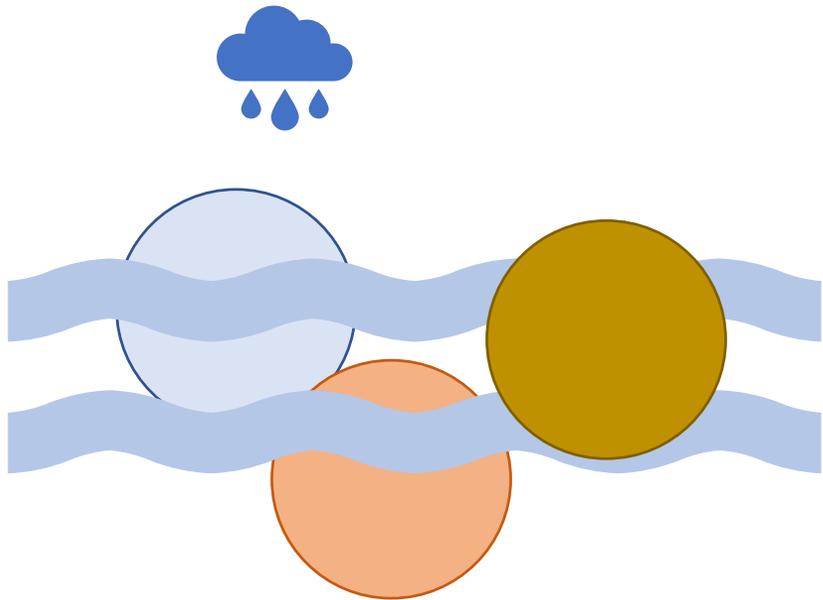


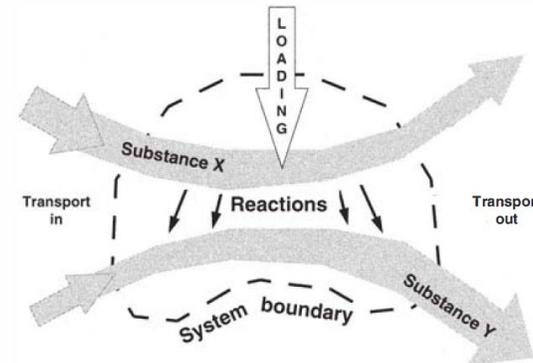
# Reaction Kinetics



# REACTION FUNDAMENTALS

Once a pollutant enters a water body many things can happen to it (some relate to transport). E.g. it can be translated and dispersed by currents within the system, it can exit the system by volatilization, by sedimentation, or by transport along with outflowing water.

The pollutant may also be transformed into other compounds via chemical and biochemical reactions.



