

# Elementary Reactions

Theories of the Kinetics of Bimolecular and  
Unimolecular Elementary Reactions  
in the Gas and Liquid Phases

Lecturer's notes, handouts and overheads for  
an eight-lecture series given in various years at  
the PTCL, University of Oxford

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SECOND YEAR

HILARY TERM

Lecture Synopsis

Dr. R.P. Wayne  
(8 lectures)

*Kinetics of Elementary Reactions*

GAS PHASE BIMOLECULAR REACTIONS

1. Elastic, inelastic and reactive encounters, and how they may be represented on potential energy surfaces.  
Why simple collision theory is likely to be inadequate.  
Macroscopic and microscopic kinetics : rate constants and cross sections.  
Averages over velocity and energy distributions.  
Activation energy in the context of averages, and a pictorial demonstration that it is temperature dependent.
2. Elementary reaction dynamics.  
Reactive and non-reactive paths.  
Probability of reaction. Reaction cross sections. Connection with measurable quantities.  
Intermolecular energy transfer in non-reactive collisions.  
Importance of energy transfer in chemistry.  
Factors influencing the efficiency of V-T and V-V processes.
3. Statistics and dynamics: transition state theory.  
What is a transition state?  
A reminder of quasi-equilibrium treatments : classical and statistical thermodynamics.  
Activation energies in TST.
4. Relation between collision frequency and TST; frequency factors.  
Some applications of TST.  
Adiabatic selection from Boltzmann population as a way of avoiding the quasi-equilibrium hypothesis.  
The real assumptions of modern TST.

## UNIMOLECULAR REACTIONS

5. Unimolecular gas reactions.  
Collisional activation : Lindemann Theory. Comparison with experiment.  
Activation in many degrees of freedom : Hinshelwood Theory.  
Intramolecular flow of energy : theory and experiment.
  
6. Free flow theories of unimolecular decomposition, leading to outline of RRKM treatment.  
Experimental tests and comparison with calculations.  
Termolecular reactions and their relationship to unimolecular reactions.

## REACTIONS IN SOLUTION

7. Liquid phase versus gas phase reactions  
Diffusion-controlled reactions  
Cage effects and recombination reactions  
Charge effects
  
8. Activation-controlled reactions  
Salt effects  
Kinetic isotope effects  
Tunnelling reactions in gases and in solution

### *Bibliography*

Laidler	:	Theories of Chemical Reaction Rates
Laidler	:	Chemical Kinetics
Pilling	:	Reaction Kinetics (OCS)
Bunker	:	Theories of Elementary Gas Phase Reactions
Wayne	:	in Comprehensive Chemical Kinetics (Vol. 2).
Pratt	:	Gas Kinetics
Smith	:	Kinetics and Dynamics of elementary gas reactions

## Elementary Reactions I

Elementary reactions. Theories of rates

Encounters

Elastic, Inelastic and Reactive: Balls, {Jelly, Bricks} and Eggs

Description of forces acting during encounter

Potential energy curves, leading to P.E. surfaces.

V1 (A, B)

TYPICAL SURFACES

First discussion in terms of A + BC, orthogonal coordinates of "r" axes

V2

SKewed

Change of coordinates for easier visualisation: effect is to skew "r" axes.

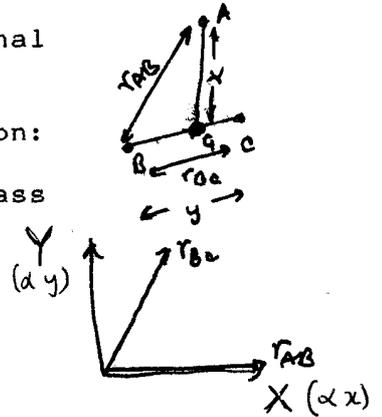
Convenience is treatment as single sliding mass system: balls or skiers

OVERLAY

V2A, B, C.

PATHWAYS -

The Arrhenius expression, and how it defines  $E_a$



$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} ; E_a = RT^2 \frac{d \ln k}{dT} = NkT^2 \frac{d \ln k}{dT}$$

V3

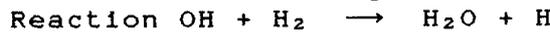
COLLISION THEORY

Collision theory, its suppositions, and its failings

Hard spheres; barrier energy

Ignores:

- orientation effect on potential
- difference collision and reactive diameters
- energies above threshold (n.b. effect of v. large energies)
- internal excitation: e.g.:-



$$k(v=0 \text{ in } \text{H}_2) = 9 \times 10^{-12} \exp(-18000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(v=1 \text{ in } \text{H}_2) = 6 \times 10^{-11} \exp(-11000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Notes: Both A and  $E_a$  are affected

1 quantum of vib = 50 kJ mol<sup>-1</sup>

so that 7000/50000 ≈ 0.14 of energy is used to overcome barrier

$$k(v=1)/k(v=0) \approx 120 \text{ at } 300\text{K}$$

$$A(v=1)/A(v=0) \approx 6.5$$

For excitation in OH, however,

$k(v=1)/k(v=0) \approx 1.5$ : that is, energy is more useful in the bond that is to be broken.

V3 (a) "b"

V3 (b) "H-S"

defines b

H<sub>2</sub>O top: conditions for HS reaction

Finally, with regard to collision theory, there is no way in which the disposition of energy in the products is predicted.

See over from D.C. Clary's lecture (11.1.91):  $\text{O}^+ + \text{HD} \rightarrow \text{OH}^+ + \text{D}$  = favoured at low J  
 $\rightarrow \text{OO}^+ + \text{H}$  = favoured at high J

\* Another example from Aspin 1990 [M.J. Frost, Birmingham]

$$\frac{k(\text{CN}, v=0 + \text{HCl}, v=1)}{k(\text{CN}, v=0 + \text{HCl}, v=0)}$$

$$\approx 200 ; \text{ Simple TST predicts } \approx 250$$



$$x = \mu \cdot r_{AB} + \mu' \cdot r_{BC} \cos \beta$$

$$\cos^2 \beta = \frac{m_A m_C}{m_A m_B + m_B m_C}$$

D. C. Clary 11 Feb 1991



f = branching ratio

f(OH <sup>+</sup> , j)	High E <sub>c</sub> '	Low E <sub>c</sub> '
J=0	0.8	0.5
J=4	0.5	0.5

Explanation : At low E<sub>c</sub>' - long distance interaction, not much influence over which end is attacked

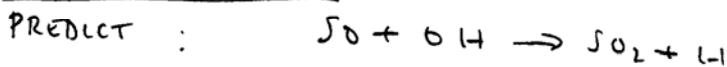
At high E<sub>c</sub>' - prefer H end, but high rotation means our effect

Reflected in T-dep of f (sum over Boltzmann)

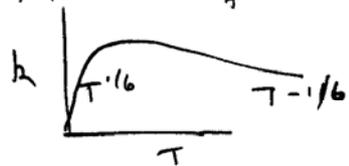
$$f \sim 0.8 \text{ at } 20K$$

$$\sim 0.7 \text{ at } 300K$$

? Matched by expt



Much faster for low J. For each J, k(J) ↑ with T ↑, but over Boltzmann pop: increased population of high J' leads to -ve T dep. However, at lower T<sub>s</sub>, k follows the J=0 curve



Reactant

Molecular beams

Laser pumping

Product

Improved chemistry.

Laser probing

Brief mention of BEAMS & IR-CL (most in ER2) - just that quantities can be selected/measured

Macroscopic and microscopic kinetics

Ideas just outlined moving towards microscopic kinetics, where rates have to be described in terms of individual encounters for particular velocities and internal excitation. Macroscopic "k" is average result of individual molecular events. Insight into "k" must start from microscopic level. Can go from microscopic rate parameters to "k", but not reverse.

Terminology of microscopic kinetics

Start from collision theory

Reminder that

$$Z'_{AB} = Z_{AB} / n_A n_B$$

Then

$$Z'_{AB} = \pi (r_A + r_B)^2 \left( \frac{8kT}{\pi\mu} \right)^{1/2} = S_c \bar{c}$$

collision cross section

$$Z'_{AB} (E' > E_c) = k$$

$$= S_c \bar{c} e^{-E_c/RT}$$

$$= S_r \bar{c}$$

reaction cross section

H10 eqs (1), (2)

Show →

H10 eq (3)

H10 eqs (4) + (5) plus HS assumptions in for it

V3

LOWER PART

We now allow that  $P_r$  is not a step function of either impact parameter,  $b$ , or of energy (velocity). So we write explicitly  $S_r(E)$  or  $S_r(c)$ , with

$$H10 eqs (6) + (7) \quad S_r(c) = \int_0^\infty P_r d(\pi b^2) = 2\pi \int_0^\infty P_r b db$$

replaces  $\pi(r_A+r_B)^2$

and

H10 eq (8)

$$k(c) = S_r(c) c$$

$$\text{That is, } k = \langle c S_r(c) \rangle$$

(with  $\bar{c}$  and a constant  $S_r$ )

Note that the previous collision expression is equivalent to

$$k = \langle S_r \rangle \langle c \rangle$$

Actual averaging procedure uses the distribution function for velocity or energy,  $f(c)$  or  $f(E)$

H10 eq (9)

or

$$k(T) = \int_0^\infty c S_r(c) f_r(c) dc$$

( $f$  may be Maxwell or Boltzmann)

V4 (shows two parts of the function)

$$k(T) = \int_0^\infty E S_r(E) f_T(E) dE$$

Note that this treatment still does not consider internal excitation ( $v, J$ ): next lecture.

Shortened version of next page:

"One conclusion is that, if  $S_r$  is  $f^2$  of  $c$  (or  $E$ ) then  $E_c$  must also be".

