

## LECTURE 3: DYNAMICS CURRENTS AND TIDES

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- **\* REACTION FUNDAMENTALS**
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## **REACTION TYPES**

- Homogeneous reaction: involve a single phase, (that is, liquid, gas, or solid)
- Heterogeneous reaction: involve more than one phase, with reaction usually occurring at the surface between phase
- Irreversible reaction: These proceed in a single direction and continue until the reactants are exhausted.
- Reversible reaction: can proceed in either direction, depending on the relative concentration of the reactants and the products.







### **ZERO-, FIRST AND SECOND – ORDER REACTIONS**

**\* Zero - order**(n = 0)

Equation (\*):  $\frac{dC}{dt} = -k$ 

Where: k has units of ML<sup>-3</sup>T<sup>-1</sup>

If  $C = C_0$  at t =0, then this equation can be integrated by separation of varibales to yield:

$$C = C_0 - kt$$

- A constant rate of depletion per unit time
- Plot of concentration versus time yields a straight line







 $\ln C_0$ 

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### **ZERO-, FIRST AND SECOND – ORDER REACTIONS**

- First order(n = 1)
- Equation(\*):  $\frac{dC}{dt} = -kC$  where k has units of T<sup>-1</sup>

If C = C<sub>0</sub> at t =0, then this equation can be integrated by separation of variables to yield: In c – In  $c_0 = -kt$ 

where  $k' = \frac{k}{2.3025}$ 

Taking the exponential of both sides gives:  $C = C_0 e^{-kt}$ 

- The concentrations decrease following exponential function
- The concentration curve asymptotically approaches zero with time
- Taking te inverse logarithm base e to base -10

$$C = C_0 10^{-k't}$$





## **ZERO-, FIRST AND SECOND – ORDER REACTIONS**

#### Second - order(n = 2)

Equation(\*):

where k has units of L<sup>3</sup>M<sup>-1</sup>T<sup>-1</sup>

 $1/C_0$ 

If  $C = C_0$  at t =0, then this equation can be integrated by separation of variables to yield 1/C

• Plot of 1/c versus t should yield a straight line

 $\frac{1}{C} = \frac{1}{C_{c}} + kt$ 

 $\frac{dC}{dt} = -kC^2$ 

The above equation can also expressed in term of concentration as a function of time by inverting to gives:

$$C = C_0 \frac{1}{1 + kC_0 t}$$





## **ZERO-, FIRST AND SECOND – ORDER REACTIONS**

- ✤ n order (n≠1)
- Equation(\*):  $\frac{dC}{dt} = -kC^n$

If  $C = C_0$  at t =0, then this equation can be integrated by separation of variables to yield

$$\frac{1}{C^{n-1}} = \frac{1}{C_0^{n-1}} + (n-1)kt$$

Plot of 1/C<sup>n-1</sup> versus t should yield a straight line

Solution for c: 
$$C = C_0 \frac{1}{\left[1 + (n-1)kC_0^{n-1}t\right]^{1/(n-1)}}$$

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#### **ANALYSIS OF RATE DATA**

A simple approach is to measuring concentrations in each bottle over time to develop a relationship between concentrations and time.







## **ANALYSIS OF RATE DATA**

### The integral method:

- Step 1: guessing n
- Step 2: Integrating equation (\*) to obtain a function, C(t)
- Step 3: Graphical methods are then employes to determine whether the model fits the data adequately

Order	Rate units	Dependent y	Independent x	Int <mark>ercep</mark> t	Slope	
n=0	M(L <sup>3</sup> T) <sup>-1</sup>	С	t	C <sub>0</sub>	-K	
n=1	T-1 '	InC	t	InC	-K	
n=2	L <sup>3</sup> (MT) <sup>-1</sup>	1/C	t	1/C <sub>0</sub>	ĸ	
n #1	(L <sup>3</sup> M <sup>-1</sup> ) <sup>n-1</sup> T <sup>-1</sup>	C <sup>1-n</sup>	t	C <sub>0</sub> <sup>1-n</sup>	(n-1)K	





## **ANALYSIS OF RATE DATA**

Example 1: Employ the integral method to determine whether the following data is zero-, first, second – order

t (day)	0	1	3	5	10	15	20
C (mg/l)	12	10.7	9	7.1	4.6	2.5	1.8

If any of these models seem to hold, evaluate k and c<sub>o</sub>





#### Solution:

To determine whether the following data is zero-, first, second – order, we will evaluate for each order.







