

### Reaction Kinetics III: Complex Reactions

- P115. The initial rate of O<sub>2</sub> production ( $v_0(\text{O}_2)$ ) by the action of an enzyme on a substrate was measured for a range of substrate concentrations ( $[\text{S}]$ ). The data obtained are collected in the table below:

$[\text{S}] / (\text{mol dm}^{-3})$	0.050	0.017	0.01	0.005	0.002
$v_0(\text{O}_2) / (\text{mm}^3 \text{ min}^{-1})$	16.6	12.4	10.1	6.6	3.3

Test the Michaelis–Menten mechanism with these data. To do it, fit the  $v_0 = \frac{a[\text{S}]}{b + [\text{S}]}$  empirical formula to the data and determine parameters  $a$  and  $b$ . ( $a = 20.0 \text{ mm}^3 \text{ min}^{-1}$ ,  $b = 0.01014 \text{ mol dm}^{-3}$ )

- P116. The isomerization of cyclopropane was examined at low pressures. They found the following effective first-order rate constants as a function of pressure:

$p / \text{Torr}$	84.1	11.0	2.89	0.569	0.120	0.067
$10^4 \cdot k_{\text{eff}} / \text{s}^{-1}$	2.98	2.23	1.54	0.857	0.392	0.303

Test the Lindemann–Hinshelwood mechanism with these data. (It is not valid for this reaction since  $1/k_{\text{eff}}$  versus  $1/p$  is not a straight line.)

- P117. The amylase enzyme decomposes starch mainly into maltose. The following set of data shows the initial rate of the reaction for different solutions. The amount of the enzyme was the same in all solutions. The initial rate here is given as the amount of maltose produced in 5.0 cm<sup>3</sup> of the reaction mixture in 1.0 min.

Starch %	0.030	0.040	0.050	0.086	0.129	0.216	0.431	0.647	1.078
Initial rate	0.140	0.165	0.180	0.260	0.305	0.345	0.400	0.435	0.445

Based on the Michaelis–Menten mechanism, propose a two-parameter empirical formula to describe the substrate concentration dependence of the initial rate and determine the parameters of this formula. ( $v_0 = \frac{a[\text{S}]}{b + [\text{S}]}$  where  $a = 0.470$  and  $b = 0.0733$ )

- P118. Fumarase catalyzed dehydration of *l*-malate results in fumarate. The following data were obtained at 25.0 °C in the presence of 5.00 mmol phosphate. The amount of the enzyme was the same in each experiment. The initial rate is given in an arbitrary unit.:

$l\text{-malate} / (\text{mmol dm}^{-3})$	0.100	0.333	1.000	3.33	10.0	33.3	100
Initial rate	1.9	4.2	6.1	6.5	7.2	7.4	6.9

Test the Michaelis–Menten mechanism with these data. Determine the two parameters of the empirical formula. ( $v_0 = \frac{a[\text{S}]}{b + [\text{S}]}$  where  $a = 7.435$  and  $b = 0.288$ )