Chapter 4 Summary–
Connection between rate equations and mechanisms.

Chapt 3 - measurement of rate laws

Chapt 4: How else can we get a rate law?

Technique:

- ♦ Find the mechanism of the reaction
  - Computationally
  - experimentally
- ♦ Use the quasi-steady state approximation to derive a rate equation

Generally more accurate - but we need a mechanism

Historically the idea that reactions follow mechanisms arose because of the observation that reaction rates did not correlate with stoichiometry

Table 2.5 Some of the rate equations which were discovered before 1886.

Reaction	Rate equation
$4PH_3 \Rightarrow P_4+6H_2$ **(2.T.1)**	$r_{PH_3}=-k_3[PH_3]$ **(2.T.2)**
$2AsH_3 \Rightarrow As_2+3H_2$ **(2.T.3)**	$r_{AsH_3}=-k_4[AsH_3]$ **(2.T.4)**
$2PH_3+4O_2 \Rightarrow P_2O_5+3H_2O$ **(2.T.5)**	$r_{PH_3}=-k_5[PH_3][O_2]^{1/2}$ **(2.T.6)**
$C_{12}H_{22}O_{11}+H_2O \overset{H+}{\Rightarrow} C_6H_{12}O_6+C_5H_9O_5CH_2OH$ **(2.T.7)**	$r_S=-k_6\,[\text{sucrose}][H^+]$ **(2.T.8)**

$$CH_3COOR + H_2O \overset{H+}{\Rightarrow} CH_3COOH + ROH$$ **(2.T.9)**

$$r_{Ac} = +k_7[CH_3COOR][H^+]$$ **(2.T.10)**

$$CH_3COOH+ROH \overset{H+}{\Rightarrow} CH_3COOR+H_2O$$

(2 .T.11)

$$r_{Ac}=-k_8[CH_3COOH][ROH][H^+]$$

(2.T.12)

$$ClCH_2COOH + H_2O \Rightarrow HOCH_2COOH + HCl$$

(2.T.13)

$$r_{C_2H_3ClO_2}=-k_9[C_2H_3ClO_2]$$

(2.T.14)

where $r_{PH_3}, r_{AH_3}, r_S, r_{Ac}, r_{C_2H_3ClO_2}$, and $r_{Fe^{3+}}$ are the rates of formation of phosphine, arsine, sucrose, acetic acid, chloroacetic acid, and Fe^{3+} respectively; $[PH_3]$, $[AsH_3]$, $[O_2]$, [sucrose], $[H^+]$, $[CH_3COOR]$, $[CH_3COOH]$, [ROH], $[Sn^{2+}]$, $[ClO_3^-]$, and $[C_2H_3ClO_2]$ are the concentrations of phosphine, arsine, oxygen, sucrose, hydrogen ion, acetate, acetic acid, alcohol, Sn^{2+}, ClO_3^-, and chloroacetic acid respectively; and k_3, k_4, k_5,

k_6, k_7, k_8, k_9, k_{10} and k_{11} are constants.

Van't hoff and Sabatier did considerable work to understand how it was possible for a reaction stoichiometry to be different than the kinetics;

Answer:

All reactions actually occur by a series of chemical transformations called Elementary reactions

Elementary reaction - a reaction which goes from reactants to products without going through any stable intermediates

Mechanism -The sequence of elementary steps which occur when the reactants come together to form products

$$\mathrm{CH_3CH_2HC = CH_2 + H^+} \rightarrow \left[\mathrm{CH_3CH_2HC'}\overset{\mathrm{H}}{-}\text{`}\mathrm{CH_2}\right]^+ \qquad \text{(a)}$$

$$\left[\mathrm{CH_3CH_2HC'}\overset{\mathrm{H}}{-}\text{`}\mathrm{CH_2}\right]^+ \rightarrow \mathrm{CH_3HC = CHCH_3 + H^+} \qquad \text{(b)}$$

$$\left[\mathrm{CH_3CH_2HC'}\overset{\mathrm{H}}{-}\text{`}\mathrm{CH_2}\right]^+ \rightarrow \mathrm{CH_3CH_2HC = CH_2 + H^+} \qquad \text{(c)}$$

$$\left[\mathrm{CH_3CH_2HC'}\overset{\mathrm{H}}{-}\text{`}\mathrm{CH_2}\right]^+ \rightarrow \mathrm{H_2C = CHCH_2CH_3 + H^+} \qquad \text{(d)}$$

