Transition State Theory

Section A

Make notes on the following:

1. The determination of equilibrium constants from partition functions.

2. The determination of rate constants in terms of partition functions (i.e. the derivation of the transition state theory expression for the rate constant). Make sure you understand the approximations involved in using transition state theory. Note that the k_BT/h factor in the rate constant expression can be obtained by treating the reaction coordinate as either a very loose vibration or a translation over the transition state region.

3. The origins of the kinetic isotope effect.

Section B

1. Theoretical expressions for the rate constant, k_2, of a bimolecular elementary reaction step include the Eyring equation from transition state theory;

$$k_2 = \kappa \frac{k_BT}{h} K^{\ddagger}$$

and the collision theory result

$$k_2 = P\,\sigma \left(\frac{8\,k_BT}{\pi\mu}\right)^{1/2} \exp(-E_a/k_BT)$$

  a) Explain the significance of the terms P, κ, $K^{\ddagger}$, σ and μ in the above expressions.

  b) For what type of reaction are the predictions of the two theories identical, with P and κ equal to unity. Obtain the specific form of the Eyring equation, in terms of partition functions, for this type of reaction.

  c) Express the rate constant for the radical reaction

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

  in terms of the molecular partition functions. Hence deduce how the pre-exponential factor for the reaction should depend on temperature (you may assume that all vibrational partition functions are equal to unity).

  d) When the experimental activation energy (50 kJ mol^{-1}) and the gas-kinetic collision cross sections are used, a P factor of 0.01 is found necessary to reconcile the collision theory result with results for the radical reaction. Explain why this factor is significantly less than one.

2. a) The following table contains data on the properties of the reactants and transition state (TS) for the reaction $D + H_2 \rightarrow DH + H$, which proceeds via a linear transition state.

Parameter	Reactants (H_2)	Transition state
r_e(DH) / Å	-	0.93
r_e(HH) / Å	0.741	0.93
Potential energy / kJ mol^{-1}	0.0	39.91
Frequencies / cm^{-1}		
Stretch	4395	1773
Bend (doubly degenerate)	-	870

Use the data to evaluate the conventional transition state theory (TST) rate constant at a temperature of 300 K

b) The experimental rate constant for this reaction at 300 K is 3.0×10^{-16} cm^3 molecule^{-1} s^{-1}, which is very close to that obtained by quantum mechanical calculation. Why is the TST result significantly lower than this value?

3. a) What temperature dependencies would be expected according to TST for the rate constants of the following reactions? (assume all vibrational partition functions are unity).

   i) A bimolecular reaction between two diatomic molecules forming a square-planar transition state.

   ii) A bimolecular reaction between an atom and a diatomic molecule which react via a linear triatomic transition state.

   iii) A bimolecular reaction between an atom and a non-linear molecule giving a non-linear transition state.

b) The reaction $2NO + Cl_2 \rightarrow 2NOCl$ is believed to be truly termolecular. The temperature dependence of the rate constant takes the form $k(T) \propto T^{-3.5}\exp(-E_0/RT)$. Account for this via transition state theory.

4. a) The oxidation of benzaldehyde by permanganate in solution is believed to involve the almost complete breaking of the aldehydic C–H bond within the transition state of the rate determining step in the reaction mechanism for this reaction. If this is so, how should the rate of this reaction at 300 K change when C_6H_5CHO is replaced by C_6H_5CDO? The wavenumber of the aldehydic C–H vibration may be taken to be 2900 cm^{-1}.

b) The following data were recorded for two isotopic variants of the reaction $Cl + HI \rightarrow HCl + I$.

Temperature / K	345	295	275	240	223
k_H/k_D	1.55	1.80	1.92	2.24	2.66

Calculate the difference in activation energies for the two reactions. Comment on this result, given that the vibrational wavenumber of HI is 2308 cm^{-1}.

5. a) Show how the equilibrium constant for a simple isomerisation reaction can be related to the partition functions of the species involved (you may want to use the expression for the Gibb's free energy derived in the last tutorial).

b) For a more general reaction, the expression for the equilibrium constant K_c is

$$K_c = \Pi_j \left(\frac{q_j}{V}\right)^{n_j} \exp(-\Delta E_0/RT)$$

where Π means the products of terms that follow, j is an index which runs over all reactants and products, ν_j is a stoichiometric factor, and ΔE_0 is the difference in energy between the ground states of the products and reactants.

The energy required to ionise the rubidium atom is 403.4 kJ mol^{-1}. Calculate the equilibrium constant K_c for the ionisation and hence the fraction of atoms ionised in a flame at 2000 K at an initial atom concentration of 6 x 10^{18} m^{-3}. The translational partition function for a one-dimensional box of length L is $(2\pi m k_B T)^{1/2} L/h$. You may assume that the extent of ionisation is small. Explain any other assumptions you have made.