

BT209

# Bioreaction Engineering

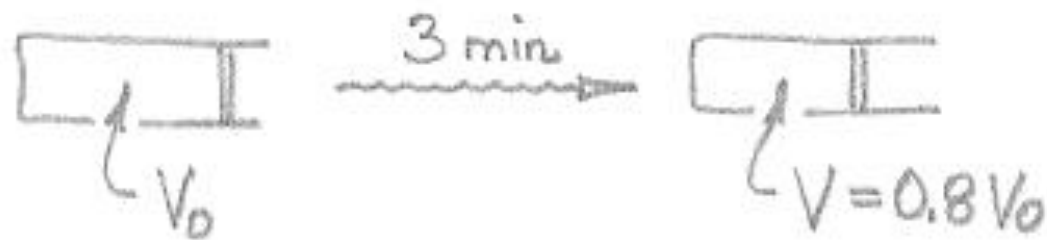
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06/02/2023

# Problem 1

Find the first-order rate constant for the disappearance of A in the gas reaction  $2A \rightarrow R$  if, on holding the pressure constant, the volume of the reaction mixture, starting with 80% A, decreases by 20% in 3 min.

# Solution: Problem 1



	$2A \longrightarrow B$	
Amount of A or B :	0.8	0.4
Amount of inert :	$\frac{0.2}{1.0}$	$\frac{0.2}{0.6}$
Total :	$\underbrace{\hspace{1cm}}$	
	$\therefore \epsilon_A = -0.4$	

For a first order reaction in a variable volume set-up, we have from Eq. 7.9 :

$$-\ln\left(\frac{\epsilon_A + 1 - V/V_0}{\epsilon_A}\right) = kt \quad \dots \text{or} \dots \quad -\ln\left(\frac{-0.4 + 1 - 0.8}{-0.4}\right) = k \cdot 3 \text{ min}$$

$$\therefore k = \frac{\ln 2}{3} = 0.231 \text{ min}^{-1} \quad \longleftarrow$$

## Problem 2

The following data are obtained at 0°C in a constant-volume batch reactor using pure gaseous A:

Time, min	0	2	4	6	8	10	12	14	$\infty$
Partial pressure of A, mm	760	600	475	390	320	275	240	215	150

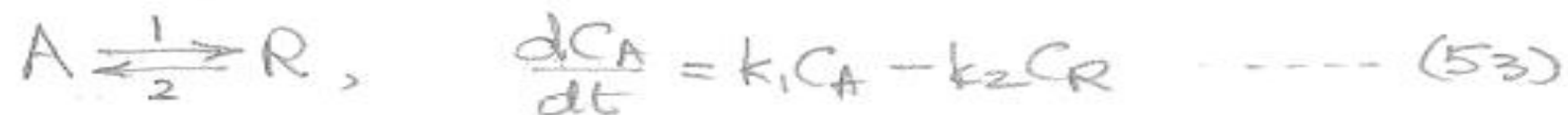
The stoichiometry of the decomposition is  $A \rightarrow 2.5R$ . Find a rate equation which satisfactorily represents this decomposition.

## Solution: Problem 2

Here we are given  $p_A$  vs  $t$  data, so we have two possible approaches

- (a) We could first transform all pressure readings into concentrations and then solve, or
- (b) We could stay with pressure readings and then transform our final equation into concentration units.

Let us stick with pressure units, and let us start by guessing first order reversible kinetics. Why reversible? Because at  $t = \infty$  there is still some unreacted  $p_A$ . So the rate equation we will test is



On integration we get

$$\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = \frac{k_1 t}{X_{Ae}} \quad \text{--- (54)}$$

