Lecture-09-Differential-Equations

Warm-up exercises
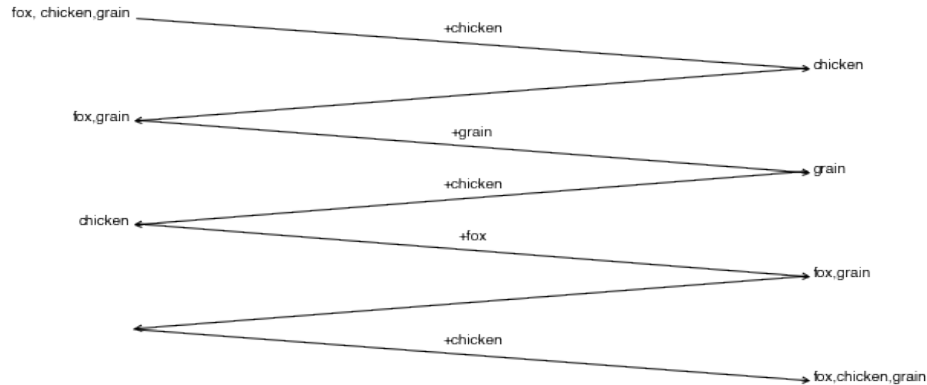
1. $\dfrac{dy}{dx} = 0$ Find $y =$

2. $\dfrac{dy}{dx} = 20x$ Find $y =$

3. $\dfrac{dy}{dx} = \dfrac{1}{x}$ Find $y =$

4. $\dfrac{dy}{dx} = \sin x$ Find $y =$

5. $\dfrac{6.1 \times 10^{-3}}{7 \times 10^5} =$

6. write 100 litres in $\text{m}^3 =$

7. $\log N - \log \dfrac{N}{2} =$

8. $\displaystyle\int_0^6 \dfrac{1}{e^x}\, dx =$

9. $\dfrac{dy}{dx} = e^x,$ Find $y =$

10. $\dfrac{9^0}{10000000} =$

11. What is the molar concentration of a solution of 500 ml water to which I have added 2.2 g KCl? (The molar mass of KCl is approx. 66 g/mol)

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fox, chicken,grain ─────── +chicken ──────→ chicken
fox,grain ←─────── +grain ───────
                  +chicken ──────→ grain
chicken ←─────── +fox ───────
                  ──────→ fox,grain
←─────── +chicken ───────
                  ──────→ fox,chicken,grain
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For you:

Week 6 challenge. There are a hundred switches. Each time you press one it goes from off to on or vice versa. Each is connected to a light bulb. 100 frogs are lined up. Frog 1 jumps on all the switches, turning on all the lights. Frog 2 jumps on switches 2,4,6,..100, turning off all the even numbered lights. Frog 3 jumps on switches 3,6,9. . . ,99 thereby turning some lights off (e.g. 3) on some back on (e.g. 6). The frogs take it in turn until Frog 100 jumps only on switch 100. After the last frog has jumped, how many lights are still on?

Differential equations

What is a differential equation?

If y depends on x, then a differential equation in x and y is one that relates one or more derivatives e.g. $\frac{dy}{dx}$ to x, to y or to both. For example

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

What is a solution to a differential equation?

For the above case, y is a solution if its derivative w.r.t. $x = f(x, y)$

To solve it, we must find y, i.e.

$$y = ?$$

But there are *many* solutions. Graph passes through one or more points already determined by theory or experiment: 'initial conditions'

How do we find these solutions?

We use the *Method of Separation of Variables*

This states that we must apply each of these mathematical operations in turn to a differential equation in order to find its solution

1. Separate
2. Integrate
3. Simplify
4. Initial conditions

The acronym **SISI** can help you remember the steps and the order to apply them! Note that not all steps may be able to be applied e.g. the equation may already be separated or we may not have any initial conditions.

