MODERN LIQUID KINETICS

PROBLEMS I

Q0 a) Estimate the translational diffusion coefficient of a spherical particle of radius 0.3 nm in water at 298 K
b) How far, on average, would such a particle diffuse in 1 s?
c) How long would it take to diffuse a distance of 1mm, on average?
d)Roughly how long would the same particle take to rotate through one radian in water?
[The viscosity of water at 298 K is 10^{-3} kg m^{-1} s^{-1}.]

Q1 Use collision theory to estimate the number of collisions per second made by a molecule (relative molecular mass 18) in
i) a gas at atmospheric pressure and 300 K;
ii) a gas with the same density as liquid water at 300 K.
Use a collision diameter of 5 Angstroms.

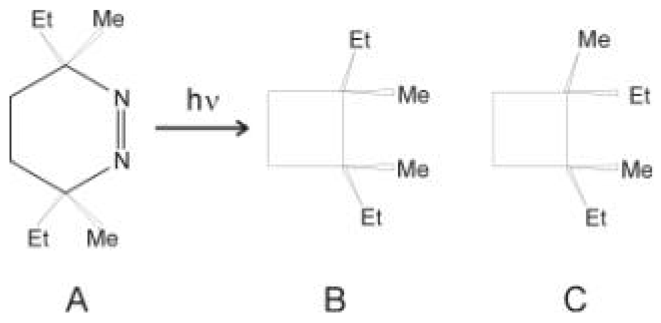
Q2 A much smaller concentration of biacetyl (butane-2,3-dione) is required to quench the fluorescence of naphthalene in solution in hexane than in glycerol (propan-1,2,3-triol). Comment.

Q3 Estimate the diffusion controlled rate constants at 298 K for the reaction of two neutral particles in
i) hexane
ii) water
Comment on the following approximate rate constants for the recombination of solvated electrons and cations in hexane (~10^{14} dm^3 mol^{-1} s^{-1}) and water (~10^{10} $dm^3mol^{-1}s^{-1}$). The viscosities of hexane and water are 3.26×10^{-4} $kgm^{-1}s^{-1}$ and 1.00×10^{-3} $kgm^{-1}s^{-1}$ respectively.

Q4 Estimate the encounter distance for the reaction of H+ and OH- in water from the following data. Diffusion coefficients: $D(H^+)=9.1\times10^{-9}$ m^2s^{-1}, $D(OH^-)=5.2\times10^{-9}$ m^2s^{-1}. Rate constant = 1.4×10^{11} $dm^3mol^{-1}s^{-1}$. Comment on your answer.

Q5 The observed activation energy for the radical recombination process $CH_3 + CH_3 \rightarrow C_2H_6$ is approximately 10-15 kJ mol^{-1}. In the gas phase, the activation energy is close to zero. Comment.

Q6. Explain why the reaction $CH_3 + CH_3 \rightarrow C_2H_6$ in solution is four times slower than might be expected on the basis of solvent viscosity, diffusion coefficients etc. Direct photolysis of compound A (below) produces a 10:1 mixture of the isomers B and C. Photolysis in the presence of a triplet sensitiser gives a 1.4:1 ratio. Comment qualitatively on this behaviour.



PROBLEMS II

Q1 The entropy of activation for a bimolecular reaction in the gas phase is usually negative, but positive activation entropies are sometimes observed for reactions between ions in solution.

Q2 The rate of reaction at 300 K is doubled when the pressure is increased from 1 to 2000 atm. Calculate the volume of activation, assuming it to be independent of pressure.

Q3 The following data relate to the reaction of iodide and persulphate ions in aqueous KCl solution at 298 K:

k/k_0	1.00	1.26	1.58	2.00
[KCl]/M	0.00	0.0025	0.010	0.023

where k_0 is the rate constant at zero ionic strength. What may be deduced about the mechanism of the reaction? You may neglect the contribution of the reactants and the products to the ionic strength.

