CH1204 Mathematics for Chemistry

Calculus for Chemists

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General Information

Calculus Context

Calculus is the branch of maths that deals with understanding **how things change**. Specifically, calculus gives us a mathematical language for talking about **rates of change**. This is very useful for us as chemists, because we are generally dealing with things like:

- **Chemical reactions**: where concentrations of reactants and products *change* over time.
- **Quantum mechanics**: we will often want to talk about how wavefunctions *change* as a function of position or time.
- **Thermodynamics**: we'll often be interested in how heat or energy changes and flows through a system.

Clearly in the first example, if we could use calculus to be able to calculate how fast a reaction will go, and thus know when to stop it for optimum yield, that would be very helpful. However, it's much more widely applicable than just these chemical examples. For instance:

- **Mechanics**: calculating how fast something is moving or accelerating - how it's position or velocity *changes* with time.
- **Biochemistry**: understanding how enzymes affect the *rate* of chemical reactions in cells.
- **Biology**: understanding how populations of animals or microbes *change* over time in response to certain factors.
- **Medicine**: understanding how diseases grow and spread within populations over time (who remembers covid?).
- **Finance**: predicting how stock market prices will change over time.

All of the above examples are places where the behaviour of real-world systems are governed by the mathematics of how things change, which is called **calculus**. What you'll learn in this course will be applicable far beyond chemistry.

Course Structure

The course will be structure in three parts:

1. Differentiation
2. Integration
3. Differential Equations

If you've done A-level maths, parts of the first two topics will be familiar to you, but we will approach things a bit differently to A level, **and there will be a lot of new content**, so you should still come to the workshops if you want to be prepared for the exam. If you've done it before, you can also help your coursemates who haven't with it.

Each week there will be a workshop where I introduce you to some topics in the first 10-15 min and you have a go at some questions for the rest of the time. Any questions you don't finish are your homework, and then later in the week there'll be a lecture where we go through the solutions together. There will also be surgeries every other week where you can get additional help if needed.

This part of the course is assessed via a written exam in summer. It'll be 5 questions, 10 marks each.

How to Study

The lecture notes for this course will be a bit more minimal than in CH1200, as the best way to learn maths is to **do maths** rather than just reading about maths. Generally, the printed notes will contain key ideas, formulae, and some minimal examples. The problem sheets will then flesh these examples out and provide more insight - **the answers you make to the problem sheets are the most important resource you'll have in this course.**

Some textbooks you can look at for extra help are:

- *Maths for Chemistry* - Monk and Munro
- *Foundations of Science Mathematics* - Sivia and Rawlings

Parts of these books go beyond what we will do - the content of the lecture notes and problem sheets determines what is examinable.

The internet is also an excellent place to learn maths, and there are some really excellent people on YouTube who make beautifully explained mathematical content. Particularly highly regarded is **3blue1brown**: `https://www.youtube.com/@3blue1brown`. His video series **The Essence Of Calculus** is essential viewing for this course, and you should all go and watch it immediately.

Chapter 1

Differentiation

To start, let's make sure we know what the **gradient** of a line is. You've seen gradients before in this course, and probably learnt them in school. However have you ever thought about what the gradient is physically telling you, about the line you have plotted? What does it mean if the gradient is large, or small? Remember that in science, when we draw graphs, they **represent something physical** - we're not talking about abstract mathematics here, but real physical, tangible things. Maths just gives us a convenient language to talk about them in.

Imagine I am throwing a ball, and have a graph that represents how far the ball is from my hand at a given time, so it's a graph of position (y-axis) against time (x-axis). If the gradient of that graph is large, it means that for a *small* increase in time (small increase along x) I get a *large* increase in position (large increase along y). Physically, this means that the ball is moving quickly - it has a high **velocity**.

This means we can interpret the gradient as follows:

> **The gradient is telling us how big a change on the y-axis we get for a given change on the x-axis.**

Or alternatively:

> **The gradient is telling us the rate of change of the thing on the y-axis as a function of the thing on the x-axis.**

Always remember that the maths we do has a physical interpretation - we're not interested in maths for the sake of maths[1].

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[1] Most of the time at least. I am unapologetically a maths fanboy.

1.1 Basics: Gradients and Curves

We know how to calculate the gradient of a straight line from school:

- 'Change in y over change in x'
- 'Rise over run'

The main idea is illustrated in Figure . For a straight line, it doesn't matter which two points on the straight line we choose, we'll always calculate the same gradient. **The gradient of a straight line is constant.**

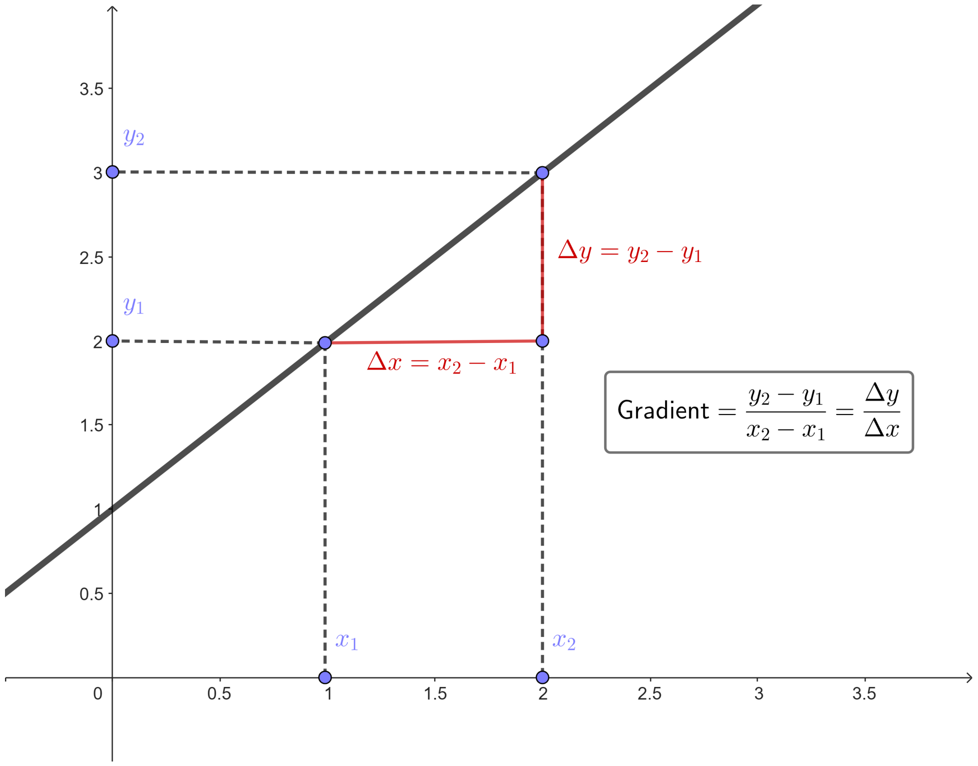

Figure 1.1: Gradient of a straight line.

What happens if we wanted to calculate the gradient of a non-linear function, like a curve? One thing we can do is draw **tangent lines** to the function at different points and calculate the gradient of those lines, as shown in Figure .

Clearly in the example in Figure , the gradient is different depending on where we draw the tangent. This means that the **gradient is no longer constant**, it varies with x. Measuring the gradient at $x = 1$ gives us a shallower gradient than at $x = 3$. This means that the gradient of this curve is also **a function of** x. This function has a name, and we call it a **derivative**. If we have a function $y = f(x)$, then we can define the **derivative** of this function with respect to x as:

$$\frac{\mathrm{d}y}{\mathrm{d}x}$$

or as

$$f'(x)$$

I'll use the first of these throughout this course, but it's useful to know both - they mean the same thing. You can remember the notation $\frac{\mathrm{d}y}{\mathrm{d}x}$ by thinking about the definition of the gradient in Figure - change in y over change in x.

So, if I can calculate the function $\frac{\mathrm{d}y}{\mathrm{d}x}$, then I have a function I can use to calculate the gradient of my original function $y = f(x)$ at any value of x. So how do I calculate it? Helpfully, clever people (notably Isaac Newton

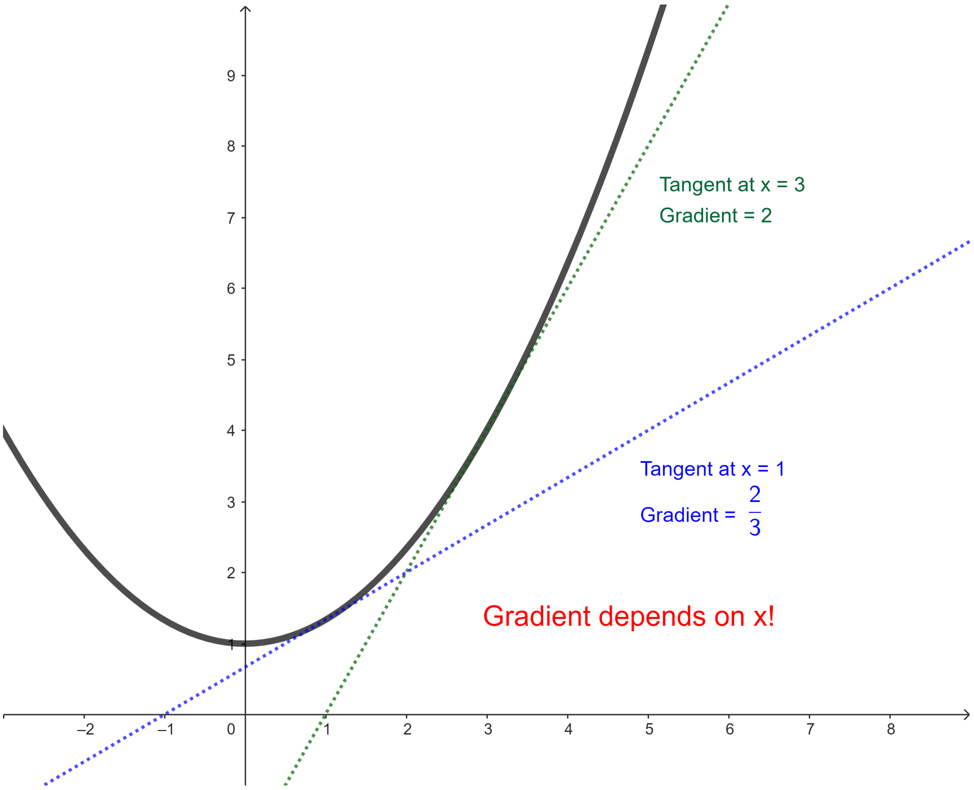

Figure 1.2: Gradient of a non-linear function - depends where we draw the tangent.

and Gottfried Leibniz) thought about this a few hundred years ago and figured it out. There's an appendix at the end of this document showing how to differentiate 'from first principles' for those of you who are interested, but for the purposes of this course, let's trust that those guys did it correctly.

1.1.1 Calculating Simple Derivatives

There are a set of rules for calculating derivatives of different functions, and we will see all the basic ones we'll need today. **I will expect you to know these**[2]. The process of calculating the derivative of a function is called **differentiating** the function - hence the name of this chapter.

Constants

If our function y is constant C:

$$y = C \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = 0$$

Think about if this makes sense, what is the gradient of the line $y = 2$?

Powers

If y is equal to x raised to some power n:

$$y = x^n \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = nx^{n-1}$$

'Multiply by the power and reduce the power by one'. This means that the gradient of a quadratic function is a straight line, and that the gradient of a straight line is a constant - can you see why?

Trigonometric Functions

If y is a sine or a cosine function:

$$y = \sin(ax) \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = a\cos(x)$$

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[2] Normally I'm not into just rote learning, as you know, but this is important.

$$y = \cos(ax) \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = -a\sin(x)$$

We will see next time why the constant a gets pulled out of the front of the derivative.

Remember that for trig functions, the derivatives go in a kind of cycle:

$$\sin(x) \xrightarrow{\text{Diff.}} \cos(x) \xrightarrow{\text{Diff.}} -\sin(x) \xrightarrow{\text{Diff.}} -\cos(x) \xrightarrow{\text{Diff.}} \sin(x)$$

We can talk about $\tan(x)$ another time.

Exponential Functions

For the exponential function, e^x:

$$y = \mathrm{e}^x \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = \mathrm{e}^x$$

Beautiful. This makes calculus with exponential functions incredibly simple, and is why we prefer natural logarithms to base-10 logarithms.

If we have a constant involved:

$$y = \mathrm{e}^{ax} \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = a\mathrm{e}^{ax}$$

Natural Logarithms

For the natural logarithm, $\ln(x)$:

$$y = \ln(x) \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = \frac{1}{x}$$

We might come onto why this is later in the course.

1.1.2 Minor Complications

If there is a constant coefficient infront of the function, then just carry it through:

$$y = Ax^2 \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = A \times 2x$$

Where $2x$ is the derivative of x^2 following the rule above for powers.

If the thing to differentiate is a sum of different functions, just differentiate each term separately.

$$y = 2x^2 + 5x + 3 \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = 4x + 5$$

Note that the above does **not** apply if y is a product of different functions, such as $y = x\sin(x)$. We will discuss this next time.

1.1.3 Second Derivatives

Sometimes, we want to differentiate a function again - to find the gradient of a gradient function, or similar. We can just repeat the operation, and this is called taking the **second derivative**. The notation for this is:

$$y = x^2 \xrightarrow{\text{Differentiate Twice}} \frac{\mathrm{d}^2y}{\mathrm{d}x^2} = 2$$

You can extend this notation to third, fourth, and higher derivatives.

1.1.4 Context: Equations of Motion

At the start we talked about how if I threw a ball and it moved a large distance in a short time, then it was moving fast (high velocity). If I had a graph of the position of the ball against time, the gradient of this graph would tell me how fast the ball was moving. The gradient is just the derivative, so:

> The derivative of position *with respect to time* is **velocity**.