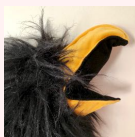These are best understood via some simple examples

Example 1. When the first derivative is zero

$$\frac{dy}{dx} = 0 \qquad \text{equation already SEPARATED, so INTEGRATE both sides w.r.t. x}$$

$$\int \frac{dy}{dx} . dx = \int 0 . dx$$

$$\int dy = \int 0 . dx$$

$$y + k = A \qquad\qquad A \text{ and } k \text{ are constants}$$

$$y = A - k$$

$$y = B \qquad \text{SIMPLIFY by writing } A - k \text{ as } B, \text{ no INITIAL CONDITIONS to apply}$$

Hence the general solution is

$$\boxed{y = B}$$

Common misconception:

Remember all the times we've talked about $\frac{dy}{dx}$ being mathematically a single object? It comes home to roost here: you are INTEGRATING both sides w.r.t x.

Example 2. When the first derivative is a constant, c

$$\frac{dy}{dx} = c \qquad \text{equation already SEPARATED, so INTEGRATE both sides w.r.t. x}$$

$$\int \frac{dy}{dx}.dx = \int c.\,dx$$

$$\int dy = \int c.\,dx$$

$$y + k = cx + A \qquad\qquad A \text{ and } k \text{ are constants}$$

$$y = cx + A - k$$

$$y = cx + B \qquad \text{SIMPLIFY by writing } A - k \text{ as } B, \text{ no INITIAL CONDITIONS to apply}$$

Hence the general solution is

$$\boxed{y = cx + B}$$

Example 3. When the first derivative is a linear function of x

$$\frac{dy}{dx} = x + c \qquad \text{equation already SEPARATED, so INTEGRATE both sides w.r.t. x}$$

$$\int \frac{dy}{dx}.dx = \int (x + c)\,dx$$

$$\int dy = \int (x + c)\,dx$$

$$y + k = \frac{x^2}{2} + cx + A \qquad\qquad A \text{ and } k \text{ are constants}$$

$$y = \frac{x^2}{2} + cx + A - k \quad \text{SIMPLIFY by writing } A - k \text{ as } B, \text{ no INITIAL CONDITIONS to apply}$$

Hence the general solution is

$$\boxed{y = \frac{x^2}{2} + cx + B}$$

Example 4. When the first derivative is a polynomial in x and y

We can't work out a general solution as it will depend on the exact form of $f(x, y)$. Consider this example:

$$\frac{dy}{dx} = 5x^{3/2}y \qquad\qquad\qquad \text{first SEPARATE the variables}$$

$$\frac{1}{y}\frac{dy}{dx} = 5x^{3/2} \qquad\qquad\qquad \text{now INTEGRATE both sides w.r.t. x}$$

$$\int \frac{1}{y}\frac{dy}{dx}.dx = \int 5x^{3/2}dx$$

$$\ln|y| + A = \frac{5x^{5/2}}{5/2} + B \qquad\qquad \text{where } A \text{ and } B \text{ are constants of integration}$$

$$\ln|y| = 2x^{5/2} + C \qquad\qquad \text{we have SIMPLIFIED by writing } C = B - A$$

$$|y| = e^{2x^{5/2}+C} \qquad\qquad \text{we can SIMPLIFY further by exponentiating both sides..}$$

$$|y| = Be^{2x^{5/2}} \qquad\qquad\qquad\qquad \text{..and defining } B = e^{C}$$

Example 5. First derivative is a complex function of x and y

Again, we cannot generalise so consider:

$$e^{x}\frac{dy}{dx} = \frac{x}{y} \qquad\qquad\qquad \text{first SEPARATE the variables}$$

$$y\frac{dy}{dx} = \frac{x}{e^{x}}$$

$$y\frac{dy}{dx} = xe^{-x} \qquad\qquad\qquad \text{now INTEGRATE both sides w.r.t. } x$$

$$\int y\frac{dy}{dx}dx = \int xe^{-x}dx$$

At this point we need to recognise that the RHS can be done using integration by parts if we identify $u = x$ and $v' = e^{-x}$!

