

Mathematics Methods and Thermodynamics

Kinetics II - Linear Differential Equations

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CLASS OVERVIEW

- ▶ Ordinary Differential Equations (ODE)
 - ▶ Classification
 - ▶ General (ODE)
 - ▶ General and particular solutions
 - ▶ Approximations

INTEGRATION IN KINETICS

- ▶ Last week we studied Kinetics and Integration
- ▶ We can use integration to work out the rate equation from the differential rate laws

INTEGRATION IN KINETICS

- Specifically the rate law can be given by the separation of variables technique:

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

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

$$\int \frac{1}{[A]} d[A] = \int -k dt$$

$$\ln([A]) + C = -kt$$

$$C = \ln(A_0)$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

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- ▶ This is an ideal unimolecular case
- ▶ For a more complex case for example

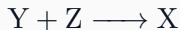


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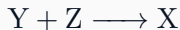


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- ▶ If one mole of Y reacts with one mole of Z to form 1 mole of X then we can write as this

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- ▶ Then we use separation of variables

$$\frac{d[X]}{dt} = k ([Y]_0 - [X]) ([Z]_0 - [X])$$

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FINDING THE ORDER

- ▶ This requires that we know the order of the reaction
- ▶ If we do not know the order we have to apply other techniques first
- ▶ For example we could break down the reaction into elementary steps and apply steady state

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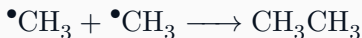
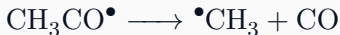
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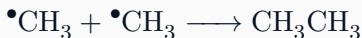
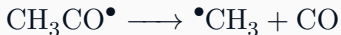
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- ▶ Consider this example
- ▶ To find the rate of CH_4 we must consider its reactants CH_3COH and $\bullet\text{CH}_3$
- ▶ The rate of generation of CH_4 is $\frac{d[\text{CH}_4]}{dt} = k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3]$ Therefore we need an expression for $[\text{CH}_3\text{CHO}]$ and $[\bullet\text{CH}_3]$.



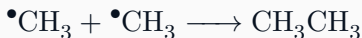
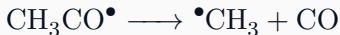
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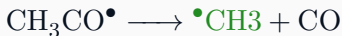
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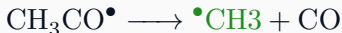
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$$\frac{d[\bullet\text{CH}_3]}{dt} = + k_i [\text{CH}_3\text{CHO}] - k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3] \\ + k_{p2} [\text{CH}_3\text{CO}\bullet] - 2k_t [\bullet\text{CH}_3] [\bullet\text{CH}_3]$$

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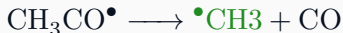
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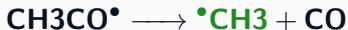
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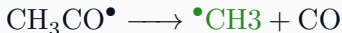
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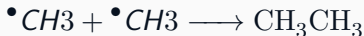
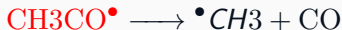
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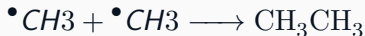
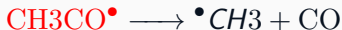
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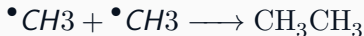
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FINDING THE ORDER

- ▶ At this point we want to apply integration to convert those differential rate equation to concentrations
- ▶ To do this we should try to put everything in terms know initial concentrations (starting materials)
- ▶ This however is a bit complex in this case we use steady the state approximation

$$\begin{aligned} \frac{d[\bullet\text{CH}_3]}{dt} &= + k_i [\text{CH}_3\text{CHO}] - k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3] \\ &\quad + k_{p2} [\text{CH}_3\text{CO}\bullet] - 2k_t [\bullet\text{CH}_3] [\bullet\text{CH}_3] \approx 0 \\ \frac{d[\text{CH}_3\text{CO}\bullet]}{dt} &= k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3] - k_{p2} [\text{CH}_3\text{CO}\bullet] \approx 0 \end{aligned}$$

