CH412 Physical Chemistry

A math-capsule for non-math students

UoH/SoC

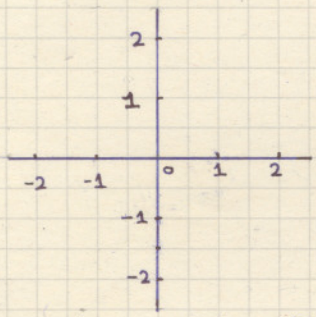
These notes summarise, for those students who didn't study mathematics in B.Sc., the important math-concepts needed for the first semester physical chemistry course. You should work through it - fill in the details which are left out - and do all the exercises. If you need more help, read a college maths text / consult your math friends / ask me (afternoons).

mvr/mons.'99

Functions in one dimension : $y = f(x)$

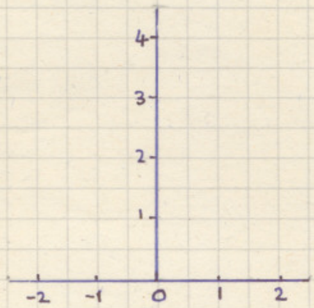
* **Plot a few simple functions below** (make smooth plots - use a sharp pencil)

$y = ax + b$



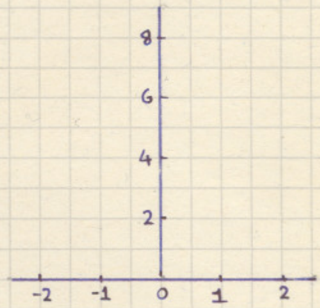
make 3 plots on this graph: (i) $a = 1$ $b = 0$
(ii) $a = \frac{1}{2}$ $b = 0$
(iii) $a = 1$ $b = 1$

$y = ax^2$



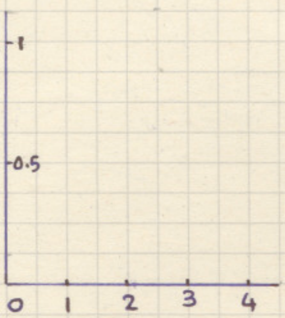
make 2 plots:
(i) $a = 1$
(ii) $a = \frac{1}{2}$

$y = e^{ax}$



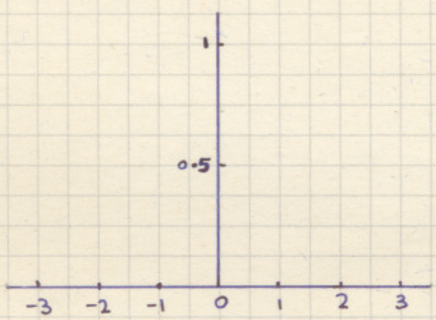
make 4 plots
(i) $a = 1$ (ii) $a = -1$
(iii) $a = \frac{1}{2}$ (iv) $a = -\frac{1}{2}$

$y = e^{ax}$



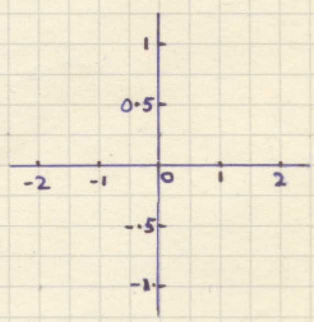
(i) $a = -\frac{1}{2}$
(ii) $a = -1$

$y = e^{-ax^2}$



(i) $a = 1$
(ii) $a = 1/2$

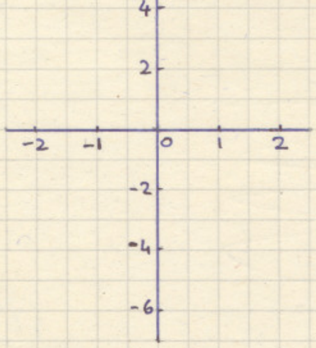
$y = \sin n\pi x$



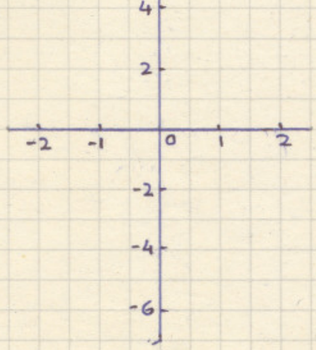
(i) $n = 1$
(ii) $n = 1/2$

* In the plots label those functions which are (i) Linear
(ii) quadratic
(iii) exponential
(iv) inverse