(4.13)

Other key terms:

- Reactive intermediate
- Molecularity
- Unimolecular
- Bimolecular
- Termolecular
- Overall reaction
- Stoichiometric reaction

All elementary reactions have at least two reactants and two products

$$\mathrm{H + HBr \rightarrow H_2 + Br}$$
(4.11)

$$\mathrm{X + H_2 \rightarrow 2H + X}$$
(4.12)

Kinetics of elementary reactions

$$\mathrm{A + B \rightarrow P + Q}$$
(4.19)

$$r_2 = k_2[A][B]$$
(4.20)

$$r_A = -k_2[A][B]$$
(4.21)

$$2A \overset{4}{\rightarrow} P + Q$$
(4.22)

$$r_4 = k_4[A]^2$$
(4.23)

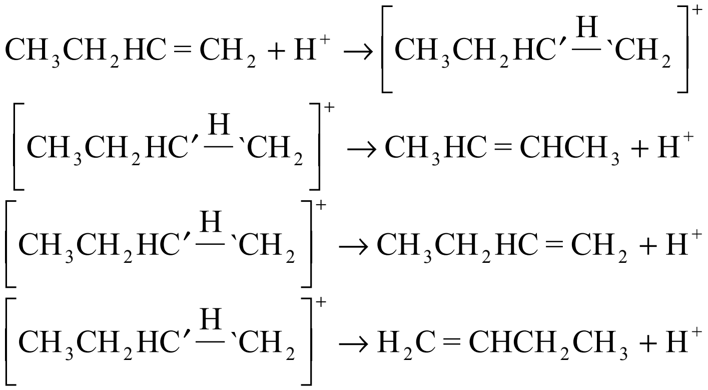
$$r_A = -2k_4[A]$$
(4.24)

The factor of -2 is very important!!

$$\boxed{r_A = \sum_{i=1}^{5} r_i \beta_{A,i}}$$
(4.25)

memorize this equation

Next: rates of overall reactions in terms of elementary rates;



$$\mathrm{CH_3CH_2HC=CH_2 + H^+ \rightarrow \left[CH_3CH_2HC'\overset{H}{—}`CH_2\right]^+} \qquad \text{(a)}$$

$$\mathrm{\left[CH_3CH_2HC'\overset{H}{—}`CH_2\right]^+ \rightarrow CH_3HC=CHCH_3 + H^+} \qquad \text{(b)}$$

$$\mathrm{\left[CH_3CH_2HC'\overset{H}{—}`CH_2\right]^+ \rightarrow CH_3CH_2HC=CH_2 + H^+} \qquad \text{(c)}$$

$$\mathrm{\left[CH_3CH_2HC'\overset{H}{—}`CH_2\right]^+ \rightarrow H_2C=CHCH_2CH_3 + H^+} \qquad \text{(d)}$$

(4.13)

$$\mathrm{A + H^+ \rightleftharpoons \underset{2}{\overset{1}{I}} \overset{3}{\rightarrow} P + H^+}$$

(4.44)

Differential equation for each species

$$\boxed{r_A = \sum_{i=1}^{5} r_i \beta_{A,i}}$$

(4.25)

$$\frac{d[\ I\ ]}{dt} = r_1 - r_2 - r_3$$

(4.45)

$$\frac{d[A]}{dt} = r_2 - r_1$$

(4.46)