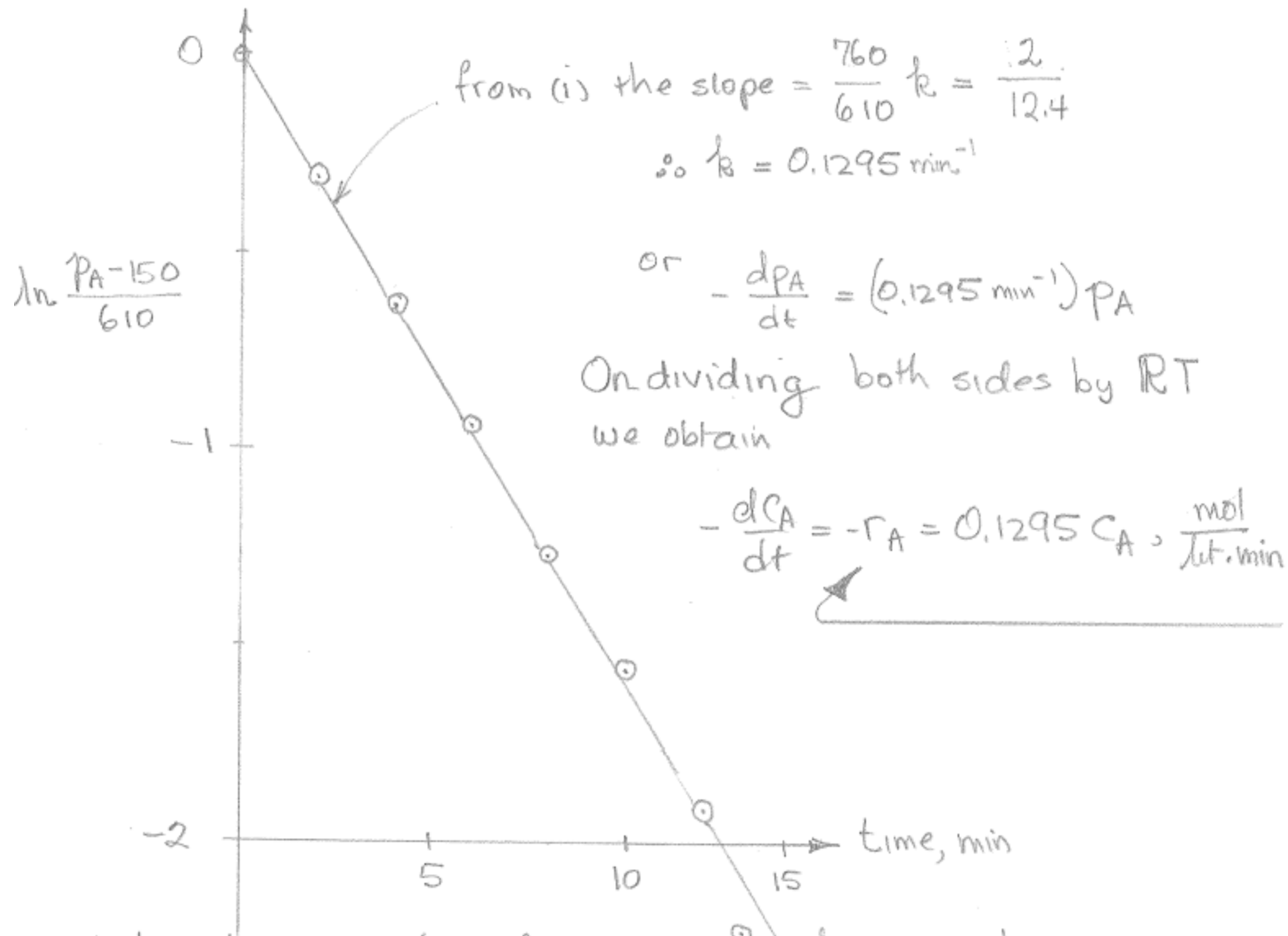
In pressure units this integrated expression becomes

$$\ln \frac{P_A - P_{Ae}}{P_{A0} - P_{Ae}} = \frac{k_1 t}{(P_{A0} - P_{Ae})/P_{A0}} \quad \dots (i)$$

Let us see whether this equation fits the facts. So tabulate & plot

$t, \text{min}$	$P_A$	$\frac{P_A - P_{Ae}}{P_{A0} - P_{Ae}}$	$\ln \frac{P_A - P_{Ae}}{P_{A0} - P_{Ae}}$
0	760	1	0
2	600	450/610	-0.3042
4	475	325/610	-0.6296
6	390	240/610	-0.9328
8	320	170/610	-1.2777
10	275	125/610	-1.5851
12	240	90/610	-1.9136
14	215	65/610	-2.2391
$\infty$	150	0	$-\infty$

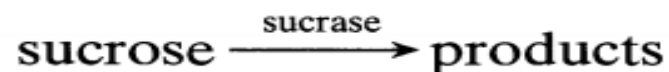
Note: For 1<sup>st</sup> order rxs  
 $k_c$  and  $k_p$  have the  
 same value,  $\text{time}^{-1}$



What this shows is that if we have isothermal  $R^{\text{th}}$  order kinetics we can use  $P_A$  or  $C_A$  without changing the rate constants

