CHAPTER 2

DIFFERENTIAL EQUATIONS

Differential equations are equations that describe the relationship between a function and its derivatives. there are two main typs **ordinary differential equations** which involved derivatives with respect to the signale variable and **partial differential equations** which involved derivatives with respect to multiple variables.
Differential equations are used in chemistry for various important applications, including:
1 Kinetics of Reactions: They describe how the concentration of reactants and products changes over time. Rate laws, which relate the rate of a reaction to the concentration of reactants, are often expressed as differential equations.
2 Chemical Equilibrium: Differential equations can model how a chemical system evolves over time until it reaches equilibrium, helping to understand the dynamics of reaction systems.
3 Thermodynamics: In thermodynamic processes, differential equations describe changes in energy, temperature, and pressure in relation to state variables.
4 Transport Phenomena: They model the movement of molecules, such as diffusion or flow in reaction media, which is essential for understanding processes like mass transfer in reactors.
5 Population Dynamics: In biochemistry and environmental chemistry, differential equations help model the growth and interaction of populations, such as bacteria or species in an ecosystem.
6 Dynamic Systems: They are used to analyze feedback systems in chemical processes, such as catalytic reactions, where the rate may depend on the concentration of intermediates.
Overall, differential equations provide a mathematical framework for understanding and predicting the behavior of chemical systems over time.

1 First-Order Differential Equation

A first-order differential equation is an equation that involves the derivative of an unknown function with respect to a certain variable. In general, it takes the form: $\frac{dy}{dx} = f(x, y)$, where $\frac{dy}{dx}$ represents the rate of change of y with respect to x, and $f(x, y)$ is a function that defines the relationship between x and y.

1.1 Types of First-Order Differential Equations

1-Separable Differential Equations

These can be written in such a way that all terms involving x are on one side, and all terms involving y are on the other.

Example :
Let's consider the following equation: $\frac{dy}{dx} = x^2 y$
Rewrite the equation as $\frac{dy}{y} = x^2 dx,$
Then, integrate both sides $\int \frac{dy}{y} = \int x^2 dx,$
the result is $\ln|y| = \frac{1}{3}x^3 + k,$ where k is the constant of integration.
the final solution is $y(x) = C \exp \frac{1}{3}x^3,$ where $C = \pm K.$

2-Linear Differential Equations

These are of the form $\frac{dy}{dx} + P(x)y = Q(x),$ where P, Q are functions of the variable$x$, and y is the unknown function we want to find.
Steps to Solve:
1-Identify the coefficients: Determine $P(x)$ and $Q(x)$.
2-Calculate the integrating factor: This is calculated as follows $\mu(x) = e^{\int P(x)dx}$
3-Multiply the equation by the integrating factor: This makes the left side integrable.
4-Integrate: Integrate both sides of the equation.
5-Solve for y: Finally, find y.

Example :
Let's consider the equation: $dy/dx + 3y = 6$.
1 Here, we identify $P(x) = 3$ and $Q(x) = 6$.
2 We calculate the integrating factor: $\mu(x) = e^{\int 3dx} = e^{3x}$.
3 We multiply the equation by e^{3x}: $e^{3x}\frac{dy}{dx} + 3ye^{3x} = 6e^{3x}$.
4 The left side becomes: $\frac{d}{dx}(ye^{3x}) = 6e^{3x}$.
5 Now we integrate both sides: $ye^{-3x} = 2e^{3x} + C.$
6 Finally, we solve for $y : y = 2 + Ce^{-3x}$

2 Second-Order Differential Equation

Definition 2.1

A second order differential equation is defined as a differential equation that includes a function and its second-order derivative and no other higher-order derivative of the function can appear in the equation. It can be of different types depending upon the power of the derivative and the functions involved. These differential equations can be solved using the auxiliary equation.