# Reaction Fundamentals

Reaction Types

Reaction Kinetics

Zero-, First-, Second-Order Reactions

## Analysis of Rate Data

Integral Method

Differential Method

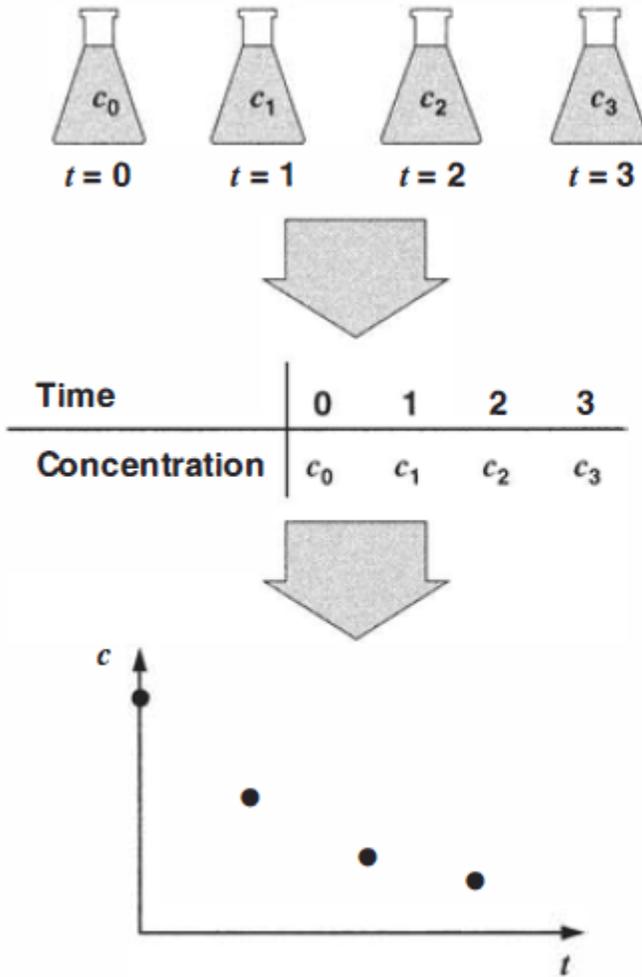
Method of Initial Rates

Method of Half-Lives

Method of Excess

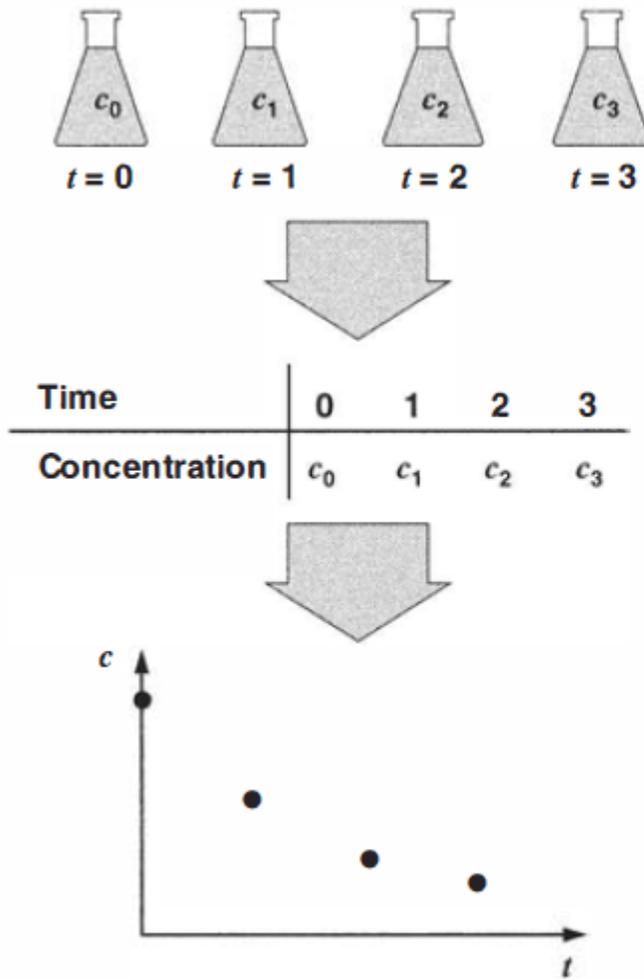
## Stoichiometry

## Temperature Effects



**FIGURE 2.1**

A simple experiment to collect rate data for a pollutant in a natural water.



Suppose you want to perform an experiment to determine how a pollutant reacts after it enters a natural water. One approach is to introduce some of the pollutant into a series of well-mixed bottles, measured over-time under well-mixed conditions (i.e. **batch reactors**).

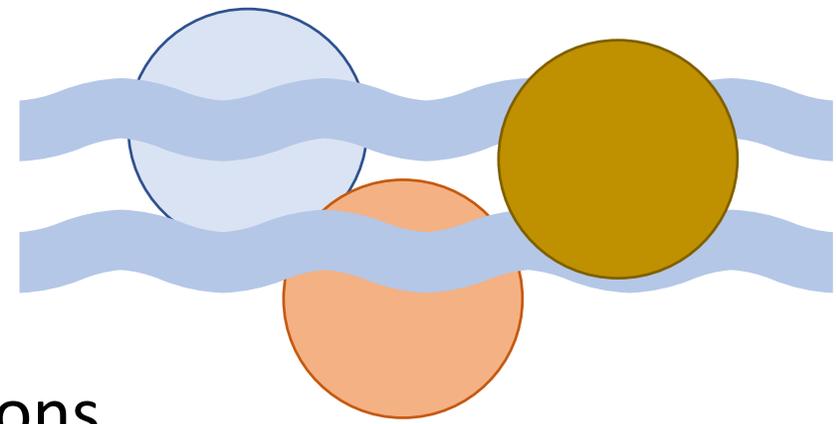
Here we explore this data to characterize the effect of the reactions on the pollutant.

**FIGURE 2.1**

A simple experiment to collect rate data for a pollutant in a natural water.

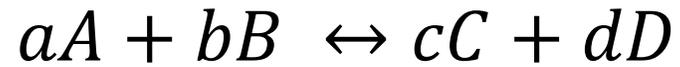


# Reaction types



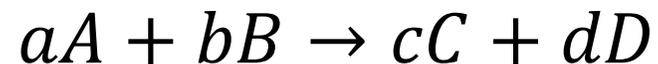
Heterogeneous reactions vs Homogeneous reactions

Reversible reaction



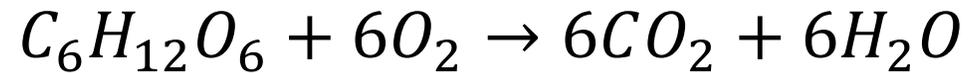
Equilibrium chemistry

Irreversible reactions



# Reaction types

A common example of an irreversible reaction is the decomposition of organic matter, represented by:



where  $C_6H_{12}O_6$  is glucose, taken to be representation of organic matter (i.e. when sewage is discharged into a receiving water). Organic matter in the sewage is oxidized by bacteria to form carbon dioxide and water.

Since it is slow, this is usually characterized as a one-way process though photosynthesis technically occurs in the reverse direction (also very slowly).