Activation Energies

Recall definition of  $E_a$  from Arrhenius expression

$$E_a = NkT^2 \frac{d \ln k}{dT}$$

Substitution in the expression for  $k(T)$  just obtained can be shown to lead to the result

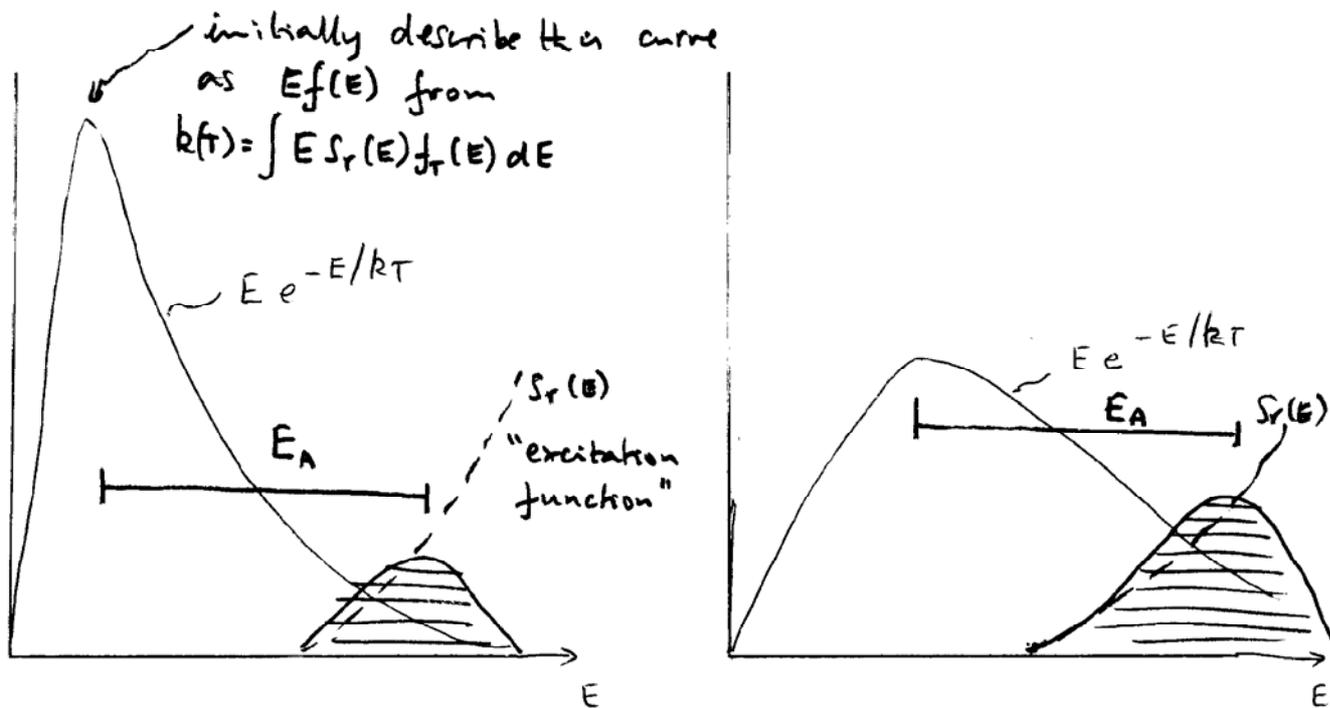
$$E_a = \langle E_r, T \rangle - \langle E_T \rangle$$

average energy of reactive collision - all collisions

Thus if  $S_r$  is a function of  $E$ , then  $E_a$  must be dependent on temperature.

$T_1$

$T_2$



Bottom of H<sub>2</sub>O : What to do in non-H<sub>2</sub> case

# ELEMENTARY REACTIONS I: VIEWGRAPHS

VIA PE SURFACE AS 3-D SKETCH  
AS CONTOUR MAP

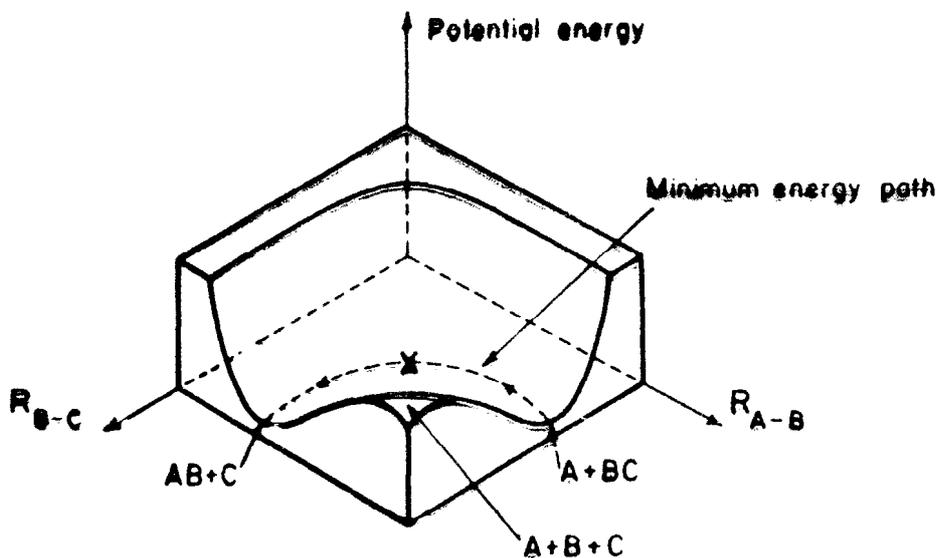
VIB SKETCH OF PE SURFACE AND  
SECTIONS THROUGH IT

V2 SKEWED SURFACE FOR  $H+Cl_2$

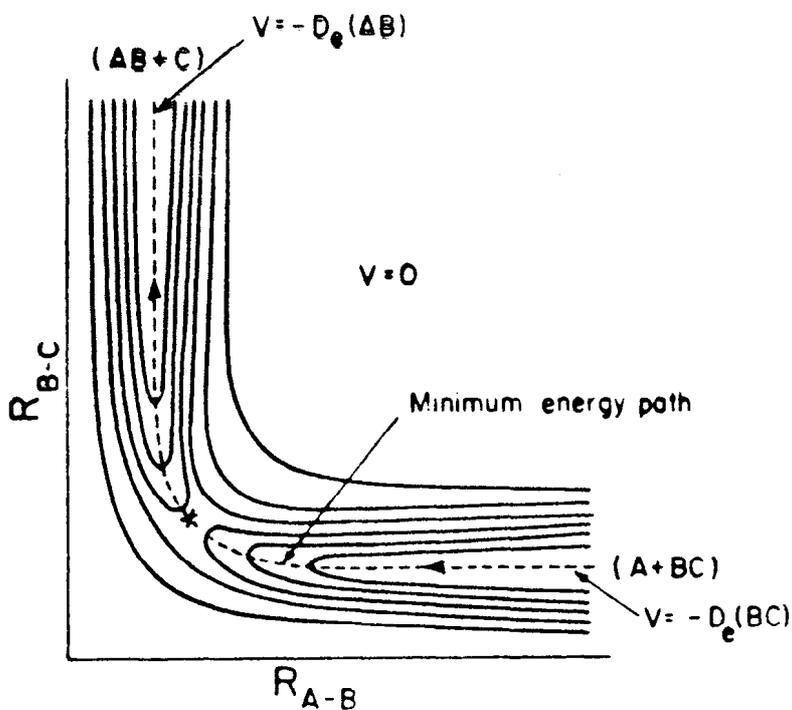
A ELASTIC  
B INELASTIC  
C REACTIVE } OVERLAYS

V3 INTERPRETATION OF IMPACT PARAMETER  
 $P_r$  vs  $b$ , vs  $E'$  IN HARD SPHERE C.T.  
 $P_r$  vs  $b$ , vs  $E'$  ALLOWING VARIATIONS

V4 COMPARISONS OF  $E e^{-E/k_B T}$ ,  $\int_r(E)$  AND  
THEIR PRODUCT:  
ACTIVATION ENERGY DEPENDS ON TEMPERATURE



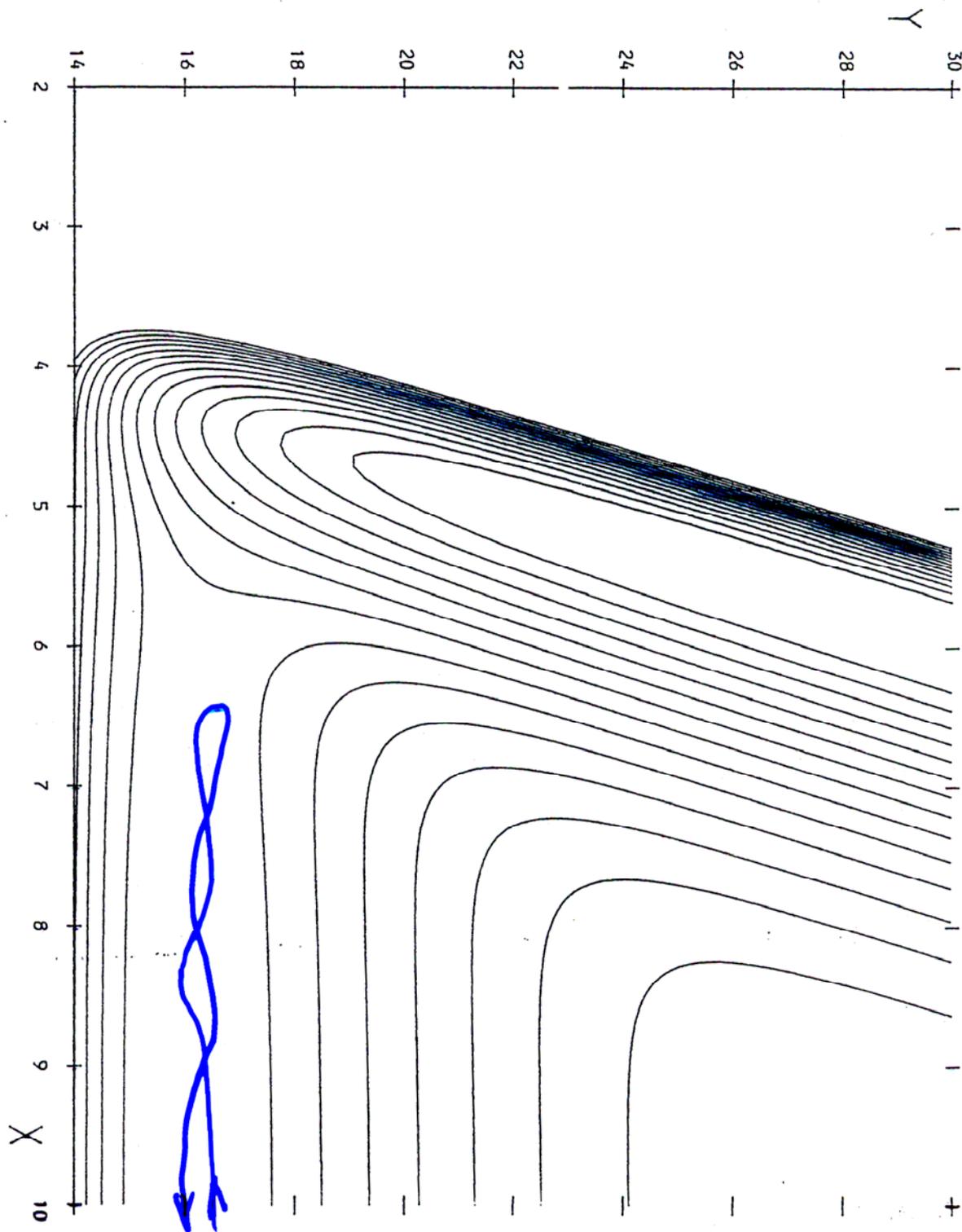
A potential energy surface for the (thermonutral)  $A + BC \rightarrow AB + C$  reaction in the 'collinear configuration' (schematic). The minimum energy route through the saddle point (x) is along the dashed curve. The plateau corresponds to the three separated atoms  $A + B + C$ .