If we define position as s, velocity as v, and time as t, then:

$$v = \frac{\mathrm{d}s}{\mathrm{d}t}$$

Furthermore, the rate of change of *velocity* with respect to time is called **acceleration**. If acceleration is a:

$$a = \frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}^2 s}{\mathrm{d}t^2}$$

So, this will come in handy if we need to work out how fast something is moving - which might be handy in the mechanics of molecular collisions.

You can now attempt the problems on **problem sheet 1**.

Problem Sheet 1 - Basics

Calculus was developed by Isaac Newton and the man pictured opposite - Gottfried Leibniz. Born in 1646 in Leipzig in the Holy Roman Empire (present day Germany), he developed calculus at about the same time as, and independently of, Isaac Newton. Unfortunately, the renaissance equivalent of a Twitter pile-on happened to him because even though Leibniz published first, Newton's friends thought he had plagiarised some of Newton's unpublished work. Recent historians have decided both men developed it independently, and so his reputation has recovered somewhat.

Remember that the reason we are doing this maths is because it's essential if you want to be a scientist. In the immortal words of Mos Def : **if you want to know how to rhyme, you'd better learn how to add, it's mathematics.** *I have it on good authority that Mos Def was talking about Chemistry and not hip-hop here.*

You should be able to complete these problems having read section 1.1 in the main handout. There are a lot of problems here, those you don't complete in the workshop are your homework. The first 3 are more pure mathematical, and the final 3 are more applied.

1. Determine the derivative of y with respect to x:

   i $y = 34$
   ii $y = x^3$
   iii $y = 5x^7$
   iv $y = \cos(4x)$
   v $y = 2\sin(8x)$
   vi $y = \mathrm{e}^{5x}$
   vii $y = 4\mathrm{e}^{3x}$
   viii $y = \ln x$
   ix $y = 2\ln(3x)$

2. Determine the derivatives of y with respect to x. Anything other than y or x is a constant.

   i $y = 6x^2 - 3x + 9$
   ii $y = 4x^5 - 3$
   iii $y = (x + 7)^2$
   iv $y = \frac{3}{x}$
   v $y = x^{\frac{1}{2}}$
   vi $y = x^{0.54}$
   vii $y = x^2(x^3 + 2x^{0.5})$
   viii $y = \frac{x^3+7}{x}$
   ix $y = ax^3 + bx^2 - 5$

3. Evaluate the following derivatives:

   i $\frac{\mathrm{d}x}{\mathrm{d}y}$ if $x = 7y^3 - 3y^2 + y - 2$
   ii $\frac{\mathrm{d}F}{\mathrm{d}t}$ if $F = 4\sin(6t) + 3t^2$
   iii $\frac{\mathrm{d}U}{\mathrm{d}t}$ if $U = at^2 + \ln t$
   iv $\frac{\mathrm{d}\Omega}{\mathrm{d}\lambda}$ if $\Omega = \frac{\lambda^2+2\lambda}{4\lambda}$

4. The relationship between force F and potential energy V is given by

   $$F = -\frac{\mathrm{d}V}{\mathrm{d}r}$$

   Where r is a distance. The Coulomb potential energy between two charged particles is given by:

   $$V = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

   where q_1 and q_2 are the charges, r is the distance between the charges, and ϵ_0 is a constant.

   Derive an expression for the force between the charged particles.

5. The distance s travelled by an bacteria moving around in a cell is given by:

$$s = at - bt^2$$

Where $a = 2\,\mu\mathrm{m\,s^{-1}}$, and $b = 0.1\,\mu\mathrm{m\,s^{-2}}$, and t is the elapsed time in seconds.

   i What is the initial velocity of the bacteria?
   ii Is the bacteria accelerating or decelerating?
   iii What is the velocity of the bacteria after $10\,\mathrm{s}$?
   iv Will the bacteria ever return to its initial position? If so, when?

6. The Schrödinger Equation for a 1D particle in a box is given by:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = E\Psi$$

A wavefunction that satisfies this equation is:

$$\Psi = N\sin\left(\frac{n\pi x}{L}\right)$$

You may assume everything apart from x is a constant.

   i Determine the first and second derivatives of Ψ with respect to position x.
   ii By substituting your result from above in into the Schrödinger Equation given, derive an expression for the energy of the particle, E.

1.2 Advanced Differentiation

Now we are going to talk about two more advanced differentiation techniques, which will expand the range of functions you are able to differentiate.

1.2.1 Products of Functions

To differentiate a function which can be expressed as the **product** of two functions, such as $x\cos x$ or $\cos(x)\sin(x)$ we can use something called the **product rule**.

For a function $y = y(x)$ that is the product of two functions $u = u(x)$ and $v = v(x)$, such that $y = uv$:

$$y = uv \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = u\frac{\mathrm{d}v}{\mathrm{d}x} + v\frac{\mathrm{d}u}{\mathrm{d}x}$$

So, you just take the first function and multiply it by the derivative of the second, then take the second function, and multiply it by the derivative of the first, and then add the two results together. For example:

$$y = x\sin(x) \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = x\cos(x) + \sin(x)$$

Because the derivative of x with respect to x is 1 (as $x = x^1$, which becomes $1 \times x^0 = 1$ when differentiated). Another example would be:

$$y = x^2\mathrm{e}^x \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = x^2\mathrm{e}^x + 2x\mathrm{e}^x$$

1.2.2 Functions of Functions

Sometimes we get functions nested inside other functions, such as:

$$y = \cos(3x + 2)$$

To differentiate this, we use something called the **chain rule**. To use the chain rule, we find a substitution that makes the function into something easily differentiable - you do this by intuition and will quickly get the hang of it. In the example above, let's use the substitution $u = 3x + 2$. Then we can write the function as:

$$y = \cos(u) \text{ where } u = 3x + 2$$

We don't have to call the new function u, it can be anything you want. Go wild.

Now we can use **the chain rule** which states that, for a function $y = y(u)$ where $u = u(x)$:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}y}{\mathrm{d}u} \times \frac{\mathrm{d}u}{\mathrm{d}x}$$

To remember which way around the derivatives go, you can look at the derivatives in the equation above and imagine the $\mathrm{d}u$ terms 'cancelling out' like in a fraction so that the RHS is equal to the LHS. However, I must stress that **this is not actually what happens** - the derivative notation merely **looks like a fraction**, but it's not **actually a fraction.** Ok?

All that remains is for us to compute the derivatives and plug them in to the chain rule formula. With our original example:

$$y = \cos(u) \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}u} = -\sin(u)$$

$$u = 3x + 2 \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}u}{\mathrm{d}x} = 3$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}y}{\mathrm{d}u} \times \frac{\mathrm{d}u}{\mathrm{d}x} = -\sin(u) \times 3 = -3\sin(3x + 2)$$

Where in the last step we undid our original substitution, and replaced u with $3x + 2$.

Let's do another example, with different letters to emphasise that it really doesn't matter what symbols we use for our derivatives. Imagine we have the function $F = F(t)$:

$$F(t) = \mathrm{e}^{4t^2+3t+6}$$

We make a substitution $\theta = 4t^2 + 3t + 6$, and get $F = \mathrm{e}^{\theta}$. We can then construct a chain rule, remembering that ultimately we want to find $\frac{\mathrm{d}F}{\mathrm{d}t}$:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \frac{\mathrm{d}F}{\mathrm{d}\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t}$$

I've dropped the × symbol for conciseness. Then we calculate:

$$\frac{\mathrm{d}F}{\mathrm{d}\theta} = \mathrm{e}^{\theta} \text{ and } \frac{\mathrm{d}\theta}{\mathrm{d}t} = 8t + 3$$

Putting it all together:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = (8t+3)\mathrm{e}^{\theta} = (8t+3)\mathrm{e}^{4t^2+3t+6}$$

Not so bad, right?

1.2.3 Combinations of Chains and Products

Sometimes we will have to do the chain rule more than once, or use the chain rule on one or both of the parts of a product rule. It can get fiddly, but it's not difficult - you just have to be systematic and careful. Let's look at two examples.

Differentiate the function:

$$y = x^3 \sin(4x + \pi)$$

We can use the product rule to find that

$$\frac{\mathrm{d}y}{\mathrm{d}x} = x^3 \frac{\mathrm{d}}{\mathrm{d}x}[\sin(4x+\pi)] + 3x^2 \sin(4x+\pi)$$

Where I've used the standard notation $\frac{\mathrm{d}}{\mathrm{d}x}[f(x)]$ to denote that we want to differentiate the thing in square brackets $(f(x))$ with respect to x, but haven't actually worked out the derivative yet[3].

To work out the derivative, we use the chain rule, with the substitution $u = 4x + \pi$. Let's also call the bit of the function we want to use the chain rule on $Z = \sin(4x + \pi)$, to tidy up notation. With our substitution, we find:

$$Z = \sin(u) \text{ where } u = 4x + \pi$$

$$\frac{\mathrm{d}Z}{\mathrm{d}x} = \frac{\mathrm{d}Z}{\mathrm{d}u}\frac{\mathrm{d}u}{\mathrm{d}x} = 4\cos(u) = 4\cos(4x+\pi)$$

Noting that:

$$\frac{\mathrm{d}Z}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}[\sin(4x+\pi)]$$

We can put the result above back into our original product rule formula to find:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 4x^3\cos(4x+\pi) + 3x^2\sin(4x+\pi)$$

Now let's look at a final example, differentiating the function:

$$y = \cos(\mathrm{e}^{6x+4})$$

Here we have a function in a function in a function! We can just use the chain rule twice, and be systematic. Firstly, let's define some substitutions:

$$y = \cos(g) \text{ where } g = \mathrm{e}^{h} \text{ where } h = 6x + 4$$

I've just broken it down into three functions that we can easily differentiate. Now let's think about chain rules, remembering we ultimately want $\frac{\mathrm{d}y}{\mathrm{d}x}$:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \frac{\mathrm{d}y}{\mathrm{d}h}\frac{\mathrm{d}h}{\mathrm{d}x}$$

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[3] Writing $\frac{\mathrm{d}}{\mathrm{d}x}$ like is is called writing it as a *differential operator*.

To find $\frac{dy}{dh}$, we can use another chain rule:

$$\frac{dy}{dh} = \frac{dy}{dg}\frac{dg}{dh}$$

So that overall:

$$\frac{dy}{dx} = \frac{dy}{dg}\frac{dg}{dh}\frac{dh}{dx}$$

We can work out these three derivatives from our substitutions:

$$\frac{dy}{dg} = -\sin(g) \text{ and } \frac{dg}{dh} = e^h \text{ and } \frac{dh}{dx} = 6$$

Combining it all and undoing our substitutions leads to:

$$\frac{dy}{dx} = -6e^{6x+4}\sin(e^{6x+4})$$

Yuk - but hopefully you can see that it's just logical. This is about as tricky as I'd ask in the exam.

1.2.4 Context: Differentiating Wavefunctions

The radial distribution function $R(r)$ for a 1s electron in a hydrogen atom is given by:

$$R(r) = Nr^2e^{-2r}$$

This function gives a measure of how likely the electron is to be found at a distance r from the nucleus, and N is a constant. The radial distribution function is derived from the wavefunction, and atomic wavefunctions (Ψ) generally tend to have a form like:

$$\Psi(r) = \text{Some polynomial in r} \times \text{Some exponential function in r}$$

So to differentiate wavefunctions, like when we are solving the Schrödinger equation, we often need to use the product rule. If we differentiate the radial distribution function above with respect to r using the product rule, we find:

$$\frac{dR(r)}{dr} = 2re^{-2r} - 2r^2e^{-2r}$$

We'll use this result next time.

You can now attempt the problems on **problem sheet 2**.

Problem Sheet 2 - Advanced Differentiation

Following formal development of calculus, there was an explosion of work in the area by mathematicians and scientists all over the world. One of these mathematicians was **Maria Agnesi***, pictured opposite. Born in Milan in present day Italy in 1718, she is credited with writing the first book on both differential and integral calculus, and was also the first woman ever appointed as a mathematics professor at a university.*

Named after Agnesi is a famous curve called the **Witch of Agnesi***. Functionally the Witch of Agnesi is identical to another function called a Lorentzian function, taking the form:*

$$\frac{1}{1+x^2}$$

This function is used in spectroscopy for modelling spectral lineshapes.

You should be able to complete these problems having read section 1.2 in the main handout. The first 5 are more pure mathematical, and the final 2 are applied. The final three questions are rather challenging and you will likely need some assistance if this is the first time you have been introduced to differentiation.

1. Using the chain rule, determine the derivative of y with respect to x:

   i $y = \mathrm{e}^{-x^2}$ ii $y = \cos(2\pi x + \pi)$ iii $y = (x^2 - 1)^7$

2. Using the product rule, determine the derivative of y with respect to x.

   i $y = x^5 \cos(3x)$ ii $y = \sin(2x)\mathrm{e}^{3x}$ iii $y = 3x^2 \ln(x)$

3. Using the chain rule and product rule together, determine the derivative of y with respect to x.

   i $y = \sin(2\pi x)(x^2 + 1)^{-1}$ ii $y = (3x^2 - 1)^7 \mathrm{e}^{4x}$

4. Find the gradient of the curve $y = x + \ln(x + 4) + 4$ when $x = 6$.

5. Using an appropriate method, determine the derivatives of y with respect to x of the following functions.

   i $y = \tan(x) = \frac{\sin(x)}{\cos(x)}$ iii $y = \sin(2\pi x)\cos(2\pi x)$

   ii $y = [5x^2 + 2x + 3]\mathrm{e}^{1-x}$ iv $y = (3x + 5)^9 (2x + 7)^5$

6. The Maxwell-Boltzmann distribution of speeds $f(c)$ for atoms with mass m at a temperature T is given by:

   $$f(c) = \sqrt{\frac{2}{\pi}\left(\frac{m}{k_B T}\right)^3} c^2 \exp\left(-\frac{mc^2}{2k_B T}\right)$$

   Find the derivative $\frac{\mathrm{d}f}{\mathrm{d}c}$. You may assume all quantities other than c are constant.