# Reaction Kinetics

Kinetics (or the rate of such reactions) can be expressed quantitatively by the law of mass action (i.e. rate law):

“ the rate is proportional to the concentration of the reactants”

$$\frac{dc_A}{dt} = -kf(c_A, c_B, \dots)$$

The functional relationship  $f(c_A, c_B, \dots)$  is almost always determined experimentally with the common general form:

$$\frac{dc_A}{dt} = -kc_A^\alpha c_B^\beta$$

# Reaction Kinetics

The powers to which the concentrations are raised (exponents) are referred to as the *reaction order*.  $\alpha$  order with respect to reactant A ( $c_A$ ),  $\beta$  order with respect to reactant B ( $c_B$ ). Overall order is:

$$n = \alpha + \beta$$

Here we focus on a single reactant and thus this simplifies to:

$$\frac{dc}{dt} = -kc^n$$

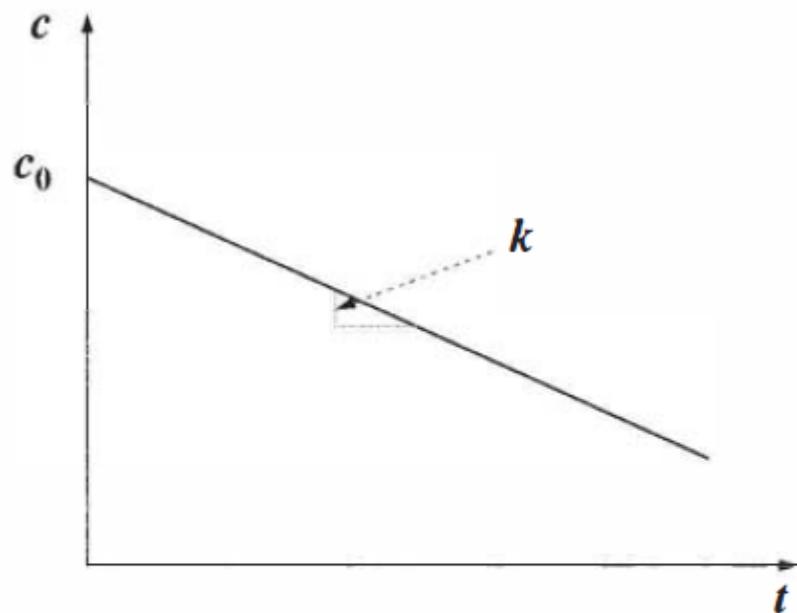
where  $c$  = the concentration of the single reactant and  $n$  = the order.

# Zero, First-, and Second-Order Reactions

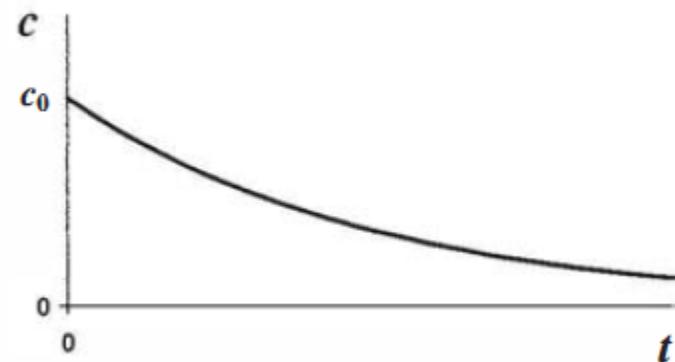
Though there are an infinite number of ways to characterize reactions, the simplified form of reactions :

$$\frac{dc}{dt} = -kc^n$$

with  $n = 0, 1, \text{ or } 2$  is the most commonly employed in natural waters.



**FIGURE 2.2**  
Plot of concentration versus time for a zero-order reaction.



**FIGURE 2.3**  
Plot of concentration versus time for a first-order reaction.

# The Integral Method

Integral method consists of guessing  $n$  and integrating simplified equation (2.7):

$$\frac{dc}{dt} = -kc^n$$

TABLE 2.1

Summary of the plotting strategy used for applying the integral method to irreversible, unimolecular reactions

Order	Rate units	Dependent (y)	Independent (x)	Intercept	Slope
Zero ( $n = 0$ )	$M(L^3 T)^{-1}$	$c$	$t$	$c_0$	$-k$
First ( $n = 1$ )	$T^{-1}$	$\ln c$	$t$	$\ln c_0$	$-k$
Second ( $n = 2$ )	$L^3(M T)^{-1}$	$1/c$	$t$	$1/c_0$	$k$
General ( $n \neq 1$ )	$(L^3 M^{-1})^{n-1}T^{-1}$	$c^{1-n}$	$t$	$c_0^{1-n}$	$(n - 1)k$

# The Integral Method

**EXAMPLE 2.1. INTEGRAL METHOD.** Employ the integral method to determine whether the following data is zero-, first-, or second-order:

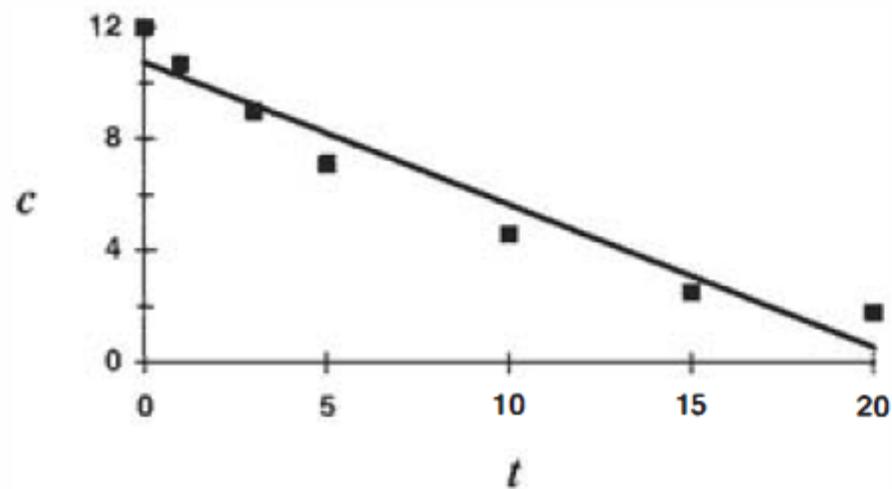
$t$ (d)	0	1	3	5	10	15	20
$c$ (mg L <sup>-1</sup> )	12	10.7	9	7.1	4.6	2.5	1.8

If any of these models seem to hold, evaluate  $k$  and  $c_0$ .

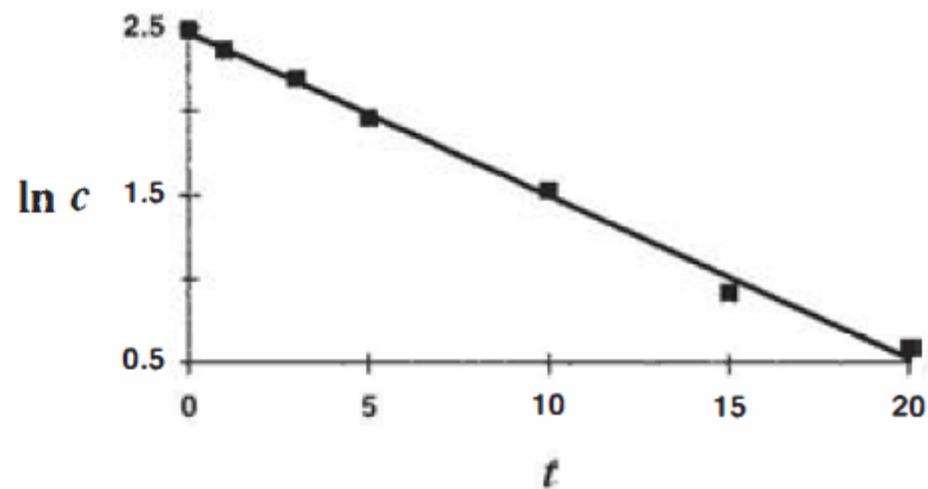
**TABLE 2.1**

Summary of the plotting strategy used for applying the integral method to irreversible, unimolecular reactions

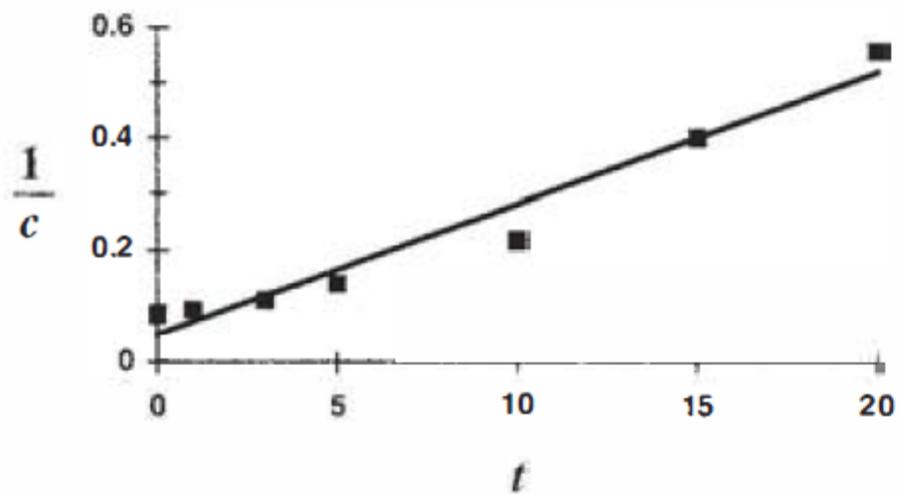
Order	Rate units	Dependent (y)	Independent (x)	Intercept	Slope
Zero ( $n = 0$ )	M(L <sup>3</sup> T) <sup>-1</sup>	$c$	$t$	$c_0$	$-k$
First ( $n = 1$ )	T <sup>-1</sup>	$\ln c$	$t$	$\ln c_0$	$-k$
Second ( $n = 2$ )	L <sup>3</sup> (M T) <sup>-1</sup>	$1/c$	$t$	$1/c_0$	$k$
General ( $n \neq 1$ )	(L <sup>3</sup> M <sup>-1</sup> ) <sup><math>n-1</math></sup> T <sup>-1</sup>	$c^{1-n}$	$t$	$c_0^{1-n}$	$(n - 1)k$



(a)



(b)



(c)

**FIGURE 2.4**

Plots to evaluate whether the reaction is (a) zero-order, (b) first-order, or (c) second-order.