FINDING THE ORDER

- Rearranging $\frac{d[\text{CH}_3\text{CO}\bullet]}{dt}$ gives

$$k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3] = k_{p2} [\text{CH}_3\text{CO}\bullet]$$

- Substituting into $\frac{d[\bullet\text{CH}_3]}{dt}$ gives

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FINDING THE ORDER

- ▶ Rearrange for $[\bullet\text{CH}_3]$

$$[\bullet\text{CH}_3] = \sqrt{\frac{k_i [\text{CH}_3\text{CHO}]}{2k_f}}$$

In steady state initial rate = final rate

$$[\bullet\text{CH}_3] = \sqrt{\frac{[\text{CH}_3\text{CHO}]}{2}}$$

FINDING THE ORDER

- ▶ The expression for $\frac{d[\text{CH}_4]}{dt} = k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3]$ can now be rewritten in terms of $[\text{CH}_3\text{CHO}]$

$$\begin{aligned}\frac{d[\text{CH}_4]}{dt} &= k_{p1} [\text{CH}_3\text{CHO}] [\bullet\text{CH}_3] \\ &= k_{p1} [\text{CH}_3\text{CHO}] \sqrt{\frac{[\text{CH}_3\text{CHO}]}{2}} \\ &= \frac{\sqrt{2}}{2} k_{p1} [\text{CH}_3\text{CHO}]^{\frac{3}{2}}\end{aligned}$$

THE INTEGRATED EQUATION

- ▶ We can now represent $[\text{CH}_3\text{CHO}]$ in terms of $[\text{CH}_4]$ and integrate. Assuming that from the stoichiometry equation that one mole goes to one mole.

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$$\frac{d[\text{CH}_4]}{dt} = \frac{\sqrt{2}}{2} k_{p1} ([\text{CH}_3\text{CHO}]_0 - [\text{CH}_4])^{\frac{3}{2}}$$

THE INTEGRATED EQUATION

- ▶ Applying the separation of variables technique

$$\int \frac{1}{([\text{CH}_3\text{CHO}]_0 - [\text{CH}_4])^{\frac{3}{2}}} d[\text{CH}_4] = \int \frac{\sqrt{2}}{2} k_{p1} dt$$
$$\frac{2}{\sqrt{[\text{CH}_3\text{CHO}]_0 - [\text{CH}_4]}} + C = \frac{\sqrt{2}}{2} k_{p1} t$$

ORDINARY DIFFERENTIAL EQUATIONS

- ▶ When dealing with differential and integrated rate equations we are dealing with *Ordinary Differential Equations* (ODEs)
- ▶ In the previous example we were dealing with a sets of ODEs
- ▶ An ODE is simply an equation that deals with not only its variable but also differentials of that variable
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ODEs

- ▶ For example Newton's law of cooling is an ODE

$$\frac{dx}{dt} + x = 2\cos(t)$$

x is some function of temperature that depends upon t and satisfies this equation

ODEs

- ▶ The equation which solves this ODE is

$$x(t) = \cos(t) + \sin(t) + Ce^{-t}$$

- ▶ The constant C can be found by applying any initial conditions for example at $x(0) = x_0$, $C = x_0 - 1$

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ODE CLASSIFICATION

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 - ▶ Linearity
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ODE CLASSIFICATION - LINEAR

- ▶ A linear ODE is one that depends the function and its derivatives in a linear manner

$$a_n \frac{d^n y}{dx^n} + a_{n-1} \frac{d^{n-1} y}{dx^{n-1}} \dots a_1 \frac{dy}{dx} + a_0 y = Q(x)$$

- ▶ For example the following is linear

$$\frac{dx}{dt} + x = 2\cos(t)$$

- ▶ Linear ODEs have exact closed form solutions

ODE CLASSIFICATION - NON-LINEAR

- ▶ A non-linear case terms such as x^2
 - ▶ For example the following is non-linear

$$\frac{dx}{dt} + x^2 = 0$$

- ▶ Non liner ODEs might be solved by observing conserved quantities (energy is often conserved in real systems) or by perturbation theory