The best-fit line for this case as below: lnC = 2.47 - 0.0972t which  $R^2 = 0.995$ Therefore the estimates of two model parameter are:  $k = 0.0972 \text{ day}^{-1}$   $C_0 = e^{2.47} = 11.8 \text{ mg/l}$ Thus the resulting model is  $C = 11.8e^{-0.0972t}$ 





log

dC<sub>A</sub> dt Co-funded by the Erasmus+ Programme of the European Union

slope = n

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## **ANALYSIS OF RATE DATA (cont.)**

### The differential Method

Taking the logarithmic of both sides of Equation(\*), to give:

$$\log\left(-\frac{dC}{dt}\right) = \log k + n\log C$$

Plot of log (-dC/dt) versus log C should yield a straight line with a slope of n and an intercept of log k

**Numerical differentiation:** Finite -Difference approximations to estimate dC/dt.

Centered Differentiation

$$\frac{\mathrm{dC}_{\mathrm{i}}}{\mathrm{dt}} \cong \frac{\Delta \mathrm{C}}{\Delta \mathrm{t}} = \frac{\mathrm{C}_{\mathrm{i+1}} - \mathrm{C}_{\mathrm{i-1}}}{\mathrm{t}_{\mathrm{i+1}} - \mathrm{t}_{\mathrm{i-1}}}$$





### **ANALYSIS OF RATE DATA (cont.)**

#### The differential Method (cont.)

<u>t</u>			t <sub>o</sub>	t <sub>1</sub>	t <sub>2</sub>	$t_3$ $t_4$ $t_5$					
С			C <sub>0</sub>	C <sub>1</sub>	C <sub>2</sub>	$C_3$ $C_4$ $C_5$					
l ▲ F	ادىتە	aroa	difforor	tiation	Drawing sm <mark>ooth cu</mark> rve that best						
V L	quar		unerer	itiation		approximates the area under the					
t	С	∆t	ΔC	∆C/∆t	dC/dt	histogram, t <mark>ry to ba</mark> lance out the histogram					
t <sub>1</sub>	C <sub>1</sub>				(dC/dt) <sub>1</sub>	areas above and below the drawn curve.					
	•	$t_2 - t_1$	$C_2 - C_1$	$(\Delta C/\Delta t)_2$		Then the de <mark>rivative</mark> estimates at the data					
t <sub>2</sub>	C <sub>2</sub>	t <sub>3</sub> – t <sub>2</sub>	$C_{3} - C_{2}$	(∆C/∆t) <sub>3</sub>	(dC/dt) <sub>2</sub>	points can be read directly from the curve. $(\Delta C / \Delta t)_2$					
t <sub>3</sub>	C <sub>3</sub>				$(dC/dt)_3$						
4	0	$t_4 - t_3$	$C_4 - C_3$	$(\Delta C/\Delta t)_4$	(-10(-14)	(dC/dt) <sub>2</sub>					
t <sub>4</sub>	$C_4$	+ +		(AC/At)	(dC/dt) <sub>4</sub>	$-\Delta C$					
<u>t<sub>5</sub></u>	C <sub>5</sub>	ι <sub>5</sub> — ι <sub>4</sub>	0 <sub>5</sub> – 0 <sub>4</sub>		(dC/dt) <sub>5</sub>	∆t					
						1 2 3 <b>t</b> 4 5					





## **ANALYSIS OF RATE DATA (cont.)**

#### The differential Method (cont.)







## **ANALYSIS OF RATE DATA (cont.)**

Example 2: Use the differential method to evaluate the order and the constant for the data from Example 1. Use equal-area differentiation to smooth the derivative estimates

t (d)	0	1	3	5	10	15	20
C (mg/l)	12	10.7	9	7.1	4.6	2.5	1.8





#### Solution:

#### Determine derivative estimate from time series of concentration

	t	С	-∆C/∆t	-dC/dt	logC	log(-dC/dt)	
	(day)	(mg/l)	mg/	/l/d			
	0	12.0		1.25	1.08	0.1	
			1.3				1.5 $_{ op}$
	1	10.7		1.1	1.03	0.04	
			0.85				
	3	9.0		0.9	0.95	-0.05	
			0.95				
	5	7.1		0.72	0.85	-0.14	
			0.50				
	10	4.6		0.45	0.66	-0.35	
			0.42				
	15	2.5		0.27	0.40	-0.57	0 5 10 15 20
			0.14				t
_	20	1.8		0.15	0.26	-0.82	Equal-area differentiation