# The Differential Method

The differential method applies a logarithmic transform of

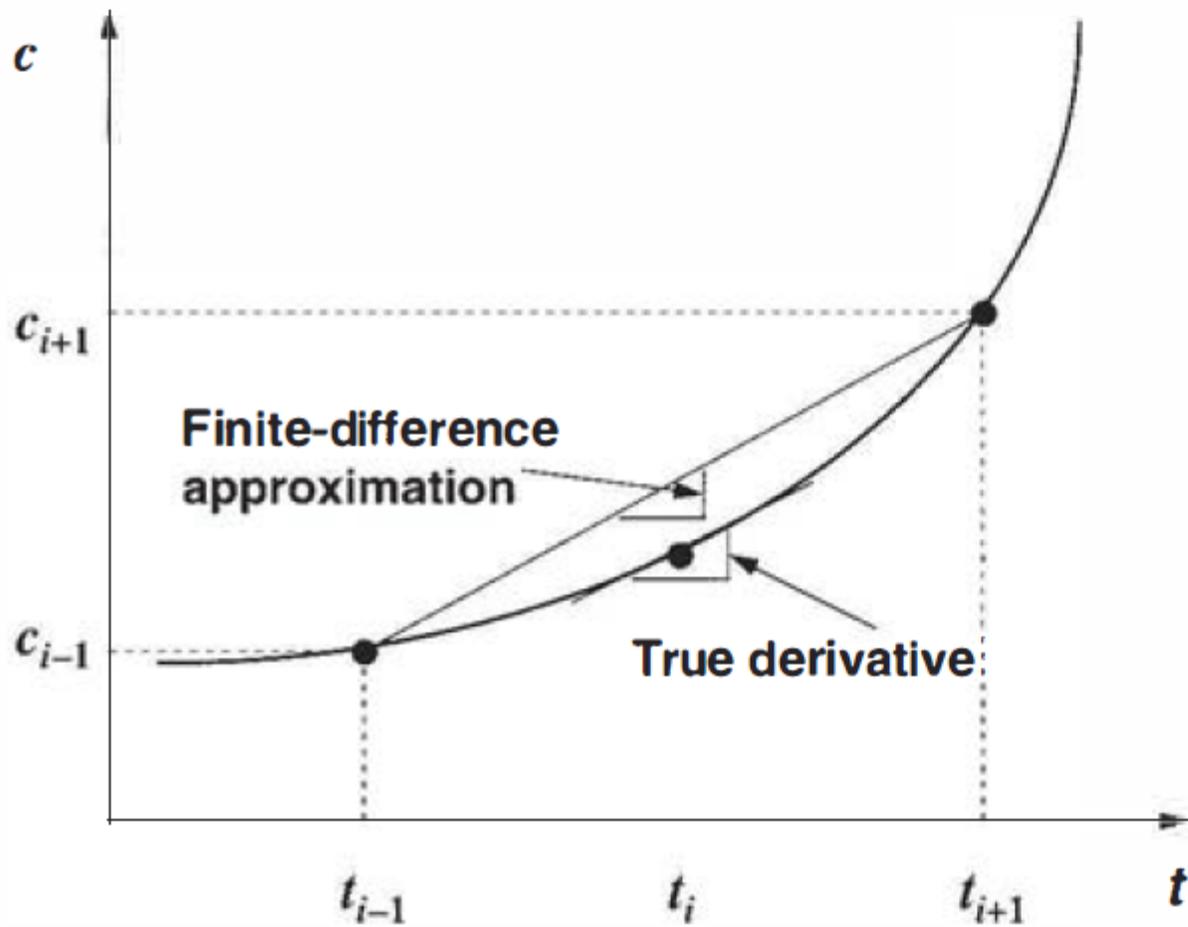
$$\frac{dc}{dt} = -kc^n$$

to give:

$$\log\left(\frac{dc}{dt}\right) = \log(k) + n\log(c)$$

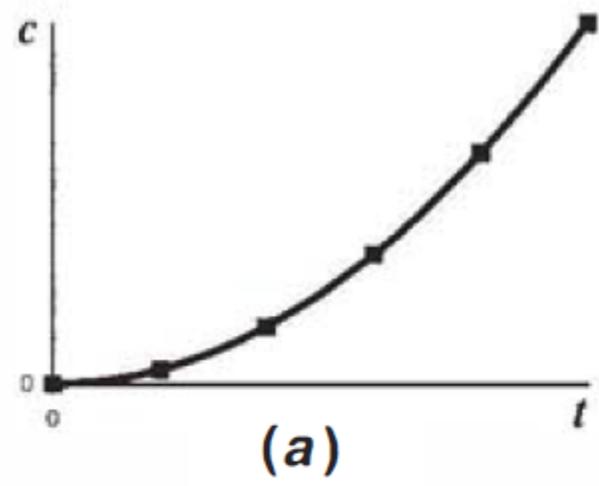
Advantage: automatically provides estimate of the order