Let us go through some special types of second order differential equations given below

2.1 Types of Second-Order Differential Equations

Linear Second Order Differential Equation

Definition 2.2

A linear second order differential equation is written as $\frac{d^2y}{dx^2} + p(x)\frac{dy}{dx} + q(x)y = f(x)$, where
- $\frac{d^2y}{dx^2} = y''$ is the second derivative of y with respect to x.
- $p(x), q(x),$ and $f(x)$ are functions depending on the variable x.

The goal is to find the function $y(x)$ that satisfies this equation.

Example :
Some of its examples are $y'' + 6x = 5, y'' + xy' + y = 0,$ etc.

Homogeneous Equations

Definition 2.3

When $f(x) = 0$, the equation is called homogeneous. The solution depends only on the intrinsic properties of the function without any external force acting on it.

Example :
Some of its examples are $y'' + y' - 6y = 0, y'' - 9y' + 20y = 0,$ etc.

Non-homogeneous Second Order Differential Equation

Definition 2.4

A differential equation of the form $y'' + p(x)y' + q(x)y = f(x)$ is said to be a non-homogeneous second order differential equation if $f(x) \neq 0,$ it means there is an external force or influence (such as a source or interference).

Example :
Some of its examples are $y'' + y' - 6y = x, y'' - 9y' + 20y = \sin x,$ etc.

2.2 Solving Second Order Differential Equation

Now that we have understood the meaning of second order differential equation and their different forms, we shall proceed towards learning how to solve them. Here, we will focus on learning to solve 2nd differential equations with constant coefficients using the method of undetermined coefficients. First, let us understand how to solve the second order homogeneous differential equations.

Solving Homogeneous Second Order Differential Equation

A homogeneous second order differential equation with constant coefficients is of the form $y'' + py' + qy = 0$, where p, q are constants. To solve, we find the roots of the characteristic equation $r^2 + pr + q = 0$. Based on the nature of the roots, the solution can be
-If the roots are real and distinct: $y(x) = C_1 e^{r_1 x} + C_2 e^{r_2 x}$
-If the roots are equal: $y(x) = C_1 e^{rx} + C_2 x e^{rx}$
-If the roots are complex: $y(x) = e^{\alpha x}(C_1 \cos \beta x + C_2 \sin \beta x)$, where $r_1, r_1 = \alpha \pm i\beta$

> ***Example :***
> Solve the 2nd order differential equation $y'' - 6y' + 5y = 0$ Assume $y = e^{rx}$ and find its first and second derivative: $y' = re^{rx}, y'' = r^2 e^{rx}$
> Next, substitute the values of y, y', and y'' in $y'' - 6y' + 5y = 0$ We have
> $r^2 e^{rx} - 6re^{rx} + 5e^{rx} = 0 \Rightarrow e^{rx}(r^2 - 6r + 5) = 0 \Rightarrow r^2 - 6r + 5 = 0$
> $\Rightarrow (r - 5)(r - 1) = 0 \Rightarrow r = 1, 5$
> Since the roots of the characteristic equation are distinct and real, therefore the general solution of the given differential equation is $y(x) = C_1 e^x + C_2 e^{5x}$. ■

> ***Example :***
> Solve the second order differential equation $y'' - 8y' + 16y = 0$
> Assume $y = e^{rx}$ and find its first and second derivative $y' = re^{rx}, y'' = r^2 e^{rx}$
> Next, substitute the values of y, y', and y'' in $y'' - 8y' + 16y = 0$. We have
> $r^2 e^{rx} - 8re^{rx} + 16e^{rx} = 0 \Rightarrow e^{rx}(r^2 - 8r + 16) = 0 \Rightarrow r^2 - 8r + 16 = 0$
> $\Rightarrow (r - 4)(r - 4) = 0 \Rightarrow r = 4, 4$
> Since the roots of the characteristic equation are identical and real, therefore the general solution of the given differential equation is $y(x) = C_1 e^{4x} + C_2 x e^{rx}$. ■