ODE CLASSIFICATION - ORDER

- ▶ The order of an ODE is the highest derivative's order
- ▶ For example
 - ▶ $y' + y = 0$ is 1st order
 - ▶ $y'' + y = 0$ is 2nd order
 - ▶ $y'' + y' + y = 0$ is 2nd order
 - ▶ $y^{(3)} + y' + y = 0$ is 3rd order

ODE - HOMOGENOUS

- ▶ An ODE is said to be homogenous if it equates to zero

$$a_n \frac{d^n y}{dx^n} + a_{n-1} \frac{d^{n-1} y}{dx^{n-1}} \dots a_1 \frac{dy}{dx} + a_0 y = 0$$

- ▶ Homogenous

$$y' + y = 0$$

$$y' = 0$$

- ▶ Non-homogenous

$$y' + y = 2$$

$$y' = -k$$

SYSTEMS OF ODES

- ▶ When there is more than 1 *dependant* variable we treat the problem as a set or system of ODEs
- ▶ In such cases the dependant variable can be rewritten as

$$\bar{x} = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix}, \quad \frac{d\bar{x}}{dt} = \begin{bmatrix} \frac{dx_1}{dt} \\ \frac{dx_2}{dt} \\ \vdots \\ \frac{dx_n}{dt} \end{bmatrix}$$

- ▶ In our differential rate equations, the concentrations are interrelated and so represent dependant variables.
- ▶ Complex reactions in chemical kinetics represent systems of ODEs

SYSTEMS OF ODES - FIRST ORDER

- ▶ A first order system of ODEs can be written in vector form as

$$\bar{F}\left(\frac{d\bar{x}}{dt}, x, t\right) = \bar{0} \quad \text{Where, } \bar{0} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

- ▶ A linear first order system can be rewritten in matrix form

$$A \frac{d\bar{x}}{dt} + B\bar{x} = \bar{G}(t)$$

Where, A and B are matrices, A is invertible and usually the identity

SYSTEMS OF ODES - HIGHER ORDER

- ▶ What about higher order?
- ▶ Higher order functions can be rewritten as first order functions but with more variables
- ▶ For example to convert the following expression:

$$x''' + 2x'' + 3x' + 4x = t$$

We define the following variables

$$y_1 = x$$

$$y_2 = x'$$

$$y_3 = x''$$

SYSTEMS OF ODES - HIGHER ORDER

- ▶ These variables gives two additional relationships, both of which are first order

$$y_1' - y_2 = 0$$

$$y_2' - y_3 = 0$$

Which gives the following set of ODEs

$$y_1' - y_2 = 0$$

$$y_2' - y_3 = 0$$

$$y_3' + 2y_3 + y_2 + 4y_1 = t$$

ODEs - ANALYTICAL VS NUMERICAL

- ▶ Some ODEs can be solved analytically by integration these include the simple ones we recently solved by separation of variables
- ▶ However in general these can only be solved approximately
- ▶ When analytical solutions do apply, we get far more information about the behaviour system without needing to justify the accuracy of any approximations
- ▶ Analytical solutions should not be shunned for numerical and modern day tools such as maple and wolfram alpha can solve many ODEs symbolically
- ▶ Numerical methods have the advantage of “always” working
- ▶ Although the success of numerical methods should be justified rather than blindly followed to avoid nonsense answers