$y = 1/x$



$y = 1/x^2$



* Also label,
(v) even functions ~~[illegible]~~
$f(x) = f(-x)$
(vi) odd functions
$f(x) = -f(-x)$
(vii) periodic functions
$f(x+T) = f(x)$

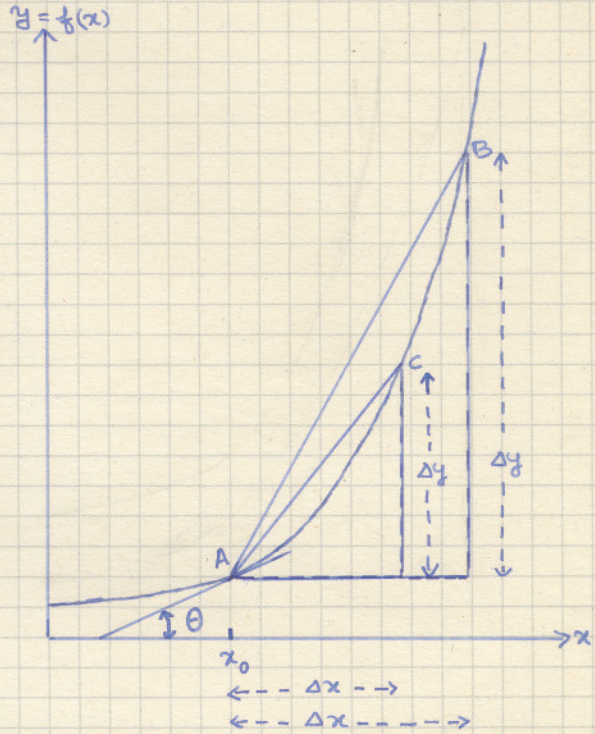
* e - the natural base for logarithm: Complete the following Table (use a calculator)

p	e^p	
1.0	2.7183	= 1 + 1.7183
0.1		= 1 +
0.01		= 1 +
0.001		= 1 +
0.0001		= 1 +

When p is small $\boxed{e^p \sim 1 + p}$

also verify that for small values of p

$10^p \sim 1 + 2.303\,p$



* Rate of change or slope of $f(x)$:

As Δx approaches zero, the slope of the chord lines (AB, AC etc..) approaches $\tan\theta$, which is the slope of the function $f(x)$ at x_0. Therefore, at any point on the function, the limit,

$$\lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x}$$ can be identified with the slope of the function.

This quantity is called the differential coefficient or derivative of $f(x)$ and is written as $\frac{dy}{dx}$. The derivative, in general, is a function of x. When is it a constant?

Let us evaluate the derivative of x^n

$$\lim_{\Delta x \to 0} \frac{(x+\Delta x)^n - x^n}{\Delta x} = \lim_{\Delta x \to 0} \frac{x^n\left(1 + \frac{\Delta x}{x}\right)^n - x^n}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \frac{x^n\left(1 + n\frac{\Delta x}{x}\right) - x^n}{\Delta x} = \underline{\underline{n x^{n-1}}}$$

Another example: e^x $\quad (e^{x+\Delta x} - e^x)/\Delta x = (e^x e^{\Delta x} - e^x)/\Delta x$

$$= e^x(e^{\Delta x} - 1)/\Delta x = e^x(1 + \Delta x - 1)/\Delta x = e^x$$

$$\therefore \lim_{\Delta x \to 0} \frac{e^{x+\Delta x} - e^x}{\Delta x} = \underline{\underline{e^x}}$$ (the derivative of e^x is e^x itself)

Yet another example : derivative of sin x

$$\frac{\sin(x+\Delta x)-\sin x}{\Delta x} = (\sin x \cos\Delta x + \cos x \sin\Delta x - \sin x)/\Delta x$$

$$= \sin x \frac{(\cos\Delta x - 1)}{\Delta x} + \cos x \frac{\sin\Delta x}{\Delta x}$$

$$\therefore \frac{d(\sin x)}{dx} = \sin x \lim_{\Delta x\to 0}\frac{(\cos\Delta x - 1)}{\Delta x} + \cos x \lim_{\Delta x\to 0}\frac{\sin\Delta x}{\Delta x}$$

To see what the two limits are, complete the following Table.