Disadvantage: hinges on obtaining a numerical estimate of the derivative

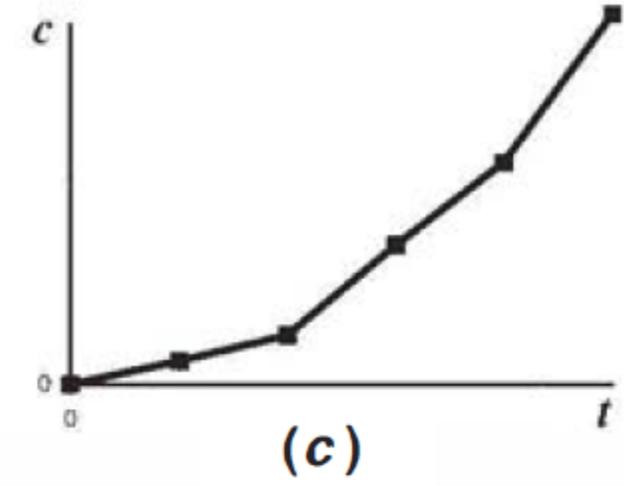
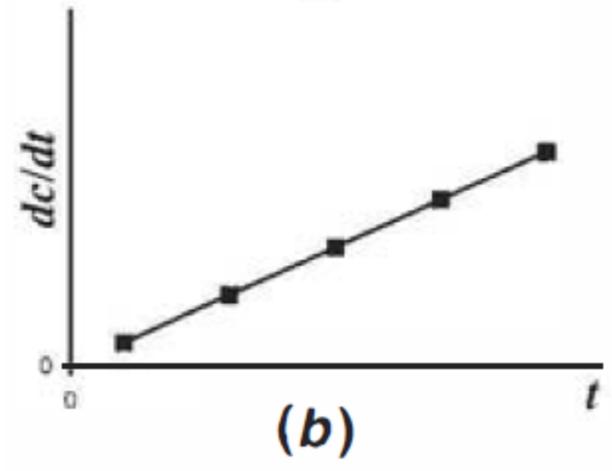


Numerical differentiation: uses finite difference approximations.

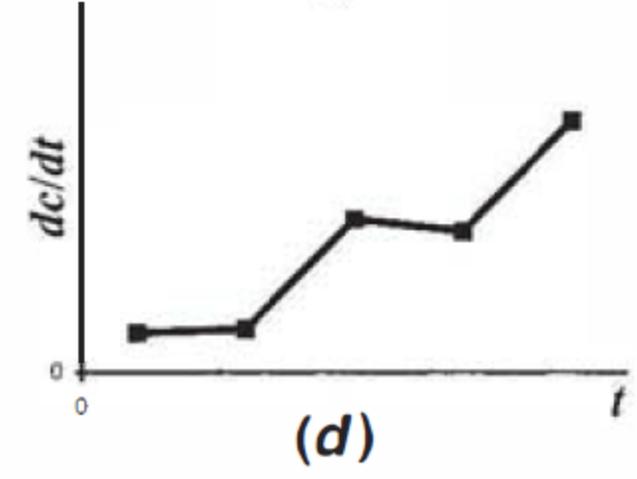
**FIGURE 2.5**  
Numerical differentiation.



Differentiate



Differentiate



**FIGURE 2.6**

Illustration of how even small data errors are amplified by numerical differentiation. (a) Data with no error; (b) the resulting numerical differentiation; (c) data modified slightly; (d) the resulting differentiation manifesting increased variability (reprinted from Chapra and Canale 1988).

# Initial Rates, Half-lives, Excess

Initial Rates

$$\log\left(\frac{dc_o}{dt}\right) = \log(k) + n\log(c_o)$$

Half-life

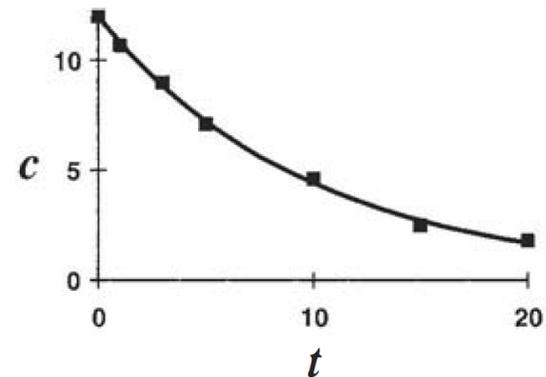
$$\log(t_{50}) = \log\left(\frac{c(t_{50})}{k(n-1)}\right) + (1-n)\log(c_0)$$