Next substitute rate laws

$$A + H^+ \underset{2}{\overset{1}{\rightleftharpoons}} I \xrightarrow{3} P + H^+$$

(4.44)

where k_1 is the rate constant for reaction 1; [A] is the concentration of A; and, $[H^+]$ is the concentration of protons. Similarly, r_2 and r_3 are given by:

$$r_2 = k_2[I]$$
(4.48)

$$r_3 = k_3[I]$$
(4.49)

Substituting equations (4.47) and (4.48) into equation (4.46) yields:

$$\frac{d[A]}{dt} = k_2[\,I\,] - k_1[A][H^+]$$

$$(4.50)$$

Similarly, substituting equations (4.47), (4.48) and (4.49) into equation (4.45) yields:

$$\frac{d[\,I\,]}{dt} = k_1[A][H^+] - (k_2 + k_3)[\,I\,]$$

$$(4.51)$$

Equations (4.50) and (4.51) are the fundamental differential equations for the behavior of the system. They are the key results in this section.

Integration of the rate equation

Next we want to integrate the equations to calculate the overall rate of reaction. There are three approaches

- Analytical integration of the differential equations
- Numerical integration of the differential equations
- Approximate integration of the rate equation

Lets start with the analytical solution:

$$\frac{d[A]}{dt} = k_2[\,I\,] - k_1[A][H^+] \qquad (4.50)$$

$$\frac{d[\,I\,]}{dt} = k_1[A][H^+] - (k_2 + k_3)[\,I\,] \qquad (4.51)$$

Analytical solution

$$[A] = [A]^0 \left\{ \frac{(k_4 - k_6)\exp(-k_5 t) - (k_5 - k_6)\exp(-k_4 t)}{(k_4 - k_5)} \right\}$$

(4.53)

$$[I] = [A]^0 \left\{ \frac{(k_4 - k_6)(k_6 - k_5)}{k_2 (k_4 - k_5)} \right\} \{\exp(-k_5 t) - \exp(-k_4 t)\}$$

(4.54)

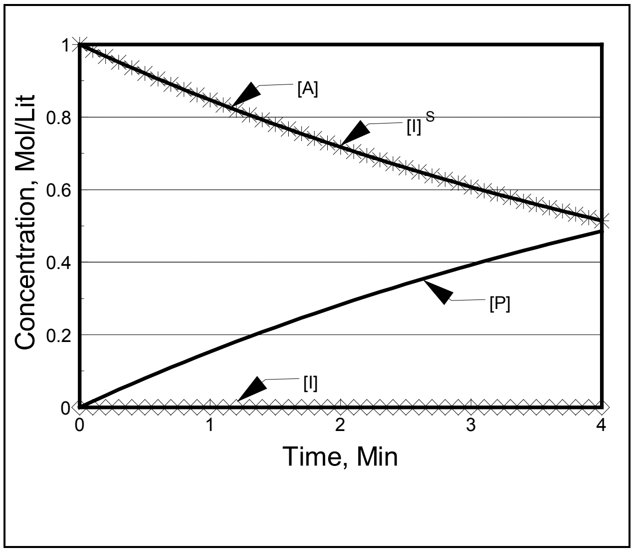


Figure 4.1 [A], [I] and [P] as a function of time calculated from equations (4.53), (4.54), and (4.55) with $k_1[H^+]= 0.2/\text{min}$, $k_2=5.7 \times 10^6/\text{min}$ and $k_3=3.8 \times 10^7/\text{min}$.