$$\frac{y^{2}}{2} + c_{1} = -x.e^{-x} + \int e^{-x}.dx$$

$$= -xe^{-x} - e^{-x} + c_{2} \qquad c_{1} \text{ and } c_{2} \text{ are constants of integration. Now SIMPLIFY.}$$

$$y^{2} = -2e^{-x}(1+x) + c_{3} \qquad\qquad \text{where } c_{3} = 2(c_{3} = c_{1})$$

$$y = \pm\sqrt{-2e^{-x}(1+x) + c_{3}} \qquad\qquad \text{could choose to write in this form}$$

A simple biochemical example: a zeroth order processes

There are many processes that occur in Nature where the **rate of growth** (or **rate of decay**) of a bacterium or compound or element is constant (i.e. does not change with time).

Let's take the rate of decay; we can write a differential equation for this

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

where $[A]$ is the concentration of compound A and t is time. The minus sign is there because k is a positive constant and the first derivative must be negative since this is decay i.e. the amount of A is decreasing with time.

Once we have separated (which there is no need here) we can classify this equation by noting that there are NO terms involving $[A]$ on the right hand side and is therefore described as a **zeroth-order process**.

$$\frac{d[A]}{dt} = -k \qquad\qquad \text{no integrate both sides w.r.t } t$$

$$\int \frac{d[A]}{dt}.dt = \int -k\,dt \qquad\qquad \text{we can take } k \text{ outside the integrand as it is constant}$$

$$\int d[A] = -k \int dt$$

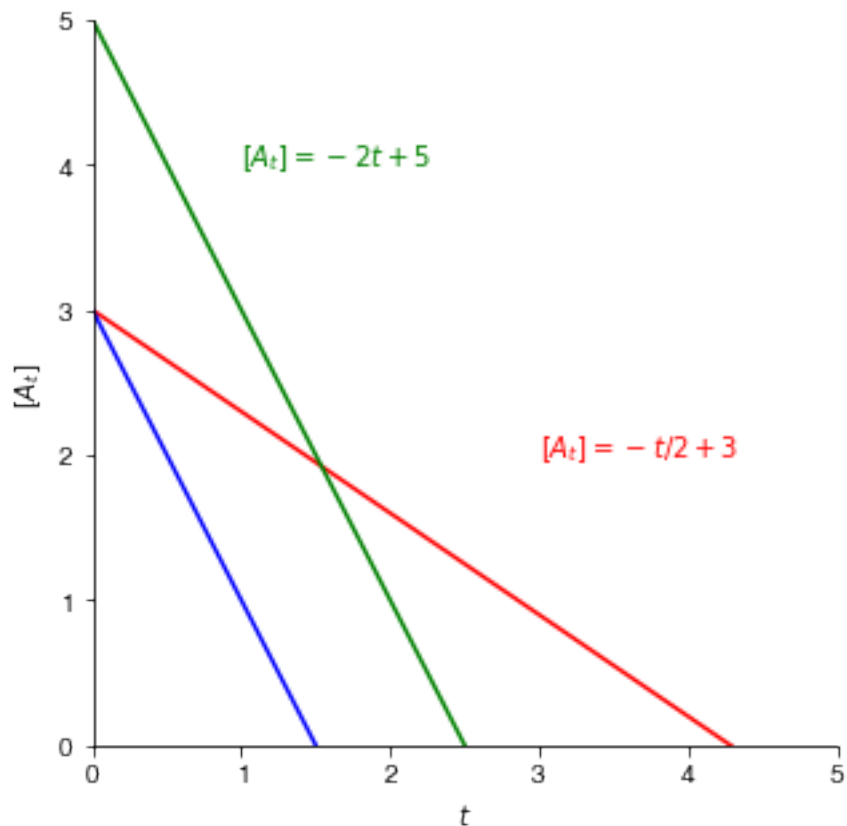$$[A_t] = -kt + c \qquad\qquad \text{note in the form } y = mx + c$$

To find out what value c takes, we have to supply some initial conditions. If we say that when $t = 0$, $[A] = [A_0]$, then we can substitute these in the equation above and solve for c.

$$[A_0] = -k \times 0 + c$$
$$c = [A_0]$$

and hence the solution is

$$\boxed{[A_t] = -kt + [A_0]}$$

Below are some example graphs showing how the values of k and $[A_0]$ affect the behaviour of the function.