# Problem 3

At room temperature sucrose is hydrolyzed by the catalytic action of the enzyme sucrase as follows:



Starting with a sucrose concentration  $C_{A0} = 1.0$  millimol/liter and an enzyme concentration  $C_{E0} = 0.01$  millimol/liter, the following kinetic data are obtained in a batch reactor (concentrations calculated from optical rotation measurements):

$C_A$ , millimol/liter	0.84	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006	0.0025
$t$ , hr	1	2	3	4	5	6	7	8	9	10	11

Determine whether these data can be reasonably fitted by a kinetic equation of the Michaelis–Menten type, or

$$-r_A = \frac{k_3 C_A C_{E0}}{C_A + C_M} \quad \text{where} \quad C_M = \text{Michaelis constant}$$

If the fit is reasonable, evaluate the constants  $k_3$  and  $C_M$ . Solve by the integral method.



# Solution: Problem 3

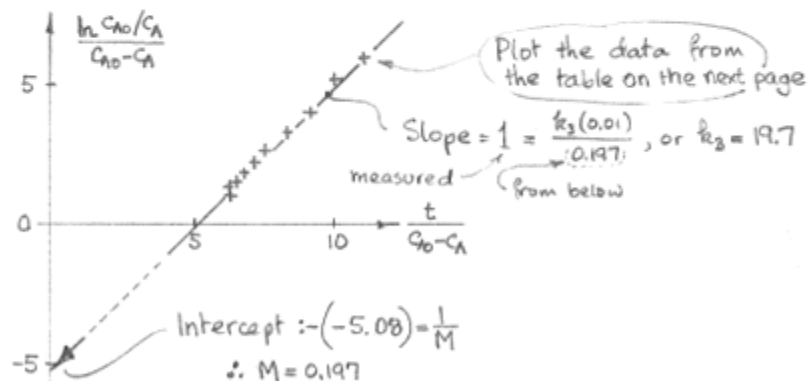
We can test the fit of the Michaelis-Menten type equation in many ways, integral or differential. We will sketch these different solutions in turn. But first let us transform the M-M equation into the following useful form

$$-r_A = \frac{k_3 C_{EO} C_A}{C_A + M} = \frac{k_4 C_A}{1 + k_5 C_A} \quad \text{--- where } \begin{cases} k_4 = \frac{k_3 C_{EO}}{M} \\ k_5 = \frac{1}{M} \end{cases} \quad \text{--- (i)}$$

use this form

Integral method Integrating (i) gives

$$\frac{\ln C_{AO}/C_A}{C_{AO} - C_A} = -k_5 + \frac{k_4 t}{C_{AO} - C_A} \quad \begin{cases} \text{slope: } k_4 = \frac{k_3 C_{EO}}{M} \\ \text{intercept: } -k_5 = \frac{1}{M} \end{cases} \quad \text{--- (i)}$$



From this figure the constants in Eq. (i) are

$$\left. \begin{array}{l} k_3 = 19.7 \text{ hr}^{-1} \\ M = 0.197 \frac{\text{millimol}}{\text{lit}} \end{array} \right\} \text{ thus } r_A = \frac{19.7 C_A C_{EO}}{0.197 + C_A}$$

t	C <sub>A</sub>	$\frac{\ln C_{AO}/C_A}{C_{AO} - C_A}$	$\frac{t}{C_{AO} - C_A}$
1	0.84	1.09	6.25
2	0.68	1.2	6.25
3	0.53	1.35	6.39
4	0.38	1.56	6.45
5	0.27	1.80	6.85
6	0.16	2.18	7.15
7	0.09	2.65	7.7
8	0.04	3.36	8.34
9	0.018	4.08	9.17
10	0.006	5.15	10.1
11	0.0025	6.01	11.0

given
for integral method, above

# Problem 4

Reactant A decomposes in a batch reactor



The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data using the half-life method.

Column 1	Column 2
Time $t, s$	Concentration $C_A, \text{mol/liter}$
0	$C_{A0} = 10$
20	8
40	6
60	5
120	3
180	2
300	1

# Solution: Problem 4

$$t_{1/2} = \frac{(0.5)^{1-n} - 1}{\tilde{k}(n-1)} C_{A0}^{1-n}$$

$C_{A0}$	$t_{1/2}$
10	60
8	(82-20)=62
4	120-40=80

plot of  $\log t_{1/2}$  vs.  $\log C_{A0}$  gives a straight line

Slope=1-n