Approximate solution of rate equation (quasi steady state approximation). Need to solve the differential equation

$$\frac{d[\,I\,]}{dt} = k_1[A][H^+] - (k_2 + k_3)[\,I\,] \qquad (4.51)$$

Consider the size of the various terms in the equation (from analytical solution)

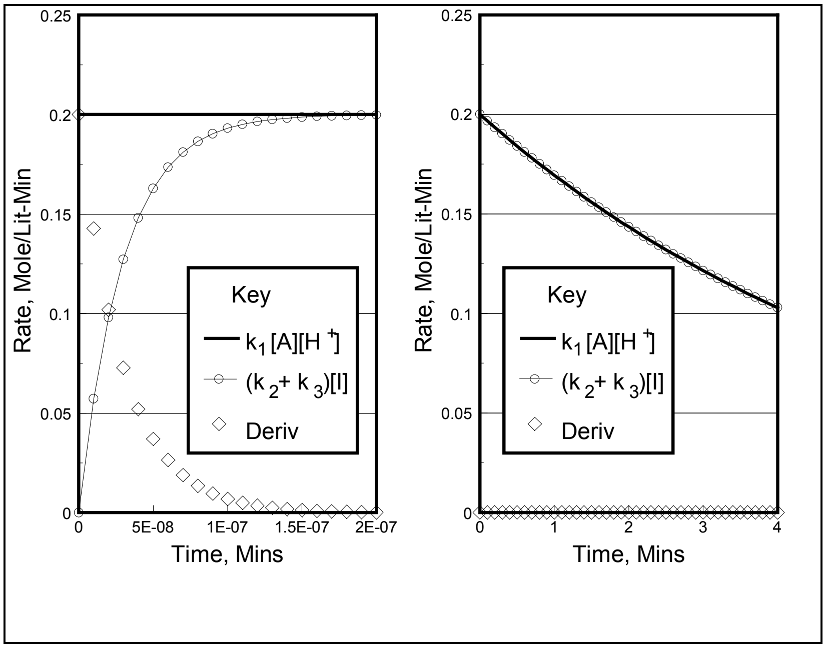


Figure 4.3 The size of various terms in equation (4.51).

Derivative much smaller than other terms in the equation

Quasi-steady state approximation. Assume the derivative is zero.

$$0 = k_1[A][H^+] - (k_2 + k_3)[I]$$

Therefore:

$$[\,I\,]^X = [A]\left(\frac{k_1[H^+]}{k_2 + k_3}\right)$$

(4.60)

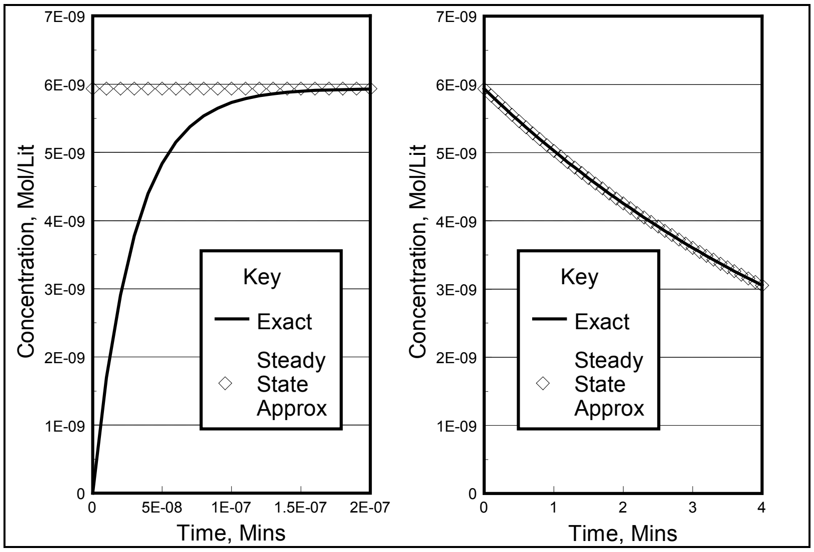


Figure 4.2 A comparison of [I] calculated from equation (4.54) and $[I]^X$ computed from equation (4.60).