A more complex biochemical example: the Michaelis-Menten equation

This states that for a large quantity of enzyme

$$-\frac{ds}{dt} = \frac{V.s}{k+s}$$

where s is the substrate concentration, t is time and V, k are constants that describe the enzyme. (Using dimensional analysis can you work out what units they have?)

Applying **SISI**:

$$-\frac{ds}{dt} = \frac{V.s}{k+s} \qquad \text{SEPARATE and get all the terms in } s \text{ on the LHS}$$

$$-\frac{k+s}{V.s}\frac{ds}{dt} = 1 \qquad \text{now INTEGRATE both sides w.r.t. t}$$

$$-\int \frac{k+s}{V.s}\frac{ds}{dt}dt = \int dt$$

$$-\int \frac{k+s}{V.s}ds = \int dt$$

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It is important to recognise that we *cannot integrate* the LHS as it is too complicated! Instead we must make some simplifying assumptions that allow us to integrate the LHS, but only in certain regimes.

Regime 1: When $s \gg k$, k in the numerator can be neglected

(remember $\gg$ means "much, much larger than")
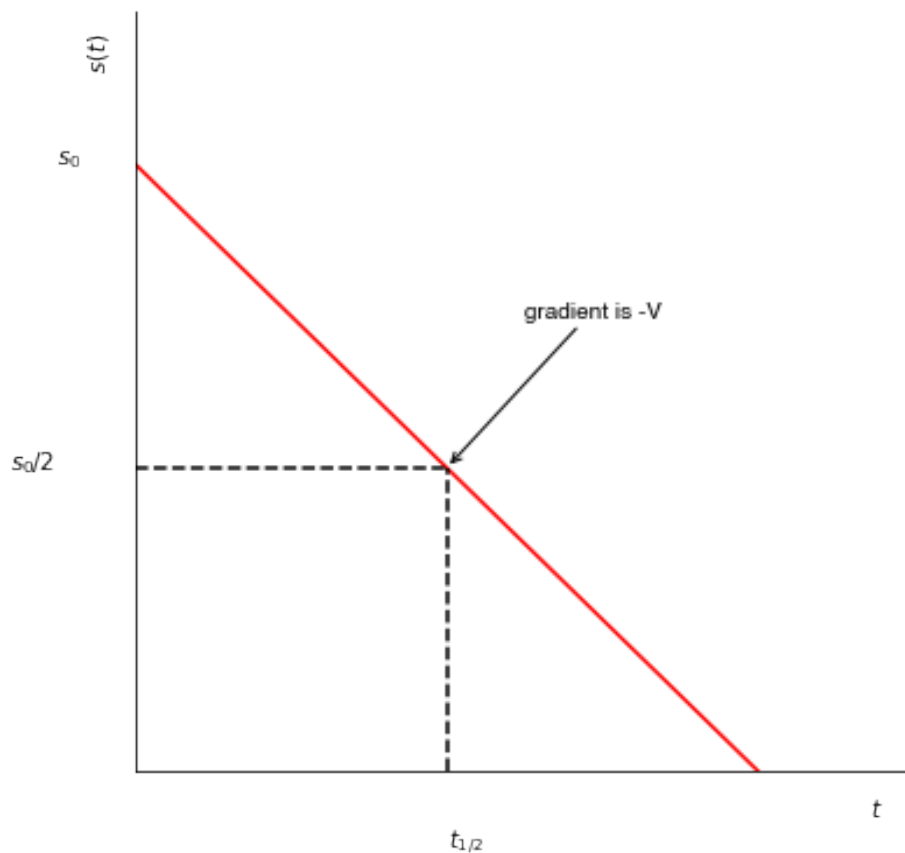
If $s \gg k$ we can rewrite the last step as

$$-\int \frac{s}{V.s}.ds = \int dt$$

$$-\int \frac{1}{V}.ds = \int dt \qquad \text{since } V \text{ is a constant we can do this}$$

$$\int ds = -V \int dt$$

$$s + a = -Vt + b \qquad \text{where } a \text{ and } b \text{ are constants of integration}$$

$$s = -Vt + c \qquad \text{where } c = b - a$$

$$\boxed{s = -Vt + c}$$

This is a straight line (i.e. in the form $y = mx + c$) and is a ZEROTH ORDER PROCESS since the rate is independent of the concentration, s, since it only depends on time t.