### ANALYSIS OF RATE DATA (cont.)

#### ✤ The method of Initial Rates

- There are cases where reactions occur in which complications arise over time. For example a significant reverse reaction might occur. Further some reactions are very slow and the time required for the complete experiment might be prohibitive.
- Using data from the beginning stages of the experiment to determine the rate constant and order
- The differential method

Taking the logarithm of the negative of Eq. (\*):

 $\log\left(-\frac{dC_{0}}{dt}\right) = \log k + n\log C_{0}$ 

Plot log(-dC0/dt) versus  $log(C_o)$  should yield a straight line can be used to estimate k and n, the slope provides an estimate of the order, whereas the intercept provides an estimate logarithm





#### **ANALYSIS OF RATE DATA (cont.)**

### The method of Half -lives

The half-lives of a reaction is the time it takes for the concentration to drop to one-half of its initial value. In other words.

 $C(t_{50}) = 0.5C_0$ 

If  $C = C_0$  at t =0, then this equation (\*) can be integrated by separation of variables to yield

Combining two equations above to give:

$$E_{50} = \frac{2^{n-1} - 1}{k(n-1)} \frac{1}{C_0^{n-1}}$$

 $t = \frac{1}{kC_0^{n-1}(n-1)} \left| \left( \frac{C_0}{C} \right)^{n-1} - 1 \right|$ 

Taking the logarithm of this equation provides a linear relationship  $\log t_{50}$ 

$$\log_{50} = \log \frac{2^{n-1} - 1}{k(n-1)} + (1 - n)\log C_0$$







### **ANALYSIS OF RATE DATA (cont.))**

### The method of Half -lives (cont.)

For general case with response time  $t_{\phi}$ , where  $\phi$  is percent reduction:

$$=\frac{\left[\frac{100}{(100-\phi)}\right]^{n-1}-1}{k(n-1)}\frac{1}{C_0^{n-1}}$$





(\*\*\*\*\* \*\*\*\*\*

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The rates of most reaction in natural waters increase with temperature. A more rigorous quantification of the temperature dependence is provided by the Arhenius equation.

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

a preexponential or frequency factor Activation energy (J.mole<sup>-1</sup>) the gas constant(8.314 J.mole<sup>-1</sup>.K<sup>-1</sup>) absolute temperature (K).

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

Compare the reaction rate constant at two different temperatures

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

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

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

Compare the reaction rate constant at 20°C:

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## **TEMPERATURE EFFECTS**



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**Example 3:** Evaluation of temperature dependency of reaction. A laboratory provides you with the flowing results for a reaction

 $T_1 = 4^{\circ}C$   $k_1 = 0.12 \text{ ng}ay^{-1}$ 

 $T_2 = 16^{\circ}C$   $k_2 = 0.20 \text{ ngày}^{-1}$ 

(a) Evaluate  $\theta$  for this reaction

(b) Determine the rate at 20°C





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#### Solution:

#### (a) Taking the logarithm and raise the results to power of 10 to give

 $logk(T_2) - logk(T_1)$  $T_2 - T_1$  $\theta = 10$ 

Substituting the data gives:

$$\theta = 10^{\frac{\log 0.12 - \log 0.20}{4 - 16}} = 1.0435$$

(b) The rate at 20°C

$$k(20) = 0.20 \times 1.0435^{20-16} = 0.237 \text{ (ngày)}$$



**BÀI TẬP** 



 We design an experiment and determine the oxygen concentration as follows:

t(d)	0	2	5	10	20	30	40	50	60	70
C(mg/l)	10	8.4	6.5	4.4	2.3	1.6	1.3	1.2	1.1	1.1

Determine the order and the rate of the reaction?



# --- THE END ----