7. The probability of finding an electron $P(r)$ at position r in a 2s orbital in hydrogen is given by:

   $$P(r) = Nr^2(2 - r)^2\mathrm{e}^{-r}$$

   Find the derivative of $P(r)$ with respect to r.

1.3 Stationary Points

A very common use of differential calculus is to find **stationary points** of a function. To understand what this means, consider the graph in Figure , which shows a plot of yield of a chemical reaction as a function of reaction progress. Ideally, we want to stop the reaction at a point where the yield is highest - so how can we determine this point?

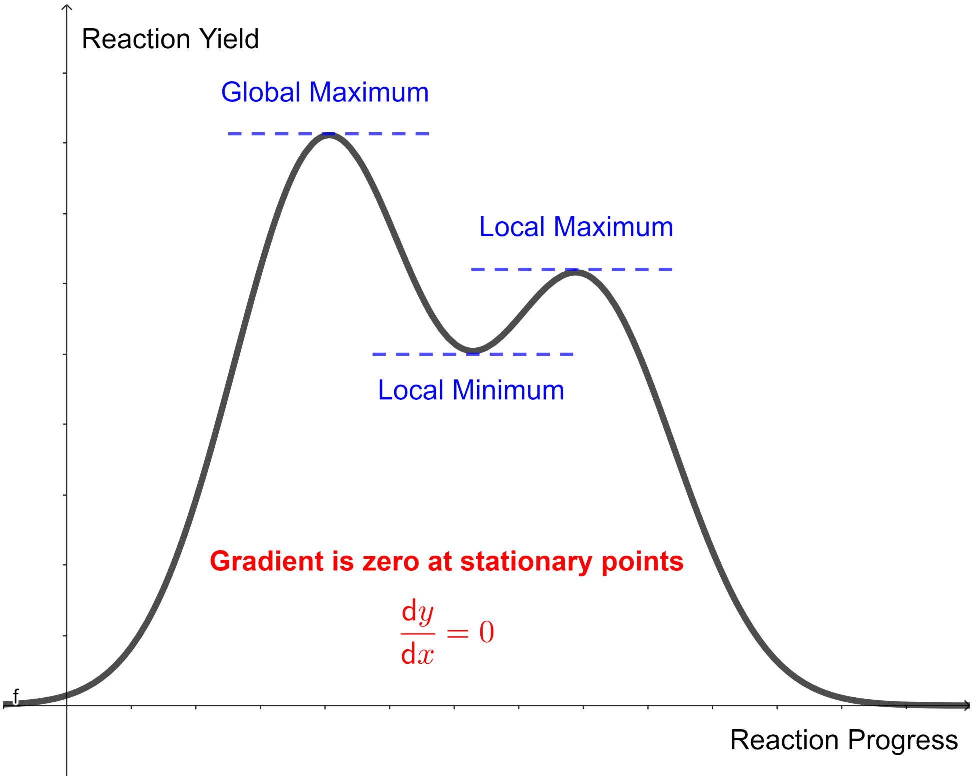

Figure 1.3: Stationary points: maxima, minima, saddle points (see later), occur when the gradient of a function passes through zero.

The key is to notice that at the maximum point, the gradient of the function is zero, because the gradient moves from being positive (on the left hand side of the maximum, where the function is rising) to negative (on the right hand side, where the function is falling). Thus, at the maximum, the gradient must pass through zero. This holds for any kind of stationary point, and we can have minima too - as shown on the diagram. The term **stationary point** simply means a point where the gradient (derivative) of the function is zero. We will see how to classify different types of stationary points soon.

1.3.1 Finding Stationary Points

Finding the stationary points of a function is as simple as setting the derivative of the function equal to zero and solving the resulting equation. For example, say we wanted to find the stationary points of $y = x^2$. First we differentiate:

$$y = x^2 \xrightarrow{\text{Differentiate}} \frac{\mathrm{d}y}{\mathrm{d}x} = 2x$$

then we set the derivative equal to zero, and solve it for x:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 2x = 0 \xrightarrow{\text{Solve}} x = 0$$

For $y = x^2$, there is one stationary point, and it occurs at $x = 0$. We could substitute this value back into our original equation to find the y coordinate, and we'd find the coordinates of the stationary point are (0,0). Does this make sense, thinking about the graph of $y = x^2$?

A more complex example could be to find the stationary points in the function $F(x)$:

$$F(x) = \frac{1}{3}x^3 - \frac{1}{2}x^2 - 6x + 3$$

First we differentiate:

$$\frac{\mathsf{d}F}{\mathsf{d}x} = x^2 - x - 6$$

Then set the equation equal to zero and solve. This time, the resulting equation is quadratic, but we can deal with that by factorisation:

$$\frac{\mathsf{d}F}{\mathsf{d}x} = x^2 - x - 6 = (x-3)(x+2) = 0 \xrightarrow{\text{Solve}} x = 3 \text{ or } x = -2$$

So now we have two stationary points, at $x = 3$ and $x = -2$. How can we know if these stationary points are maxima or minima?

1.3.2 Classifying Stationary Points

One simple way to classify stationary points is to simply look at a graph of the function and do it visually - looking at the example in Figure , it's clear that (from left to right), we have a maximum, minimum, and another maximum. The highest point of the function is called the **global maximum**, and any other maxima are called **local maxima**. Similarly, we have a **local minimum** - this is not the global minimum, because the function goes to zero, and so the lowest point of this function is lower than the local minimum.

However, it won't always be possible to easily sketch functions, so we can use algebra to classify stationary points too. The trick is to realise:

- At a **maximum**, the gradient changes from **positive** on the left side to **negative** on the right side.
- At a **minimum**, the gradient changes from **negative** on the left side to **positive** on the right side.

So we now need to think about the **rate of change of the gradient**, which requires we use the **second derivative**, as illustrated in Figure .

- At a **maximum**, the gradient is decreasing (+ve to -ve) so the second derivative is **negative** (or zero).
- At a **minimum**, the gradient is increasing (-ve to +ve) so the second derivative is **positive** (or zero).

To illustrate this, let's use the example we had earlier of the function $F(x)$, which had stationary points at $x = 3$ and $x = -2$. To classify these, we first calculate the second derivative:

$$\frac{\mathsf{d}^2F}{\mathsf{d}x^2} = 2x - 1$$

We then plug in each value of x and check the sign of the second derivative at each point:

$$x = 3 \rightarrow \frac{\mathsf{d}^2F}{\mathsf{d}x^2} = 5 \rightarrow \text{ Positive } \therefore \text{ Minimum}$$

$$x = -2 \rightarrow \frac{\mathsf{d}^2F}{\mathsf{d}x^2} = -5 \rightarrow \text{ Negative } \therefore \text{ Maximum}$$

1.3.3 Saddle Points

What happens if the second derivative of a function is zero? In this case, there are three options. The stationary point could be a higher order maximum or a minimum, or it could be a **saddle point**. A saddle point is a stationary point where the gradient has the same sign on both sides of the point. You may have heard this called a **point of inflection** in A level maths, but strictly you can have non-stationary points of inflection, so saddle point is a better term. Saddle points look something like the example in Figure . To classify a point with zero second derivative, you need to analyse the sign of the gradient on either side of the point:

- For a **maximum**, the gradient will be positive before and negative after the point.

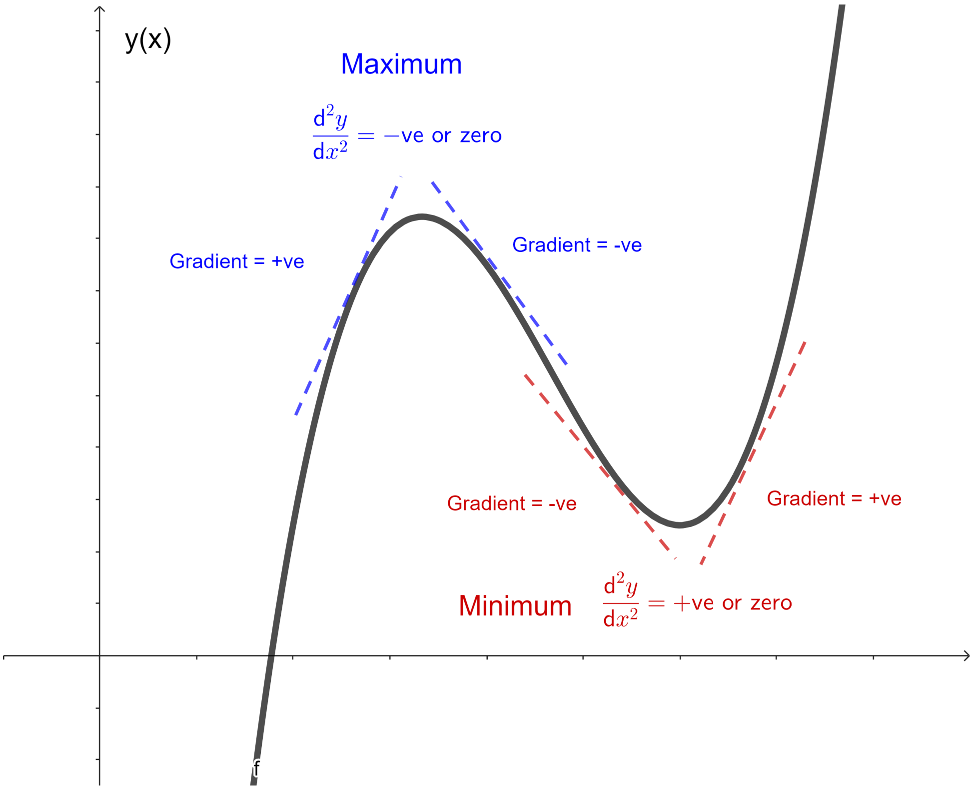

Figure 1.4: Classification of maxima and minima. If the second derivative is zero, further checks are needed.

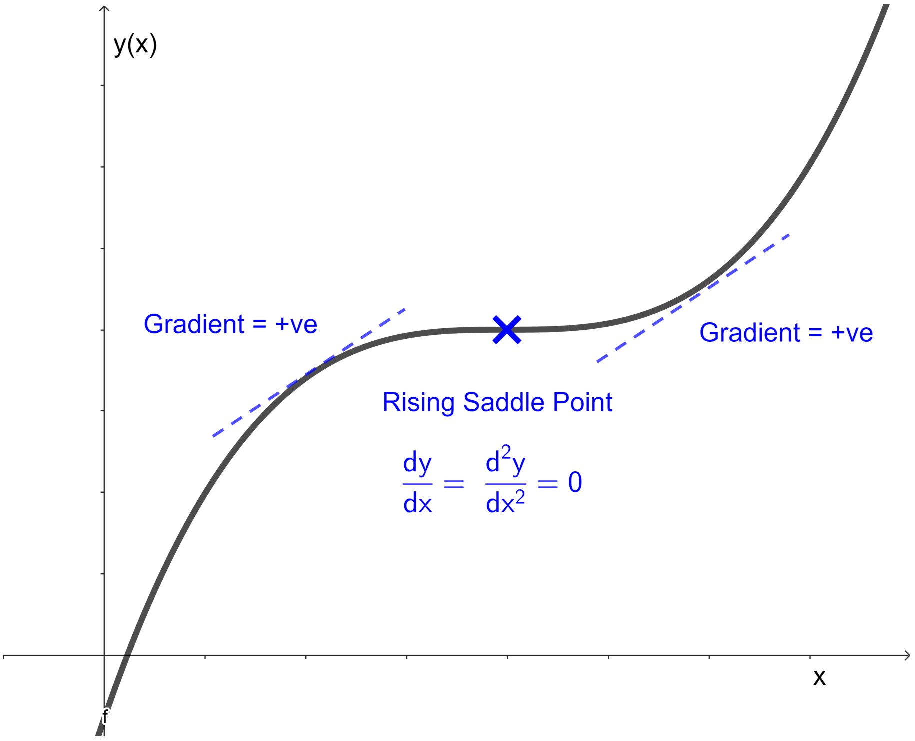

Figure 1.5: A rising saddle point - both the first and second derivatives are zero.

- For a **minimum**, the gradient will be negative before and positive after the point.
- For a **saddle point**, the gradient will have the same sign before and after the point. If the gradients are positive, it is a **rising saddle point**, and a **falling saddle point** if they are negative.

To check the sign of the gradient on each side, simply substitute the x-coordinate either side of the stationary point into your function for the derivative.

1.3.4 Context: Where is the electron?

Previously we had a radial distribution function $R(r)$ for a 1s electron in a hydrogen atom. This function tells us the probability of finding an electron at a distance r from the nucleus. Can we use our new knowledge of stationary points to find out the most likely distance that the electron will be found?

This amounts to finding the position of the maximum in $R(r)$, so we take the derivative and set it equal to zero:

$$\frac{\mathrm{d}R(r)}{\mathrm{d}r} = 2r\mathrm{e}^{-2r} - 2r^2\mathrm{e}^{-2r} = 0$$

Solving this equation:

$$2r - 2r^2 = 0 \rightarrow r = 1$$

So the electron is most likely to be found at a distance of $r = 1$, but one what? The function $R(r)$ is written in **atomic units**, where the standard unit of length is the **Bohr radius**, a_0. Thus, the 1s electron in a hydrogen atom is most likely to be found at $r = a_0$.

You can now attempt the problems on **problem sheet 3**.

Problem Sheet 3 - Stationary Points

Today, research in calculus is called **analysis**. *Analysis deals with the study of functions, limits, and related things such as differentiation and integration. A well-known current researcher in analysis is* **Kate Okikiolu**, *who works at John Hopkins University in the USA.*

Okikiolu has worked a lot on something called the **Laplacian**, *which is a differential operator that is central to quantum mechanics and quantum chemistry. Given the symbol ∇^2, it finds a use in, amongst other things, a compact statement of the Schrödinger Equation for a hydrogen atom:*

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

This equation ultimately governs the whole subject of chemistry, and you'll hear a lot more about it in the next couple of years.