A potential contour map for the potential energy surface of Fig. 4.1. The entrance valley has a depth  $-V = D_e(BC)$ , the dissociation energy of BC (as measured from the bottom of the valley) and similarly for the exit valley. At the saddle point (x) the potential energy is above that of either valley but below that of the plateau.

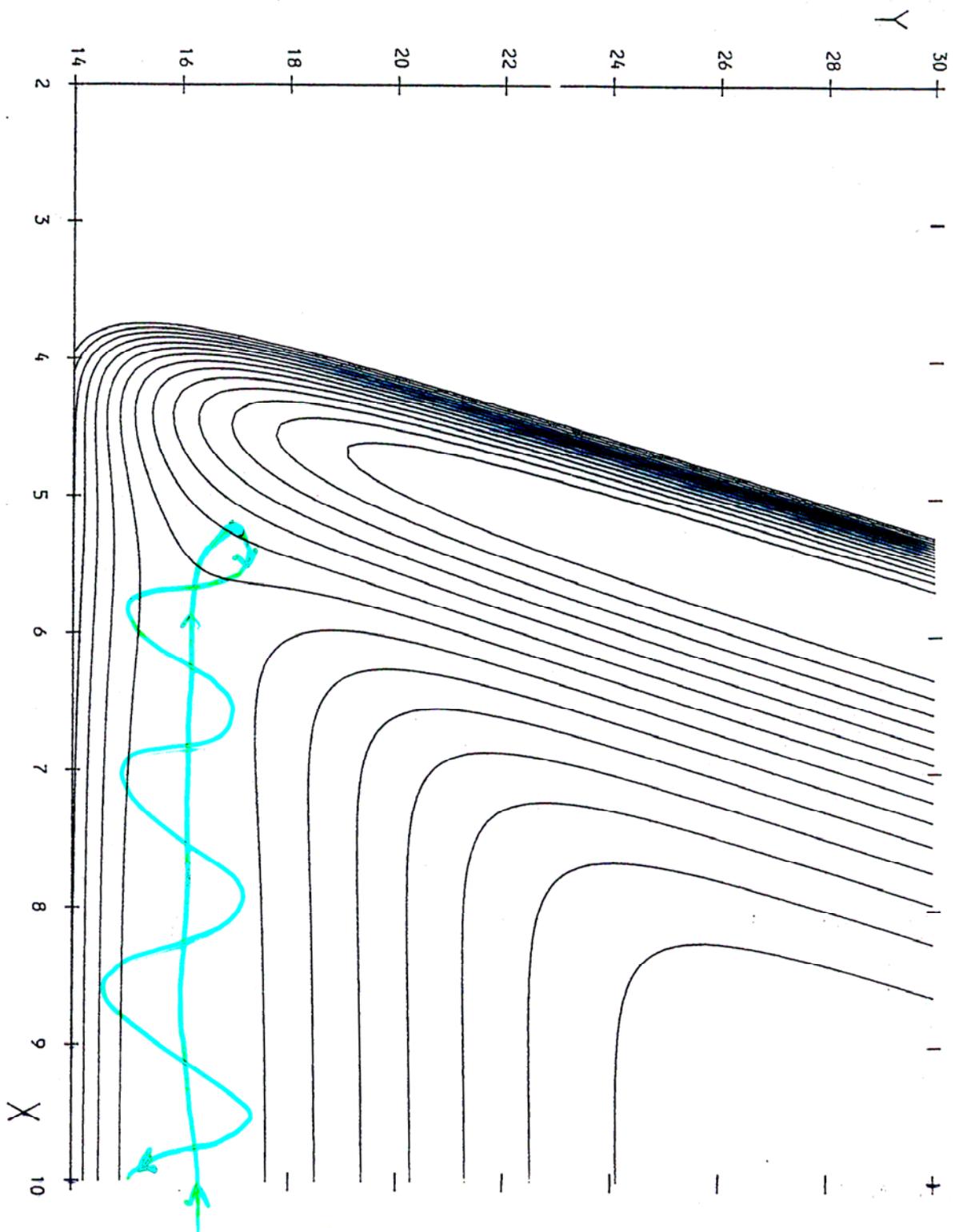
ERI  
V2a

# Elastic Collision



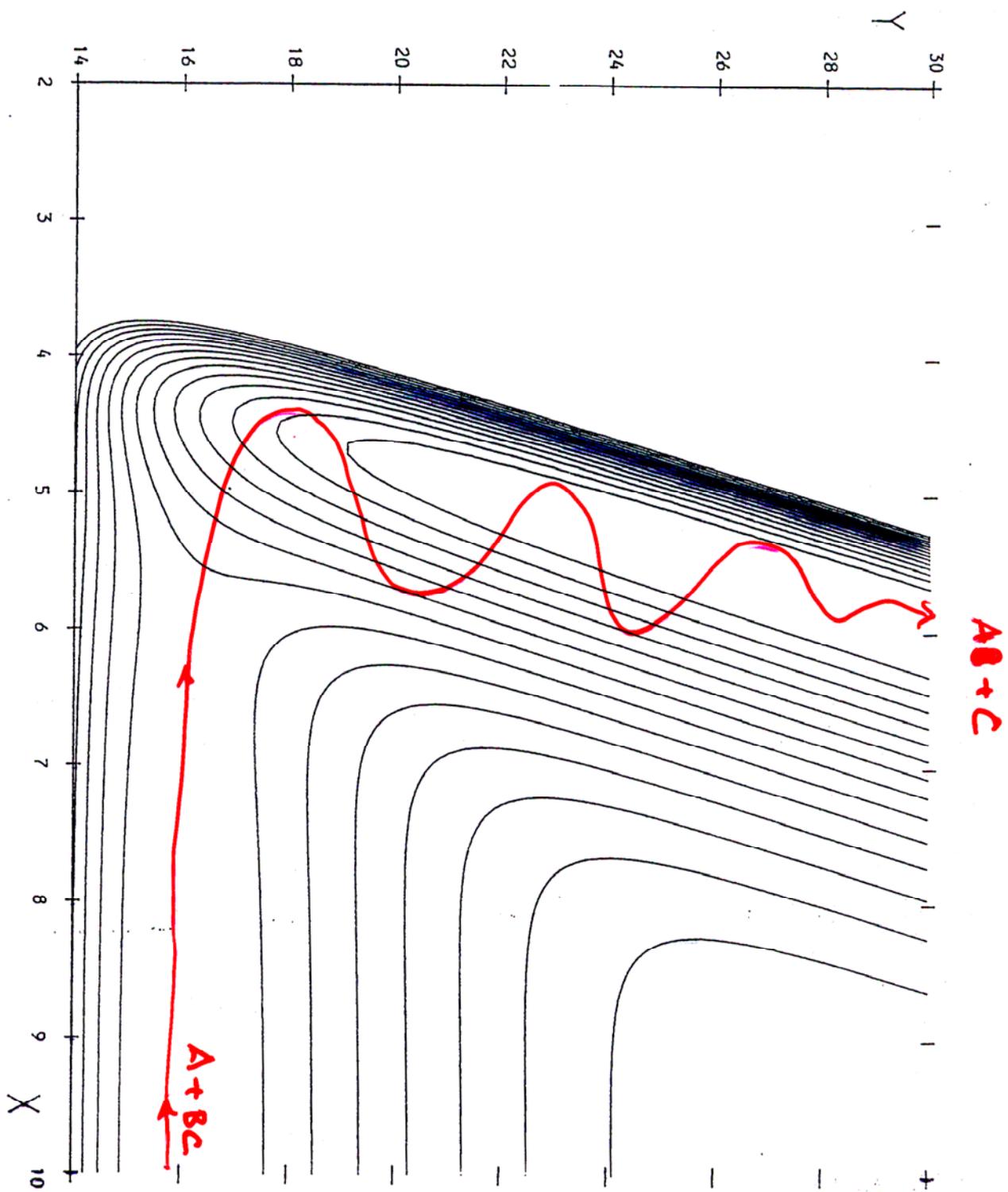
ERI  
V2b

