CHEMICAL REACTION RATES   Dr M. BROUARD

Trinity Term 2003

A. Bimolecular Reactions   5 Lectures

1. *Introduction*

   Simple collision theory.

   Potential energy curves and surfaces.

   The reaction coordinate and barriers to reaction.

   Types of potential energy pathway.

2. *Collision Theory*

   Collision versus reaction cross-sections.

   Dependence of reaction cross-sections collision energy and reactant state.

   Cross-sections as average over reactant orientation and impact parameter.

   Microscopic to macroscopic rate constants.

3. *Transition State Theory*

   Reaction coordinate and the Transition State.

   The quasi-equilibrium assumption.

   Comparison with simple collision theory.

4. *Applications of Transition State Theory*

   The pre-exponential factor and the temperature dependence of reaction rate constants.

   Kinetic isotope effects.

   Quantum mechanical tunnelling.

   Transition state spectroscopy.

5. *Thermodynamic formulation of Transition State Theory*

   Entropy of activation.

   Thermochemical kinetics.

B. Unimolecular Reactions   3 Lectures

1. *Thermally Activated Unimolecular Reactions*

   The Lindemann and Lindemann-Hinshelwood theories of unimolecular reaction rates and their limitations.

   Types of potential energy surface.

   Energy dependent reaction rates.

   Strong collision assumption.

2. *Energy Dependent Reaction Rates*

   RRK theory for the energy dependent activation and reaction rate constants.

   Intramolecular vibrational redistribution.

3. *RRK Theory of Unimolecular Reactions and Beyond*

   Thermally and Chemically activated reactions.

   Transition state (and RRKM) theory of unimolecular reactions in the high pressure limit.

Suggested Reading

A. General Texts

1. P.W. Atkins *Physical Chemistry*, OUP, 6th Edition (1998), Chapters 25 and 27.

2. K J Laidler, *Chemical Kinetics*, Harper and Row, 3rd Edition (1987), Chapters 5 and 12.

3. M J Pilling and P W Seakins, *Reaction Kinetics*, Oxford University Press, (1995), Chapters 3 to 5.

4. M J Pilling and I W M Smith (Ed), *Modern Gas Kinetics*, Blackwells (1987), Chapters A.3, B.1, B.2 and C.6.

5. J L Steinfeld, J S Francisco and W L Hase, *Chemical Kinetics and Dynamics*, Prentice Hall (1989), Chapters 6, 8, 9 and 11.

6. M. Brouard, *Reaction Dynamics*, OUP Primer (1998), Chapters 1, 2, 5 and 6.

B. More Detailed Texts

1. R D Levine and R B Bernstein, *Molecular Reaction Dynamics*, OUP (1987), Chapters 1, 4, 5 and 7.

2. R B Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques*, OUP (1982), Chapters 3, 4, 6 and 7.

3. P J Robinson and K A Holbrook, *Unimolecular Reactions*, Wiley-Interscience (1972), Chapters 1 and 3.

4. J H Beynon, J R Gilbert, *Applications of Transition State Theory to Unimolecular Reactions*, Wiley and Sons (1984).

Problems

The problems given below are not all short and straightforward, and this is to be expected in a course which tries to link non-trivial theory with experimental data. The problems involving calculations of rate constants are necessarily quite tricky, and for these some hints are given. Most problems are longer than you would expect to find in a Finals General Paper.

Bimolecular Reactions

1. (a) The following table contains data on the properties of the reactants and transition state (TS) for the reaction

$$D + H_2 \longrightarrow DH + H .$$
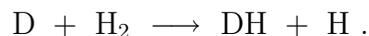
obtained from an *ab initio* potential energy surface. Like the other isotopic variants of this reaction, the TS is linear.

Parameter	Reactants (H_2)	Transition State
$r_{e, DH}/\text{Å}$	—	0.93
$r_{e, HH}/\text{Å}$	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 300 K.

Hints

i. Only a ratio of rotational partition functions is required: the moment of inertia of the TS may be calculated from the expression for a linear ABC molecule with equal bond lengths given in Atkins, 'Physical Chemistry' or the lectures.

ii. The exponential term in the rate constant expression, ϵ_0, refers to the difference in zero-point energies, which is not quite the same as the potential energy barrier, $V^{\ddagger}$.

(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 answer you obtain in (a) significantly lower than this value? The quasi-classical trajectory calculated rate constant for the same potential energy surface as used in the quantum mechanical calculations is 1.9×10^{-16} cm^{3}molecule^{-1}s^{-1} at 300 K. Suggest a reason why this classical result is much closer to experiment than the TST calculated value.

(c) Based on your answer to part (a), and the TST results given in the lecture course for the reaction

$$H + D_2 \longrightarrow HD + D ,$$
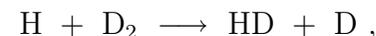
evaluate the isotope effect predicted by TST. Compare this value with that obtained by considering vibrational zero-point energy differences alone (i.e. ignoring the differences in A-factors). On the basis of TST, what is the dominant contribution to the isotope effect for this reaction at 300 K?