What is the half-life, $t_{1/2}$? The half-life is the length of time it takes for the amount to half (e.g. decay). As shown above, when $t = t_{1/2}$, $s = s_0/2$. We can substitute these above leading to

$$-\int_{s_0}^{s_0/2} \frac{ds}{V} = \int_0^{t_{1/2}} dt$$

$$-\left[\frac{s}{V}\right]_{s_0}^{s_0/2} = [t]_0^{t_{1/2}}$$

$$-\frac{s_0}{2V} + \frac{s_0}{V} = t_{1/2}$$

$$-\frac{s_0}{2V} = t_{1/2}$$

$$\boxed{t_{1/2} = \frac{s_0}{2V}}$$

Hence $t_{1/2}$ depends on s_0. Since t has the dimensions of time and s_0 has the dimensions of concentration, then V in this regime has dimensions of "concentration per time" e.g. $V = 10\,\mu\text{mol.dm}^{-3}.\text{min}^{-1}$

Regime 2: When $s \ll k$, s in the denominator can be neglected

$$-\frac{ds}{dt} = \frac{V.s}{k+s}$$

If $s \ll k$ we can rewrite the differential equation as

$$-\frac{ds}{dt} = \frac{V.s}{k}$$

$$-\int \frac{k}{V.s} .ds = \int dt$$

$$-\frac{k}{V} \int \frac{1}{s} .ds = \int dt \qquad \text{since } k \text{ and } V \text{ are both constants we can take them out of the integrand}$$

$$D - \frac{k}{V} \ln s = t + c \qquad \text{where } D \text{ and } c \text{ are constants of integration}$$

$$ln \left| \frac{B}{s} \right| = \frac{Vt}{k} \qquad \text{where } \ln B = D - c$$

$$\frac{B}{s} = \pm e^{Vt/k} \qquad \text{have to choose the positive or negative solution; let's choose the positive solution}$$

$$s = Be^{-Vt/k}$$

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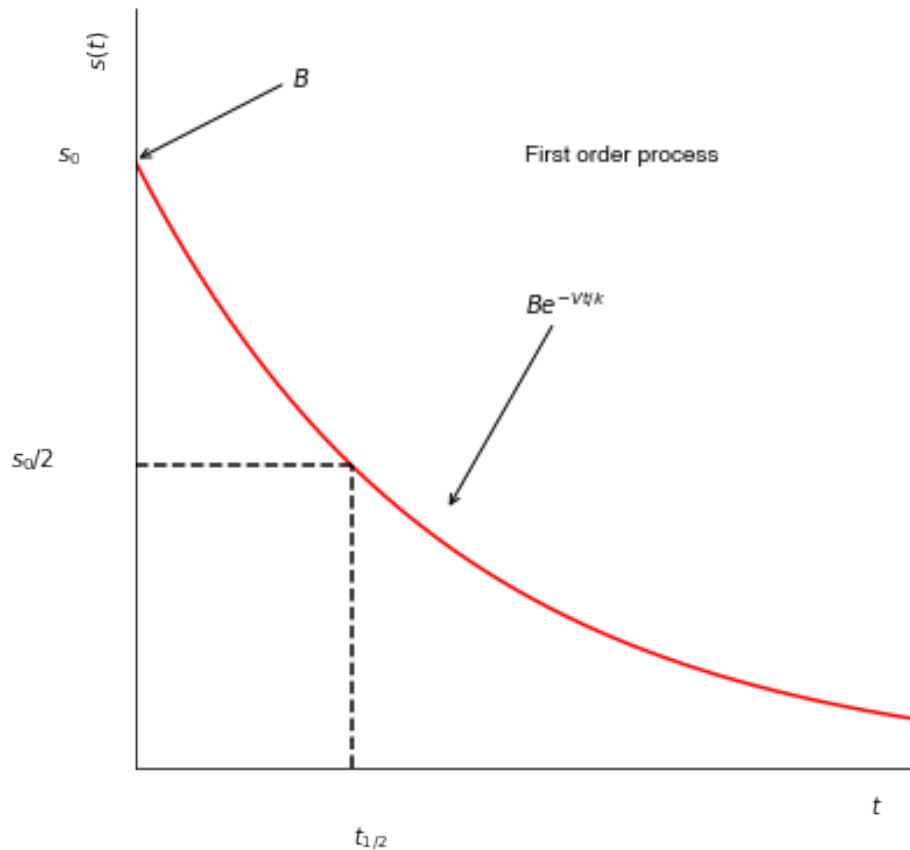
What is the half-life, $t_{1/2}$? As shown above, when $t = t_{1/2}$, $s = s_0/2$. We can substitute these above leading to