Δx	$(\cos\Delta x - 1)/\Delta x$	$\sin\Delta x/\Delta x$
0.1π	-0.1558	0.9836
0.001π		
0.00001π		

So, what is the derivative of sin(x)?

Proceeding along similar lines, complete the following Table of derivatives

$f(x)$	$d\, f(x)/dx$
x^n	$n x^{n-1}$
e^x	e^x
$\sin x$	
$\cos x$	
$\log x$	
$1/x$	

Here is an important formula.

If $f(x) = u(x)\, v(x)$, then

$$\frac{d\, f(x)}{dx} = u(x)\frac{d\, v(x)}{dx} + v(x)\frac{d\, u(x)}{dx}$$

Try to prove it. (Write $u(x+\Delta x) = u(x) + \Delta x \frac{dy}{dx}$ etc.)

Another short-cut : example e^{3x}

$$\frac{d e^{3x}}{dx} = \frac{d e^{3x}}{d(3x)} \cdot \frac{d(3x)}{dx} = e^{3x}\cdot 3 = 3e^{3x}$$

Similarly, $$\frac{d e^{x^2}}{dx} = \frac{d(e^{x^2})}{d(x^2)} \cdot \frac{d(x^2)}{dx} = e^{x^2}\cdot 2x = 2x e^{x^2}$$

These are examples of function of a function – and the rule is 'work inwards'

Try to differentiate the following functions:

$4x^3$ $\quad x\sin x$ $\quad 2x^3 - x + 4$ $\quad \frac{1}{\log x}$ $\quad \frac{\cos x}{x^2}$

$\cos\sqrt{t}$ $\quad e^{-t^2}$ $\quad x^2 e^x$

It is possible to differentiate a function more than once.

For eg. $\frac{d^2 f(x)}{dx^2}$ is called the second derivative of $f(x)$.

Let us find the second derivative of x^3

$$\frac{dx^3}{dx} = 3x^2 \quad \therefore \quad \frac{d^2x^3}{dx^2} = \frac{d}{dx}(3x^2) = 6x$$

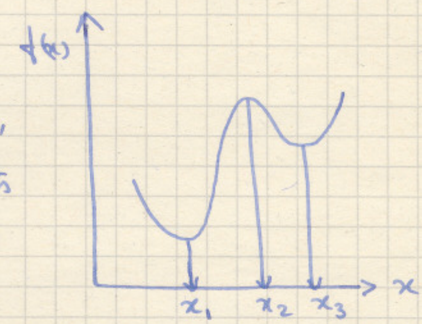
If $f(x) = xe^{2x}$ 1st derivative : $df/dx = 2xe^{2x} + e^{2x}$

2nd " : $d^2f/dx^2 = 4xe^{2x} + 2e^{2x} + 2e^{2x}$

$= 4(xe^{2x} + e^{2x})$

What is the fourth derivative of sin(x)?

Extrema points of a function:



At x_1, x_2 and x_3 the function passes through a minimum, a maximum and another minimum, respectively. Since the tangents at these points are parellel to the x axis, the derivatives of $f(x)$ at these points will be zero.

Finding max and/min points is an important application of the first derivative.

Eg. Let us find the value of x at which the function $x^2 - 2x$ will pass through a maximum or minimum.

$df(x)/dx = 2x - 2$. Equating it to zero, we have $2x = 2$, or $x = 1$

Do a similar calculatiion for the function re^{-2r}.

In the expressions df/dx and d^2f/dx^2, $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ can be thought of as operators. They operate on the function $f(x)$ to give the first derivative and second derivative, respectively.