# Inelastic Collision



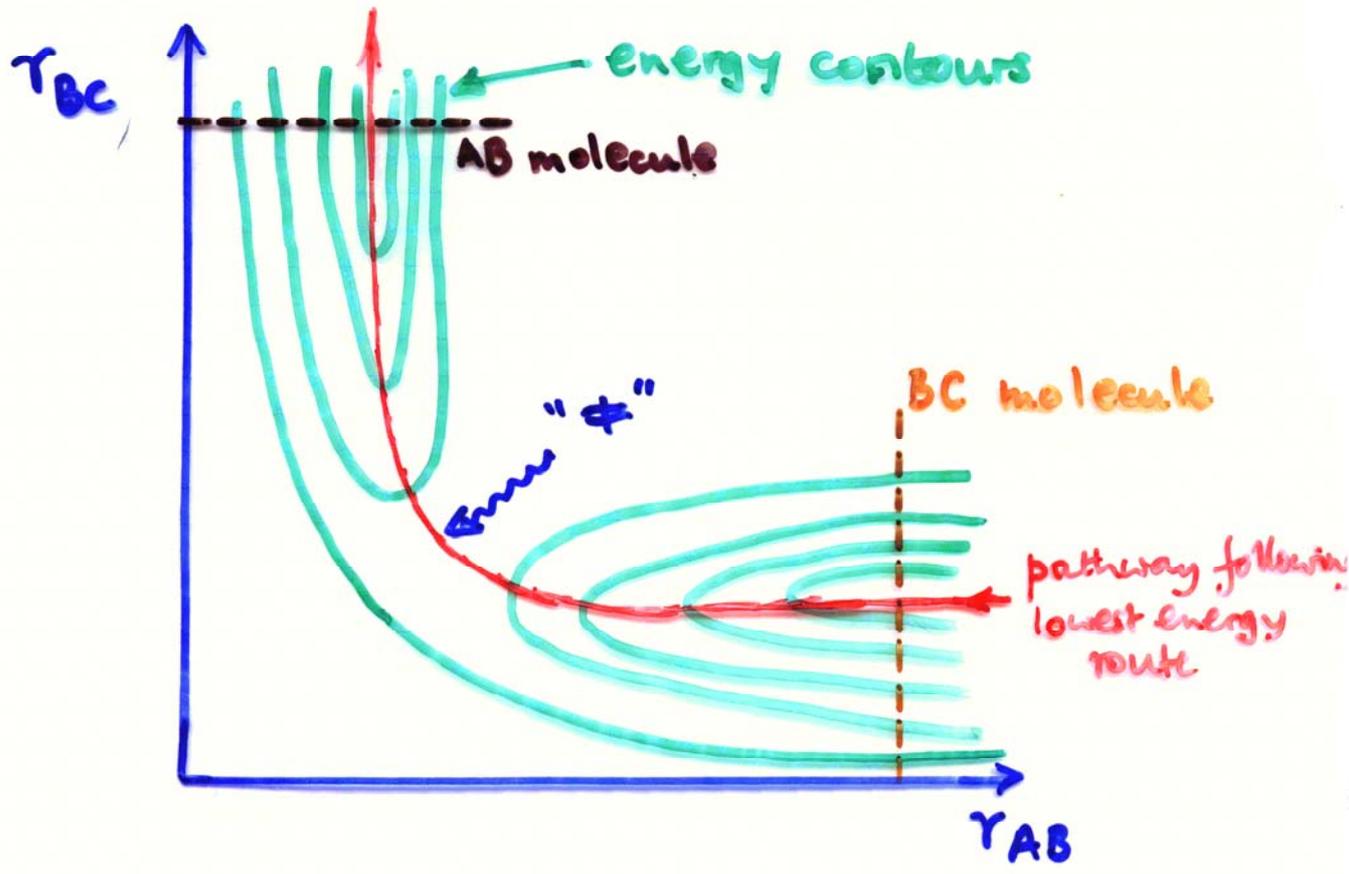
ERI  
V2c

Reactive Collision

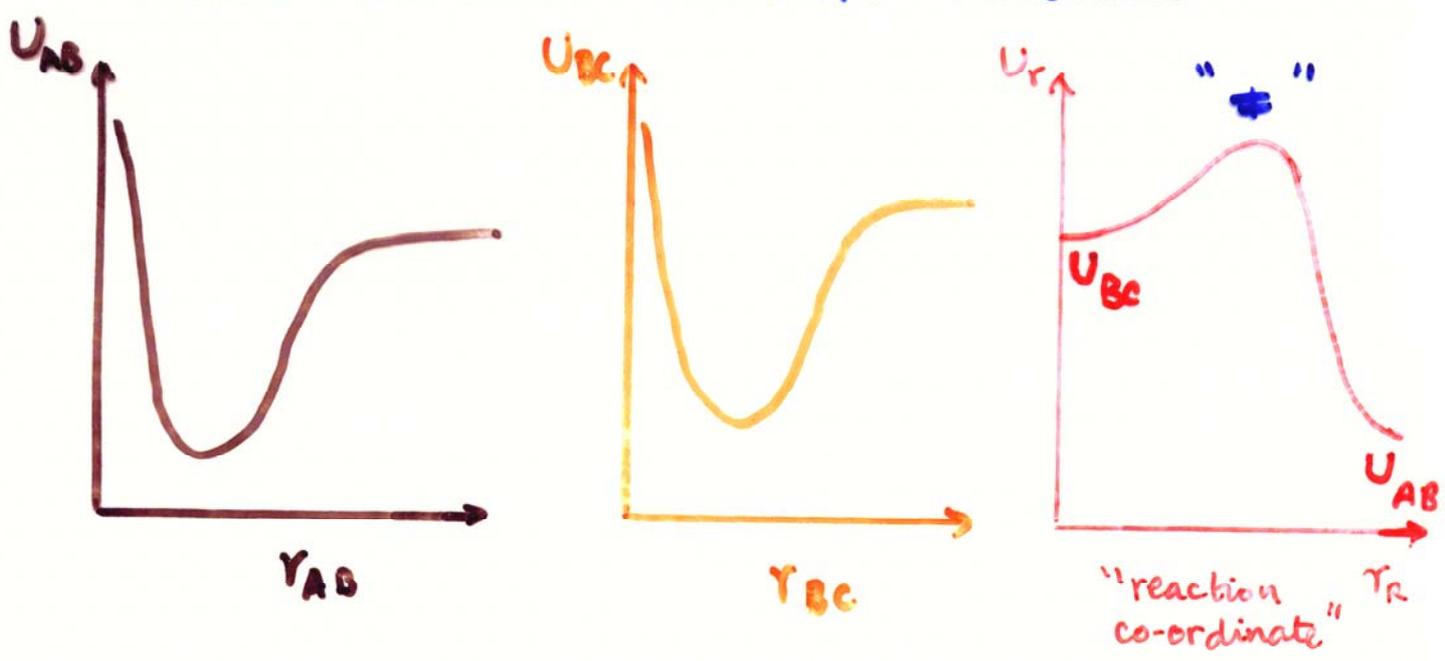


ER I  
VIB

# A POTENTIAL ENERGY SURFACE FOR REACTION $A + BC \rightarrow AB + C$

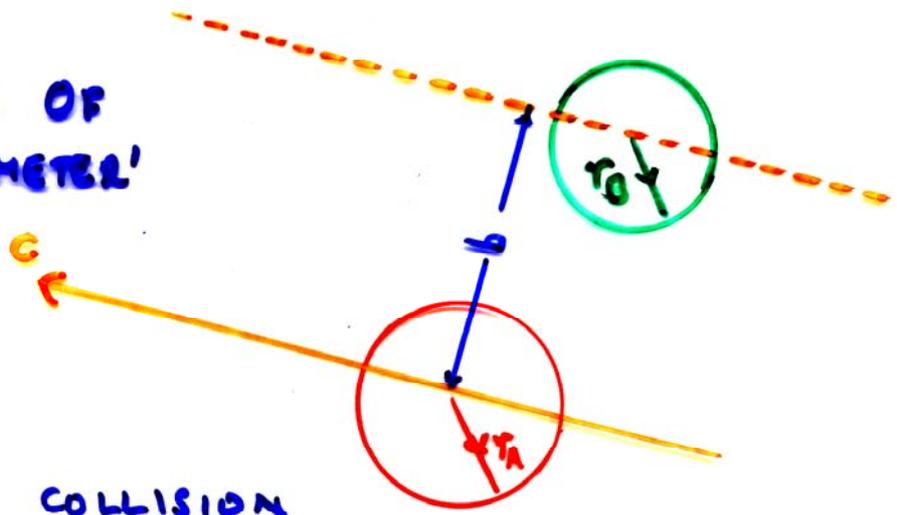


## CROSS SECTIONS THROUGH SURFACE

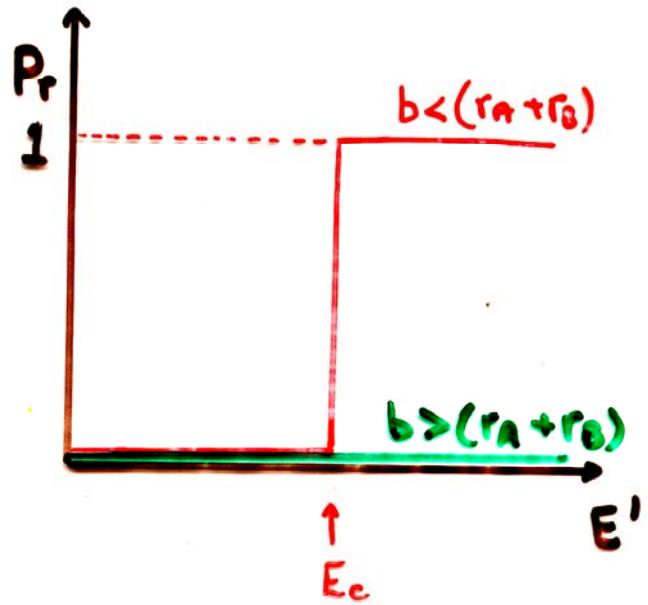
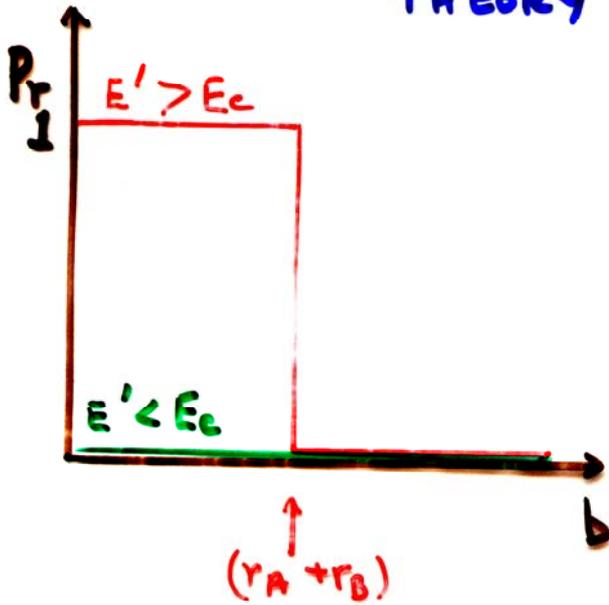


EKI  
V3

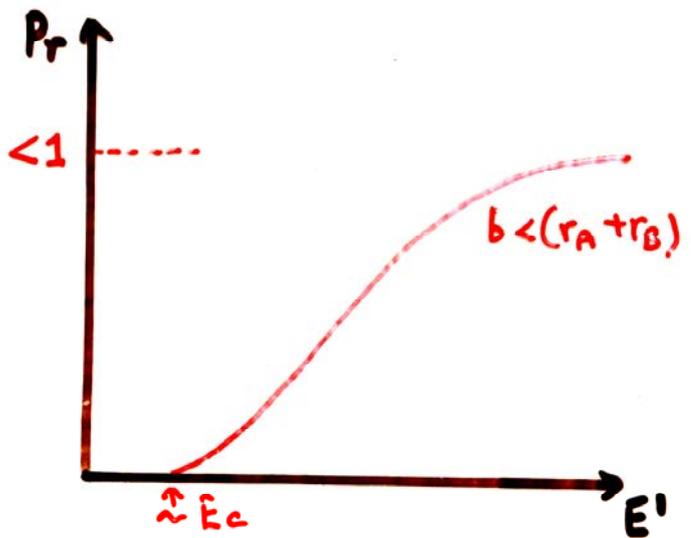
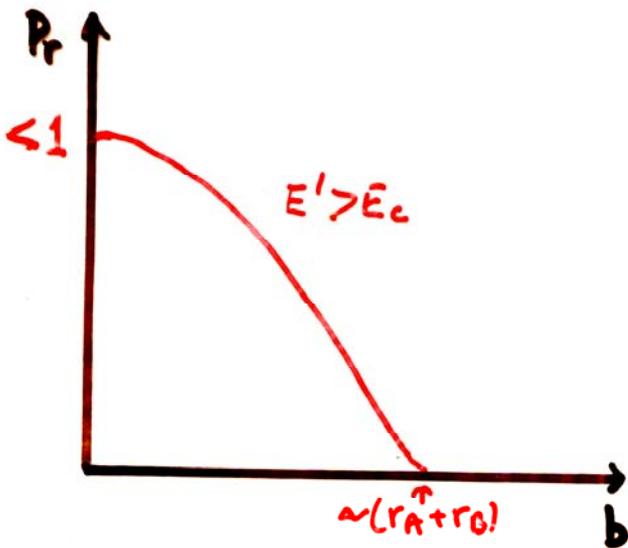
# INTERPRETATION OF 'IMPACT PARAMETER' "b"

