

T. D. n° 2 (reaction kinetics and chemical equilibria)

Exercise n° 1 :

During a transformation, the concentrations of reactant A were measured over time. The results are as follows :

Time (S)	0	2	6	10	14	20
[A] (M)	0,398	0,385	0,366	0,341	0,315	0,282

Determine the reaction order, rate constant, and period.

Exercise n° 2 :

Adenosine diphosphate (ADP) can be oxidized with sodium periodate. Oxidized ADP binds covalently to proteins, which leads to inactivation in the case of certain enzymes. The kinetics of isocitrate dehydrogenase inactivation by 0.1 mM oxidized ADP were studied at 25°C :

Time (min)	0	6	12	18	24	30	36	42	48	54
Activity (%)	100	93	87	82	77,5	74	70,7	68	65,5	63,3
Time (h)	1	1,5	2	3	4	5	6	7	8	9
Activity (%)	61,4	54,3	49,5	42,3	36,5	31,6	27,4	23,7	20,5	17,8

This inactivation occurs in two phases.

- Determine the reaction order, rate constant, and half-reaction time for each phase.

Exercise n° 3 :

The thermal denaturation of a protein was studied in a concentrated solution (20.2 mg/mL). By measuring the concentration of native protein remaining over time, the following results were obtained :

Time (min)	2	4	6	8	10	12	14	16	18	20	30	60	90	120	180
[P] _n mg/ml	18.6	17.2	15.9	14.8	13.7	12.9	12	11.4	10.7	10.1	8	5.7	5.3	5.2	5.2

1. Determine the order of this reaction and its rate constant.

2. Calculate each of the specific constants.

Exercise n° 4 :

The interaction between α -chymotrypsin and Kunitz inhibitor (a protein extracted from the pancreas) occurs with a stoichiometry of **1:1** and can be considered complete. This interaction was studied over time : in an incubation mixture containing 36 nM chymotrypsin and 110 nM inhibitor, aliquots were taken and the remaining enzyme activity was determined :

Incubation time (min)	0	0,25	0,5	1	2
Enzymatic activity (%)	100	81,2	67	46	27,5

- Determine the order of the reaction and the corresponding rate constant.

Exercise n° 5 :

Pyruvate dehydrogenase is phosphorylated in the presence of a protein kinase. This phosphorylation can be easily measured using ATP labeled with ^{32}P in the γ position and determining the incorporation of phosphoryl residues into pyruvate dehydrogenase.

The table shows the number of nanomoles of ^{32}P incorporated in 1 minute for different amounts of protein kinase in the assay :

Protein kinase (μg)	2.5	10	15	20
^{32}P incorporated (nmol/min)	0.33	1.22	1.83	2.45

1. Write the reaction studied.
2. Determine the partial order of the reaction with respect to protein kinase.