You should be able to complete these problems having read section 1.3 in the main handout. Today most of the problems are applied (only the first is not), because unlike Kate Okikiolu, we are not mathematicians, but chemists.

1. Find the values of x at the stationary points of the following functions, and classify the stationary points in each case.

   i $y = 6x^4$ ii $y = 6x^4 - 2x^3$ iii $y = \sin(x)$ (for $0 \leq x \leq \pi$)

2. The vibrations of a diatomic molecule can be simply modelled as a harmonic oscillator (imagine a spring between two atoms). The energy of the molecule $E(r)$ is a function of the bond length, r:

   $$E(r) = \frac{1}{2}k(r - r_0)^2$$

   Where k is a positive constant and r_0 is the equilibrium bond length. Find the value of r where the energy of the molecule is at a minimum, and annotate this value on a sketch of $E(r)$.

3. The displacement x as a function of time t of a colloidal particle moving in a straight line is given by:

   $$x(t) = 2t - 0.1t^2$$

   Determine the maximum displacement of the object.

4. The Maxwell-Boltzmann distribution of speeds $f(c)$ for atoms with mass m at a temperature T is given by:

   $$f(c) = \sqrt{\frac{2}{\pi}\left(\frac{m}{k_B T}\right)^3} c^2 \exp\left(-\frac{mc^2}{2k_B T}\right)$$

   You determined the derivative $\frac{\mathrm{d}f}{\mathrm{d}c}$ last week (problem sheet 2). Now use this result to find the most probable speed of the molecules in the gas.

5. The probability of finding an electron $P(r)$ at position r in a 2s orbital in hydrogen is given by:

   $$P(r) = Nr^2(2 - r)^2\mathrm{e}^{-r}$$

   You determined the derivative of $P(r)$ with respect to r last week (problem sheet 2). Use this result to find the value of r at the stationary points in P.

   Bonus: Explain the physical significance of the result (a sketch may help).

1.4 Partial Differentiation

So far we have only considered functions of one variable, like $y = f(x)$, or $F = z(t)$. Lots of useful functions are functions of more than one variable, such as:

$$p = p(V, T) = \frac{nRT}{V}$$

the ideal gas equation that we are familiar with. How do we think about these functions? Unlike a function of one variable, which we can represent with a 2D graph, a function of two variables needs to be represented as a **3D surface**, as in Figure .

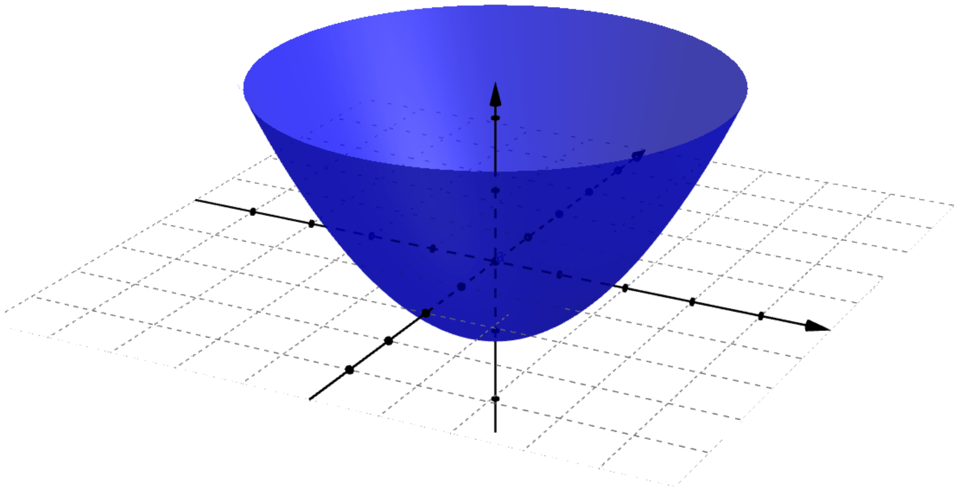

Figure 1.6: An example of a function of two variables, plotted in 3D. This function clearly has a minimum.

Clearly the function shown in Figure has a minimum, but how do we find out where it is? To do this, we need to be able to differentiate this function somehow, and one way to do that is to take something called a **partial derivative**.

1.4.1 Partial Derivatives

Take the function $z = z(x, y)$ with two arguments:

$$z(x, y) = x^2 + y^2$$

To take **partial derivatives** of this function, we simply differentiate with respect to each variable, treating the other variable as a constant, and we use some new notation:

$$\left(\frac{\partial z}{\partial x}\right)_y = 2x$$

The notation $\left(\frac{\partial z}{\partial x}\right)_y$ means 'partial derivative of z with respect to x whilst holding y constant'. To calculate the derivative, we just treated every single y as a constant, and differentiated the x terms as normal. We could also calculate the other partial derivative:

$$\left(\frac{\partial z}{\partial y}\right)_x = 2y$$

Note that the partial derivative uses a funny d (∂) rather than the normal d, to differentiate it from the normal derivative. That's all there is to it though - just normal differentiation, but treating one variable as a constant. This amounts to taking a 'slice' through our 3D plot in Figure , and then calculating the derivative of that slice. We could work out the coordinates of the minimum of our 3D function by setting each of the partial derivatives equal to zero, but we don't do that in this course.

1.4.2 Chemistry Examples

A classic place where this gets used in chemistry is when describing gases, as the pressure of a gas depends on both volume and temperature - $p = p(V, T)$.

Take the ideal gas equation:

$$p = \frac{nRT}{V}$$

We can calculate the two partial derivatives:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}\left(\frac{\partial}{\partial T}\right)_V (T) = \frac{nR}{V}$$

by treating V as a constant, and

$$\left(\frac{\partial p}{\partial V}\right)_T = nRT\left(\frac{\partial}{\partial V}\right)_t (V^{-1}) = -\frac{nRT}{V^2}$$

Now treating T as a constant - remember that n and R are constants by definition.

1.4.3 Context: Error Propagation

When analysing experimental errors, we often need to think about how the error in one variable affects our result. For example, we might be calculating the gradient of a straight line, and need to know how the error in y and x combine to give us an error in the gradient m. We do this by **error propagation**. Start with an expression for the thing we want to calculate in terms of the variables, for the gradient example:

$$m = \frac{y - c}{x}$$

Imagine we know the errors in y and x, called Δy and Δx respectively. It turns out[4] that the error in m, Δm is given by:

$$(\Delta m)^2 = \left(\frac{\partial m}{\partial x}\right)_y^2 (\Delta x)^2 + \left(\frac{\partial m}{\partial y}\right)_x^2 (\Delta y)^2$$

This expression holds for **any** function $m = m(x, y)$, not just the one above. We can understand it as follows:

- The first term is the product of how strongly m depends on x (the derivative) with the size of the error in x.
- The second term is the product of how strongly m depends on y with the size of the error in y.
- The total error in m is then given by the sum of these two - as both the size of the errors in the individual components x and y matter, and how strongly our desired result m depends on x and y. We might have a situation where there is a really large error in x, but actually x doesn't really affect m (small partial derivative), so that error doesn't affect m very much.

We'll see this more next year.

You can now attempt the problems on **problem sheet 4**.

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[4] I can prove this, and we'll see it next year - ask if you're impatient.

Problem Sheet 4 - Partial Differentiation

An important use of partial derivatives in chemistry is in thermodynamics, via the **Maxwell relations**. *Named after the Scottish scientist* **James Clerk Maxwell**, *they mathematically relate the partial derivatives of various thermodynamic quantities to one another. An example is given below.*

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

It's not physically obvious that the rate of change of temperature with volume should be equal to the rate of change of pressure with entropy - Maxwell relations are a classic example of how we often need to use mathematics to guide us in our physical observations. Maxwell, for completeness, also developed **Maxwell's equations** *for describing propagation of waves, and many more things – to the extent that when Einstein was asked if he stood on the shoulders of Newton, he replied 'no, I stand on the shoulders of Maxwell'.*

You should be able to complete these problems having read section 1.4 in the main handout. Today we have a mix of pure and applied problems. The final extended problem is about error propagation, which is an important application of of partial differentiation in analytical chemistry.

1. Find the partial derivatives $\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial z}{\partial x}\right)_y$ for the following:

   i $z = xy$
   ii $z = \mathrm{e}^{2xy}$
   iii $z = \cos(x) + \sin(y)$
   iv $z = y\cos(x)$
   v $z = \cos(x^2y^3)$
   vi $z = \frac{x-3}{y}$

2. The isothermal compressibility, κ, of a gas is defined as:

   $$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

   Derive an expression for κ for an ideal gas (i.e. one where $pV = nRT$).

3. The van der Waals' equation of state for one mole of gas is given by:

   $$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

   Where p, V, T, and R have their usual meanings, and a and b are constants.

   Determine the partial derivatives (i) $\left(\frac{\partial T}{\partial p}\right)_V$ and (ii) $\left(\frac{\partial p}{\partial V}\right)_T$. (Hint: rearrange the equation first, to make either T (i) or p (ii) the explicit subject, i.e. in the form $T = \ldots$ or $p = \ldots$)

4. If we measure a two quantities, x and y, and use them to calculate a third quantity, f such that $f = f(x, y)$, then the error in f, Δf, is given by:

   $$(\Delta f)^2 = \left(\frac{\partial f}{\partial x}\right)_y^2 (\Delta x)^2 + \left(\frac{\partial f}{\partial y}\right)_x^2 (\Delta y)^2$$

   Where Δx and Δy are the errors in x and y respectively.

   i $x = 2.0 \pm 0.2\mathrm{cm}$ and $\theta = 53 \pm 2°$. Given that $S = x\cos(\theta)$, find S and the error in S (ΔS). Note that you should convert the angle to radians for your answer to be meaningful.

   ii A $0.2181\,\mathrm{g}$ ($\pm$ $0.0001\,\mathrm{g}$) sample of KHP was titrated with $8.98\,\mathrm{mL}$ ($\pm$ $0.01\,\mathrm{mL}$) of NaOH. What is the concentration, and the error in the concentration, of the resulting solution?

   Note that KHP has a molecular weight of $206.227\,\mathrm{g\,mol^{-1}}$. *You may assume there is zero error associated with this molecular weight.*

Chapter 2

Integration

We've talked about differentiation, and know that if we have a function like $y = x^2$, we can define the derivative as:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 2x$$

However, what if we only knew the derivative, and not the original function? This might happen if we could only measure the change in something, and not it's actual value (like the speed of a car from a speed camera doesn't allow you to directly work out the position of the car). Is there a way we can 'undo' the derivative and get back our original function, y?

It turns out there is, and this process is called **integration**:

$$y \xrightarrow{\text{Differentiation}} \frac{\mathrm{d}y}{\mathrm{d}x}$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} \xrightarrow{\text{Integration}} y$$

Integration is useful in chemistry, for example because we might know a chemical reaction rate (a derivative) and want to work out the concentration of product at a certain time:

$$\frac{\mathrm{d}[\text{Product}]}{\mathrm{d}t} \xrightarrow{\text{Integrate}} [\text{Product}]$$

2.1 Integration Basics

Initially we think of integration as the reverse of differentiation, and integration operation has a special symbol. The **integral** of a function $f(x)$ is denoted by:

$$\int f(x)\ \mathrm{d}x$$

In this notation, the thing inside the integral sign $(f(x))$ is called the **integrand**.

2.1.1 Indefinite Integration

To evaluate the derivative of a function, we just do the opposite of whatever we did to find the derivative. For example:

$$\int 2x\ \mathrm{d}x = \frac{2}{2}x^2 + C = x^2 + C$$

Let's unpack this:

- To differentiate an expression like x^n, we multiplied by the power and then reduced the power by one. To integrate, we do the opposite - raise the power by one, and then divide by the *new* power.
- We add a constant C to our result. This is called the **constant of integration**.

Why do we add a constant C? Remember any constants in our original expression are lost when we take a derivative, because the derivative of a constant is zero. This means that we need to add on a constant to fully reconstruct our original function when we integrate it. We'll see soon how to determine the value of this constant. Let's see how to integrate some common functions - remembering that it's just the inverse of differentiation that we had before.

Constants

If our function y is constant k:

$$y = k \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = kx + C$$

Powers

If y is equal to x raised to some power n:

$$y = x^n \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = \frac{x^{n+1}}{n+1} + C$$

The inverse function x^{-1} is special and:

$$y = x^{-1} \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = \ln(x) + C$$

Try applying the normal rule to the inverse function and you'll see why it's weird.

Trigonometric Functions

If y is a sine or a cosine function:

$$y = \sin(ax) \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = -\frac{1}{a}\cos(x) + C$$

$$y = \cos(ax) \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = -\frac{1}{a}\sin(x) + C$$

Note that we divide by the constant, rather that multiplying now.

We just reverse the cycle of derivatives for integration:

$$\sin(x) \xleftarrow{\text{Int.}} \cos(x) \xleftarrow{\text{Int.}} -\sin(x) \xleftarrow{\text{Int.}} -\cos(x) \xleftarrow{\text{Int.}} \sin(x)$$

Exponential Functions

For the exponential function, e^x:

$$y = \mathrm{e}^x \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = \mathrm{e}^x + C$$

If we have a constant involved:

$$y = \mathrm{e}^{ax} \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = \frac{1}{a}\mathrm{e}^{ax} + C$$

Natural Logarithms

For the natural logarithm, $\ln(x)$:

$$y = \ln(x) \xrightarrow{\text{Integrate}} \int y \, \mathrm{d}x = x\ln x - x + C$$

Remember to always put in the constant of integration when doing an . The same rules regarding constants and expressions that are sums of terms that we saw for derivatives also apply:

$$\int Af(x) \, \mathrm{d}x = A\int f(x) \, \mathrm{d}x \text{ where A is a constant}$$

$$\int f(x) + g(x) + h(x) \; \mathrm{d}x = \int f(x) \; \mathrm{d}x + \int g(x) \; \mathrm{d}x + \int h(x) \; \mathrm{d}x$$

For example, I could simplify the integral below as:

$$\int 3x^2 + 6x + 7 \; \mathrm{d}x = 3 \int x^2 \; \mathrm{d}x + 6 \int x \; \mathrm{d}x + \int 7 \; \mathrm{d}x$$

To determine the constant of integration, we simply need to know a point on our integrated function. We'll see how this works in one of the problems. We call these kinds of integrals **indefinite integrals** because they are not evaluated between specific **limits**. To understand what this means, we have to think about integration graphically.