The pseudo-steady state approximation

According to the pseudo steady state approximation, one can compute accurate values of the concentrations of all of the intermediates in a reaction by assuming that the net rate of formation of the intermediates is negligible (i.e., the derivatives with respect to time of the concentrations of all intermediates are negligible compared to other terms in the equation.)

$$A \xrightarrow{1} I \xrightarrow{2} P$$

(4.64)

$$O = r_I = k_1[A] - k_2[I]$$

(4.65)

Therefore

$$[\,I\,] = \frac{k_1}{k_2}[A]$$

(4.66)

We can extend this procedure to any reaction. The general steps are:

1)Set up the differential equation for the species of interest in terms of rate of all of the elementary reactions using equation (4.25) to keep track of the coefficients.
2)Substitute the expression for the rate of each of the elementary reactions using equations from section 4.3.
3)Set the derivatives of the intermediate concentrations to zero.
4)Eliminate terms in the expression in (1) which contain the concentrations of unstable intermediates other than the species of interest.
(Usually done by adding equations together)
5)Solve the reactant expression for the concentration of the species of interest.

Next: Numerical solution at rate equation

Consider $A + H^{+} \underset{2}{\overset{1}{\leftrightharpoons}} I \xrightarrow{3} P$

The differential equations are

$$\frac{d[A]}{dt} = -k_6[A] + k_2[I] \tag{4.B.1}$$

$$\frac{d[I]}{dt} = +k_6[A] - (k_2 + k_3)[I] \tag{4.B.2}$$

$$\frac{d[P]}{dt} = k_3[I] \tag{4.B.3}$$

with $k_6 = k_1[H]$

4.B.1 Numerical Methods

Let’s define two new vectors $\vec{C}$ and $\vec{R}$ by:

C(1) = [A], C(2) = [I], C(3) = [P]

$$R(1) = \frac{dC(1)}{dt}$$

$$R(2) = \frac{dC(2)}{dt} \qquad \textbf{(4.B.}$$

$$R(3) = \frac{dC(3)}{dt}$$

Physically, $\vec{C}$ is a vector containing the concentrations of all of the species while $\vec{R}$ is a vector containing all of the rates of reaction. For our example

$$\begin{aligned} R(1) &= -k_6[A] + k_2[\,I\,] \\ R(2) &= +k_6[A]-(k_2 + k_3)[\,I\,] \qquad \textbf{(4.B.5)} \\ R(3) &= k_3[\,I\,] \end{aligned}$$

Equations 4.B.1, 4.B.2, and 4.B.3 become:

$$\frac{d\vec{C}}{dt} = \vec{R}(\vec{C}, t) \qquad \textbf{(4.B.6)}$$

Numerical methods start by looking at some small time increment Δt and approximating $d\vec{C}/dt$ by $\Delta\vec{C}/\Delta t$. According to the mean value theorem:

$$\frac{\Delta\vec{C}}{\Delta t} = \vec{R}(\zeta, \xi) \qquad \textbf{(4.B.7)}$$

where $\vec{R}(\zeta, \xi)$ is an average value of $\vec{R}$ time between t and $t + \Delta t$.

Rearranging equation 4.B.6 yields:

$$\vec{C}(t+\Delta t)=\vec{C}(t)+\Delta t\vec{R}(\zeta,\xi) \qquad \textbf{(4.B.8)}$$

where $\vec{C}(t)$ is the value of the concentrations at time = t, $\vec{C}(t+\Delta t)$ is the value at t + Δt.

Eulers method

$$\vec{C}(t+\Delta t)=\vec{C}(t)+\Delta t\,\vec{R}(\vec{C}(t),t) \qquad \textbf{(4.B.9)}$$

Where $\vec{R}(\vec{C}(t),t)$ is the value of $\vec{R}$ calculated at a concentration equal to the concentration at time t.

Equation 4.B.9 says that if you know the concentration of any time t, and the rate equation you can calculate the concentration at some time t + Δt, by plugging into equation 4.B.9

In practice, you use equation 4.B.9 iteratively.