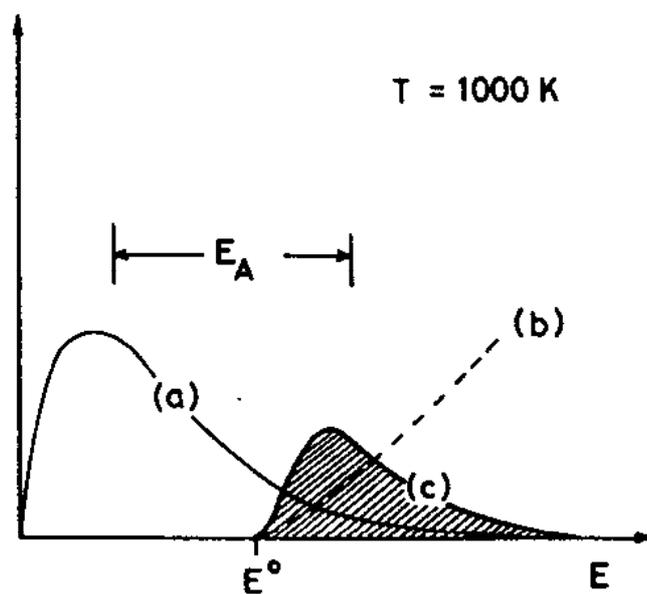
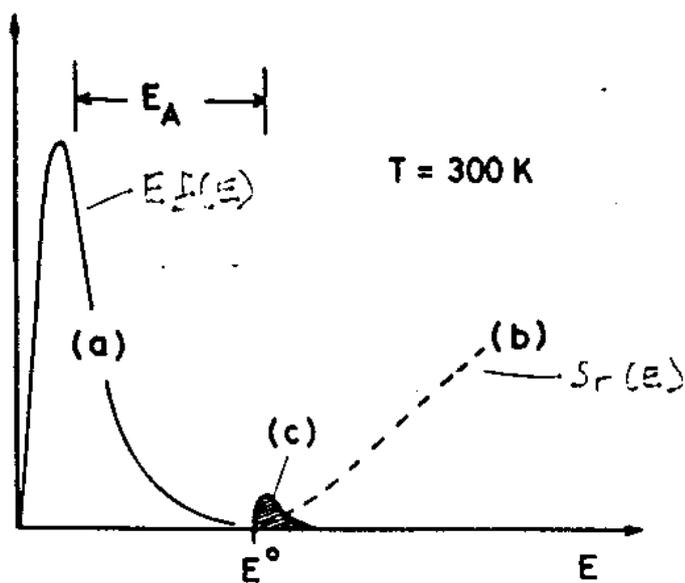


## HARD SPHERE COLLISION THEORY



## SOPHISTICATED COLLISION THEORY





Comparison of energy distribution function  $E \exp(-E/k_b T)$  (a); excitation function  $\sigma(E)$  (b); and their product, the reaction function (c) at two different temperatures. The integral of (c) is proportional to the rate coefficient  $k$ . Also indicated is the difference between the average energy of reactive collisions and the average energy of all collision, the activation energy  $E_A$ .

# **Handouts for Lecture I**

NOTES ON COLLISION THEORY AND REACTION PROBABILITY

The collision theory requires

- (i) that the impact parameter,  $b$ , is less than the sum  $(r_A + r_B)$
- (ii) that the energy of collision  $E$  is greater than a critical amount  $E_c$ .

For a system in thermal equilibrium (i.e. subject to the Maxwell-Boltzmann distribution) this theory predicts that the rate constant,  $k$ , should be given by

$$k = \pi(r_A + r_B)^2 \sqrt{\frac{8kT}{\pi\mu}} \cdot e^{-E_c/RT} \quad (1)$$

$$= S_c \bar{c} e^{-E_c/RT} \quad (2)$$

where  $S_c$  is the collision cross-section. Since the theory and practice require a "P" factor to be reconciled, it is useful to define a reaction cross-section,  $S_r$ , which includes both P and exponential terms

$$k = S_r \bar{c} \quad (3)$$

The hard sphere collision theory indicates that for any individual collision\*

$$\left. \begin{aligned} \text{(i)} \quad S_r &= 0 \quad \text{if } b > r_A + r_B \\ &= \pi(r_A + r_B)^2 \quad \text{if } b < r_A + r_B \end{aligned} \right\} \text{for } E' > E_c \quad (4)$$

$$\left. \begin{aligned} \text{(ii)} \quad S_r &= 0 \quad \text{if } E' < E_c \\ &= \pi(r_A + r_B)^2 \quad \text{if } E' > E_c \end{aligned} \right\} \text{for } b < r_A + r_B \quad (5)$$

In any more general case it is necessary to investigate how  $S_r$  depends on  $E$  (related to  $c$ ) and  $b$  and then to sum over the distributions of  $c$  and  $b$  to obtain the overall rate constant at any temperature  $T$ , as shown below in equations (6) to (9). For a thermally equilibrated system, the distribution of  $c$  is the Maxwell distribution, but the method is also applicable to any other (non-equilibrated) system.

\* In (i) and (ii)  $E'$  has the rather special meaning of energy resolved along the line of centres at the impact. If  $E$  is the relative energy of the spheres, then (i) becomes  $S_r = \pi(r_A + r_B)^2 (1 - E_c/E)$  for  $E > E_c$ ; (ii) is also more complicated.

If the probability of reaction for an impact parameter  $b$  and relative velocity  $c$  is  $P_r$  then  $S_r(c)$  (written this way to indicate that  $S_r$  is now dependent on  $c$ ) is given by

$$S_r(c) = \int_0^{\infty} P_r d(\pi b^2) \quad (6)$$

$$= 2\pi \int_0^{\infty} P_r b db \quad (7)$$

The general rate constant  $k(c)$  is thus

$$k(c) = S_r(c) c \quad (8)$$

and at any temperature  $T$  the overall rate constant  $k_T$  is given by

$$k_T = \int_0^{\infty} f_T(c) S_r(c) c dc \quad (9)$$

where  $f_T(c)$  is the distribution function appropriate to  $c$  (n.b. summation rather than integration may be necessary for non-continuous distributions).

This treatment may be extended to reactants which are not hard spheres by

- (i) allowing that  $P_r$  is now a function of  $c$ ,  $J$ ,  $v$  and  $b$  ( $J$  and  $v$  are rotational and vibrational quantum numbers)
- (ii) obtaining  $P_r(c, J, v, b)$  by obtaining the probability of reaction as a function of orientation and summing over random distributions
- (iii) carrying out the final summations or integrations over appropriate distributions of  $c$ ,  $J$ ,  $v$  and  $b$ .

Elementary Reactions II

Recap on cross section and rate constant

Introduce  $S_r$  by analogy with  $S_c$ : "reactive area" presented in a collision

That is,  $S_r$  is a way of expressing the velocity (collisional energy, temperature) independent part of the reactivity

Summing  $S_r$  over appropriate velocity distribution gives  $k(T)$

$S_r$  probably depends also on internal energy

$$k(T) = \int S_r(c) c f(c) dc$$

Measurability of  $S_r(c)$ , and maybe of  $S_r(n|n'; c)$

$$S_r(c) = \sum_n \sum_{n'} f_n S_r(n|n'; c)$$

$n'$  depends on  $n$

Beam experiments: also angular scattering, and translational and internal energy in products

Calculations of  $S_r(c)$

Need to know  $P_r$  and integrate over impact parameters

$$S_r = \int_0^{\infty} P_r d(\pi b^2) = 2\pi \int_0^{\infty} P_r b db$$

$P_r$  itself can be obtained by trial "experiments" that solve the equations of motion on the potential energy surface for a large number of trial orientations of reactants and for a fixed  $b$  and  $c$ .  $P_r$  is then the ratio of the number of events that led to reaction to the total number of trials. "Monte Carlo" methods.

$$P_r = \lim_{N \rightarrow \infty} \left( \frac{N_r}{N} \right)$$

Defined in this way,  $P_r$  is obviously a function of  $b$  as well as  $c$  and internal excitation ( $v, J$ )

Thus to obtain  $S_r(c)$ , further sequences of trials must be performed for many different values of  $b$ .

Finally, the whole procedure is repeated for a new  $c$ , and so on.

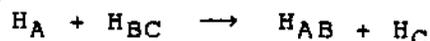
So far, we have been dealing with a fixed  $v$  and  $J$ : now it is possible to assess the effects of internal excitation by choosing new starting  $v$  and  $J$

V1: THE SURFACE

Some results of dynamics calculations on  $H + H_2$

V2

Typical reactive and non-reactive paths for



- a) Non-reactive -- little energy transfer
- b) Reactive -- crossing of BC, AB curves indicates change of partners ("reaction")
- crossing of BC, AC curves indicates rotation of new AB
- interaction period in both cases not much greater than single vibrational period ("direct interaction")

V3 TOP

Results for  $P_r$  vs  $b$

- a)  $b_{max} =$  collision diameter (but NOT a step function)
- b)  $P_r, max < 1$  (steric effect)

Now get  $S_r$  by summing  $P_r$  over  $b$

V3 BOTTOM

Note that threshold is 22 kJ mol<sup>-1</sup>, while difference between barrier and ZPE is ≈ 12 kJ mol<sup>-1</sup>  
 Extra energy is needed, because much energy is forced into symmetric and bending vibrations of the complex.

