

Reaction Kinetics IV.: Molecular reaction dynamics

- P119. Collision theory demands knowing the factor of molecular collisions having at least the kinetic energy E_a along the line of flight. What is this fraction at 298 K and 1000 K when
- $E_a = 10.0 \text{ kJ mol}^{-1}$ and (0.01766 and 0.3004)
 - $E_a = 100 \text{ kJ mol}^{-1}$? ($2.96 \cdot 10^{-18}$ and $5.975 \cdot 10^{-6}$)

- P120. In the dimerization of methyl radicals, the pre-exponential factor is $2.4 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C. What is the reactive cross-section (σ) and the P -factor for the reaction if the C–H bond length is 154 pm? ($\sigma = 2.98 \cdot 10^{-19} \text{ m}^2$, $P = 0.146$)

- P121. The rates of thermolysis of a variety of *cis*- and *trans*-azoalkanes have been measured over a range of temperature to settle a controversy concerning the mechanism of the reaction. In ethanol an unstable *cis*-azoalkane decomposed at a rate that was followed by observing the N_2 evolution. The following rate constants were determined:

T/K	248.36	252.42	256.13	260.15	264.20
$10^4 \cdot k/\text{s}^{-1}$	1.22	2.31	4.39	8.50	14.3

Calculate the enthalpy, entropy, energy, and Gibbs free energy of activation at $-20.0 \text{ }^\circ\text{C}$. ($\Delta H^\ddagger = 84.05 \text{ kJ/mol}$, $\Delta S^\ddagger = 20.11 \text{ J mol}^{-1} \text{ K}^{-1}$, $E_a = 86.18 \text{ kJ/mol}$, $\Delta G^\ddagger = 78.96 \text{ kJ/mol}$)

- P122. Calculate the entropy of activation for a collision between two structureless particles at 300 K, taking $M = 50 \text{ g mol}^{-1}$ and reactive cross-section (σ^*) = 0.4 nm^2 . ($\Delta S^\ddagger = -76.14 \text{ J mol}^{-1} \text{ K}^{-1}$)

- P123. In an experimental study of a bimolecular reaction in aqueous solution, the second-order rate constant was measured at 25.0 °C and at a variety of ionic strengths:

$I/(\text{mol kg}^{-1})$	0.0025	0.0037	0.0045	0.0065	0.0085
$k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	1.05	1.12	1.16	1.18	1.26

It is known that a singly charged ion is involved in the rate-determining step. What is the charge on the other ion involved? In the Debye–Hückel limiting law, $A = 0.509 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ at this temperature. ($z = +2$)

- P124. Between the neutral particles A and B, a diffusion-controlled ($A + B \rightarrow P$) reaction occurs at 40.0 °C in a solvent having a viscosity of 2.37 cP at this temperature. Calculate the initial rate of product formation if the initial concentrations of the reactants are as: $[A]_0 = 0.150 \text{ mol dm}^{-3}$ and $[B]_0 = 0.330 \text{ mol dm}^{-3}$. ($v_0 = 1.450 \cdot 10^8 \text{ M/s}$)

- P125. In HI gas at 1.00 mol dm^{-3} concentration and 283 °C, the number of molecular collisions per unit of time and volume is $6.0 \cdot 10^{31} \text{ cm}^{-3} \text{ s}^{-1}$. The activation energy of the reaction is 187 kJ mol^{-1} . Calculate the number of reacting molecules in a volume of 1.00 cm^3 in 1.0 s. Calculate also the rate constant. ($1.6 \cdot 10^{14}$ molecules; $k = 2.72 \cdot 10^{-7} \text{ M s}^{-1}$)

- P126. The activation energy for the bimolecular $2\text{HI}(\text{g}) = \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ reaction is $186.7 \text{ kJ mol}^{-1}$. The diameter of the ball-shaped HI molecule is 350 pm. Use the collision theory to estimate the rate constant of the reaction at six different temperatures and then, compare the estimated values with the experimentally measured ones:

T/K	556	629	666	683	716	781
$k_{\text{exp}}/(\text{M}^{-1} \text{ s}^{-1})$	$3,517 \cdot 10^{-7}$	$3,02 \cdot 10^{-5}$	$2,195 \cdot 10^{-4}$	$5,115 \cdot 10^{-4}$	$2,501 \cdot 10^{-3}$	$3,954 \cdot 10^{-2}$

(With increasing temperature: $k = 2.86 \cdot 10^{-7}, 3.31 \cdot 10^{-5}, 2.47 \cdot 10^{-4}, 5.79 \cdot 10^{-4}, 2.70 \cdot 10^{-3}$ and $3.84 \cdot 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)

- P127. For the $2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g})$ second-order reaction, $k \cdot p^{\ominus}/(RT)^2 = 1.819 \cdot 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1} \text{ s}^{-1}$ and $5.668 \cdot 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1} \text{ s}^{-1}$ at 1423 K and 1681 K, respectively. Calculate the value of ΔS^{\ddagger} and ΔH^{\ddagger} . ($\Delta S^{\ddagger} = -84.4 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H^{\ddagger} = 265.1 \text{ kJ mol}^{-1}$)

- P128. The pre-exponential factor for the gas phase decomposition of ozone at low pressure is $4.60 \cdot 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the activation energy is 10.0 kJ mol^{-1} . Calculate the
- entropy of activation, ($-45.8 \text{ J mol}^{-1} \text{ K}^{-1}$)
 - enthalpy of activation and (5.04 kJ mol^{-1})
 - Gibbs free energy of activation at 298 K. (18.7 kJ mol^{-1})