> ***Example :***
> Solve the second order differential equation $9y'' + 12y' + 29y = 0$
> Assume $y = e^{rx}$ and find its first and second derivative $y' = re^{rx}, y'' = r^2 e^{rx}$
> Next, substitute the values of y, y', and y'' in $9y'' + 12y' + 29y = 0$. We have
> $9r^2 e^{rx} + 12re^{rx} + 29e^{rx} = 0 \Rightarrow e^{rx}(9r^2 + 12r + 29) = 0 \Rightarrow 9r^2 + 12r + 29 = 0$
> $\Rightarrow r = \frac{-12 \pm \sqrt{1380i}}{18} \Rightarrow r = \frac{-2}{3} \pm \frac{5}{3} i$ Since the roots of the characteristic equation are complex conjugates, therefore the general solution of the given second order differential equation is $y = e^{\frac{-2}{3} x}[C_1 \sin \frac{5}{3} x + C_2 \cos \frac{5}{3} x]$. ■

Solving Non-Homogeneous Second Order Differential Equation

the general solution is of the form $y = y_h + y_p$, where y_h is the complementary solution of the homogeneous second order differential equation and y_p is the particular solution of the non-homogeneous differential equation $y'' + py' + qy = f(x)$.
Since y_h is the solution of the homogeneous differential equation, we can determine its value

using the methods that we discussed in the previous section.

Solving the particular solution by undetermined coefficients method

Which only works when $f(x)$ is a polynomial, exponential, sine, cosine or a linear combination of those, to find the particular solution y_p, we can guess the solution depending upon the value of $f(x)$. The table given below shows the possible particular solution y_p corresponding to each $f(x)$.

f(x)	y_p
be^{ax}	Ae^{ax}
a$x^n + lowerorderpowersofx$	$C_n x^n + C_{n-1}x^{n-1} + ... + C_0$
Pcos(ax) or Q sin(ax)	A cos(ax)+B sin(ax)

Let us now consider a few examples of second order differential equations and solve them using the method of undetermined coefficients

Example :

Find the complete solution of the second order differential equation $y'' - 6y' + 5y = e^{-3x}$. first we will find the general solution of the homogeneous differential equation $y'' - 6y' + 5y = 0$. We have solved this equation in the previous section in the solved examples and hence the complementary solution is $y_h = C_1 e^x + C_2 e^{5x}$.

Next, we will find the particular solution y_p. Since $f(x) = e^{-3x}$ is of the form Ae^{-3x}, let us assume $y_p = Ae^{-3x}$.

Now differentiating y_p, we have $y_p' = -3Ae^{-3x}$ and $y_p'' = 9Ae^{-3x}$.

Substituting these values in the given second order differential equation, we have $y_p'' - 6y_p' + 5y_p = e^{-3x} \Rightarrow 9Ae^{-3x} - 6(-3Ae - 3x) + 5Ae^{-3x} = e^{-3x} Ae^{-3x}(9 + 18 + 5) = e^{-3x} \Rightarrow 32Ae - 3x = e^{-3x} \Rightarrow A = \frac{1}{32}$

Hence, the particular solution $y_p = \frac{1}{32}e^{-3x}$.

Therefore, the complete solution of the given non-homogeneous $2nd$ order differential equation is $y = C_1 e^x + C_2 e^{5x} + \frac{1}{32}e^{-3x}$. ■

Example :

Consider the equation $\frac{d^2y}{dx^2} + y = \sin x$

First, solve the homogeneous equation: $\frac{d^2y}{dx^2} + y = 0 \Rightarrow r^2 + 1 = 0 \Rightarrow r = \pm i$,

so the homogeneous solution is $y_h(x) = C_1 \cos x + C_2 \sin x$

Now, we look for a particular solution $y_p(x)$ Since the right-hand side is $\sin x$, we try $y_p = Ax\cos x + Bx\sin x$, so we get $y_p' = (A + Bx)\cos x + (B - Ax)\sin x$,

and $y_p'' = (-Ax + 2B)\cos x - (Bx + 2A)\sin x$

After differentiating and substituting, we obtain $y_p = -\frac{1}{2}x\cos x$

Thus, the general solution is $y = y_h + y_p = C_1 \cos x + C_2 \sin x - \frac{1}{2}x\cos x$. ■