$$-\int_{s_0}^{s_0/2} \frac{k}{V} \frac{ds}{s} = \int_0^{t_{1/2}} dt$$

$$-\left[\frac{k}{V} \ln |s|\right]_{s_0}^{s_0/2} = [t]_0^{t_{1/2}}$$

$$-\frac{k}{V} \ln |\frac{s_0}{2}| + \frac{k}{V} \ln |s_0| = t_{1/2}$$

$$-\frac{k}{V} \ln \left|\frac{s_0}{s_0/2}\right| = t_{1/2}$$

$$\boxed{t_{1/2} = \frac{k}{V} \ln 2}$$

Hence $t_{1/2}$ depends on k and V. e.g. if $V = 10\,\mu\text{mol.dm}^{-3}.\text{min}^{-1}$ and $k = 100\,\mu\text{mol.dm}^{-3}$, $t_{1/2} = 10 \ln 2 = 6.93$ min.

Summary

Zeroth order process

The rate of change is INDEPENDENT of concentration (or equivalently $\propto s^0$ which is a constant). Characterised by a single positive constant, k.

$$\frac{dA}{dt} = k \qquad\qquad\qquad \text{GROWTH}$$

$$\frac{dA}{dt} = -k \qquad\qquad\qquad \text{DECAY}$$

First order process

The rate of change is PROPORTIONAL to concentration (i.e. $\propto s^1$). Characterised by a single positive constant, k.

$$\frac{dA}{dt} = kA \qquad\qquad\qquad \text{GROWTH}$$

$$\frac{dA}{dt} = -kA \qquad\qquad\qquad \text{DECAY}$$

Motivating example from Thermodynamics

We are told that the change in free energy ΔG is related to the equilibrium constant, K, via

$$\Delta G^o = -RT \ln K$$

where R is the Rydberg gas constant and T is the absolute temperature. Can rewrite the above as

$$\ln K = -\frac{\Delta G^o}{RT}$$
$$= -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

If we assume that ΔH^o and ΔS^o are independent of T, then we can write

$$\frac{d \ln K}{dT} = \frac{d}{dT} \left(-\frac{\Delta H^o}{R} T^{-1} \right)$$
$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \qquad\qquad \text{this is the VAN T'HOFF ISOCHORE}$$

Reintegrating this equation gives

$$\int_{K_1}^{K_2} \frac{d \ln K}{dT} . dT = \int_{T_1}^{T_2} \frac{\Delta H^o}{RT^2} . dT$$
$$\int_{K_1}^{K_2} d(\ln K) = \left[-\frac{\Delta H^o}{RT} \right]_{T_1}^{T_2}$$
$$\ln K_2 - \ln K_1 = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$
$$\ln \left| \frac{K_2}{K_1} \right| = -\frac{\Delta H^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

as per your Thermodynamics notes.