Experimental data: $a_i$ at various $t_i$

Problem: what elementary rxns & k's?
Given $t_0$ and $c_0$, calculate $c_n$ at $t_n$

$a_1$ at $t_1 = t_0 + \delta t$ given by Taylor series

$$a_1 = a_0 + \left( \frac{d}{dt} a_0 \right) \delta t + \left( \frac{d^2}{dt^2} a_0 \right) \frac{(\delta t)^2}{2!} + \cdots$$

$$= a_0 + f(a_0) \delta t + \frac{f''(a_0)}{2} \frac{(\delta t)^2}{2!} + \cdots$$

Once $a_1$ is determined, then $a_2$ can be determined from $a_1$, and so on.
Chemical kinetics allows $f(a_t)$ to be determined from $a_t$

Example:

$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ \hspace{1cm} (1)

$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$ \hspace{1cm} (2)

If $O_2$ essentially constant, then

$$\frac{d[\text{CH}_3]}{dt} = -k_1[\text{CH}_3]^2 - k_2[\text{CH}_3][O_2] = f([\text{CH}_3(t)])$$

Various methods for truncating Taylor’s expansion

Euler’s method: $a_1 = a_0 + f(a_0)\delta t$

Modified Euler method:

$$a_1 = a_0 + f(a_0)\delta t + f@a_0 \left(\frac{(\delta t)^2}{2!}\right)$$
But--$f'(a(0))$ cannot be determined from rate eqns

$f(a(0))$ can be

$$f(a_0) \approx \frac{f(a_1) - f(a_0)}{\delta t}$$

$$a_1 = a_0 + f(a_0)\delta t + \frac{f(a_1) - f(a_0)}{\delta t} \left(\frac{\delta t}{2}\right)^2$$

$$a_1 = a_0 + \frac{1}{2} \left[ f(a_0) + f(a_1) \right] \delta t$$
But we need to know $a_1$ to get $f(a_1)$, so approximate as

$$a_1 \approx a_0 + f(a_0)\delta t = a_0 + \beta_0$$

with $\beta_0 = f(a_0)\delta t$.

And a better approximation to $a_1$ is

$$a_1 = a_0 + \frac{1}{2} \left[ f(a_0) + f(a_1) \right] \delta t$$

$$a_1 = a_0 + \frac{1}{2} \left[ f(a_0) + f(a_0 + \beta_0) \right] \delta t$$

$$a_1 = a_0 + \frac{1}{2} \left[ \beta_0 + \beta_1 \right]$$

with $\beta_1 = f(a_0 + \beta_0)\delta t$.
Example

CH$_3$ + CH$_3$ = C$_2$H$_6$

$[CH_3]_0 = 1 \times 10^{13}$ cc$^{-1}$

$K_1 = 5 \times 10^{-11}$ cc s$^{-1}$

$\delta t = 5 \times 10^{-4}$ s

Euler's method: $a_1 = a_0 + \beta_0$

$\beta_0 = f(a_0)\delta t = \frac{d[CH_3]}{dt} \delta t = -k_1[CH_3]^2 \delta t$

$= (-5 \times 10^{-11})(1 \times 10^{13})^2 (5 \times 10^{-4}) = -2.5 \times 10^{12}$

$a_1 = 1 \times 10^{13} - 2.5 \times 10^{12} = 7.5 \times 10^{12}$
\[ a_1 = a_0 + f(a_0) \delta t \]
Modified Euler’s Method

\[ a_1 = a_0 + \frac{\beta_0 + \beta_1}{2} \]

\[ \beta_0 = f(a_0)\delta t = -2.5 \times 10^{12} \]

\[ \beta_1 = f(a_0 + \beta_0)\delta t \]

\[ = f(1 \times 10^{13} - 2.5 \times 10^{12})\delta t = f(7.5 \times 10^{12})\delta t \]

\[ = (-5 \times 10^{-11})(7.5 \times 10^{12})^2(5 \times 10^{-4}) \]

\[ = -1.41 \times 10^{12} \]

\[ a_1 = a_0 + \frac{1}{2} [\beta_0 + \beta_1] = 1 \times 10^{13} + \frac{(12.5 \times 10^{12} - 1.41 \times 10^{12})}{2} \]

\[ = 8.05 \times 10^{12} \]