Example :

Solve the second order differential equation $y'' - 6y' + 5y = cos2x + e^{-3x}$

As we have solved the homogeneous differential equation, we have solved this equation in the previous section in the solved examples and hence the complementary solution is $y_h = C_1 e^x + C_2 e^{5x}$.

Next, we will find the particular solution of the given differential equation individually for $\cos 2x$ and e^{-3x}, that is, determine the particular solution of $y'' - 6y' + 5y = \cos 2x$ and

$y'' - 6y' + 5y = e^{-3x}$ separately.
From example above, we have the particular solution of the differential equation $y'' - 6y' + 5y = e^{-3x}$ as $\frac{1}{32}e^{-3x}$.
Now, we will find the particular solution of the equation $y'' - 6y' + 5y = \cos 2x$ using the table. Assume the particular solution of the form $y_p = A\cos 2x + B\sin 2x$. Differentiating this, we have $y_p' = -2A\sin 2x + 2B\cos 2x$ and $y_p'' = -4A\cos 2x - 4B\sin 2x$.
Substituting these values in the differential equation $y'' - 6y' + 5y = cos2x$, we have
$-4Acos2x - 4Bsin2x - 6(-2Asin2x + 2Bcos2x) + 5(Acos2x + Bsin2x) = cos2x$
$\Rightarrow (A-12B)cos2x+(B+12A)sin2x = cos2x \Rightarrow A-12B = 1$ and $B+12A = 0 \Rightarrow A = \frac{1}{145}$ and $B = \frac{-12}{145} \Rightarrow y_p = (\frac{1}{145})cos2x - (\frac{12}{145})sin2x$
Now, taking the sum of both particular solutions, the final particular solution of the given second order differential equation $y'' - 6y' + 5y = cos2x + e^{-3x}$ is
$y_p = (\frac{1}{32})e^{-3x} + (\frac{1}{145})cos2x - (\frac{12}{145})sin2x$.
Therefore, the complete solution of the differential equation is
$y = C_1e^x + C_2e^{5x} + \frac{1}{32}e^{-3x} + \frac{1}{145}cos2x - (\frac{12}{145})sin2x$ ■

Solving the particular solution by variation of parameters method

Which works on a wide range of functions but is a little messy to use.
To keep things simple, we are only going to look at the case $y'' + py' + qy = f(x)$
The complete solution to such an equation can be found by combining two types of solution
-The general solution of the homogeneous equation $y'' + py' + qy = 0$
-Particular solutions of the non-homogeneous equation $y'' + py' + qy = f(x)$
Note that $f(x)$ could be a single function or a sum of two or more functions. Once we have found the general solution and all the particular solutions, then the final complete solution is found by adding all the solutions together. This method relies on integration, the problem with this method is that, although it may yield a solution, in some cases the solution has to be left as an integral.
The fundamental solutions of the equation:
- If $y_h(x) = C_1e^{r_1x} + C_2e^{r_2x} \Longrightarrow y_1 = e^{r_1x}, y_2 = e^{r_2x}$.
- If $y_h(x) = C_1e^{rx} + C_2xe^{rx} \Longrightarrow y_1 = e^{rx}, y_2 = xe^{rx}$.
- If $y_h(x) = e^{\alpha x}(C_1\cos\beta x + C_2\sin\beta x) \Longrightarrow y_1 = e^{\alpha x}\cos\beta x, y_2 = e^{\alpha x}\sin\beta x$.