V4

Arrhenius plot for calculated results of  $k_T$

### Selectivity of Energy Consumption

Reminder of effect of vib excitation in H<sub>2</sub> in OH + H<sub>2</sub> reaction

Even when  $E_v$  exceeds barrier height, still need translation (cf 50 kJ mol<sup>-1</sup> only reduces activation energy by 7 kJ mol<sup>-1</sup>)

For thermoneutral reactions less dramatic effects, but still apparent in the H + H<sub>2</sub> results

Probability of reaction REDUCED for rotational excitation, and for very high  $c$

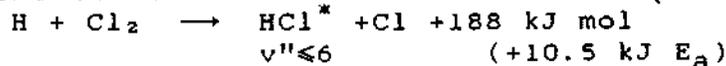
How excitation affects reactivity for different types of system:  
 Dynamic effects of "early" and "late" barriers

V5

### Specificity of Energy Disposal

Vibrational release

Infrared chemiluminescence



Disequilibrium of vibration, BUT only ≈ 7 percent of energy released as vibration

Predicted effects of early ("attractive") and late ("repulsive") barriers

V6

Rotational release

Generally rotational excitation is weak, suggesting collinear approach

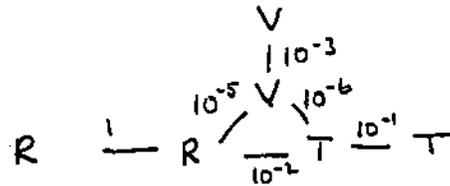
However, M + X<sub>2</sub> occurs at large impact parameters (long range interaction) and much rotational excitation as angular momentum is conserved

10.47

Energy Transfer

Reminder about elastic and inelastic collisions

Diagram showing approximate probabilities of e.t. per collision



Note, especially, low efficiency of V-T process  
Importance of e.t. in determining redistribution of energy within and between modes of a system that has been perturbed.

Significance in situations where collisions may be infrequent

Importance in fields ranging from astronomy and aerodynamics through laser physics to biochemistry

In chemistry, e.t. is intimately bound up with how collisions lead to reaction (motions that are more or less vibrational overcome the activation barrier).

Idea of vibrational excitation becomes explicit in unimolecular reactions, and we need to know the rates both of excitation and of de-excitation

Indication of what controls efficiency of V-T transfer can be obtained from simple picture



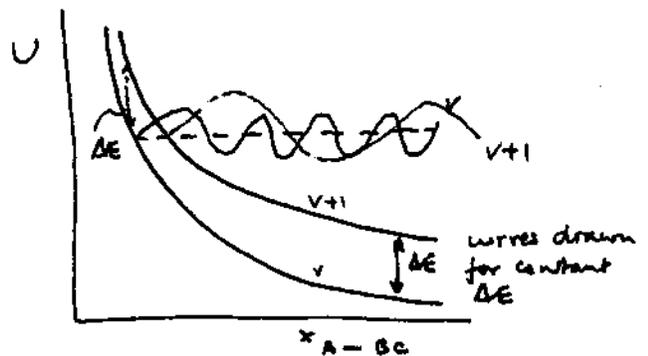
Curves represent A — BC potential for v, v+1 in BC

Waves are for translation  
Overlap is zero for pure sine waves

Thus effective overlap is where two distorted waves interact near turning point (viz. during collision)

Best when

- (i) Curves are close: i.e. Low energy to be transferred
- (ii) For a given set of curves, at high kinetic energy
- (iii) When  $\lambda$  is large: i.e. Low mass of system



Quantitative: Schwartz, Slawsky, and Herzfeld (SSH) theory

$$\log P = A - B \left( \frac{\omega^2 \mu}{T} \right)^{\frac{1}{3}}$$

- V7 Variation with T
- V8 Variation with  $\mu$
- V9 Variation with  $\omega$

V-V transfer

Theory: modified SSH (i.e. extension of idea of harmonic oscillator perturbed by exponential repulsive potential)

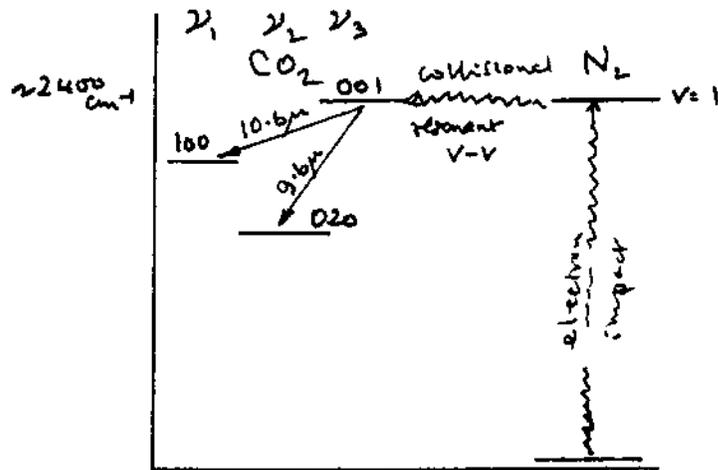
Theory gives

$$\log P = \alpha - \Delta E$$

For exact resonance,  $P \approx 10^{-3}$ , and decreases by a factor of 10 for each  $200 \text{ cm}^{-1}$  of  $\Delta E$

$$P \propto T \quad \text{if short range repulsion is dominant}$$

Very important resonant system:  $\text{CO}_2$  laser



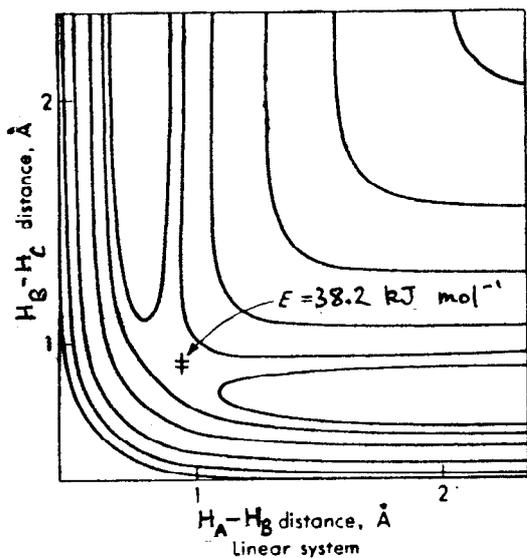
Long range electrostatic interactions can greatly increase P

e.g. For  $\text{CO}_2(001) + \text{C}^{16}\text{O}^{18}\text{O}$   $P \approx 0.5$  at 300K.

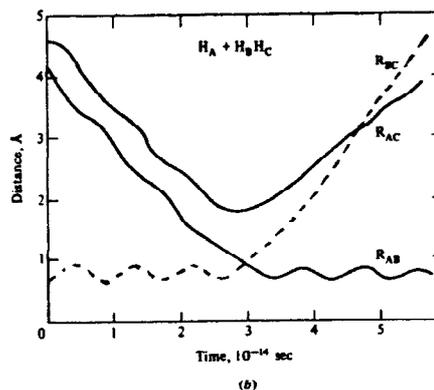
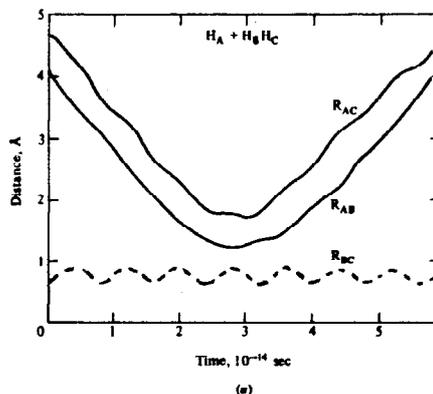
$$P \propto 1/T \quad \text{if long range attraction is dominant}$$

## **Handouts and overheads for Lecture II**

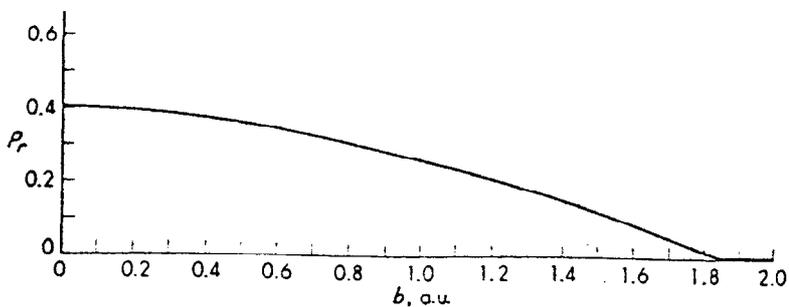
**Overheads V1 – V6 are identical to H1 – H6**



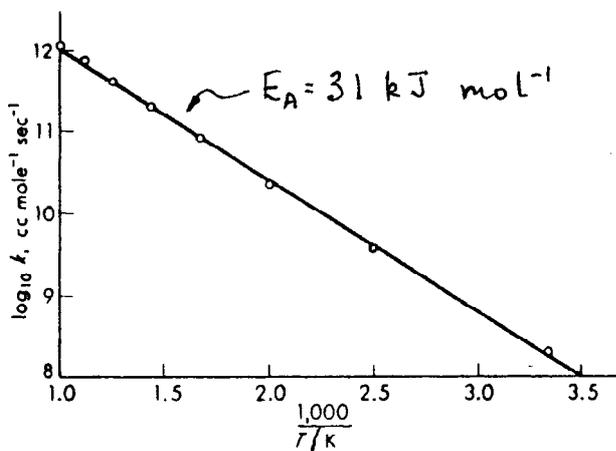
1 Potential-energy surfaces for the  $H + H_2$  reaction, as calculated by Porter and Karplus using a modified LEP procedure.



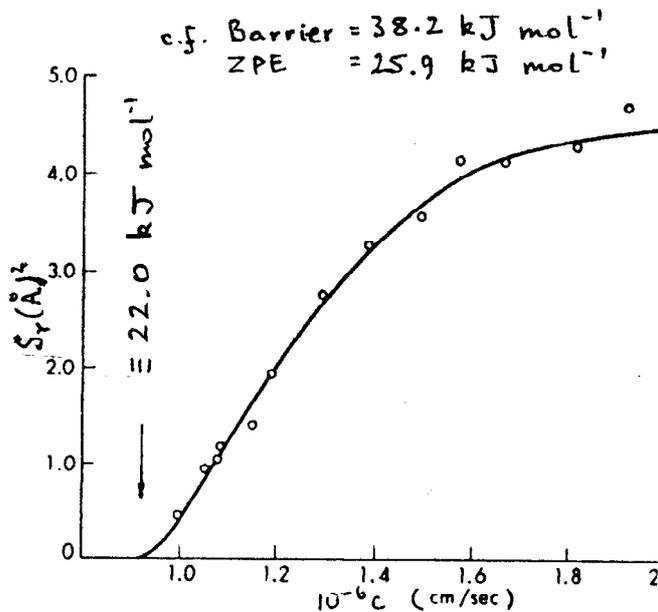
2 Internuclear distances in the reaction  $H_A + H_B H_C$  as a function of time: (a) a non-reactive collision; the small fluctuations in  $R_{BC}$  are due to molecular vibration; (b) a reactive collision; crossing of  $R_{AC}$  and  $R_{BC}$  at  $4 \times 10^{-14}$  secs indicates a rotation of  $H_A H_B$ . [From Karplus, Porter, and Sharma, *J. Chem. Phys.* 43, 3259 (1965).]