2.1.2 Definite Integration

We interpreted differentiation graphically as giving us the gradient of non-linear functions. We can think of integration graphically as giving us the **area between the function and the x-axis**. This is illustrated in Figure .

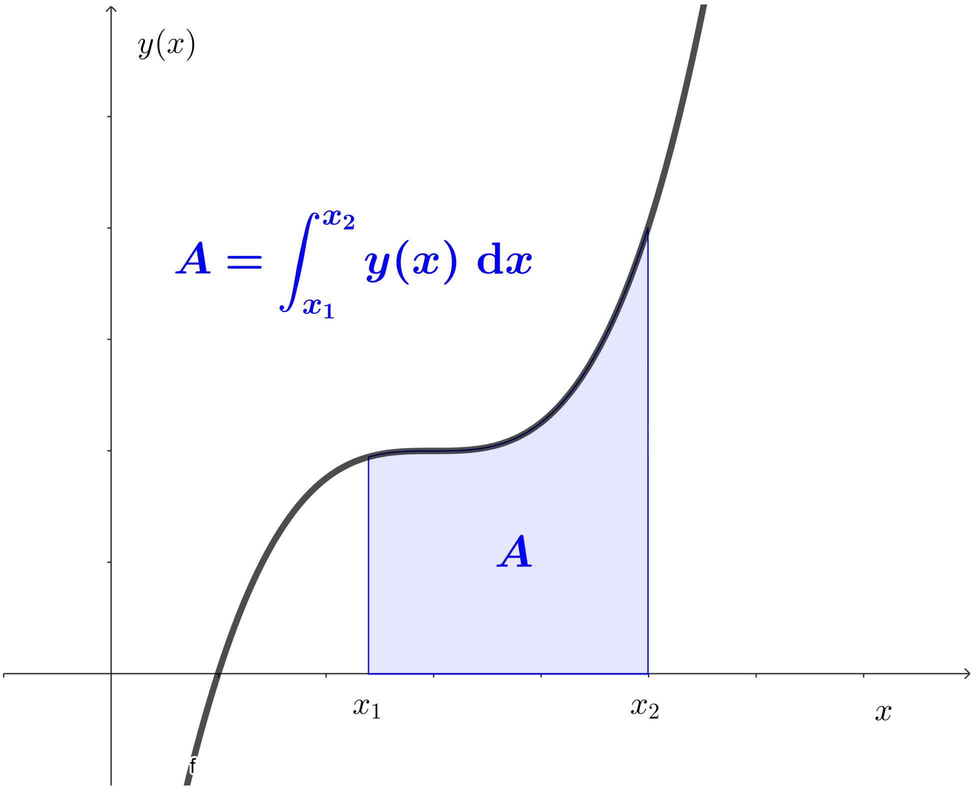

Figure 2.1: The definite integral of a function between x_1 and x_2 is defined as the area between the function and the x axis, evaluated between x_1 and x_2.

Evaluating an integral between two limits to calculate the area between a function an the x-axis is called doing a **definite integral**. To show this works, let's calculate the area between the curve $y = x^2 + 1$ and the x-axis between the limits 0 and 2.

$$\int_0^2 y(x) \; \mathrm{d}x = \int_0^2 x^2 + 1 \; \mathrm{d}x$$

We now evaluate the integral as normal, but put the limits around the result. We also don't need a constant of integration when doing definite integrals[1].

$$\int_0^2 x^2 + 1 \; \mathrm{d}x = \left[\frac{1}{3}x^3 + x\right]_0^2$$

---

[1] To understand why, do this example again leaving the constant of integration in.

To evaluate this, we simply evaluate the expression in the square bracket at the first limit, then at the second limit, and subtract them from each other:

$$\left[\frac{1}{3}x^3 + x\right]_0^2 = \left[\frac{1}{3}2^3 + 2\right] - \left[\frac{1}{3}0^3 + 0\right] = \frac{8}{3} + 2 = \frac{14}{3}$$

Leaving the answer answer as a fraction is fine, or you could convert it to decimals. To reiterate, this number is the area between the function $y = x^2 + 1$ and the x-axis, evaluated between $x = 0$ and $x = 2$. Remember that we **do not** need a constant of integration when evaluating a definite integral.

2.1.3 Context: Normalising Wavefunctions

In quantum mechanics, we have to ensure that our wavefunctions are **normalised**, which means that the integral of the square of the wavefunction $\Psi(x)$ over all space is equal to one:

$$\int_{-\infty}^{\infty} \Psi(x)^2 \, \mathrm{d}x = 1$$

Evaluating this integral for given wavefunctions enables us to calculate **normalisation constants** for the wavefunctions. We'll see this again next year.

You can now attempt the problems on **problem sheet 5**.

Problem Sheet 5 - Integration

Integration is the sister technique to differentiation, and has been around for longer (in forms that were not called 'integration' at the time). In particular, the mathematician **Hasan Ibn-al Haytham**[a] *developed a method for finding out the volumes of paraboloids. This method was basically integration, although he didn't call it this.*

Born in around 965 in Basra (modern day Iraq, then the Buyid Emirate) Ibn-al Haytham is often called 'the first true scientist'. He was a pioneer of the idea that ideas must be supported by experimental observation - an early precursor of what we now call the **scientific method**. *His 'Book of Optics' is an early classic in the theory of light and optics.*

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[a] Described as Arabic or Persian depending on which book you read.

You should be able to complete these problems having read section 2.1 in the main handout. The first five problems are pure, the final one is more applied.

1. Determine the integral of y with respect to x of the following:

   i $y = 59$
   ii $y = 2x^3$
   iii $y = \sin(10x)$
   iv $y = 2\cos(8x)$
   v $y = \mathrm{e}^{5x}$
   vi $y = 4\mathrm{e}^{3x}$
   vii $y = 5x^{-1}$
   viii $y = \frac{5}{x^2}$
   ix $y = \sqrt{x}$

2. Evaluate the following indefinite integrals:

   i $\int 3x^2 + 2x^7 \mathrm{d}x$
   ii $\int 6\mathrm{e}^{2x} - 2\mathrm{e}^{-3x} \mathrm{d}x$
   iii $\int \frac{1}{x^{4.75}} \mathrm{d}x$
   iv $\int \frac{1}{t^3} + t^3 \mathrm{d}t$
   v $\int 4(y^3 + y^2 + 1)\mathrm{d}y$
   vi $\int \sin(3\theta) + \cos(3\theta)\mathrm{d}\theta$

3. Evaluate the following definite integrals:

   i $\int_0^2 0.5\mathrm{e}^x \mathrm{d}x$
   ii $\int_2^4 \frac{1}{\sqrt{\mathrm{e}^x}} \mathrm{d}x$

4. Find the area bounded by the curve $y = \sin(x)$ and the x-axis, between $x = 0$ and π.

   Bonus: repeat the calculation between $x = 0$ and $x = 2\pi$. Can you explain the result?

5. (Harder) Find the equation of the curve that has a gradient function given by $\mathrm{e}^x + 2x$, given that the curve passes through the point (0, -3). Find the area enclosed between this curve and the x-axis between $x = 0$ and $x = 1$.

6. (Looks harder than it is) The heat capacity of quartz at constant pressure (C_p) is given approximately by:

   $$C_p = a + bT + cT^{-2} + dT^{-0.5}$$

   Where $a = 104.35\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $b = 6.07\times10^{-3}\mathrm{J\,K^{-2}\,mol^{-1}}$, $c = 3.0\times10^{4}\,\mathrm{J\,K\,mol^{-1}}$, and $d = -1070\,\mathrm{JK^{-0.5}mol^{-1}}$. T is temperature.

   Determine the enthalpy and entropy change of quartz on heating from $298\,\mathrm{K}$ to $1000\,\mathrm{K}$, given that:

   $$\Delta H = \int_{T1}^{T2} C_p \mathrm{d}T \text{ and } \Delta S = \int_{T1}^{T2} \frac{C_p}{T} \mathrm{d}T$$

2.2 Integration Hacks

Last time we saw how to integrate lots of things, and this'll serve us well for our needs as chemists. Calculating integrals quickly and efficiently is a large part of what computational and quantum chemistry is about, and to do this it's often possible to exploit symmetry, or other things, to make our lives easier (and calculations faster).

Note that in a previous version of this course, some other techniques for analysing integrals: 'integration by parts' and 'integration by substitution'. These are no longer part of the course, so don't panic if you see these on exam papers and cannot answer them.

2.2.1 Simple Shortcuts

The integral of anything multiplied by zero is still zero, even if that thing is very complicated:

$$\int_0^{\pi} \frac{\cos^2(x)\sin(\pi)}{x^3 + x^{1.5} - 5}\ \mathrm{d}x = 0$$

Because $\sin(\pi) = 0$.

The integral of anything between identical limits is zero by definition:

$$\int_{\pi}^{\pi} \frac{\Gamma(x)\mathrm{e}^{-x^2}}{1 + \ln(x)}\mathrm{d}x = 0$$

Because in this case the area must be zero - imagine shrinking the limits in Figure until there was no area between them.

We can also split up the limits of integration which can sometimes render the integral more straightforward to evaluate:

$$\int_{-2}^{3} f(x)\ \mathrm{d}x = \int_{-2}^{0} f(x)\ \mathrm{d}x + \int_{0}^{3} f(x)\ \mathrm{d}x$$

You can think of this as just doing the integral 'in stages' rather than all at once.

2.2.2 Exploiting Symmetry

The area produced by an integral is the area between the function and the x-axis - but what happens if the function is below the x-axis? By convention, this is defined as a **negative area**[2]. So what does this mean when we calculate an area like the one shown in Figure ?

Clearly, if the area below the x-axis is defined as negative area, the total area defined by this integral (the blue area in Figure) must be zero. This is because the function used here is an **odd function**, which means it satisfies the relationship:

$$f(-x) = -f(x)$$

By symmetry, the integral of an odd function between symmetrical limits (i.e. between $-a$ and a) is zero:

$$\int_{-a}^{a} f(x)\ \mathrm{d}x = 0 \text{ if } f(x) \text{ is an odd function}$$

Knowing this trick can make evaluating some horrific-looking integrals very easy.

Similarly, we can also have functions that are **even functions**, this means they satisfy the relationship:

$$f(-x) = f(x)$$

By symmetry, the integral of an even function between symmetrical limits is given by:

$$\int_{-a}^{a} f(x)\ \mathrm{d}x = 2\int_{0}^{a} f(x)\ \mathrm{d}x \text{ if } f(x) \text{ is an even function}$$

An example of this is shown in Figure . When evaluating difficult looking integrals between symmetrical limits, **always check if the function is even or odd first** - it can save you a lot of time!

---

[2] You might have learned in school that in this case you have to break the integral up into pieces that are above/below the axis and add them up at the end. This is only true if the integral you are evaluating physically represents something that cannot be negative - like the area of a field, or something. In general, treat things below the x-axis as negative area.

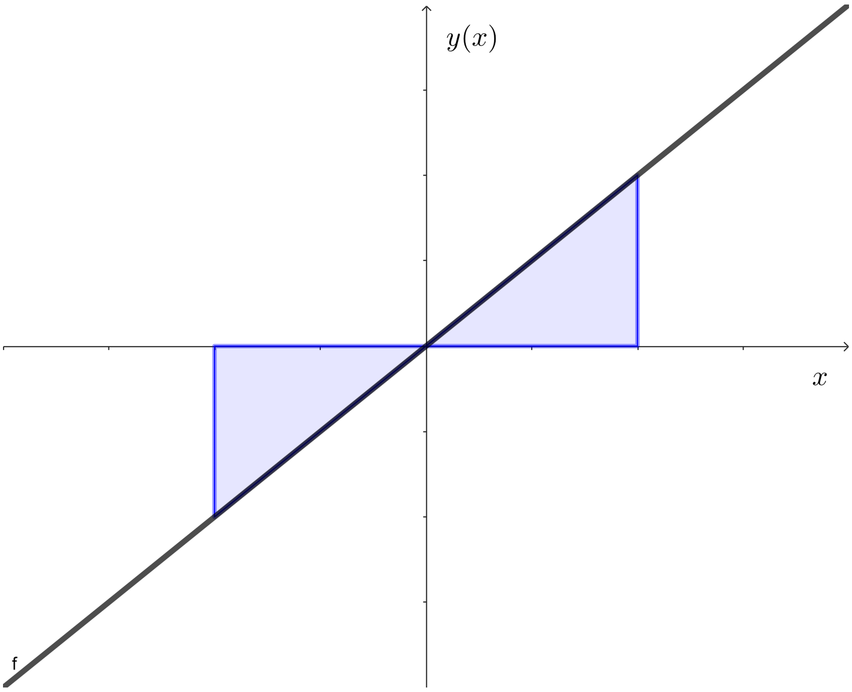

Figure 2.2: The integral of this function (an odd function) between symmetrical limits is zero, shown by the blue area.