(d) The experimental isotope effect for the two reactions at 300 K is

$$\frac{k_{D+H_2}}{k_{H+D_2}} \sim 14$$

at 300 K. Why is the experimentally derived kinetic isotope effect larger than the one predicted by TST?

2. Try another TST calculation, this time of the 300 K rate constant for the reaction

$$H + HBr \longrightarrow H_2 + Br .$$

The relevant data are collected in the table below: once again you may assume the TS to be linear. E_0 is the zero-point energy difference between the TS and the reactants.

Parameter	Reactants (HBr)	Transition State
$r_{e, HBr}/\text{Å}$	1.414	1.42
$r_{e, HH}/\text{Å}$	—	1.50
$E_0/\text{kJ mol}^{-1}$	—	5.0
Frequencies/cm^{-1}		
Stretch	2650	2340
Bend (doubly degenerate)	—	460

Hint

You may have difficulty calculating the moment of inertia for the complex (the relevant equation is in Atkins 'Physical Chemistry'). You should get 1.74×10^{-46} kg m^2.

3. (a) What temperature dependences 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 TS.

   ii. A bimolecular reaction between an atom and a diatomic molecule which react *via* a linear triatomic TS.

   iii. A bimolecular reaction between an atom and a non-linear molecule giving a non-linear TS.

(b) The reaction

$$2\,NO + Cl_2 \longrightarrow 2\,NOCl$$
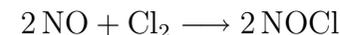
is believed to be truely termolecular. The temperature dependence of the rate constant takes the form

$$k(T) \propto T^{-3.5}e^{-E_0/RT} .$$

Account for this *via* TST.

(c) The rate constant for the reaction

$$OH + H_2(v = 0, 1) \longrightarrow H_2O + H$$
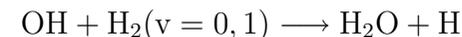
has been measured for translationally and rotationally thermalized H$_2$ molecules in vibrational levels v $= 0, 1$. The results are

$$k_{v=0}(T) = 9.3 \times 10^{-12}\,e^{-18000/RT}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_{v=1}(T) = 6.0 \times 10^{-11}\,e^{-11000/RT}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

where the activation energies are in J mol^{-1}. Calculate the rate constants $k_{v=0,1}(T)$ at five temperatures over the range 300-2500 K, and comment on the relative magnitudes of the two state-specific rate constants.

Next use these data to calculate the thermal rate constant (i.e. that for a Boltzmann vibrational distribution in the reactants) over the same temperature range, and plot the results in Arrhenius form, commenting on the shape of the plot you obtain. You may neglect contributions from vibrational levels v ≥ 2, and take the energy difference between H$_2(v = 1)$ and H$_2(v = 0)$ to be 49.6 kJ mol^{-1}.

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 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 as 2900 cm^{-1}.

(b) The following data were recorded for two isotopic variants of the reaction

$$Cl + HI \longrightarrow HCl + I .$$

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. If very little is known about the detailed structure of the transition state, pre-exponential factors may still be estimated by considering the entropy change on forming the transition state.

Consider the reaction

$$H + C_2H_6 \longrightarrow C_2H_7^\ddagger \longrightarrow H_2 + C_2H_5$$

in the gas phase: estimate the A-factor at 400 K

Hints

(a) Proceed by calculating a lower limit to $\Delta^\ddagger S^\ominus$, the difference between the *standard* ($p^\ominus = 10^5$ Pa) entropies of the TS and the reactants. For $S_\ddagger^\ominus$ (i.e. $S^\ominus$ for $C_2H_7^\ddagger$) use C_2H_6 as a 'model'.

(b) The addition of an H atom makes minimal differences to mass and moments of inertia of C_2H_6, so the contributions to the standard entropy of the complex from translation and rotation may be set equal to their contribution to $S_{C_2H_6}^\ominus$, but with the addition of a positive term which accounts for the reduction in symmetry on forming the TS. For this system, the *ratio* of the appropriate symmetry numbers for C_2H_6 and $C_2H_7^\ddagger$ is 6. What should this term be?

(c) A term needs to be added which accounts for the increase in electronic degeneracy in going from C_2H_6 (a singlet) to $C_2H_7^\ddagger$ (a doublet).

(d) There are changes in vibrational and internal rotational partition functions in forming the H—H—C structure. A lower limit on $S_\ddagger^\ominus$ and thus on $\Delta^\ddagger S^\ominus$ is obtained by neglecting them, i.e.

$$S_\ddagger^\ominus \geq S_{C_2H_6}^\ominus + \text{two positive terms} ,$$

where the latter terms account for the decrease in symmetry and the increase in electronic degeneracy.

(e) Finally, $S^\ominus$ for the H atoms is required. Use the Sackur-Terode equation (Atkins, 5th Ed. p686). However, remember that H is a ^{2}S atom.