$c(t_{50}) = 0.5c_0$

Excess

$$\frac{dc_a}{dt} = -kc_a c_b$$
$$\frac{dc}{dt} = -(kc_{b0})c_a = -(k_{b2})c_a$$

	A	B	C	D	E	F	G	H
1	Fitting of reaction rate							
2	data with the integral/least-squares approach							
3	k	0.091528						
4	n	1.044425						
5	dt	t						
6	t	k1	k2	k3	k4	cp	cm	(cp-cm)^2
7	0	-1.22653	-1.16114	-1.16462	-1.10248	12	12	0
8	1	-1.10261	-1.04409	-1.04719	-0.99157	10.83658	10.7	0.018653
9	2	-0.99169	-0.93929	-0.94206	-0.89225	9.790448		
10	3	-0.89235	-0.84541	-0.84788	-0.80325	8.849344	9	0.022697
11	4	-0.80334	-0.76127	-0.76347	-0.72346	8.002317		
12	5	-0.72354	-0.68582	-0.68779	-0.65191	7.239604	7.1	0.019489
13	6	-0.65198	-0.61814	-0.61989	-0.5877	6.552494		
14	7	-0.58776	-0.55739	-0.55895	-0.53005	5.933207		
15	8	-0.53011	-0.50283	-0.50424	-0.47828	5.374791		
16	9	-0.47833	-0.45383	-0.45508	-0.43175	4.871037		
17	10	-0.4318	-0.40978	-0.4109	-0.38993	4.416389	4.6	0.033713
18	11	-0.38997	-0.37016	-0.37117	-0.35231	4.005877		
19	12	-0.35234	-0.33453	-0.33543	-0.31846	3.635053		
20	13	-0.31849	-0.30246	-0.30326	-0.28798	3.299934		
21	14	-0.28801	-0.27357	-0.2743	-0.26054	2.996949		
22	15	-0.26056	-0.24756	-0.24821	-0.23581	2.7229	2.5	0.049684
23	16	-0.23583	-0.22411	-0.22469	-0.21352	2.474917		
24	17	-0.21354	-0.20297	-0.20349	-0.19341	2.250426		
25	18	-0.19343	-0.18389	-0.18436	-0.17527	2.047117		
26	19	-0.17529	-0.16668	-0.16711	-0.1589	1.862914		
27	20	-0.15891	-0.15115	-0.15153	-0.14412	1.695953	1.8	0.010826
28								
29							SSR =	0.155062



**FIGURE 2.10**  
Plot of fit generated with the integral/least-squares approach.

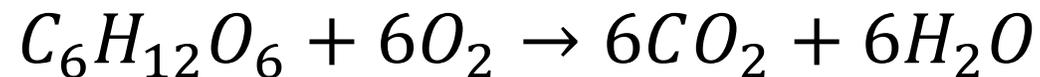
**FIGURE 2.9**  
The application of the integral least-squares method to determine the order and rate coefficient of reaction data. This application was performed with the Excel spreadsheet.

# STOICHIOMETRY

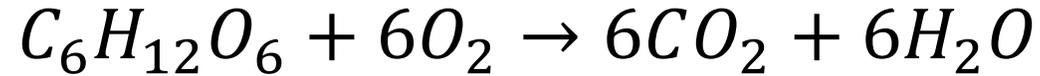
Several compounds may react to form other compounds.

Thus we may want to determine “how much” of a reactant or product is consumed or created as the reaction proceeds.

The answer resides in the *stoichiometry*, or the number of moles, taking part in the reaction.



# STOICHIOMETRY



How much of an individual element would be contained in the production or consumption within reaction? E.g. how much oxygen would be consumed if 40gC m<sup>-3</sup> of glucose reacted according to above?

$$r_{oc} = \frac{6 \text{ moles } O_2 \times 32 \text{ gO/mole } O_2}{6 \text{ moles } C \times 12 \text{ gC/mole } C} = 2.67 \text{ gO gC}^{-1}$$

$$2.67 \frac{\text{gO}}{\text{gC}} \left( 40 \frac{\text{gC}}{\text{m}^3} \right) = 106.67 \text{ gO m}^{-3}$$

# TEMPERATURE EFFECTS

The rates of most reactions in natural waters increase with temperature. A general rule of thumb is that the rate will roughly double for a temperature rise of 10° C.

The *Arrhenius equation* quantifies this temperature dependence more rigorously:

$$k(T_a) = Ae^{\frac{-E}{RT_a}}$$

where A = a preexponential or frequency factor

$E$  = activation energy (J mole<sup>-1</sup>)

$R$  = the gas constant (8.314 J mole<sup>-1</sup> K<sup>-1</sup>)

$T_a$  = absolute temperature (K)

# TEMPERATURE EFFECTS

The *Arrhenius equation* is often used to compare reaction rate constant at two different temperatures by expressing the ratio of the rates:

$$\frac{k(T_{a2})}{k(T_{a1})} = e^{\frac{-E(T_{a2}-T_{a1})}{RT_{a2}T_{a1}}}$$

which can then be simplified with the following being defined as a constant:

$$\theta \equiv e^{\frac{E}{RT_{a2}T_{a1}}}$$

And subsequently:

$$\frac{k(T_2)}{k(T_1)} = \theta^{T_2-T_1}$$

where temperature (T) is expressed in °C.