Consider t = 0, 1, 2, 3…

t = 0 Know $C_A(0)$ calculate $C_A(1)$
t = 1 Know $C_A(1)$ calculate $C_A(2)$
t = 2 Know $C_A(2)$ can calculate $C_A(3)$

Can calculate C_A at all times

Example 4.B.A

Consider solving the differential equation:

$$\frac{dC_A}{dt} = (-k_1)C_A = r_A \qquad \textbf{(4.B.10)}$$

with an initial concentration of 1 mole/liter, and k_1 = -2/sec.

Solution

In equation 4.B.10:

$$\vec{R} = r_A(C_A(t)) \tag{4.B.11}$$

Combining equations 4.B.9 and 4.B.11 yields:

$$\begin{aligned} C_A(t+\Delta t) &= C_A(t) + \Delta t\, r_A(C_A(t)) \\ &= C(t) - k_1(\Delta t)C(t) \end{aligned} \tag{4.B.12}$$

Equation 4.B.12 gives us a way to solve for $C_A(t+\Delta t)$ given $C_A(t)$.

Next, we will use a spreadsheet to solve this problem. Table 4.B.1 shows my spreadsheet. I set up the spreadsheet so column T is time, column CA is the concentration of A and

column DA is $\frac{dC_A}{dt}$. I named cell CA1 dt, and CA2 k_1. I then hid all of the rest of the columns so the spreadsheet was easy to see.

Table 4.B.1 The formulas used to integrate equation 4.B.10

	T	CA	DA
01	dt=	0.1	
02	k_1=	2	
03	0	1	=-k_1*CA3
04	=T3+dt	=CA3+dt*DA3	=-k_1*CA4
05	=T4+dt	=CA4+dt*DA4	=-k_1*CA5
06	=T5+dt	=CA5+dt*DA5	=-k_1*CA6
07	=T6+dt	=CA6+dt*DA6	=-k_1*CA7
08	=T7+dt	=CA7+dt*DA7	=-k_1*CA8
09	=T8+dt	=CA8+dt*DA8	=-k_1*CA9
10	=T9+dt	=CA9+dt*DA9	=-k_1*CA10
11	=T10+dt	=CA10+dt*DA10	=-k_1*CA11
12	=T11+dt	=CA11+dt*DA11	=-k_1*CA12
13	=T12+dt	=CA12+dt*DA12	=-k_1*CA13
14	=T13+dt	=CA13+dt*DA13	=-k_1*CA14
15	=T14+dt	=CA14+dt*DA14	=-k_1*CA15
16	=T15+dt	=CA15+dt*DA15	=-k_1*CA16
17	=T16+dt	=CA16+dt*DA16	=-k_1*CA17
18	=T17+dt	=CA17+dt*DA17	=-k_1*CA18

Table 4.B.2 The numerical values in the spreadsheet in 4.B.1

	T	CA	DA	
01	dt=	0.1		Exact concentration
02	k_1=	2		
03	0	1	-2	1
04	0.1	0.8	-1.6	0.818731
05	0.2	0.64	-1.28	0.67032
06	0.3	0.512	-1.024	0.548812
07	0.4	0.4096	-0.8192	0.449329
08	0.5	0.32768	-0.65536	0.367879
09	0.6	0.262144	-0.52429	0.301194
10	0.7	0.209715	-0.41943	0.246597
11	0.8	0.167772	-0.33554	0.201897
12	0.9	0.134218	-0.26844	0.165299
13	1	0.107374	-0.21475	0.135335
14	1.1	0.085899	-0.1718	0.110803
15	1.2	0.068719	-0.13744	0.090718
16	1.3	0.054976	-0.10995	0.074274
17	1.4	0.04398	-0.08796	0.06081
18	1.5	0.035184	-0.07037	0.049787

Notice that Euler’s method gives a fair approximation to the concentration, but the results are by no means exact.