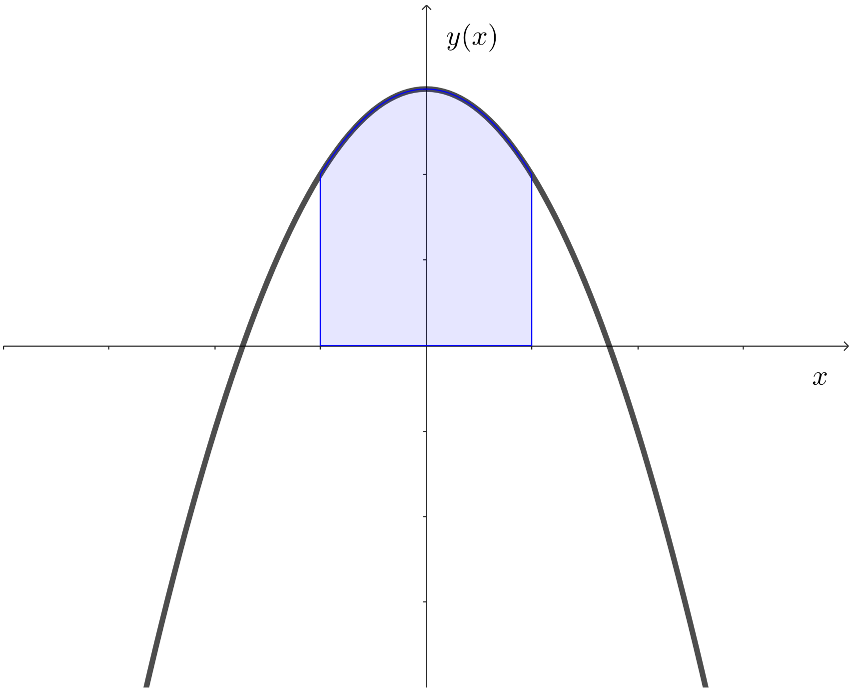

Figure 2.3: The integral of this function (an even function) between symmetrical limits is twice the integral of the function between 0 and the upper limit.

2.2.3 Standard Integrals

Sometimes, and especially in quantum chemistry, there are integrals which cannot be evaluated in an indefinite way. A classic example of this is the integral of a **Gaussian function**:

$$\int \mathrm{e}^{-x^2}\,\mathrm{d}x = \text{ undefined!}$$

However, many of these integrals can be evaluated as definite integrals, such as:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2}\ \mathrm{d}x = \sqrt{\pi}$$

That this happens to become the square root of π is pretty beautiful, I think.

The point is that quite a lot of the time we can look up these **standard integrals**, or just do them on a computer[3]. There's no shame in just using a result like this, as we're chemists, not mathematicians. I Google integrals all the time when I can't remember how they work.

In an exam, you'll be given any standard integrals you need - but remember for your future life and career that if you need to find out what a certain integral is and can't work it out - Google, or standard maths textbooks, will contain lists of standard integrals that can help.

2.2.4 Context: Computational Chemistry

In computational chemistry, you often use software packages (such as *Gaussian* or *Orca*) to calculate the structure and dynamics of molecules. Often, this amounts to solving the Schrödinger equation for the molecules, and in practice the computer ends up evaluating tens of thousands of integrals (or more) to accomplish this.

When setting up a job in computational chemistry, you'll often define something called a **basis set**, which is a set of mathematical functions that can be used to approximate the orbitals on the atoms in your molecule. Generally, these basis sets are made up of different kinds of Gaussian functions, because they have well known standard integrals. This means that it's blazingly fast for a computer to calculate the integrals - as you can just program the computer to know all the standard integrals. In fact, to calculate complex orbitals, one common strategy is to approximate the orbital as a series of different Gaussian functions, to increase the speed of the computation. You may see basis sets called things like *3-21G* or *6-31+G* - the numbers in these names refer to the number of different Gaussian functions that are used to approximate the orbitals. Larger numbers increase accuracy, but take longer to compute. Some basis sets go beyond Gaussian orbitals, to get increased accuracy, but at the expense of computational cost - integrating Gaussian functions like the one described above is really fast!

You can now attempt the problems on **problem sheet 6**.

Please note - there are many other tricks that people use to evaluate integrals than we have covered here. If you are interested in going deeper into physical chemistry/chemical physics/anything mathematical later on, it might be worth looking up things like **integration by parts** and **integration by substitution** in any maths textbook (or online). What we've learnt about integration here will suffice for most of what you see in the main chemistry course.

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[3] I'll add some information at the end of this course about doing calculus on computers with Python, for interest.

Problem Sheet 6 - Integration Tricks

Integration lies at the heart of quantum and computational chemistry. The Schrödinger Equation is a differential equation (see next week), and as such it's solutions tend to involve a lot of integration. Calculating integrals quickly and efficiently using computers is what computational chemists, such as **Anna Krylov** *do.*

Born in Donetsk, Ukraine, in 1967, Anna Krylov has made a number of significant breakthroughs in the efficient modelling of complex open-shell molecules. This computational chemistry underlies all the other chemistry everyone does - nobody can do chemistry without comparing their results to theoretical calculation, and scientists like Anna Krylov facilitate this. She is pictured here drinking coffee at her computer - stereotypical theoretical chemist behaviour.

You should be able to complete these problems having read section 2.2 in the main handout. You will find some of the standard integrals (reverse of this sheet) invaluable for questions 2-5.

1. Evaluate the following integrals, giving a reason for your answers:

   i $F = \int_{\pi}^{\pi} \tanh(x^2 - 3)\ \mathrm{d}x$

   ii $\Omega = \int_{0}^{\infty} \cos(^{\pi}/_{2})\ \mathrm{d}x$

   iii $y = \int_{-3}^{3} (x^2 + 4x - 3)\sin(n\pi)\ \mathrm{d}x$ where $n = 1, 2, 3\ldots$

2. Evaluate the following definite integrals, giving a reason for your answers:

   i $\int_{-2}^{2} x^3\ \mathrm{d}x$

   ii $\int_{-2}^{2} x^2\ \mathrm{d}x$

   iii $\int_{-4}^{4} x^{19}\cos(x)\ \mathrm{d}x$

   iv $\int_{-\infty}^{\infty} x^2 \mathrm{e}^{-ax^2}\ \mathrm{d}x$

3. For each of the functions below, sketch the function and evaluate the definite integral between the specified limits. Explain all answers fully.

   i $\sin(x)$ between $x = -2\pi$ and 2π

   ii $\cos^2(x)$ between $x = -\pi$ and π

   iii $\frac{\sin(x)}{x}$ between $x = -\infty$ and ∞

   iv $\sum_{n=1}^{100} \sin(n\pi)x$ between $x = 0$ and π.

4. Evaluate the following sum of integrals, explaining your answer:

$$\int_{0}^{3} \mathrm{e}^{-2x^2}\ \mathrm{d}x + \int_{3}^{13} \mathrm{e}^{-2x^2}\ \mathrm{d}x + \int_{13}^{250} \mathrm{e}^{-2x^2}\ \mathrm{d}x + \int_{250}^{\infty} \mathrm{e}^{-2x^2}\ \mathrm{d}x$$

5. The power P of a symmetrical Gaussian laser beam is given by the following expression:

$$P = I_0 \int_{-\infty}^{\infty} \exp\left(\frac{-2x^2}{\omega^2}\right) \mathrm{d}x \int_{-\infty}^{\infty} \exp\left(\frac{-2y^2}{\omega^2}\right) \mathrm{d}y$$

   Where I_0 is the intensity at the center of the beam, and ω is the width of the beam. Using the standard integrals below, calculate the power of a laser beam with $I_0 = 1 \times 10^{12}\ \mathrm{W\,m^{-2}}$ and $\omega = 6\ \mu\mathrm{m}$.

List of Standard Integrals

$$\int\limits_0^\infty \mathsf{e}^{-ax^2}\ \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$\int\limits_0^\infty \sqrt{x}\mathsf{e}^{-x}\ \mathrm{d}x = \frac{1}{2}\sqrt{\pi}$$

$$\int\limits_0^\infty x^2\mathsf{e}^{-ax^2}\ \mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$\int\limits_0^\infty \frac{\sin x}{x}\ \mathrm{d}x = \frac{\pi}{2}$$

$$\int\limits_{-\infty}^\infty \mathsf{e}^{-a(x+b)^2}\ \mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

Chapter 3

Differential Equations

Finally, we are going to talk about **differential equations**. These are equations which involve some kind of derivative, such as:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = x$$

Equations like this are incredibly commonplace in science, mathematics, and economics. This is because they allow us to relate *how things are going to change* (via derivatives) to *how things currently are* (via the other terms in the equation). There are entire university departments devoted just to studying differential equations, so we can only scratch the surface in two sessions - have a look online (3blue1brown has a nice series of videos) for more depth if you find this interesting. Differential equations are really beautiful.

These equations pop up in chemistry all the time in fields like **chemical kinetics**, where we are studying rates of reaction via **rate equations**:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k[\mathrm{A}]$$

These are equations that relate the rate of a chemical reaction (on the left - change in concentration [A] with time t) to concentration of reactants/products [A]. They also pop up in quantum mechanics - such as the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} = E\Psi$$

Other examples of things that ultimately come from differential equations are the Beer-Lambert law; the equations that govern radioactive decay; and the Clausius-Clapeyron and van t'Hoff equations from thermodynamics. We will start to see how these equations can be solved in the next two sessions.

3.1 First-Order Differential Equations

A **first-order** differential equation is one where the highest order derivative is $\frac{\mathrm{d}y}{\mathrm{d}x}$ - so there are no second or third derivatives. A simple example of an equation like this is:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = x$$

You can solve an equation like this in a couple of ways:

- **By inspection**: we want a function $y = y(x)$ that will differentiate to just x. What about the function $y = \frac{1}{2}x^2 + C$, where C is a constant. This is often an quick way to solve simple equations.
- **By integration** - we can integrate both sides with respect to x:

$$\int \frac{\mathrm{d}y}{\mathrm{d}x}\,\mathrm{d}x = \int x\,\mathrm{d}x$$

$$\int \mathrm{d}y = y = \frac{1}{2}x^2 + C$$

> On the LHS of the equation, you can imagine that the $\mathrm{d}x$ terms cancel under the integral sign - **again, this is not really what happens**. Note that we only need to add one constant of integration - if we added two, we could just as easily combine them into one, so we might as well just have one.

So we see for this simple example, the function that solves the equation is:

$$y = \frac{1}{2}x^2 + C$$

It's always a good idea to plug this function back into the equation and check that it solves it.

This function is known as the **general solution** to the differential equation, because we haven't yet determined C. To determine C we have to know something else about our system - for example, we might be told that $y = 1$ when $x = 2$. In this case, we can work out C:

$$1 = \frac{1}{2}2^2 + C \Rightarrow 1 = 2 + C \Rightarrow C = -1$$

Thus, in this situation, we can write down the **particular solution**:

$$y = \frac{1}{2}x^2 - 1$$

3.1.1 Separation of Variables

It's not always the case that we can just directly integrate our differential equations to solve them. Sometimes, we have to do some algebra before we can integrate them, and this is called **separating the variables**. We need to get it so that one side of the equation has all the y terms and the other has all the x terms (or whatever our variables are called). We'll illustrate this with an example from chemical kinetics - for the rate of a first order reaction of molecule A:

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k[\mathrm{A}]$$

In this equation, [A] is the concentration of molecule A, t is time, and k is the rate coefficient. However, equations of this form govern all kinds of things - we'll see one of them later. This equation tells us that the rate of change of concentration of A (the thing on the LHS) depends on the concentration of A (on the RHS). If there is a lot of A, then our rate will be a large - does it make sense?

To solve this equation, we first need to separate the variables:

$$\frac{1}{[\mathrm{A}]}\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k$$

Now we can integrate this equation with respect to t:

$$\int \frac{1}{[\mathrm{A}]}\frac{\mathrm{d[A]}}{\mathrm{d}t}\,\mathrm{d}t = \int -k\,\mathrm{d}t$$

Which simplifies to:

$$\int \frac{1}{[\mathrm{A}]}\,\mathrm{d[A]} = \int -k\,\mathrm{d}t$$

Doing the integrals results in:

$$\ln[\mathrm{A}] = -kt + C$$

Which we could recast as:

$$[\mathrm{A}] = \mathrm{e}^{-kt+c} = \mathrm{e}^{-kt}\mathrm{e}^{c}$$

This is fine as a general solution, but we would normally also told something else, like that the initial concentration of A $[\mathrm{A}] = [\mathrm{A}]_0$ at time $t = 0$. Then we can find a particular solution:

$$[\mathrm{A}]_0 = \mathrm{e}^{c} \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0\mathrm{e}^{-kt}$$

Which might look like a familiar result from CH1203.

3.1.2 Context: Beer-Lambert Law

The Beer-Lambert law looks a lot like the solution we've just shown above for that differential equation - and that's no accident. We can derive[1] it as follow. The Beer-Lambert law says that the rate of change of intensity of light I as it passes through a volume of solution of depth L is proportional the concentration of the solution c, the molar absorptivity of the molecule in solution ϵ, and the intensity of light in the solution I:

$$\frac{\mathrm{d}I}{\mathrm{d}L} = -Ic\epsilon$$

Looks familiar! Separating the variables and integrating, we find:

$$\ln I = -\epsilon c L + k$$

Where I've called the integration constant k to avoid confusion. We know that the transmitted intensity when $L = 0$ is just the incident intensity, I_0, so we can say:

$$\ln I_0 = k$$

and therefore, if we rearrange it all:

$$\ln\left(\frac{I}{I_0}\right) = -\epsilon c L = -A$$

where A is the absorbance. Equally, we could write the above as:

$$I = I_0 \mathrm{e}^{-\epsilon c L}$$

Nice.

You can now attempt the problems on **problem sheet 7**.

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[1] I've skipped a couple of steps but the main idea is fine - look up *integrating factors* if you want a deeper derivation.

Problem Sheet 7 - Differential Equations I

Differential equations are used everywhere in the world, as we are normally trying to figure out how to predict how certain things will change in response to some stimulus - whether that thing is the weather, stock prices, reaction yields, or spread of an infectious disease. Mathematical modelling to understand systems like these is what a lot of professional mathematicians spend their life doing.

