

CHEM2024 – Week 20 Lecture 2 – Ordinary differential equations

- Sections 11.1-11.6 of Steiner, "The Chemistry Maths Book", 2nd edition.
- Sections 7.1-7.3 of Cockett and Doggett, "Maths for Chemists", Vol 1.

1. Classification of differential equations

A *differential equation* is an equation that involves derivatives of a function. Such equations are ubiquitous in science and engineering – the most powerful models of reality (general relativity theory, quantum field theory, hydrodynamics, etc.) are formulated in terms of differential equations. In chemistry, their primary application is chemical kinetics.

Differential equations are classified into *ordinary differential equations* (ODEs) that involve derivatives with respect to one variable only, for example time:

$$\frac{d^2}{dt^2} I(t) + \frac{1}{LC} I(t) = 0 \quad \text{[current in a resonant electrical circuit]} \quad (1)$$

and *partial differential equations* (PDEs) that involve derivatives with respect to multiple variables, e.g.:

$$\frac{\partial}{\partial t} c(\vec{r}, t) = D \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] c(\vec{r}, t) \quad \text{[diffusion in three dimensions]} \quad (2)$$

The task of solving a differential equation consists in finding a function that satisfies it.

2. Classification of ODEs

ODEs come in two major classes: *linear* and *non-linear*. A *linear differential equation* is a differential equation that is linear with respect to all of the derivatives. It can be written in the following form:

$$p_n(x) f^{(n)}(x) + p_{n-1}(x) f^{(n-1)}(x) + \dots + p_1(x) f'(x) + p_0(x) f(x) = g(x) \quad (3)$$

where $f^{(n)}(x)$ is the n -th derivative of $f(x)$, and $p_n(x)$ with $g(x)$ are arbitrary functions of x . When $g(x) = 0$, the equation is called *homogeneous*; otherwise, it is *inhomogeneous*. Any ODE that cannot be written in the form prescribed by Equation (3) is called *non-linear*. Examples:

$$\frac{dA(t)}{dt} = -kA(t) \quad \text{[first order kinetics]} \quad - \text{linear, homogeneous}$$

$$\frac{dA(t)}{dt} = -kA^2(t) \quad \text{[second order kinetics]} \quad - \text{nonlinear}$$

$$\frac{dA(t)}{dt} = -kA(t) + s(t) \quad \text{[first order kinetics with a source]} \quad - \text{linear, inhomogeneous}$$

A differential equation is called *autonomous* if it can be written in the form

$$f^{(n)}(x) = g \left[f(x), f'(x), \dots, f^{(n-1)}(x) \right] \quad (4)$$

In other words, autonomous differential equations are those where the independent variable (x in the equation above) does not appear explicitly. Examples:

$$\frac{dA(t)}{dt} = -kA^2(t) \quad [\text{second order kinetics}] \quad - \textit{autonomous}$$

$$\frac{dA(t)}{dt} = -kA^2(t) + s(t) \quad [\text{second order kinetics with a source}] \quad - \textit{not autonomous}$$

The term *autonomous* originated in physical sciences: autonomous differential equations appear in the description of physical systems that are not subject to time-dependent external influences.

The *order* of the differential equation is the order of the highest derivative of the unknown function that it contains. Examples:

$$\frac{d^2 f(t)}{dt^2} = -\omega^2 f(t) \quad [\text{wave equation in 1D}] \quad - \textit{second order}$$

$$\frac{d^4 f(x)}{dx^4} = g(x) \quad [\text{Euler-Bernoulli beam deflection equation}] \quad - \textit{fourth order}$$

A homogeneous first order ODE is called *separable* if it may be written in the following form:

$$f(x)dx = g(y)dy \quad (5)$$

All other homogeneous first order ODEs are *inseparable*. Examples:

$$\frac{dy}{dx} = 6y^2x \quad - \textit{separable} \qquad \frac{dy}{dx} = x^2 \cos(xy) \quad - \textit{inseparable}$$

3. Simple homogeneous first-order ODEs

The general form of a homogeneous first-order ODE is:

$$\frac{dy}{dx} = f(x, y) \quad (6)$$

In many cases it is possible to split $f(x, y)$ into a function of just x and another function of just y . In that case, the recipe is roughly as follows:

1. Using appropriate transformations, bring the equation to the following form:

$$g(y)dy = h(x)dx \quad (7)$$

2. Integrate both sides and note that a sum or difference of two unknown constants is a *single* unknown constant. The solution that contains this constant is called the *general solution*.
3. Use the initial condition to determine the constant. The solution with all unknown constants eliminated is called the *particular solution*.
4. Check the solution by substituting it back into the differential equation and the initial condition. If both are satisfied, the solution is correct.

Example 1: find the general solution of the equation

$$\frac{dy}{dx} = x + 10 \sin x \quad (8)$$

and the particular solution for which $y(0) = 0$.

Solution:

1. Multiplying by dx brings the equation into the separated form:

$$dy = (x + 10 \sin x) dx \quad (9)$$

2. Integrating both sides creates the general solution:

$$\int dy = \int (x + 10 \sin x) dx \quad \Rightarrow \quad y = \frac{x^2}{2} - 10 \cos x + C \quad (10)$$

3. Using the initial condition creates an algebraic equation for the constant C :

$$0 = -10 \cos(0) + C \quad \Rightarrow \quad C = 10 \quad (11)$$

The particular solution therefore is:

$$y = \frac{x^2}{2} - 10 \cos x + 10 \quad (12)$$

4. Substituting Equation (12) back into Equation (8) and the initial condition confirms that it is the correct solution.

Not all first-order ODEs are instantly separable – considerable effort and skill may be required to bring an ODE into the form prescribed by Equation (7).

3. Simple inhomogeneous first-order ODEs

The general form of a linear inhomogeneous first-order ODE is:

$$f'(x) + a(x)f(x) = b(x) \quad (13)$$

Such equations are solved by first solving the corresponding homogeneous equation:

$$g'(x) + a(x)g(x) = 0 \quad (14)$$

for the function $g(x)$ and then looking for the solution of the original equation of the following form:

$$f(x) = c(x)g(x) \quad (15)$$

where $c(x)$ is an unknown function. This has a formal proof, but we do not have sufficient time here.

Example 2: find the general solution of the differential equation describing first order chemical reaction with the reagent being continuously fed into the system

$$\frac{dS}{dt} = -k_1 S + k_2 \quad (16)$$

Solution: the homogeneous part of Equation (16) is simple first order kinetics

$$\frac{dg}{dt} = -k_1 g \quad \Rightarrow \quad g(t) = C e^{-k_1 t} \quad (17)$$

where C is a constant. The ansatz that we must use for the solution of the inhomogeneous equation is therefore:

$$S(t) = c(t)e^{-k_1 t} \quad (18)$$

where $c(t)$ is an unknown function. Substituting this into Equation (16) yields:

$$\frac{dc}{dt}e^{-k_1 t} - k_1 c e^{-k_1 t} = -k_1 c e^{-k_1 t} + k_2 \quad \Rightarrow \quad \frac{dc}{dt} = k_2 e^{k_1 t} \quad (19)$$

This equation may be integrated directly:

$$c(t) = \frac{k_2}{k_1} e^{k_1 t} + C \quad (20)$$

Substitution back into Equation (18) yields the general solution:

$$S(t) = \frac{k_2}{k_1} + C e^{-k_1 t} \quad (21)$$

where the coefficient C depends on the initial condition.