The reason Euler's method has failed is that it assumes that the rate is constant over the entire time increment. For example during the first time increment, the concentration of A drops from 1.0, to 0.8. The rate of reaction changes from -2.0 to -1.6. However, Euler's method ignores the change in rate. Instead it assumes that the rate stays at -2.0 for the entire time increment. This leads to errors.

4.B.3 Implicit Methods

$$\vec{C}_A(t+\Delta t) = \vec{C}_A(t) + \Delta t\left(\vec{R}_A(t) + \vec{R}_A(t+\Delta t)\right)/2$$

(4.B.17)

Equation 4.B.17 replaces the exact value of the rate, with an average of the initial and final values of the rate so it gives much more accurate values than Euler's method.

Table 4.B.3 The formulas used to integrate equation 4.B.10 according to equation (4.B.17)

	T	CA	DA
01	dt=	0.1	
02	k_1=	2	
03	0	1	=-k_1*CA3
04	=T3+dt	=CA3+dt*(DA3+DA4)/2	=-k_1*CA4
05	=T4+dt	=CA4+dt*(DA4+DA5)/2	=-k_1*CA5
06	=T5+dt	=CA5+dt*(DA5+DA6)/2	=-k_1*CA6
07	=T6+dt	=CA6+dt*(DA6+DA7)/2	=-k_1*CA7
08	=T7+dt	=CA7+dt*(DA7+DA8)/2	=-k_1*CA8
09	=T8+dt	=CA8+dt*(DA8+DA9)/2	=-k_1*CA9
10	=T9+dt	=CA9+dt*(DA9+DA10)/2	=-k_1*CA10
11	=T10+dt	=CA10+dt*(DA10+DA11)/2	=-k_1*CA11
12	=T11+dt	=CA11+dt*(DA11+DA12)/2	=-k_1*CA12
13	=T12+dt	=CA12+dt*(DA12+DA13)/2	=-k_1*CA13
14	=T13+dt	=CA13+dt*(DA13+DA14)/2	=-k_1*CA14
15	=T14+dt	=CA14+dt*(DA14+DA15)/2	=-k_1*CA15
16	=T15+dt	=CA15+dt*(DA15+DA16)/2	=-k_1*CA16
17	=T16+dt	=CA16+dt*(DA16+DA17)/2	=-k_1*CA17
18	=T17+dt	=CA17+dt*(DA17+DA18)/2	=-k_1*CA18

Table 4.B.4 The numerical values in the spreadsheet in Table 4.B.3. I also added column for the exact concentration

	T	CA	DA	Exact concentration
01	dt=	0.1		
02	k_1=	2		
03	0	1	-2	1
04	0.1	0.818182	-1.63636	0.818731
05	0.2	0.669421	-1.33884	0.67032
06	0.3	0.547708	-1.09542	0.548812
07	0.4	0.448125	-0.89625	0.449329
08	0.5	0.366648	-0.7333	0.367879
09	0.6	0.299985	-0.59997	0.301194
10	0.7	0.245442	-0.49088	0.246597
11	0.8	0.200816	-0.40163	0.201897
12	0.9	0.164304	-0.32861	0.165299
13	1	0.134431	-0.26886	0.135335
14	1.1	0.109989	-0.21998	0.110803
15	1.2	0.089991	-0.17998	0.090718
16	1.3	0.073629	-0.14726	0.074274
17	1.4	0.060242	-0.12048	0.06081
18	1.5	0.049289	-0.09858	0.049787

4.B.5 Other Methods

Table 4.B.7 Some of the common numerical methods used to solve differential equations

