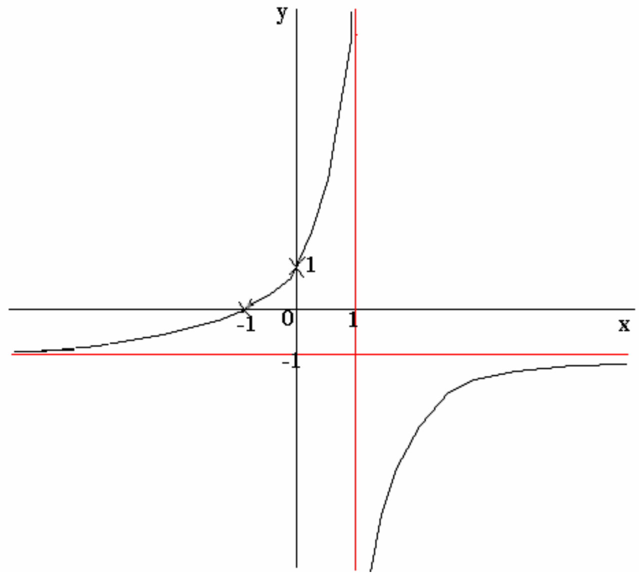
2) Where the axes are crossed: When $x = 0$, $y = 1$. Therefore the curve crosses the y-axis at (0,1).

When $y = 0$, $1 + x = 0$ so $x = -1$. Therefore the curve crosses the x-axis at (-1, 0).

3) As x becomes large, 1 + x will become large and positive and 1 - x will become large and negative. Therefore as x becomes large, y = large/-large = -1. As x becomes very large and negative, 1 + x will become very large and negative and 1 - x will become very large and positive. Therefore y = -large/large = -1.

4) By substituting in -x for x it can be seen that the graph is not symmetrical in the x axis.

The sketch of the graph would therefore look something like this:



Note that the curve does not cut the lines that we have found to be asymptotes, but it gets extremely close to them.

Integration

There are two processes with an especially important role, not only because they arise in many different connections, but mainly due to their very close reciprocal relationship. differentiation and integration are complementary in nature**.** Integration is the reverse of differentiation. With differentiation breaking a process down to look at the instantaneous process, integration sums up the information from small time intervals to give a total result over a larger time period. Like area under the curve can be obtained by integration.

Definite Integrals

Definite Integrals are defined as:

$$\int_a^b f(x)dx = \lim_{n\to\infty}\sum_{i=1}^{n} f(x_i)\Delta x \quad \int f'(u)du = I \qquad 7.2.1$$

and

$$\int_a^b f(x)dx = F(b) - F(a) \qquad 7.2.2$$

which is the fundamental theorem of calculus, where [a,b].

Special Integrals:

$$\int_a^a f(x)dx = 0 \qquad 7.3.1$$

If *f* is integrable on [a,b] and a < b then

$$\int_a^b f(x)dx = -\int_b^a f(x)dx \qquad 7.3.2$$

Properties of Definite Integrals:

$$\int_a^b kf(x)dx = k\int_a^b f(x)dx \qquad 7.4.1$$

$$\int_a^b (f(x) \pm g(x))dx = \int_a^b f(x)dx \pm \int_a^b g(x)dx \qquad 7.4.2$$

$$\int_a^b f(x)dx = \int_a^c f(x)dx + \int_c^b f(x)dx \qquad 7.4.3$$

Indefinite Integrals

The indefinite integral of a function *f*, denoted as □ *f*(x) dx, is the set of all the antiderivatives of *f*.

Properties of Indefinite Integrals

If *f*(x) and *g*(x) are integradable, then

$$\int x^n dx = x^{n+1} \big/ n+1 \qquad 7.6.1$$

$$\int kf(x)dx = k\int f(x)dx \qquad 7.6.2$$

$$\int \left[f(x) \pm g(x) \right] dx = \int f(x)dx \pm \int g(x)dx \qquad 7.6.3$$

Methods of Integration

Integration by Substitution

Integration by substitution allows change of basic variable of an integrand.

$$\int f'(g(x))g'(x)dx = I \qquad 7.8.1a$$

Let $u = g(x)$. Then $du = g'(x)dx$. Substituting we get

$$\int f'(u)du = I \qquad 7.8.1b$$

Rules.

