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:

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

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

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

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:

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

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:

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

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

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

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

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

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

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

$$\frac{dA(t)}{dt} = -kA^2(t) + s(t)$$ [second order kinetics with a source] - *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:

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

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

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

$$f(x)\,dx = g(y)\,dy \tag{5}$$

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

$$\frac{dy}{dx} = 6y^2 x$$ - *separable*

$$\frac{dy}{dx} = x^2 \cos(xy)$$ - *inseparable*

3. Simple homogeneous first-order ODEs

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

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

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:

$$g(y)\,dy = h(x)\,dx \tag{7}$$

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

$$\frac{dy}{dx} = x + 10\sin x \tag{8}$$

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

Solution:

1. Multiplying by dx brings the equation into the separated form:
$$dy=(x+10\sin x)\,dx \tag{9}$$
2. Integrating both sides creates the general solution:
$$\int dy=\int(x+10\sin x)\,dx \quad\Rightarrow\quad y=\frac{x^2}{2}-10\cos x+C \tag{10}$$
3. Using the initial condition creates an algebraic equation for the constant C:
$$0=-10\cos(0)+C \quad\Rightarrow\quad C=10 \tag{11}$$
The particular solution therefore is:
$$y=\frac{x^2}{2}-10\cos x+10 \tag{12}$$
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:
$$f'(x)+a(x)f(x)=b(x) \tag{13}$$
Such equations are solved by first solving the corresponding homogeneous equation:
$$g'(x)+a(x)g(x)=0 \tag{14}$$
for the function $g(x)$ and then looking for the solution of the original equation of the following form:
$$f(x)=c(x)g(x) \tag{15}$$
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
$$\frac{dS}{dt}=-k_1S+k_2 \tag{16}$$

Solution: the homogeneous part of Equation (16) is simple first order kinetics
$$\frac{dg}{dt}=-k_1g \quad\Rightarrow\quad g(t)=Ce^{-k_1t} \tag{17}$$
where C is a constant. The ansatz that we must use for the solution of the inhomogeneous equation is therefore:

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

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

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

This equation may be integrated directly:

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

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

$$S(t) = \frac{k_2}{k_1} + Ce^{-k_1 t} \tag{21}$$

where the coefficient C depends on the initial condition.