Method	Formula	Speed	Accuracy	Useful for stiff equations
Explicit Methods				
Eulers	$\vec{C}(t+\Delta t)=\vec{C}(t)+\Delta t\vec{R}(t)$	Slow	Poor	No
Runge Kutta second order	$\vec{C}(t+\Delta t)=\vec{C}(t)+\Delta\vec{R}(t)$	Fair	Good	No
Runge Kutta Fourth Order	$\vec{C}(t+\Delta t)=\vec{C}(t)+\frac{\Delta t}{6}(\vec{R}_1+2\vec{R}_2+2\vec{R}_3+\vec{R}_4)$ $\vec{R}_1=\vec{R}(\vec{C}(t),\ t)\vec{C}_1=C(t)+\frac{\Delta t}{2}\vec{R}_1$ $\vec{R}_2=\vec{R}\left(\vec{C}_1(t)+\frac{\Delta t}{2}\right),\quad \vec{C}_2=\vec{C}(t)+\frac{\Delta t}{2}\vec{R}_2$ $\vec{R}_3=\vec{R}\left(\vec{C}_2,t+\frac{\Delta t}{2}\right),\quad \vec{C}_3=\vec{C}(t)+\vec{R}_3\Delta t$ $\vec{R}_4=\vec{R}\left(\vec{C}_3,t+\frac{\Delta t}{2}\right)$	Excellent	Good	No
Runge-Kutta Gill	$\vec{C}(t+\Delta t)=\vec{C}(t)+\frac{\Delta t}{\vec{C}}(\vec{R}_1+0.586\vec{R}_2+3.414\vec{R}_3+\vec{R}_4)$ $\vec{R}_1=\vec{R}(\vec{C}(t),\ t),\vec{C}_1=\vec{C}(t)+\frac{\Delta t}{2}\vec{R}_2$ $\vec{R}_2=\vec{R}\left(\vec{C}_1,t+\frac{\Delta t}{2}\right)\vec{C}_2=\vec{C}(t)+\left(0.207\vec{R}_1+0.293\vec{R}_2\right)\Delta t$ $\vec{R}_3=\vec{R}\left(\vec{C}_2(t)+\frac{\Delta t}{2}\right)\vec{C}_3=C(t)+\Delta t\left(1.707\vec{R}_3-.707\vec{R}_2\right)$ $\vec{R}_4=\vec{R}\left(\vec{C}_3,t+\frac{\Delta t}{2}\right)$	Outstanding	Excellent	No

Bulirsch-Stoer	Extrapolate 2nd order Runge Kutta to 0 Step size	Good	Outstanding	Maybe
Adam's-Milne predictor correcter	Iteratively solve equation 4.B.10	Good	Fair	No
Implicit Methods				
Gear	Iterative solution of: $C(t+\Delta t) = C(t) + \Delta t \eta \vec{R}\big(C(t+\Delta t), t+\Delta t\big)$	Slow	Fair	Yes
Rosenbrock	$\vec{C}(t+\Delta t) = \vec{C}(t) + \frac{\Delta t}{4}\left(\frac{19}{9}\vec{R}_1 + \frac{1}{2}\vec{R}_2 + \frac{25}{108}\vec{R}_3 + \frac{125}{108}\vec{R}_4\right)$ $\vec{R}_1 = \vec{R}\big(C(t)t\big) + \vec{R}\left(C(t) + \vec{R}_1 C\left(t + \frac{\Delta t}{2}\right), t + \Delta t\right)$etc	Fair	Excellent	Yes

4.B.6 Stiff Equations

In kinetics the equations are hard to solve numerically.

$$\frac{d[I]}{dt} = +k_6[A] - (k_2 + k_3)[I] \qquad \textbf{(4.B.2)}$$

Recall that equation (4.B.2) computes d[I]/dt as a difference between two big numbers. If you make an error in the calculations, that error is amplified. This makes the calculations difficult.

Implicit methods work much better.

Summary: Chapter 4 discusses

Can derive rate equations from a mechanism by

- Write down the differential equations in terms of the rates and then substitute in the rate equations.
- Keep track of what terms you want to eliminate and eliminate them.
- Adding equations together helps.