One such person is **Nira Chamberlain***, who develops mathematical models for solving industrial problems (and is a Professor at Loughborough University). In 2014 he was one of only five mathematicians named by the Science Council as one of the top 100 UK scientists. He likens doing maths to fighting an invisible boxer, saying that: 'the harder the battle, the sweeter the victory!'.*

You should be able to complete these problems having read section 3.1 in the main handout.

1. Find the general solution to the following differential equations:

   i $\sin y \frac{dy}{dx} = 1$

   ii $y \frac{dy}{dx} = \sin x$

   iii $\frac{dy}{dx} + xy = 0$

   iv $\frac{1}{3+5x+x^2+2x^3} \frac{dy}{dx} = 1$

2. Find the particular solution to the differential equation in Q1 (iv), given that when $y = 0$, $x = 1$.

3. The rate equation for the first order reaction A $\rightarrow$ B is given by:

$$-\frac{d[A]}{dt} = k[A]$$

   Where k is the rate constant.

   i Solve the above differential equation to find an expression for [A], given that when $t = 0$, $[A] = [A]_0$, where $[A]_0$ is the initial concentration of [A].

   ii The half-life of [A], $t_{1/2}$, is defined as the time taken for the the concentration of [A] to drop to half the initial concentration. Derive an expression for $t_{1/2}$.

4. The intensity of light I passing a distance z through an absorbing medium is given by:

$$\frac{dI}{dz} = -\alpha I$$

   Solve this differential equation and explain the significance of the result (the equation should be one you recognise from CH1200, CH1206, and many other modules).

5. The differential form of the Clausius-Clapeyron Equation is:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

   This equation is used for understanding phase transitions in substances.

   a) Assuming that the phase transition is from one mole of liquid to one mole of ideal gas, find an approximate expression for ΔV in terms of p and T.

   b) Find the general solution of the resulting differential equation.

   The result you should find is the integrated (perhaps more familiar) form of the Clausius-Clapeyron Equation.

3.2 Second-Order Differential Equations

Finally, we will talk briefly about **second-order** differential equations - these are equations where the highest order term is a second derivative, such as:

$$\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + \frac{\mathrm{d}y}{\mathrm{d}x} = 2y$$

These kinds of equations occur all the time in scientific problems - the Schrödinger equation is an example, as are many of the classical equations of motion. We're going to wrap up this course by doing a brief overview of solving these equations.

3.2.1 Educated Guessing

We don't solve equations like the ones above by integrating them twice (though you could do this in some circumstances). Instead, what we do is use our mathematical intuition to make some sort of educated guess as to what the solution is. This might seem odd - you are used to mathematics where you can solve equations by rearranging them to make a certain variable the subject, but this is only one way to solve the equation. For example, if I wanted to solve the equation:

$$x + 2 = 4$$

I could just rearrange and find that $x = 2$. However, another equally legitimate approach would be to make an educated guess at the value of x, substitute it into the equation, and see if it works. For simple equations like the one above, it is easier to just rearrange the equation – but for complex differential equations it's often impossible to rearrange them. So instead, we make an educated guess as to what the solution is, plug it into the equation, and see if it works.

To see how this works, let's look back at the second-order differential equation at the top of the page. To solve this equation we need to find the function $y = y(x)$ that satisfies it. Making an educated guess, we can see that the function $y = y(x)$ which solves this equation is a function that will differentiate to a multiple of itself, and also differentiate again to a multiple of itself. An obvious function that would fit this description is some kind of exponential function, as these differentiate to a multiple of themselves:

$$y = \mathrm{e}^{ax}$$

Plugging this into our equation at the top will result in:

$$a^2\mathrm{e}^{ax} + a\mathrm{e}^{ax} = 2\mathrm{e}^{ax}$$

We can tidy this up by factorising the exponential and collecting everything on one side:

$$(a^2 + a - 2)\mathrm{e}^{ax} = 0$$

How do we proceed from here? We can divide by the exponential term (as this can't ever be equal to zero), and are left with:

$$a^2 + a - 2 = 0$$

This is called the **auxiliary equation** for our differential equation.

3.2.2 The Auxiliary Equation

The auxiliary equation is what tells us the possible values of a that solve our equation, so we just need to solve it like any other equation. In this case, we can factorise it:

$$(a + 1)(a - 2) = 0 \Rightarrow a = -1 \text{ or } a = 2$$

So there are two possible values of a that satisfy our original equation, so we have two solutions:

$$y_1 = \mathrm{e}^{-x} \text{ and } y_2 = \mathrm{e}^{2x}$$

It turns out that actually any linear combination of these two solutions will also solve our equation, so we can write down the **general solution** as:

$$y = A\mathrm{e}^{-x} + B\mathrm{e}^{2x}$$

Where A and B are constants. We'll leave that here for now. Just remember that the main idea with solving differential equations is to **find functions that differentiate to themselves as guesses** - exponential functions always work. An old professor of mine used to say *'the solution's always some kind of exponential, just write that'* whenever he couldn't work one out.

3.2.3 Context: The Schrödinger Equation

We saw the Schrödinger equation at the start of this chapter, which is an example of a second-order differential equation. So can we solve it?

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi(x)}{\mathrm{d}x^2} = E\Psi$$

We can, let's guess a wavefunction like:

$$\Psi = \mathrm{e}^{-kx}$$

Plugging this in, we'll find:

$$\frac{\hbar^2 k^2}{2m}\mathrm{e}^{-kx} = E\mathrm{e}^{-kx}$$

So we can clearly identify:

$$E = \frac{\hbar^2 k^2}{2m}$$

We just solved the Schrödinger Equation! We haven't determined k yet, because this requires that we impose some **boundary conditions**, which are ultimately what make our energy **quantised**. We'll talk about this over the next couple of years.

A final note, is that you've seen functions like:

$$\Psi = \sin(kx)$$

as solutions before too - these will also solve the equation above (try and see). The reason for this is that **sines and cosines are just exponential functions, but in a different form**. To go into this in more depth requires that we talk about **complex numbers**, which we don't have time to do now. But as a teaser, I can tell you that:

$$\sin(x) = \frac{\mathrm{e}^{ix} - \mathrm{e}^{-ix}}{2i} \text{ and } \cos(x) = \frac{\mathrm{e}^{ix} + \mathrm{e}^{-ix}}{2}$$

Where i is defined as $i^2 = -1$. We can talk about this another time, if you're interested :)

You can now attempt problems on **problem sheet 8**.

Problem Sheet 8 - Differential Equations II

You could, if you wanted to, succinctly summarise the entire subject of chemistry by saying that our ultimate aim is to solve one differential equation - The Schrödinger Equation. Unfortunately, it's basically impossible to solve this equation for anything but the most simple systems, so we have to do experiments and find other methods instead to make discoveries.

Named after **Erwin Schrödinger***, the Schrödinger Equation (as used most widely in chemistry) allows us to calculate the energy of a quantum system (such as a molecule) provided we know a suitable wavefunction for that system. Finding these wavefunctions is very difficult, which is why energy is quantised and why chemistry is complicated. We'll talk about this a lot more in future.*

You should be able to complete these problems having read section 3.2 in the main handout.

1. Show that the function $\Psi = N\cos(ax)$ is a solution to the second order differential equation:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = E\Psi$$

This equation is one form of the **Schrödinger Equation** (one we can actually solve).

2. Find general solutions to the following second order differential equations:

   i $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + \frac{\mathrm{d}y}{\mathrm{d}x} = 6y$

   ii $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} = 3\frac{\mathrm{d}y}{\mathrm{d}x} + 4y$

   iii $4\frac{\mathrm{d}^2y}{\mathrm{d}x^2} - y = 0$

3. Find general solutions to the following second order differential equations:

   i $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + 3\frac{\mathrm{d}y}{\mathrm{d}x} + y = 0$

   ii $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + 4\frac{\mathrm{d}y}{\mathrm{d}x} = -1$

   iii $\frac{1}{2}\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + \frac{\mathrm{d}y}{\mathrm{d}x} - \frac{3}{2}y = 0$

4. An equation of motion for a vibrating diatomic molecule with reduced mass μ and force constant k is given by:

$$\mu\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = -kx$$

Where x is the change in bond length as the molecule vibrates.

   i Identify the physical meaning of the LHS of the above equation.

   ii By using a trial solution of the form $x = A\cos(\omega t)$, find an expression for ω in terms of k and μ. What is the physical interpretation of ω?

   iii Sketch the motion of the molecule as a function of time (i.e. sketch x against t).

This is the end of the main material for this course! From now on, we will be doing exam-style revision problems. But, just today, turn over for a **much** more challenging problem.

5. **(V hard)** So far we have seen auxiliary equations that have two solutions, but we could have an auxiliary equation of the form:

$$(a-1)^2 = 0$$

In that case, the resulting quadratic equation has only one solution (technical term: 'repeated roots'). We would expect then that the general solution to our differential equation would only contain one term:

$$y = A\mathrm{e}^{ax}$$

However, this is not the most general solution. In this situation, $y = x\mathrm{e}^{ax}$ is also a solution. You are about to prove why.

Consider a general differential equation:

$$\alpha\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + \beta\frac{\mathrm{d}y}{\mathrm{d}x} + \gamma y = 0 \tag{3.1}$$

i Show that $y = \mathrm{e}^{ax}$ is a solution to this equation if it satisfies the auxiliary equation:

$$\alpha a^2 + \beta a + \gamma = 0 \tag{3.2}$$

ii Write down the values of a that satisfy this equation.

iii Substitute $y = x\mathrm{e}^{ax}$ into equation (1), and write down the resulting expression.

iv Show that $y = x\mathrm{e}^{ax}$ satisfies equation (1) provided that a satisfies equation (2) and also satisfies:

$$a = -\frac{\beta}{2\alpha}$$

v Why does the result from (iv) mean that $y = x\mathrm{e}^{ax}$ is only a solution if the auxiliary equation has only one distinct solution?

If you finish this problem, I will be very impressed.

Revision Problems I

These problems are the kind of problems you should expect to see in the written exam in May. If you can do all of these problems without looking at your notes, you should feel prepared for the exam. Each full question would be worth roughly 10 marks in the exam.

1. A missile is fired from a submarine, and it's height above sea level, h (in metres), as a function of time t (in seconds), is given by:
$$h = 230t - 4.2t^2$$
   i Derive an expression for the vertical velocity v, and vertical acceleration a, of the missile.
   ii At what time would the missile reach it's maximum height?
   iii What is the maximum height the missile reaches?
   iv Determine how long it takes the missile to hit the ground again after launch.
2. Differentiate the following expressions with respect to z, where a and b are constants:
   i $y = z^3 + 3z$
   ii $y = a\mathrm{e}^{bz} + z^{-2}$
   iii $y = z^2 \sin(z)$
   iv $y = \cos(z^2 + bz)$
3. Determine the following definite integrals, explaining your answers where necessary:
   i $\int_0^1 x^2 + 3x \, \mathrm{d}x$
   ii $\int_1^2 x + \frac{1}{x} \, \mathrm{d}x$
   iii $\int_{-1}^1 x^3 + \sin(x) \, \mathrm{d}x$
4. The van der Waals equation of state is:
$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$
   i Determine the two partial derivatives:
$$\left(\frac{\partial p}{\partial V}\right)_T \text{, and } \left(\frac{\partial T}{\partial p}\right)_V$$
   ii Hence show that:
$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -1$$
   given that:
$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2}$$
5. NO_2 can react to form NO and O_2. The reaction kinetics are second order and follow the rate law:
$$\frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = -k[NO_2]^2$$
   Where k is a rate constant.
   i Derive the integrated rate law for this reaction, using the symbol $[NO_2]_0$ for the initial concentration of NO_2.
   ii Show that the half-life, $t_{\frac{1}{2}}$, of NO_2 is given by:
$$t_{\frac{1}{2}} = \frac{1}{k[NO_2]_0}$$
   iii The half-life of NO_2 is 35 minutes when the initial concentration of NO_2 is $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. What is the rate constant for the reaction?

Revision Problems II

These problems are the kind of problems you should expect to see in the written exam in May. If you can do all of these problems without looking at your notes, you should feel prepared for the exam. Each full question would be worth roughly 10 marks in the exam.

1. **Sketch** a graph of y, $\frac{\mathrm{d}y}{\mathrm{d}x}$, and $\frac{\mathrm{d}^2y}{\mathrm{d}x^2}$ for the following functions:

   i $y = \frac{1}{3}x^3$ ii $y = x^2 + 1$ iii $y = \sin(x)$

   For each function, you can either sketch the function and derivatives overlaid on the same graph, or on separate graphs.

2. Find general solutions to the following differential equations:

   i $\frac{\mathrm{d}y}{\mathrm{d}x} = y^3$ ii $\sin(x)\frac{\mathrm{d}y}{\mathrm{d}x} = y$ iii $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + \frac{\mathrm{d}y}{\mathrm{d}x} = 12y$

   Note that $\int \sin(x)^{-1}\ \mathrm{d}x = -\ln(\csc x + \cot x) + c$.

3. The ideal gas equation is given by:

   $$p = \frac{nRT}{V}$$

   i Calculate the three partial derivatives:

   $$\left(\frac{\partial p}{\partial V}\right)_T, \left(\frac{\partial V}{\partial T}\right)_p, \text{and } \left(\frac{\partial T}{\partial p}\right)_V$$

   ii Hence show that the product of these three partial derivatives is equal to -1.

   iii The Dieterici equation of state is given by:

   $$p = \frac{RT}{V-b}\exp\left(-\frac{a}{RVT}\right)$$

   where a and b are constants. Determine the partial derivatives $\left(\frac{\partial p}{\partial V}\right)_T$ and $\left(\frac{\partial p}{\partial T}\right)_V$.