**Exact solution**

\[ -d[CH_3]\frac{dt}{dt} = k_i[CH_3]^2 \]

\[ \frac{1}{[CH_3]} - \frac{1}{[CH_3]_0} = k_it \]

\[ \frac{1}{[CH_3]} = 1 \times 10^{-13} + (5 \times 10^{-11})(5 \times 10^{-4}) \]

\[ = 1.25 \times 10^{-13} \]

\[ [CH_3] = 8.00 \times 10^{12} \]
\[ a_1 = a_0 + f(a_0) \delta t \]

\[ a_1 = a_0 + \left[ f(a_0) \delta t + f(a_1) \right] / 2 \]
4th order Runge-Kutta method

“Numerical Recipes: the Art of Scientific Computing”

Press, Flannery, Teukolsky, Vettering

\[ a_{n+1} = a_0 + \frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} + \text{terms}(\delta t)^5 \]
Using ODE45 in MATLAB to solve differential equations

Consider the simple unimolecular reaction

\[ A \rightarrow B \]

the rate equation is \( \frac{dA}{dt} = -kA \)

which can be integrated to give \( A = A_0 \exp(-kt) \). We can also use ODE45 to give a numerical solution. The MATLAB command

```matlab
>> help ODE45
```

gives us the following information:

**ODE45** Solve non-stiff differential equations, medium order method.

\[ [T,Y] = \text{ODE45}('F',\text{TSPAN},\text{Y0}) \]

with \( \text{TSPAN} = [\text{T0 TFINAL}] \) integrates the system of differential equations \( y' = F(t,y) \) from time \( \text{T0} \) to \( \text{TFINAL} \) with initial conditions \( \text{Y0} \). 'F' is a string containing the name of an ODE file. Function \( F(T,Y) \) must return a column vector. Each row in solution array \( Y \) corresponds to a time returned in column vector \( T \). To obtain solutions at specific times \( \text{T0}, \text{T1}, \ldots, \text{TFINAL} \) (all increasing or all decreasing), use \( \text{TSPAN} = [\text{T0 T1 \ldots TFINAL}] \).
In order to solve this equation, we need to write a MATLAB function file \( y' = F(t,y) \) that will calculate the derivatives \( y' \) as a function of time, \( t \), and concentrations, \( y \). For the simple first order equation we have considered, the derivative is independent of time and dependent only on the concentration: \( y' = -k y \). We thus write (and save) the following file which we will choose to call yexample.m:

```matlab
function yp = first(t,y);

%this file calculates the time derivatives of the concentrations
%using the rate constant k1
k1= 3e-2;
yp = -k1*y;
```

The function ODE45 will calculate a series of concentrations \([A]\) at various times using a variable step Runge-Kutta approximation. According to the help information, we need the function file yexample that we have just written, the time span \([T0 Tfinal]\) and the initial value, \([A0]\). Let us choose \(T0 = 0\), \(Tfinal = 100\), and \([A0] = 3\). Then the matlab call to find \([A]\) as a function of time is

\[
[T,A] = ODE45('yexample',[0 100],3);
\]
This call uses unequally spaced values of $T$, and we can write out in neat form values of $T$ and $A$ by defining a new variable, 

$B_2 = [T \ A]$ 

which gives the following values:

$$
B_2 = \\
0 \quad 3.0000 \\
1.6746 \quad 2.8530 \\
3.3492 \quad 2.7132 \\
5.0238 \quad 2.5803 \\
6.6984 \quad 2.4539 \\
9.1984 \quad 2.2765 \\
11.6984 \quad 2.1121 \\
14.1984 \quad 1.9594 \\
16.6984 \quad 1.8179 \\
19.1984 \quad 1.6865 \\
21.6984 \quad 1.5646 \\
24.1984 \quad 1.4516 \\
26.6984 \quad 1.3467 \\
29.1984 \quad 1.2494 \\
31.6984 \quad 1.1591 \\
34.1984 \quad 1.0754 \\
36.6984 \quad 0.9977 \\
39.1984 \quad 0.9256
$$
Example plot showing numerical solution