Comment on your answer, given that the experimental A-factor is 1.0×10^{11} dm^{3}mol^{-1}s^{-1}.

Unimolecular Reactions

1. The table below shows the variation of the unimolecular rate constant, k_{uni}, with pressure at 763 K for the isomerization of cyclopropane to propene.

$k_{\mathrm{uni}}/10^{-4}\,s^{-1}$	0.55	0.95	1.78	2.40	3.39	4.07	4.79	5.37
p/Torr	0.10	0.32	1.0	3.2	10	32	100	320

(a) By graphical means, use the data to test Lindemann theory.

(b) Estimate (as best you can) the high pressure limiting rate constant, k_∞.

(c) Based on your answer to (b), find a value for $p_{1/2}$. Hence estimate k_1, clearly stating the units employed.

(d) The critical energy, E_0, for the reaction is $274\,\mathrm{kJ\,mol^{-1}}$ and the collision number under the above conditions is $Z^o_{\mathrm{AM}} = 2.9 \times 10^{11}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Show that the approximate number of 'active' oscillators, s, required by the Hinshelwood model is eight. Comment on this result.

2. *Trans*-diphenylbutadiene undergoes unimolecular photoisomerization in one of its low lying electronically excited states. The rate constants for isomerization (determined from 'real-time' fluorescence lifetime measurements) vary with energy in the excited butadiene in the following way:

$\epsilon/\mathrm{cm^{-1}}$	2000	3000	4000	5000	6000	7000	8000
$k_2(\epsilon)/10^{10}\mathrm{s^{-1}}$	0.36	1.1	1.9	2.7	3.5	4.1	4.8

(a) Use the data to make a classical RRK estimate of the number of active oscillators, s, and calculate the rate constant $k^\ddagger$, given that the critical energy $\epsilon_0 = 1100\,\mathrm{cm^{-1}}$.

(b) Implicit in the free energy flow assumption, upon which RRK theory (and RRKM theory) is (are) based, is that *all* vibrational modes should be active (ie. vibrational energy is assumed to be distributed randomly among all the vibrational modes of the molecule). Using your estimate of $k^\ddagger$ in (a), calculate $k_2(\epsilon)$ assuming all the modes in diphenylbutadiene are active. Comment on the answers you obtain.

3. (The following question is adapted from the Advanced Physical Chemistry paper, 1994.)

Free-flow (statistical) theories of redistribution of energy often yield an equation for the rate of dissociation of a vibrationally excited molecule of the form

$$k(E) = A\left(\frac{E - E_0}{E}\right)^{s-1}$$

where A is a constant, E is the total internal energy, E_0 is the bond-dissociation energy and s the number of vibrational modes. The molecule ClONO can fragment in two ways

$$\mathrm{ClONO} \longrightarrow \mathrm{Cl} + \mathrm{NO_2} \qquad \Delta_r H^\ominus(298) = +72\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

$$\mathrm{ClONO} \longrightarrow \mathrm{ClO} + \mathrm{NO} \qquad \Delta_r H^\ominus(298) = +111\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

(a) If a reaction system contains both ClO and NO, energy-rich ClONO* may be formed by combination. Assuming that A is the same for both channels, estimate the relative importance of fragmentation into products (1) and redissociation to reactants

(2) for a total energy of ClO + NO of (i) 10 kJ mol^{-1} above the threshold for channel (2); and (ii) 50 kJ mol^{-1} above the threshold.

(b) How can stabilized ClONO be formed?

(c) What do the data suggest about the products of the reaction between Cl and NO$_2$?

(d) To what extent can the constant A be predicted? Is it really likely to be the same for differing dissociation pathways?

4. The RRK rate constant $k^{\ddagger}$ is used as an adjustable parameter to fit limiting high pressure A-factors, A_{∞}. Thus the theory provides no explanation for the wide variation of experimental A_{∞} values from one reaction to another, for example:

Reaction	A_{∞}/s^{-1} at $T \simeq 1000$ K
$C_3H_8 \rightarrow CH_3 + C_2H_5$	1.5×10^{17}
	3.2×10^{15}
$(CHO)_2 \rightarrow 2CO + H_2$	1.0×10^{14}
	2.0×10^{11}
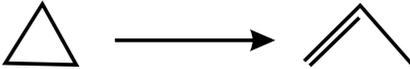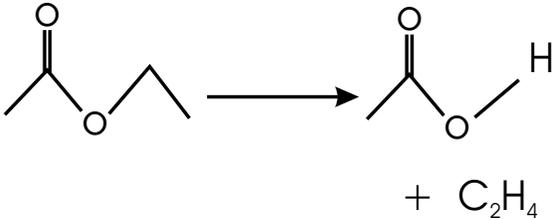
(a) Use transition state theory (which is equivalent to RRKM theory in the high pressure limit) to estimate the entropy of activation and the ratio of transition state to reagent partition functions, $q^{\ddagger}/q_A$, for each of the above reactions.

(b) How are the values you obtain in (a) related to the nature of the transition states involved?