

Tutorial 1: Chemical Kinetics Answers

1. Consider the following concentration-time data for the reaction of iodide ion and hypochlorite ion (OCl^-). The products are chloride ion and hypiodite ion (OI^-).

Experiment	Time (s)	$[\text{I}^-]$	$[\text{OCl}^-]$	$[\text{OH}^-]$
1	0	2.40×10^{-4}	1.60×10^{-3}	1.00
	10	2.16×10^{-4}	1.36×10^{-3}	1.00
2	0	1.20×10^{-4}	1.60×10^{-3}	1.00
	10	1.08×10^{-4}	1.48×10^{-3}	1.00
3	0	2.40×10^{-4}	4.00×10^{-5}	1.00
	10	2.34×10^{-4}	3.40×10^{-5}	1.00
4	0	1.20×10^{-4}	1.60×10^{-3}	2.00
	10	1.14×10^{-4}	1.54×10^{-3}	2.00

- (a) Write a balanced equation for the reaction.
 (b) Determine the rate law, and calculate the value of the rate constant.
 (c) Does the reaction occur by a single-step mechanism? Explain.
 (d) Propose a mechanism that is consistent with the rate law, and express the rate constant in terms of the rate constants for elementary steps in your mechanism. (Hint: Transfer of an H^+ ion between H_2O and OCl^- is a rapid reversible reaction.)



- b) assume that $\text{rate} = \frac{-\Delta[\text{I}^-]}{\Delta t} = k[\text{OCl}^-]^a[\text{I}^-]^b[\text{OH}^-]^c$
 compare experiments 1 and 3:

$$\frac{2.4 \times 10^{-4} - 2.17 \times 10^{-4}}{2.4 \times 10^{-4} - 2.34 \times 10^{-4}} = \left(\frac{1.6 \times 10^{-3}}{4 \times 10^{-5}} \right)^a$$

$$4^a \approx 4$$

$$\therefore a = 1$$

compare experiments 1 and 2:

$$\frac{2.4 \times 10^{-4} - 2.17 \times 10^{-4}}{1.2 \times 10^{-4} - 1.08 \times 10^{-4}} = \left(\frac{2.4}{1.2} \right)^b$$

$$2^b \approx 2$$

$$\therefore b = 1$$

compare experiments 1 and 4:

$$\frac{2.4 \times 10^{-4} - 2.17 \times 10^{-4}}{1.2 \times 10^{-4} - 1.14 \times 10^{-4}} = 2 \left(\frac{1}{2} \right)^c$$

$$2 \left(\frac{1}{2} \right)^c \approx 4$$

$$\therefore c = -1$$

$$\text{rate} = \frac{-\Delta[\text{I}^-]}{\Delta t} = k \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

$$\frac{1.2 \times 10^{-4} - 1.08 \times 10^{-4}}{10} = k \frac{1.2 \times 10^{-4}(1.6 \times 10^{-3})}{1}$$

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Clemens Wendtner



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method described in this book is to develop the original discrete optimization problems or game models in the space of

randomized formulations where the variables stand in for the distributions mixed strategies or preferences of the original discrete pure strategies in the use The following suppositions are made a finite state space a limited action space continuity of the probabilities and rewards associated with the actions and a necessity for accessibility These hypotheses lead to the existence of an optimal policy The best course of action is always stationary It is either simple i e nonrandomized stationary or composed of two nonrandomized policies which is equivalent to randomly selecting one of two simple policies throughout each epoch by tossing a biased coin As a bonus the optimization procedure just has to repeatedly solve the time average dynamic programming equation making it theoretically feasible to choose the optimum course of action under the global restriction In the ergodic cases the state distributions generated by the corresponding transition equations exponentially quickly converge to their stationary final values This makes it possible to employ all widely used optimization methods such as Gradient like procedures Extra proximal method Lagrange s multipliers Tikhonov s regularization including the related numerical techniques In the book we tackle different problems and theoretical Markov models like controllable and ergodic Markov chains multi objective Pareto front solutions partially observable Markov chains continuous time Markov chains Nash equilibrium and Stackelberg equilibrium Lyapunov like function in Markov chains Best reply strategy Bayesian incentive compatible mechanisms Bayesian Partially Observable Markov Games bargaining solutions for Nash and Kalai Smorodinsky formulations multi traffic signal control synchronization problem Rubinstein s non cooperative bargaining solutions the transfer pricing problem as bargaining

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