* The indefinite integral:

If $f(x)$ is the first derivative of the function $g(x)$, then $g(x)$ is called the indefinite integral of $f(x)$.

$$\frac{d\,g(x)}{dx} = f(x) \qquad \int f(x)\,dx = g(x) + c,$$ where c is any constant (in what follows we will omit c)

Why is g(x) called an indefinite integral?

Examples: $\int x\,dx = \frac{x^2}{2}$ $\quad \int \sin x\,dx = -\cos x$ $\quad \int e^x\,dx = e^x$ $\quad \int \frac{dt}{t} = \log t$ — These can be verified by differentiating the right side.

There is no straightforward general method for finding the indefinite integral of a function. Two of the simpler methods are illustrated below:

(i) Substitution: eg: $\int x\,e^{x^2}\,dx$

put $x^2 = t$ $\quad \therefore \int x e^{x^2} dx = \frac{1}{2}\int e^t\,dt = \frac{1}{2}e^t = \frac{1}{2}e^{x^2}$

$2x\frac{dx}{dt} = 1$

$(x\,dx = \frac{1}{2}dt)$ $\qquad$ (verify this result by back-differentiation)

(ii) product rule $\int u\,dv = uv - \int v\,du$

eg: $\int x\cos x\,dx$ $\quad$ put $u = x$ and $dv = \cos x\,dx$

$\therefore v = \int dv = \sin x$ and $du = dx$

$\therefore \int x\cos x\,dx = x\sin x - \int \sin x\,dx$

$= x\sin x + \cos x$ (verify the result by differentiation)

Certain functions cannot be integrated. For eg: e^{-x^2} (ie., there is no function, which upon differentiation will give e^{-x^2})

Try to integrate the following functions.

(i) $x\cos(x^2)$ $\quad$ (ii) $r e^r$ $\quad$ (iii) $\cos^2 x$ $\quad$ (iv) $\log x$ $\quad$ (v) $x^2 e^{-x}$

* <u>The definite integral</u>

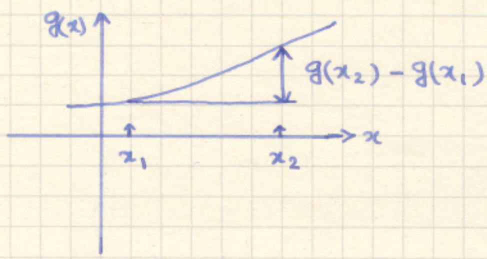
If $g(x)$ is the indefinite integral of $f(x)$, we have

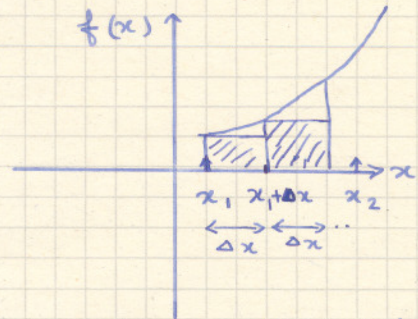
$$\frac{dg(x)}{dx} = f(x)$$

For small Δx, we can write $\Delta g(x) \sim f(x)\,\Delta x$

Let us now look at the plots of $f(x)$ and $g(x)$

between two points x_1 and x_2.





The interval $x_2 - x_1$ is divided into a number of smaller intervals (Δx). When Δx is small the shaded rectangles will have area approximately equal to the area between the x axis and the function between x and $x + \Delta x$ (for the left most segment in the figure this is equal to $f(x_1)\,\Delta x$)

$\therefore$ We can write,

$$g(x_2) - g(x_1) = \sum_{\substack{k=0 \\ n\to\infty \\ \Delta x \to 0}}^{n} f(x_1 + k\Delta x)\,\Delta x \quad = \text{area under } f(x) \text{ between } x_1 \text{ and } x_2$$

The quantity on the right hand side is called the definite integral of the function $f(x)$ between limits, x_1 and x_2. It is written as $\int_{x_1}^{x_2} f(x)\,dx = g(x_2) - g(x_1)$

eg: $\int_1^2 2x\,dx = x^2\Big]_1^2 = 4 - 1 = 3$

Evaluate $\int_0^{\pi/4} \cos 2x\,dx$

A short table of integrals:

$f(x)$	$g(x) = \int f(x)\,dx$
x^n	$x^{n+1}/(n+1)$
$1/x$	$\log x$
$\log x$	$x \log x - x$
e^{ax}	$(e^{ax})/a$
$\sin x$	$-\cos x$
$\cos x$	$\sin x$
$\tan x$	$-\log(\cos x)$

$$\int_0^{\pi} \sin^2 x\,dx = \pi/2$$

$$\int_0^{\pi} \sin x \cos x\,dx = 0$$

$$\int_0^{\infty} e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{2a} \quad (a>0)$$

$$\int_0^1 (\log x)^n\,dx = (-1)^n n!$$

$$\int_0^{\infty} x^{n-1} e^{-x}\,dx = \int_0^1 \{\log(1/x)\}^{n-1}\,dx = \Gamma(n) \quad \text{(Gama function)}$$

$$\Gamma(n+1) = n\,\Gamma(n), \quad n>0$$

$$\Gamma(1) = 1 \qquad \Gamma(\tfrac{1}{2}) = \sqrt{\pi}$$

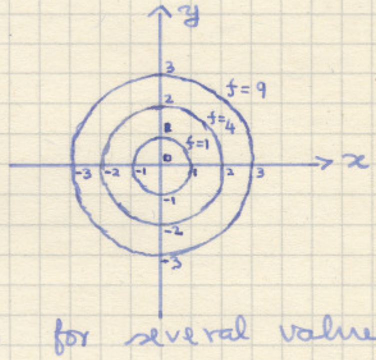
Functions in three dimensions: $f(x, y, z)$

x, y, z are usually coordinate variables.

eg: $x^2 - xy + z$, $\quad 3x^2 + z^2 \quad \frac{x}{z}\cos y$ etc..

Such functions are difficult to represent graphically. Usually contour maps are made – often several sections will be needed for two dimensional representation.

Here is a plot of $x^2 + y^2 + z^2$ in the (x, y) plane for $z = 0$.



Value of the function are marked at each point on a coordinate grid. Points of equal value are joined to give a contour plot of the function. A collection of such plots for several values of z (level 0, 1, 2, 3 etc..), together form ~~#~~ a three-dimensional representation of the function $f(x, y, z)$

Such functions can be differentiated independently with respect to each variable. This is called <u>partial differentiation</u>.

eg: $f(x,y,z) = x^2 - xy + z \qquad \partial f/\partial x = 2x - y$

$\partial f/\partial y = -x \qquad \partial f/\partial z = 1$

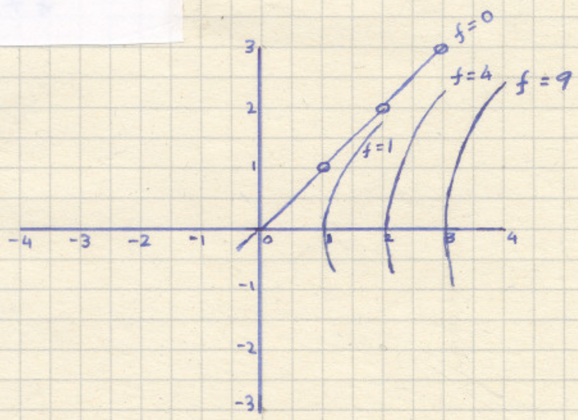
Try this: $f(x,y,z) = x^2 + y^2 + z^2$. Find $\partial f/\partial x$, $\partial^2 f/\partial x^2$, $\partial^2 f/\partial x \partial y$, $\partial^2 f/\partial x \partial z$, $\partial^2 f/\partial y \partial z$

The quantity $\partial^2 f/\partial x^2 + \partial^2 f/\partial y^2 + \partial^2 f/\partial z^2$ is called the Laplacian of the function $f(x,y,z)$ and is written as $\nabla^2 f(x,y,z)$.

∇^2 is known as the <u>Laplacian operator</u>.

Find the Laplacian of $x^2 + y^2 + z^2$

Complete the following contour plot



$f = x^2 - y^2$

Do you see two nodal lines in the plot, along which $f(x,y)$ is zero?