1. Start with the Integral

2. Let u=g(x)

3. Calculate du

4. Substitute u and du

5. Integrate

6. Replace u by g(x)

Integration by Parts

$$\int f(x)g'(x) = f(x)g(x) - \int g(x)f'(x)dx \int f(x)g'(x) = f(x)g(x) - \int g(x)f'(x)dx$$

$u = f(x)$; $du = f'(x)dx$

$v = g(x)$; $dv = g'(x)dx$

$$\int udv = uv - \int vdu$$

Applications in Chemistry

To normalize the wavefunction integration is used

$$\int \psi^* \psi d\tau = N$$

To find the expectation value of any operator we need integration

$$\int \psi^* A\psi d\tau = \langle \hat{A} \rangle$$

In spectroscopy transition moments are calculated using $\int \psi^* \mu_x \psi dx = TM$

8.1 Least Square fitting

Least squares is a mathematical optimization procedure/technique used to find a function which fits the data closely. Method assumes that the best-fited curve is the one that has the minimal sum of the deviations squared (*least square error*) from a given set of data. The least square method is widely used to fit a function to a set of data or to characterize the statistical properties or estimates. Several variants of the method exists. The oldest version is called ordinary least squares (OLS), the more sophisticated version is called weighted least squares (WLS). Which ofcourse is expected to do better than OLS.

The least squares method will work best if errors in each measurement are randomly distributed. The least squares technique is commonly used in curve fitting. Many other optimization problems can also be expressed in a least squares form.

The oldest use of least squares was to fit the best curve for a given set of data. Suppose that we are fitting N date points (x_i,y_i) i=1…N, where x is the independent variable and y is the dependent variable. We want to find he function f which predicts or fits best the functional relation between the dependent variables Y and independent variables x. According to the method of least squares, the best fitting curve has the property that:

$$D = \sum_{i=1}^{N} \left[Yi - f(x_i) \right]^2 \text{ is a minimum}$$

This is achieved using one variable and a linear function. The least-squares line method uses a straight line $y = ax + b$ to approximate the given set of data(xi,yi). $y = a + bx + cx^2$ is min

Here, a and b are unknown coefficients while all x_i and y_i are given. To obtain the least square error, the unknown coefficients a and b must give zero first derivatives.

$$\partial D / \partial a = 2\sum_{i=1}^{N} \left[Y_i - (a + bx_i) \right] = 0$$

$$\partial D / \partial b = 2x_i \sum_{i=1}^{N} \left[Y_i - (a + bx_i) \right] = 0$$

from above equations we have

$$\sum_{i=1}^{N} Y_i = a + b\sum_{i=1}^{N} x_i \quad \text{and} \quad \sum_{i=1}^{N} x_i Y_i = a\sum_{i=1}^{N} x_i + b\sum_{i=1}^{N} x_i^2$$

unknown coefficients a and b can be obtained. For more accurate curve fitting we can use higher degree of fitting instead of straight line one can use parabole fitting. In this, a second degree curve $y = a + bx + cx^2$ is used for fitting the data (x_i,y_i). The unknown coefficients a,b, and c can be obtained in a similar fashion as before.

Exercises

1. How many different committees of 4 students can be chosen from a group of 15

2. There are 15 boys and 13 girls in a class. Find the number of ways to form a team of 3 students from the class to work on a group project. The team consists of 1 girl and 2 boys.

3. Express $^{10}P_4$ in terms of factorials

4. Five different books are on a shelf. In how many different ways could you arrange them?

5. How many different arrangements can be made using two of the letters of the word TEXAS if no letter is to be used more than once?

6. Find number of valence diagrams for naphthalene and anthracene.

7. Find dy/dx for a) $9x^3 + 8xy - 9y^2 = 3$ b) $\cos(x) + \sin(x)\cos(y)$

8. Consider the ideal gas $P = nRT/V$ and obtain partial derivatives of P with respect to V,T and n.

9. The 1S orbital wavefunction of hydrogen atom is given by $\psi_{1s} = (1/\pi a_o^3)^{1/2} \exp(-r/a_o)$, where r is the distance of the electron from the nucleus. The radial probability density of an electron in an orbital of hydrogen atom is given by, $4\ \Pi r^2\ |\Psi|^2$. Find r at which the maximum radial probability density of the electron in hydrogen atom 1S orbital can be obtained.

10. Find the stationary points of the functions
(i) $y=4x^2-4x+7$ (ii) $y=x^2/2 - \cos(x)$

11. Find the limit for the function

a) $\lim_{x\to 0} x^2 - 9/x + 3$

12. Normalize the ground state wavefunction of a particle in one-dimensional box, where $\Psi_1 = k\ \sin(\Pi x/a)$, for x between 0 and a and is equal to zero for other values of x., a being the length of the box, i.e. find the value of k, such that integral of $|\Psi_n|^2$ over all x is equal to 1.