If y_1 and y_2 are two linearly independent solutions (because neither function is a constant multiple of the other) of the homogeneous second order differential equation $y''+py'+qy = 0$, then the particular solution of the corresponding second order non-homogeneous differential equation $y'' + py' + qy = f(x)$ can be determined using the formula
$y_p = -y_1\int[y_2\frac{f(x)}{W(y_1,y_2)}]dx + y_2\int[y_1\frac{f(x)}{W(y_1,y_2)}]dx$, where
$W(y_1, y_2) = y_1y_2' - y_2y_1'$
is called the **Wronskian**. This method of finding the solution is called the method of variation of parameters.

Example :
Find a general solution to the following differential equation $y'' - 2y' + y = \frac{e^t}{t^2+1}$
The characteristic equation is $r^2 - 2r + 1 = 0 \Rightarrow (r1)(r1) = 0 \Rightarrow r = 1$
The general solution of the differential equation is $y_h = C_1e^x + C_2xe^x$
So, we have $y_1 = e^x, y_2 = xe^x$
The Wronskian of these two functions is

$$\begin{vmatrix} e^x & xe^x \\ e^x & (x+1)e^x \end{vmatrix} = (x+1)e^x - xe^x = e^{2x}$$

Find the particular solution using the above formula, so solve the integrals

$$\int [y_2 \frac{f(x)}{W(y_1,y_2)}]dx = \int \frac{xe^x e^x}{e^{2x}(t^2+1)}dx = \int \frac{x}{x^2+1}dx = \ln(x^2+1)$$

and

$$\int [y_1 \frac{f(x)}{W(y_1,y_2)}]dx = \frac{e^x e^x}{e^{2x}(t^2+1)}dx = \int \frac{1}{x^2+1}dx = \arctan(x)$$

The general solution is $y_g = C_1 e^x + C_2 xe^x - \frac{1}{2}e^x \ln(x^2+1) + xe^x \arctan(x)$ ■

Remark.

> This method can also be used on non-constant coefficient differential equations, provided we know a fundamental set of solutions for the associated homogeneous differential equation.

3 Some common First-order differential equations in Chemistry

First-order differential equations are widely used in chemistry, especially in studying chemical reactions and the kinetics of chemical systems. Here are some commonly used first-order differential equations in chemistry

First-Order Reaction Rate Equation

In first-order chemical reactions, the reaction rate depends on the concentration of a single substance. The equation takes the form $\frac{d[A]}{dt} = -k[A]$, where
$[A]$ is the concentration of reactant A, k is the reaction rate constant and the negative sign indicates that the concentration of the reactant decreases over time.

Zero-Order Reaction Equation

$\frac{d[A]}{dt} = -k$, This means that the concentration of the substance decreases linearly over time.

Exponential Growth Equation

This equation describes systems where the number of molecules increases over time, such as in chain reactions or the accumulation of a chemical product. The equation is $\frac{dN}{dt} = rN$, where N is the number of molecules or concentration of the substance, r is the growth rate.

4 Some common Second-order differential equations in Chemistry

The Diffusion Equation (Fick's Second Law of Diffusion)

This equation is important for studying how molecules diffuse through a medium over time. The general form of Fick's second law is $\frac{\rho C}{\rho t} = D\frac{\rho^2 C}{\rho x^2}$, where C is the concentration of the substance (a function of position x and time t, D is the diffusion coefficient, and $\frac{\rho^2 C}{\rho x^2}$ is the second derivative of the concentration with respect to position, representing the change in diffusion with distance.

Heat Equation

In physical chemistry, this equation is used to study the transfer of heat in bodies or materials $\frac{\rho T}{\rho t} = \alpha \frac{\rho^2 t}{\rho x^2}$, where T is the temperature and α is the thermal diffusivity.

Quantum Harmonics (Schrödinger Equation)

This equation is essential for understanding the behavior of electrons in atoms and molecules and is central to theoretical chemistry $\frac{-h^2}{2m} \frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = E\Psi$