Q4 Estimate the maximum kinetic isotope effect associated with breaking a C-X bond ($X={}^1H$ or ${}^3H$) at 298 K. Assume that the C atom is infinitely heavy, and that the force constant of a C-H bond is 450 N m^{-1}.

Q5 The following reactions have rate constants in the order $k_1 > k_2 > k_3 > k_4$. Comment.

$D + H_2 \rightarrow DH + H$	k_1
$H + H_2 \rightarrow H_2 + H$	k_2
$D + D_2 \rightarrow D_2 + H$	k_3
$H + D_2 \rightarrow HD + D$	k_4

Q6 Muonium (Mu) is a light isotope of hydrogen, consisting of a positively charged muon (8.83 times lighter than a proton) and an electron. Comment on the following experimental rate constants, pre-exponential factors, activation energies and Mu/H kinetic isotope effects for reactions of muonium in water at 298 K.

Reaction	k / $dm^3mol^{-1}s^{-1}$	A / $dm^3mol^{-1}s^{-1}$	E_a / $kJmol^{-1}$	k_{Mu}/k_H
i) $Mu+MnO_4^-$ (reduction)	$2.5x10^{10}$	$3.5x10^{13}$	18	1.0
ii) Mu+maleic acid (addition)	$1.1x10^{10}$	$2.3x10^{13}$	19	1.4
iii) Mu + $HCOO^-$ (abstraction)	$8.0x10^6$	$4.0x10^{12}$	33	0.03
iv) Mu + NO_3^- (unknown)	$1.5x10^9$	$2.0x10^{10}$	6	155

Q7 The decomposition of ethyl diazoacetate ($N_2CHCO_2C_2H_5$) is followed by measuring the loss of N_2. The reaction is faster in a solution of $DClO_4$ in D_2O than in a solutoin of $HClO_4$ in H_2O. Comment.

PROBLEMS III

Q1 a) A simplified form of the Marcus theory expression for the rate of an electron transfer reaction in solution is:

$$k = Z \exp\left[\frac{-(\Delta G^0+\lambda)^2}{4\lambda RT}\right]$$

where Z is a constant for the solvent, ΔG^0 the standard free energy for the reaction and λ is a free energy of reorganization of the system in passing from reactants to products. Sketch how ln(k) is predicted to vary for different reactions as ΔG^0 alters from being slightly positive to being less than $-\lambda$. Explain the chemical reasons for the behaviour that you have predicted.

b) In a hypothetical photochemically induced electron transfer reaction in solution, a donor molecule D becomes excited to D*, which then transfers an electron to an acceptor A.

$$D^* + A \rightarrow D^+ + A^- \qquad \Delta G^0 = -10 \text{ kJ mol}^{-1} \qquad \text{(a)}$$

Charge neutralisation

$$D^+ + A^- \rightarrow D + A \qquad \Delta G^0 = -100 \text{ kJ mol}^{-1} \qquad \text{(b)}$$

is energetically more favourable. Assuming that the reorganisation energy λ is +30 kJ mol^{-1}, calculate the ratio k_b/k_a at 298 K using the above expression for k.

Q2 In photosynthesis involving bacteria, an early process in a complex reaction pathway is the photo-induced charge separation

$$D^*A \rightarrow D^+A^-$$

where D is the primary electron donor (formed in the electronically excited state D*) and A the primary electron acceptor (‘primary’ because later on in photosynthesis another such step occurs). This reaction is activationless and occurs at a rate of $3x10^{11}$ s^{-1}.

For such an electron transfer reaction involving molecules embedded in a protein matrix, the pre-exponential factor in the Marcus expression (see Q1 of this section) is approximately $Z = 7.4\times10^{14}\exp(-1.4R)$, where Z is in s^{-1} and R, the separation between donor and acceptor, is in Angstroms. Derive a value for R.

Predict the rate of reaction at 298 K of a similar electron transfer reaction in a second photosystem in which R is the same but $\Delta G^0 = -16$ kJ mol^{-1}, given that the reorganisation energy $\lambda = 70$ kJ mol-1.