13. Sketch the graph of a) y =xe^x b) $y = e^x \cos(x)$ c) $y = x\sqrt{4-x^2}$ d) $y = x^2 + bx + a$ e) y=|x|

APPENDIX I Some Differentiation Formulas

Let c, a_0, a_1,...,a_n be real numbers, then	**Trigonometric Functions:**
$\frac{dc}{dx} = 0$	$\frac{d\sin x}{dx} = \cos x$
$\frac{dx}{dx} = 1$	$\frac{d\cos x}{dx} = -\sin x$
$\frac{d(x^c)}{dx} = cx^{c-1}$	$\frac{d\tan x}{dx} = \sec^2 x$
$\frac{d\sqrt{x}}{dx} = \frac{1}{2\sqrt{x}}$	$\frac{d\cot x}{dx} = -\operatorname{cosec}^2 x$
$\frac{d(1/x)}{dx} = -\frac{1}{x^2}$	$\frac{d\sec x}{dx} = \sec x\tan x$
$\frac{d(a_nx^n + a_{n-1}x^{n-1} + \ldots.. + a_1x + a_0)}{dx} = na_nx^{n-1} + \ldots.. + a_1$	$\frac{d\operatorname{cosec} x}{dx} = -\operatorname{cosec} x\cot x$
<u>Techniques of differentiation:</u> If f and g are differentiable at x, and α a constant then:	
$[f(x) \pm g(x)]' = [f(x)]' \pm [g(x)]'$	
$[\alpha f(x)]' = \alpha * [f(x)]'$	
$[f(x)/g(x)]' = [f(x)]' * g(x) - [g(x)]' * f(x)/[g(x)]^2$	
Let $y=f(u)$ and $u=g(x)$, then $\frac{dy}{dx} = \frac{dy}{du} * \frac{du}{dx}$ chain rule	

Appendix II : Basic Integration Formulas

Function	Indefinite Integral
x^n	$x^{(n+1)}/(n+1)$
1/x	ln |x|
lnx	x ln x-x
1/x ln x	Ln (ln x)
x ln x	$X^2/2$ ln x -1/4 x^2
$(a+bx)^n$	$(a+bx)^{(n+1)}$ /(n+1)b n≠-1

1/(ax+b)	(1/a) ln |ax+b|
x/(ax+b)	$(1/a^2)$(ax + b - b ln|ax + b|)
$1/(a^2+x^2)$	(1/a) arctan (x/a)
$1/(a^2-x^2)$	(1/a) arctanh (x/a)
$1/\mathrm{sqrt}(a^2-x^2)$	arcsin (x/a)
$1/\mathrm{sqrt}(x^2-a^2)$	$\ln(x + \mathrm{sqrt}(x^2-a^2))$
$x\ \mathrm{sqrt}(a^2-x^2)$	$(-1/3)(a^2-x^2)\ \mathrm{sqrt}(a^2-x^2)$
$x\ \mathrm{sqrt}(x^2-a^2)$	$(1/3)(x^2-a^2)\ \mathrm{sqrt}(x^2-a^2)$
$x\ \mathrm{sqrt}(x^2+a^2)$	$(1/3)(x^2+a^2)\ \mathrm{sqrt}(x^2+a^2)$
sin x	-cos x
cos x	sin x
$\sec^2 x$	tan x
tan x	-ln cos x
1/(tan x) = cot x	ln sin x
sec x	ln(sec x + tan x)
csc x	ln(csc x - cot x)
$\sin^2 x$	x/2 - sin(2x)/4
$\cos^2 x$	x/2 + sin(2x)/4
$\tan^2 x$	tan(x) - x
sin(ax)sin(bx)	(1/2)(sin(a-b)x/(a-b) - sin(a+b)x/(a+b))
sin(ax)cos(bx)	-(1/2)(cos(a-b)x/(a-b) + cos(a+b)x/(a+b))
cos(ax)cos(bx)	(1/2)(sin(a-b)x/(a-b) + sin(a+b)x/(a+b))

Sources for this e-chapter:

1. “Mathematics in Chemistry”, by K.V.Raman and Sourav Pal, Vikas publishing, India, 2004
2. http://www.projectalevel.co.uk/maths/curve.htm