# TEMPERATURE EFFECTS

$$\theta \equiv e^{\frac{E}{RT_2 - T_1}}$$

$$\frac{k(T_2)}{k(T_1)} = \theta^{T_2 - T_1}$$

TABLE 2.3

Some typical values of  $\theta$  used in water-quality modeling

$\theta$	$Q_{10}$	Reaction
1.024	1.27	Oxygen reaeration
1.047	1.58	BOD decomposition
1.066	1.89	Phytoplankton growth
1.08	2.16	Sediment oxygen demand (SOD)

# TEMPERATURE EFFECTS

In water-quality modeling many reactions are reported at 20°C. Then this usually simplifies the equation further to:

$$k(T) = k(20)\theta^{T-20}$$

$$Q_{10} = \frac{k(20)}{k(10)}$$

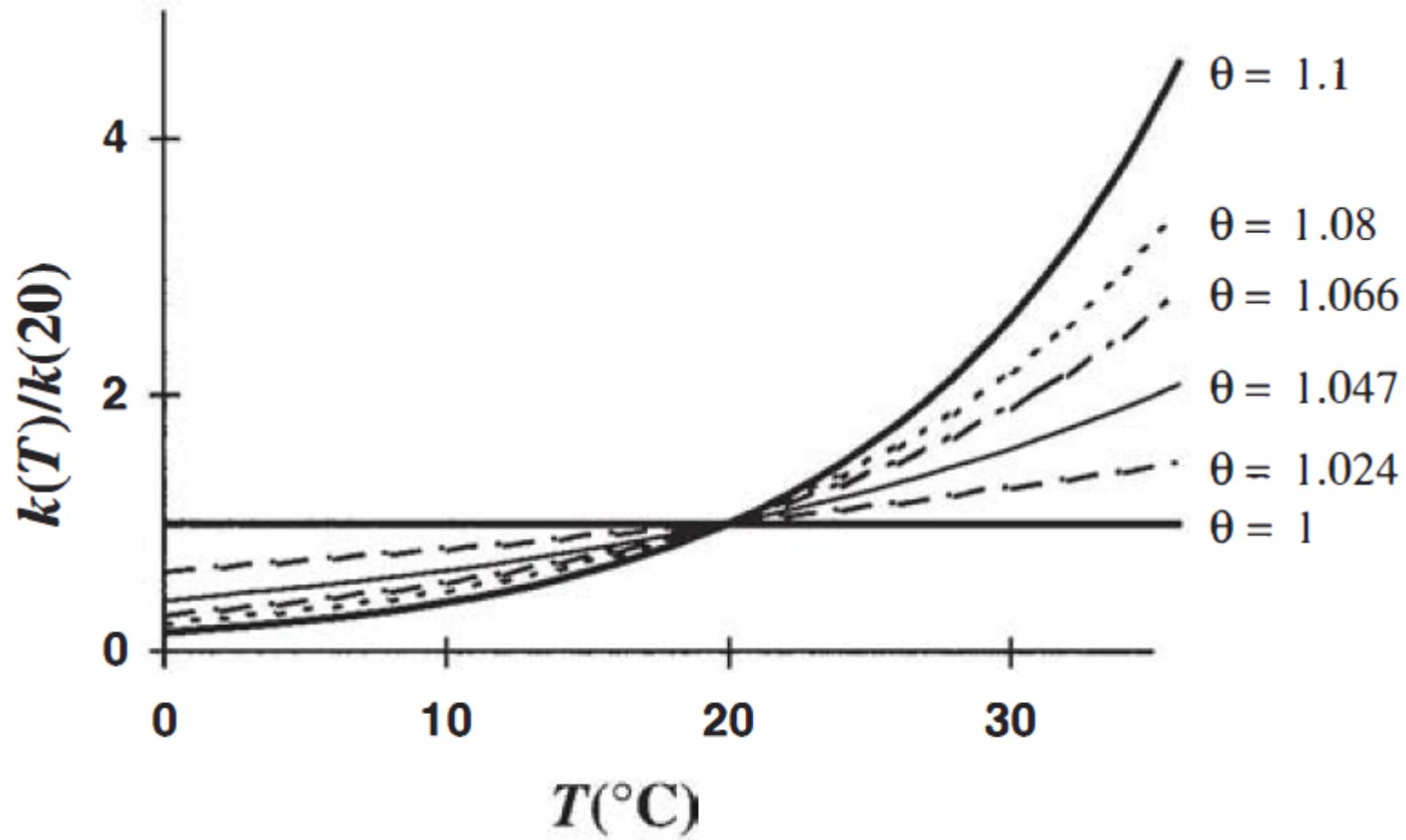
Substituting yields

$$Q_{10} = \theta^{10}$$

TABLE 2.3

Some typical values of  $\theta$  used in water-quality modeling

$\theta$	$Q_{10}$	Reaction
1.024	1.27	Oxygen reaeration
1.047	1.58	BOD decomposition
1.066	1.89	Phytoplankton growth
1.08	2.16	Sediment oxygen demand (SOD)



**FIGURE 2.11**

The effect of temperature on reaction rate for various values of  $\theta$ .