4. The wavefunction Ψ of a 1s electron in a hydrogen atom is given by:

   $$\Psi = N\mathrm{e}^{-r}$$

   Where r is the distance of the electron from the nucleus, and N is a normalisation constant. N is defined such that:

   $$\int_0^\infty \Psi^2 4\pi r^2\ \mathrm{d}r = 1 \tag{3.3}$$

   i Substitute the wavefunction of a 1s electron Ψ into equation (1) above.

   ii By using the standard integral:

   $$\int_0^\infty r^2\mathrm{e}^{-ar}\ \mathrm{d}r = \frac{2}{a^3}$$

   Show that the normalisation constant, N is given by:

   $$N = \sqrt{\frac{1}{\pi}}$$

5. Find and classify the stationary points in the following functions:

   i $y = x^3 - 2x + 1$

   ii $y = \mathrm{e}^{-x^2}$

Revision Problems III

These problems are the kind of problems you should expect to see in the written exam in May. If you can do all of these problems without looking at your notes, you should feel prepared for the exam. Each full question would be worth roughly 10 marks in the exam.

1. The rate constant, k, for a unimolecular reaction can be estimated using a formula derived from transition state theory:
$$k = \frac{k_B T}{h} \times \mathrm{e}^{\Delta S/R} \times \mathrm{e}^{\Delta H/RT}$$
Where all symbols have their usual meanings. You can assume everything except T is a constant.
   - i Write down an expression for the natural logarithm of the rate constant, $\ln k$.
   - ii Determine the derivative:
$$\frac{\mathrm{d}\ln k}{\mathrm{d}T}$$
   - iii The Arrhenius equation is given by:
$$k = A \times \mathrm{e}^{E_a/RT}$$
Determine the derivative $\frac{\mathrm{d}\ln k}{\mathrm{d}T}$ for the Arrhenius equation.
   - iv By comparing the answers to (ii) and (iii), find the relationship between ΔH and E_a.

2. For each of the following functions F, determine the partial derivatives:
$$\left(\frac{\partial F}{\partial t}\right)_x \text{ and } \left(\frac{\partial F}{\partial x}\right)_t$$
   - i $F = x^2\cos(2t)$
   - ii $F = x^{2.25} + t^{-2.25}$
   - iii $F = 3xt^3 + x$
   - iv $F = \cos^2(xt)$

3. The high-temperature heat capacity C_V of tungsten can be approximated using the Debye model for heat capacity:
$$C_V = 9R\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} x^2 \,\mathrm{d}x$$
Where R is the gas constant, T is the temperature of the solid, T_D is the Debye temperature of the solid, and x is a variable that accounts for the energy of different quantised levels within the solid. The Debye temperature of tungsten is $400\,\mathrm{K}$.
   - i Write down the value of T_D/T for tungsten at a temperature of $1600\,\mathrm{K}$.
   - ii Evaluate the integral above to derive an expression for the heat capacity.
   - iii How does the heat capacity of tungsten change if the temperature is increased to $2000\,\mathrm{K}$? Explain your answer.

4.
   - i Expand and simplify the following expression:
$$(x-3)(x-2)(x+1)(x-4)$$
   - ii Hence identify and classify the stationary points in the function:
$$y = \frac{1}{5}x^5 - 2x^4 + \frac{17}{3}x^3 + x^2 - 24x + 4$$

5. Given the differential equation:
$$\frac{\mathrm{d}y}{\mathrm{d}x} = 1 + x + y + xy$$
   - i Find the general solution.
   - ii Find the particular solution, given that the general solution passes through the point $(0, 1)$.

   Hint: you may find it useful to try and factorise the RHS of the equation, and to know that:
$$\int \frac{1}{1+x}\,\mathrm{d}x = \ln(x+1)$$

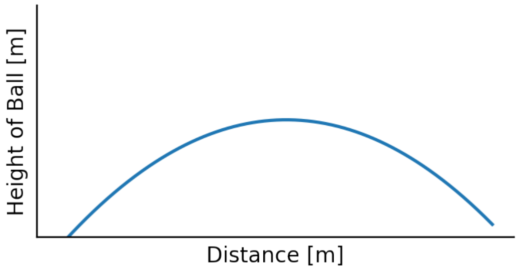
Extra Exam Style Problems

Here are some further exam style problems for you to practice with. Each problem would be worth approximately 10 marks in an exam.

1. Inflation rate, I, is equal to the rate of change of the price index, p, with time, t.
   a) Write down a differential equation linking inflation rate to price index.
   b) Find the general solution of this differential equation. You may assume the inflation rate does not depend on time.
   c) At the start of a given forecasting period, the price index was £45. Hence find the particular solution to this differential equation.
   d) Given an inflation rate of 3p per day, calculate the price index 200 days into the forecasting period.
2. Given the function:
   $$Y(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\mathrm{e}^{-2i\phi}\sin^2\theta\cos\theta$$
   Find the partial derivatives:
   $$\left(\frac{\partial Y}{\partial \phi}\right)_\theta \text{ and } \left(\frac{\partial Y}{\partial \theta}\right)_\phi$$
   You may treat i as a constant.
3. Differentiate the following functions F with respect to z:
   i $F = 3z^2 + z$
   ii $F = 3z^{-2} - z + 2$
   iii $F = z^3\mathrm{e}^{4z}$
   iv $F = \cos(z^4 + z^3 - 1)$
4. i Evaluate the following integral, showing all working:
   $$\int_{-1}^{1} x\mathrm{e}^{x^2}\ \mathrm{d}x$$
   ii Find the positive number n such that:
   $$\int_0^n 2x + 1\ \mathrm{d}x = 2$$
5. The *12-6 potential*, $V(r)$, is a potential energy function used for modelling van der Waals interactions between atoms and molecules as a function of their separation r:
   $$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
   Where σ and ϵ are constants.
   i Find the intermolecular separation, r_{min} where the potential energy is at a minimum.
   ii Find the value of the potential energy $V(r)$ at this minimum point.
   iii By considering the behaviour of the potential at small and large r, or otherwise, **sketch** the form of the 12-6 potential.
6. Find general solutions to the following differential equations:
   i $\frac{\mathrm{d}y}{\mathrm{d}x} = 3x^2y^{-1}$
   ii $(\frac{\mathrm{d}y}{\mathrm{d}x})^2 = x^2y^{-2}$
   iii $\frac{\mathrm{d}^2y}{\mathrm{d}x^2} + 6\frac{\mathrm{d}y}{\mathrm{d}x} - 16y = 0$

   Note that $(\frac{\mathrm{d}y}{\mathrm{d}x})^2 \neq \frac{\mathrm{d}^2y}{\mathrm{d}x^2}$!

7. The height of the ball above the pitch following the free kick that Marcus Rashford creamed into the top corner of the net against Wales in the 2022 World Cup looked like the diagram below, when viewed from the side of the pitch.



The following information about the motion of the ball is available:

- The height of the ball exhibits quadratic dependence as a function of time.
- The maximum height of the ball was $1.25\,\mathrm{m}$, and the ball reached this height after travelling for a time of $0.5\,\mathrm{s}$.
- The vertical acceleration of the ball was $-2\,\mathrm{m/s^2}$ due to bizarre climatic conditions in Qatar.
- The height of the ball when placed on the free kick spot by the referee (i.e. at a time of $0\,\mathrm{s}$) was $1\,\mathrm{m}$.

Derive an expression for the height of the ball as a function of time.

Hint: to start, try annotating the sketch of the ball with the information given above.

8. Evaluate the following integrals:

   i $\int_0^1 x^2\ \mathrm{d}x$ ii $\int_{-1}^1 4x^2\ \mathrm{d}x$ iii $\int_1^2 x + \sin(x) + \cos(x)\ \mathrm{d}x$

9. In electrochemistry, the *Nernst Equation* relates cell potential E to reaction quotient Q:

$$E = E^\circ - \frac{RT}{zF} \ln Q$$

Where E° is the standard cell potential, R is the gas constant, T is temperature, z is the number of electrons transferred in the reaction, and F is the Faraday constant.

   i Determine the partial derviatives:

$$\left(\frac{\partial E}{\partial T}\right)_{Q,z}, \left(\frac{\partial E}{\partial Q}\right)_{T,z} \text{ and } \left(\frac{\partial E}{\partial z}\right)_{Q,T}$$

   ii For a given reaction, the cell potential increases by a factor of two when the reaction quotient increases by a factor of four (with other variables held constant). Write down the value of $\left(\frac{\partial E}{\partial Q}\right)_{T,z}$ for this reaction (units are not required).

10. Differentiate the following functions:

   i $y = x^{2.5} \sin(x^2 + 3)$

   ii $y = 2\cos(3x^2 + 2x) + x\sin(x)$

Calculus Drill Problems

Here are some questions for you to just practice the key processes in calculus - differentiation and integration. The idea is that you can just work through these many examples as ‘drill’ practice.

In all problems, **Greek letters are constants** and **Latin letters are variables**. The answers are at the end of the sheet.

1. Differentiate the following functions:
    - i $y = x^2$
    - ii $y = \alpha x^4 + x^2$
    - iii $F = \beta t^3 + t + 1$
    - iv $y = \cos(4t)$
    - v $G = 2\sin(4x) + 2\cos(3x)$
    - vi $F = \mathrm{e}^{\alpha t} + \mathrm{e}^{\alpha^2 t}$
    - vii $T = r(r-1) + 3$
    - viii $y = \ln x + \ln\theta$
    - ix $F = \ln(\alpha x)$
    - x $y = x^2\mathrm{e}^x$
    - xi $L = t^3\sin(\gamma t)$
    - xii $R = \cos(3r + 4r^2)$
    - xiii $F = x^4\mathrm{e}^{\beta x^2}$
    - xiv $K = t^2 + 3t^4\cos(\omega t^2)$
    - xv $y = (1+x)(1-x)^{-1}$
    - xvi $p = (2J+1)\mathrm{e}^{\frac{J(J+1)}{\theta}}$
    - xvii $L = 4\pi\rho^2\sigma T^4$
    - xviii $U = r^3(\mathrm{e}^{\kappa r} + 1)^{-1}$

2. Evaluate the following indefinite integrals:
    - i $\int 5x^{3.5}\mathrm{d}x$
    - ii $\int 3x^2 + x^{-2}\mathrm{d}x$
    - iii $\int 14x^{13} + 13x^{12} + 12x^{11}\mathrm{d}x$
    - iv $\int 0.25x^2 + 0.5x^4\mathrm{d}x$
    - v $\int \pi y^3 + \pi y^{-3}\mathrm{d}y$
    - vi $\int (1+t)(2+t)(3+t)\mathrm{d}t$
    - vii $\int (1+t)(1-t)\mathrm{d}t$
    - viii $\int \sin(3z) + \cos(\alpha z)\mathrm{d}z$
    - ix $\int z^{-1} + \theta z^2\mathrm{d}z$

3. Evaluate the following definite integrals:
    - i $\int_1^2 x^2 + x + 1\mathrm{d}x$
    - ii $\int_{-3}^3 (x+2)^3\mathrm{d}x$
    - iii $\int_{-6}^6 x\mathrm{e}^{x^2}\mathrm{d}x$
    - iv $\int_2^4 x^3 + 2x^{-2}\mathrm{d}x$
    - v $\int_\pi^{2\pi} \sin(2y)\mathrm{d}y$
    - vi $\int_{-\pi}^{\pi} \sin(t) + \cos(t)\mathrm{d}t$
    - vii $\int_2^8 (1+t)(1-t)\mathrm{d}t$
    - viii $\int_{-2}^2 x^3\sin(x)\mathrm{d}x$
    - ix $\int_0^{100} r^3(r^2-1)\sin(\pi)\mathrm{d}r$

Answers

1. Derivative symbols are not shown to keep it relatively tidy:

    i $2x$
    ii $4\alpha x^3 + 2x$
    iii $3\beta t^2 + 1$
    iv $-4\sin(4t)$
    v $8\cos(4x) - 6\sin(3x)$
    vi $\alpha \mathrm{e}^{\alpha t} + \alpha^2 \mathrm{e}^{\alpha^2 t}$
    vii $2r - 1$
    viii ${}^1\!/_x$
    ix ${}^1\!/_x$
    x $x^2\mathrm{e}^x + 2x\mathrm{e}^x$
    xi $\gamma t^3 \cos(\gamma t) + 3t^2 \sin(\gamma t)$
    xii $-(8r + 3)\sin(3r + 4r^2)$
    xiii $2\beta x^5 \mathrm{e}^{\beta x^2} + 4x^3 \mathrm{e}^{\beta x^2}$
    xiv $2t - 6\omega t^5 \sin(\omega t^2) + 12t^3 \cos(\omega t^2)$
    xv $-2x$
    xvi $(2J + 1)^2\theta^{-1} + 2)\mathrm{e}^{\frac{J(J+1)}{\theta}}$
    xvii $16\pi\rho^2\sigma T^3$
    xviii $-r^4\mathrm{e}^{\kappa r}(\mathrm{e}^{\kappa r} + 1)^{-2} + 3r^2(\mathrm{e}^{\kappa r} + 1)^{-1}$

2. Fractions or decimals are fine. Remember constants of integration for indefinite integrals!

    i $1.111x^{4.5} + c$
    ii $x^3 - \frac{1}{3x^3} + c$
    iii $x^{14} + x^{13} + x^{12} + c$
    iv $0.083x^3 + 0.1x^5 + c$
    v $\frac{\pi y^4}{4} - \frac{\pi}{2y^{-2}} + c$
    vi $\frac{t^4}{4} + 2t^3 + \frac{11t^2}{2} + 6t + c$
    vii $t - \frac{t^3}{3} + c$
    viii $-\frac{\cos(3z)}{3} + \frac{\sin(\alpha z)}{\alpha} + c$
    ix $\ln z + \frac{\theta z^3}{3} + c$

3. Remember to state reasoning if a trick is used.

    i $\frac{29}{6}$
    ii 156
    iii $0 \because$ odd function.
    iv 60.5
    v 0
    vi 0
    vii -162
    viii $0 \because$ odd function.
    ix $0 \because$ integrand is zero.