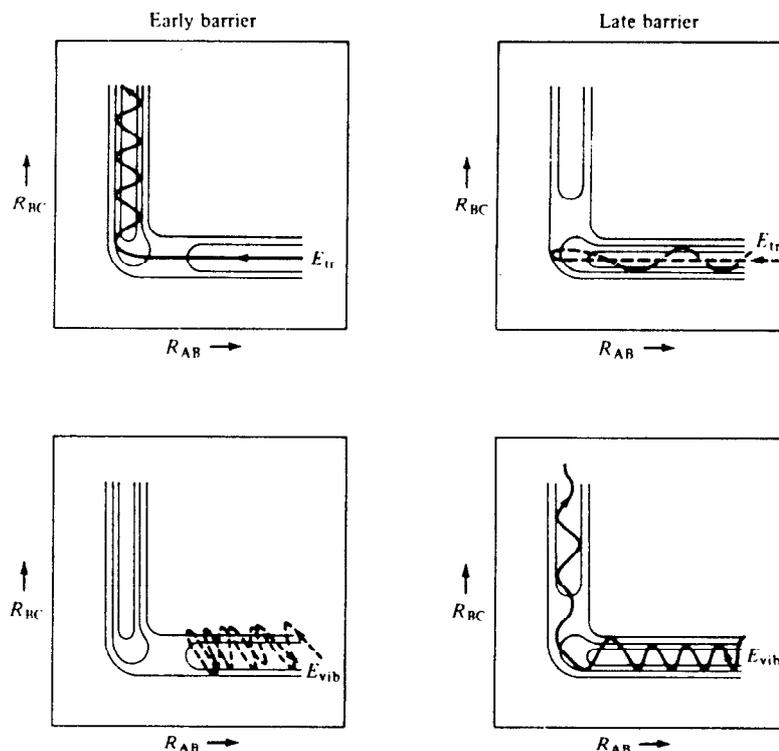
3 The variation of the reaction probability  $P_r$  with the impact parameter, for  $V_R = 1.17 \times 10^4$  cm/sec,  $J = 0$ , and  $v = 0$ .



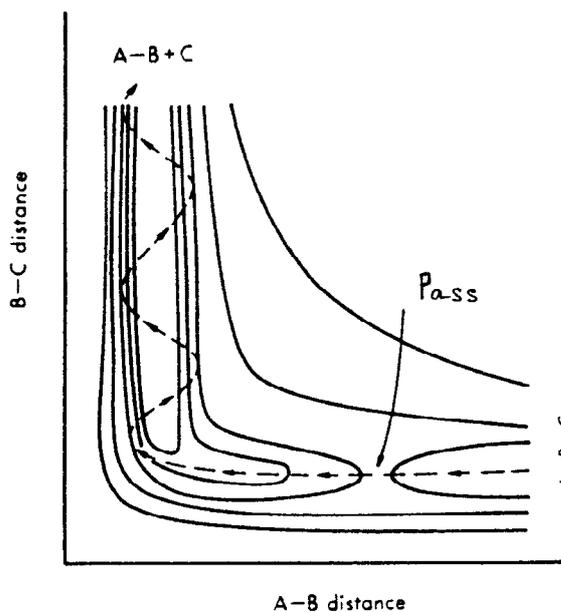
5 Arrhenius plot for the calculated dynamical rate constants for the  $H + H_2$  reaction.



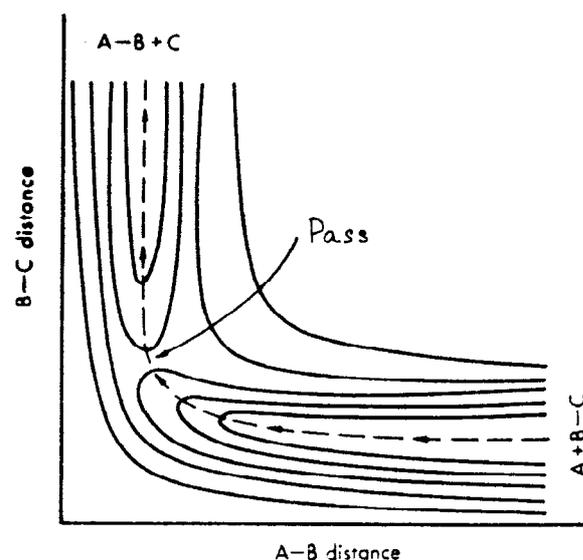
4 Reaction cross section  $S_r(c, J, v)$  as a function of  $c$   $H + H_2$ ;  $v = 0$  and  $J = 0$ .



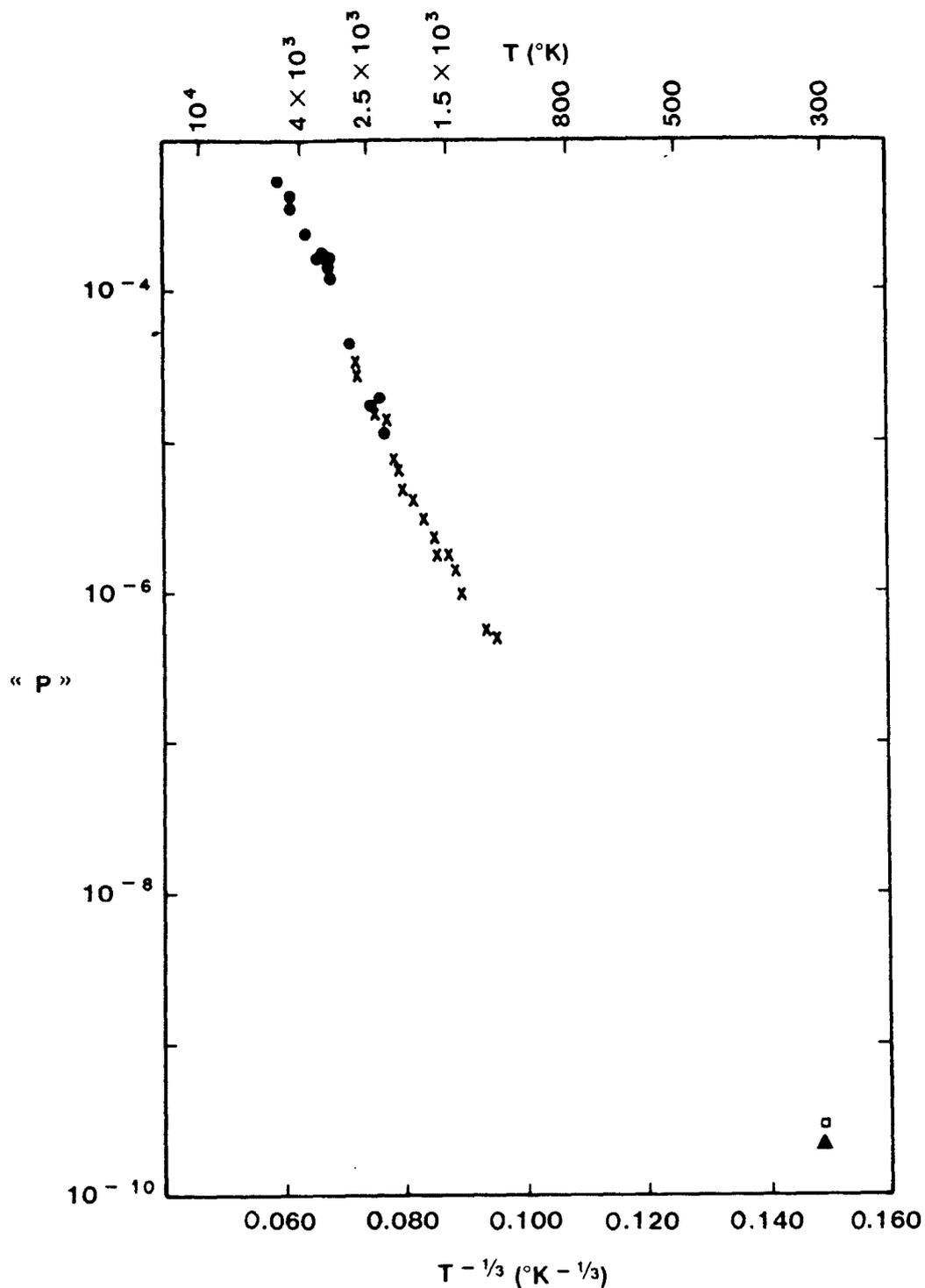
**6** Classically calculated trajectories on stylized potential surfaces for collinear  $A + BC$  reactions, showing dynamic effect of early versus late barrier. For high relative translational energies, reaction occurs for early barrier (top left) but not for late barrier (top right). For high vibrational energy of the  $BC$  reagent, reaction fails for early barrier (bottom left) but occurs for late barrier, i.e., the reagent's vibration assists in surmounting the (late) barrier. Adapted from J. C. Polanyi and W. H. Wong, *J. Chem. Phys.* **51**, 1439 (1969).