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ODEs - ANALYTICAL METHODS

- ▶ We have seen one of the most common cases of an ODE already

$$\frac{dx}{dt} = kx$$

- ▶ This ODE represent exponential growth and its solution is

$$x = Ce^{kt}$$

ODEs - REPRESENTATION

- ▶ A first order differential can be represented as

$$\frac{dx}{dt} = f(t, x)$$

- ▶ It has an initial condition that can be represented as

$$x(t_0) = x_0$$

ODEs - PICARD'S THEOREM

- ▶ For such an ODE Picard's theorem states
 - ▶ If near (t_0, x_0) the function is continuous and that if $\frac{df}{dt}$ is also continuous, then there exists a solution that is unique
 - ▶ This theorem states that around (t_0, x_0) a solution exists but says nothing about other regions
 - ▶ For example

$$\frac{dx}{dt} = x^2$$

$$x(t_0) = 1$$

Then the solution is

$$x = \frac{1}{1-t}$$

Which is valid around (t_0, x_0) but blows up at around $t = 1$

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ODEs - SEPARATION OF VARIABLES

- ▶ So far we have been using separation of variables to solve ODEs
- ▶ This works for simple ODEs of the form

$$\frac{dx}{dt} = f(x)$$

- ▶ By applying the inverse function theorem

$$\frac{dx}{f(x)} = dt$$

- ▶ Then integrating

$$\int \frac{1}{f(x)} dx = t + C$$

ODEs - HIGHER ORDER SYSTEM OF ODEs

- ▶ A real system tends to be a set of ODEs
- ▶ For a system of k n^{th} ODEs they can be rewritten as a system of $n \times k$ first order equations with $n \times k$ unknowns

ODEs - SYSTEM OF LINEAR ODEs

- ▶ Many practical example are sets of linear ODEs, or ones that can be rewritten as such through linearisation
- ▶ In such cases we can construct a matrix

$$\vec{x}' = A\vec{x} + \vec{F}(t)$$

And solve the matrix as an eigenvalue problem

NUMERICAL - ODEs

- ▶ In many cases a solution of $\frac{dx}{dt} = F(t, x)$ at $x(t_0) = x_0$ is impossible or very difficult to solve
- ▶ Practically we use approximate methods to solve the equations and obtain values for our range of interest

NUMERICAL - EULER'S METHOD

- ▶ Euler's method is a very simple approximate ODE solver
- ▶ It operates by starting at a known point $F(t_0) = x_0$
- ▶ Then taking the gradient at that point $k = F'(t_0, x_i)$
- ▶ Moving along the tangent by step h to find an approximate t_1, x_1
- ▶ Repeating the process from this point
- ▶ Generally:

$$t_{i+1} = t_i + h$$

$$x_{i+1} = x_i + hF'(t_i, x_i)$$

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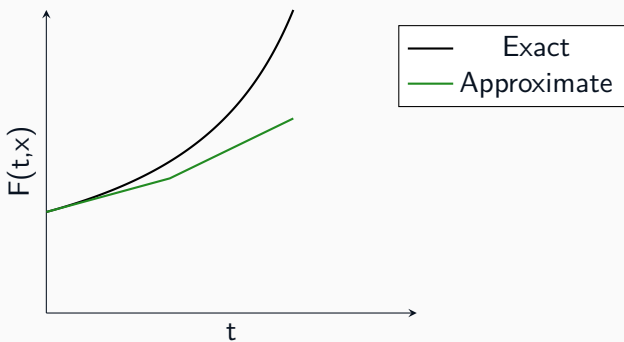
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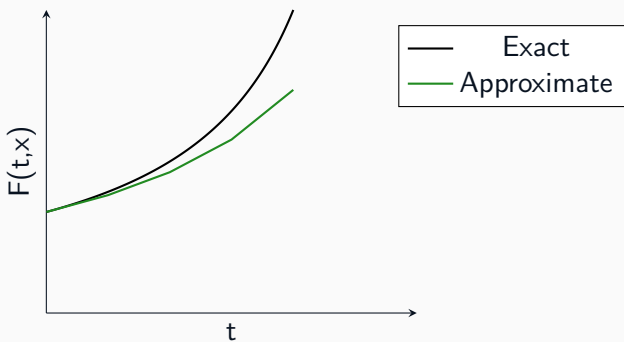
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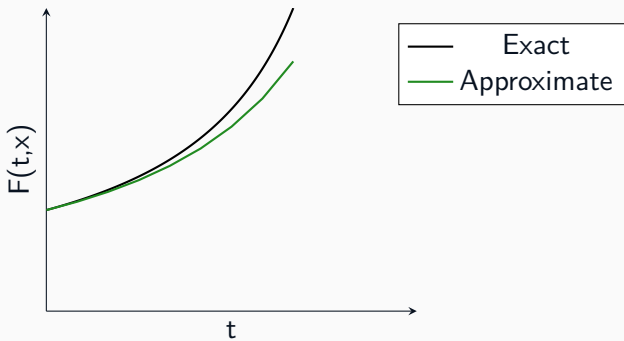
$$h = 1$$

NUMERICAL - EULER'S METHOD



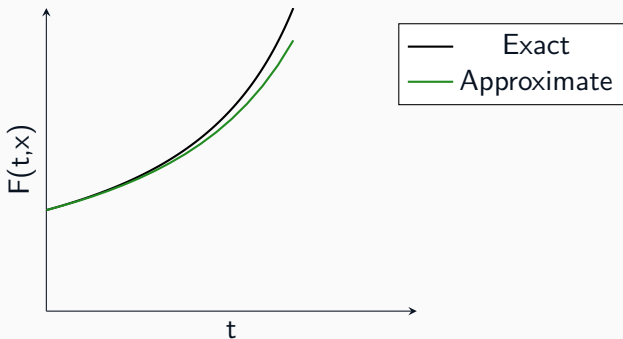
$$h = 0.5$$

NUMERICAL - EULER'S METHOD



$$h = 0.25$$

NUMERICAL - EULER'S METHOD



$$h = 0.125$$

NUMERICAL - EULER'S METHOD

- ▶ Euler's method is a first order method
- ▶ This means that by halving h the error is approximately halved
- ▶ This is computationally inefficient
- ▶ For this example we get an error of ≈ 0.1 when $h = 0.03125$ requiring 64 evaluations in the range of 0 to 1
- ▶ To get an error of 0.01 it would need to be halved 3 to 4 more times are require 512-1024 steps
- ▶ Generally errors in approximate methods is approximately

$$\frac{1}{2^n}$$

Where n is the order of the method

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NUMERICAL - RUNGE-KUTTA

- ▶ A more efficient method would be the Runge-Kutta method which is fourth order
- ▶ For each point it calculates four approximations with different methods and then takes a linear combination of them

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NUMERICAL - RUNGE-KUTTA

- ▶ The Runge-Kutta approximation uses the following logic where $\frac{dx}{dt} = f(x, t)$

$$k_1 = f(t_i, x_i)$$

$$k_2 = f\left(t_i + \frac{h}{2}, x_i + k_1 \frac{h}{2}\right)$$

$$k_3 = f\left(t_i + \frac{h}{2}, x_i + k_2 \frac{h}{2}\right)$$

$$k_4 = f(t_i + h, x_i + k_3 h)$$

$$t_{i+1} = t_i + h$$

$$x_{i+1} = x_i + h \frac{k_1 + 2k_2 + 2k_3 + k_4}{6}$$

NUMERICAL CONSIDERATION

- ▶ When consider numerical approximations a few considerations need to be made
 - ▶ Computational time: Even though each computation may be fast to get high accuracy often many thousands of computations must be performed this can become quite time consuming
 - ▶ Roundoff errors: Computers have a limit of precision this means they can only divide by small h values up to a certain point before the number becomes too large to hold (without special techniques). From experience for standard float type numbers this is 4 significant figures for double type numbers this is 7 significant figures
 - ▶ Stability Some equations are numerically unstable, this means that they fluctuate widely and that values converge slowly if at all

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- ▶ These solutions often depend on ordinary differential equations (ODEs)
- ▶ ODEs can be classified by their order, linearity and homogeneity
- ▶ ODEs can be solved by techniques such as separation of variables
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