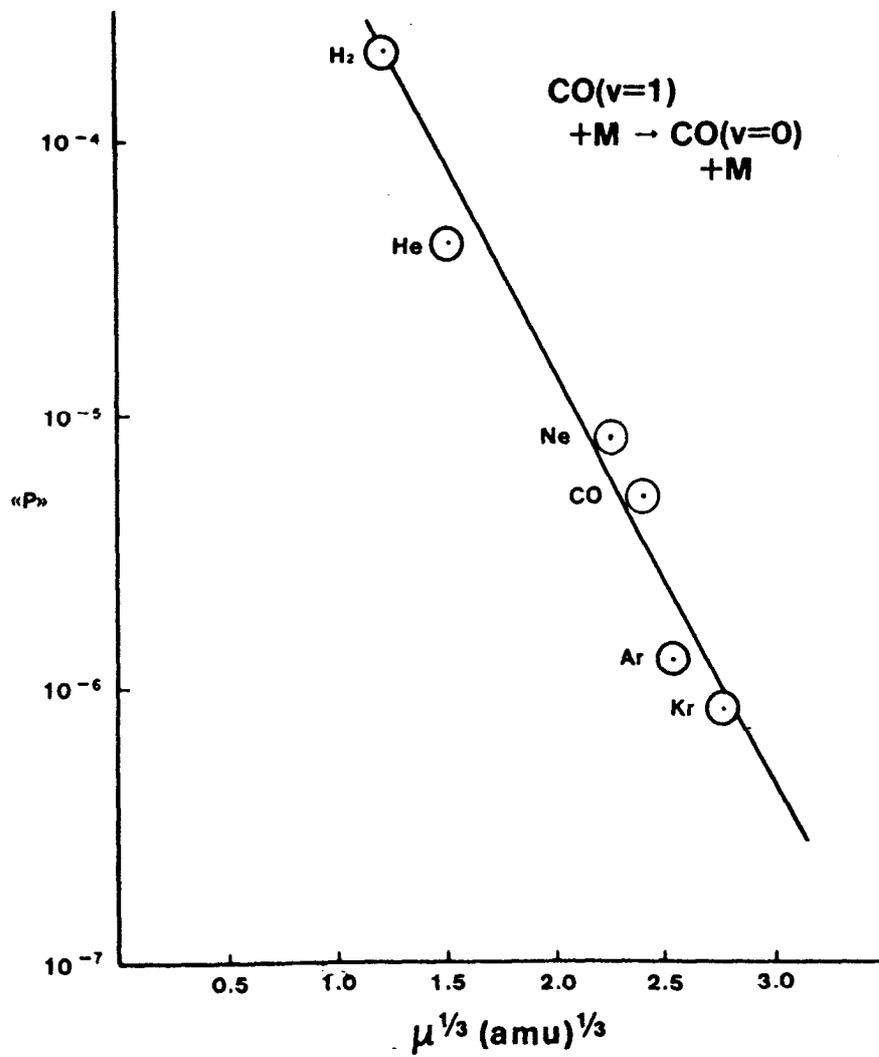
**7A** A potential-energy surface of the attractive type, for the reaction  $A + BC \rightarrow AB + C$ . The dashed line shows a typical reaction path, in which much of the energy released passes into vibration of the  $AB$  molecule.



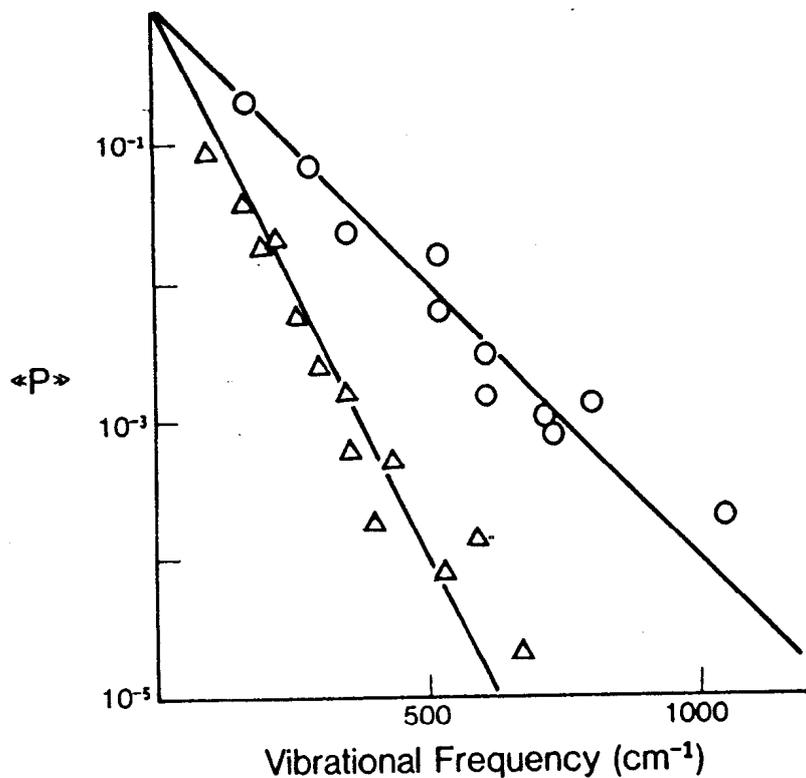
**7B** A repulsive surface, showing a typical reaction path. Little energy now goes into vibration of  $AB$ ; most goes into relative translational energy.



Vibrational relaxation probabilities for pure CO plotted as a function of temperature. ●, D. L. Matthews, *J. Chem. Phys.* **34**, 639 (1961); ×, W. J. Hookers and R. C. Milliken, *Chem. Phys.* **38**, 214 (1963); ▲, M. A. Kovacs and M. E. Mack, *Appl. Phys. Lett.* **20**, 487 (1972); ■, R. C. Milliken, *J. Chem. Phys.* **38**, 2855 (1963).



Vibrational relaxation probabilities for CO( $v = 1$ ) with different collision partners plotted logarithmically against collision reduced mass to the  $\frac{1}{3}$  power. Temperature is 295°



Vibrational relaxation probabilities at 300° K plotted as a function of vibrational frequency for nonhydrides ( $\Delta$ ) and hydrides ( $\circ$ ). [Data from tabulations by B. Stevens, "Collision Activation in Gases." Pergamon, Oxford, 1967.]

T. L. Cottrell and A. J. Matheson, *Trans. Faraday Soc.* **58**, 2336 (1962); **59**, 824 (1963).  
C. B. Moore, *J. Chem. Phys.* **43**, 2979 (1965).

This lecture needs a PE curve, such as VIB from ERI

### Elementary Reactions III

#### Historical

SCT → TST

Also called Activated Complex Theory; even Absolute Rate Theory in heyday: Write  $A + BC \rightleftharpoons A-B-C \ddagger \rightarrow A + BC$

Problems: Evaluation requires knowledge of surface near TS - can explain, but not predict

Newer expts provide data of a kind not considered by TST

However, full dynamical scattering calculations have promoted further interest in the fundamental assumptions of TST. For example, one first question might be to compare TST and full scattering (classical or quantum) using the same PE surface.

#### Basic Idea

Combination of statistics ("how many" TS species?) with dynamics ("how fast" do those species pass over into products?)

What is a transition state?

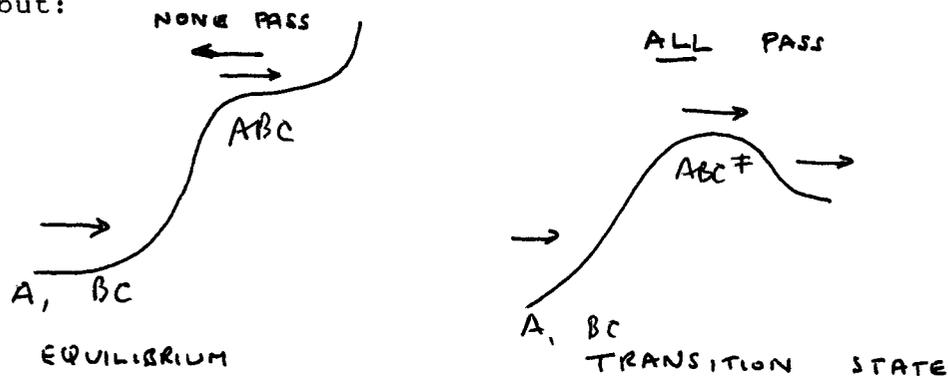
Surface (line, point) dividing reactants from products, in such a way that once system has reached TS from reactant side, it is bound to carry on to products without turning back.

#### Formulation

Deal with formulation is several stages

First ordinary derivations in terms of quasi-equilibrium, then in next lecture show how same result can be obtained without assuming equilibrium (and therefore justifying its application).

What is quasiequilibrium? Idea is to calculate concentrations of activated complexes on the basis of equilibrium between AC and reactants: NOT equilibrium, but:



So long as none return after TS, then concentration of ACs will be as for equilibrium

VIEW  
ERS/VIB

VIEW  
ERI/VIB

We thus assume that we can write

$$[ABC^*] = K^*[A][BC]$$

and

$$\text{Rate} = \nu^*[ABC^*]$$

Thus

$$k_2 = \text{Rate}/[A][BC] = \nu^*K^*$$

and the problem is of evaluating  $\nu^*$  and  $K^*$

We shall be looking at Classical Thermodynamic and Statistical Thermodynamic formulations

H/O 5-6  
V1 V2

\*\*\*\*\* DON'T TAKE NOTES: ALL ON H/O  
\*Remedial Statistical Thermodynamics! \* USE TWO O/H PROJECTORS TO  
\*\*\*\*\* BE ABLE TO REFER BACK TO V1 (p5)

Thermodynamic evaluation

H/O 7-8  
V3 V4

Rate expression

Temperature dependence: relation between  $\Delta H^\ddagger$  and  $E_a$

Statistical evaluation

H/O 8  
V4

Point out that  $q' = q/V$  and that  $q'' = q'$  with motion leading to reaction being factorized out

Activation Energies in TST, and whether they are T-dependent

Again use definition of  $E_a$  from Arrhenius expression. Implicit that  $E_a$  should be constant with T. But examination of any of the rate expressions obtained so far shows that it is likely to vary: ie curved Arrhenius plots

Indeed, TST is in some ways more useful for predicting such T-dependences than for predicting absolute rate constants (because TST makes no predictions about the heights of barriers.

We remember that  $\Delta \epsilon_0/kT = \Delta E_0/RT$  and write the statistical expression in the form

$$k_2 = \frac{kT}{h} \frac{q''_{ABC}}{q'_A q'_{BC}} e^{-\Delta E_0/kT} = \frac{kT}{h} \frac{q''_{ABC}}{q'_A q'_{BC}} e^{-\Delta E_0/RT}$$

per molecule ↑ per mole

Then

$$E_a = RT^2 \frac{d \ln k_2}{dT} = \Delta E_0 + RT + RT^2 \frac{d \ln q''_{ABC}}{dT} - RT^2 \frac{d \ln q'_A q'_{BC}}{dT}$$

Temperature dependence will thus be determined by how the partition functions vary with T.

In general,  $d \ln(q''_{ABC})/dT$  increases more rapidly than  $d \ln(q'_A q'_{BC})/dT$ , so that  $E_a$  increases with increasing temperature.

importance of being able to make extrapolation →

## **Handouts and overheads for Lecture III**

REMEDIAL STATISTICAL THERMODYNAMICS

The Boltzmann distribution tells us that

$$n_i = \text{const.} \times g_i e^{-\epsilon_i/kT}$$

where  $n_i$  is the number of particles possessing energy  $\epsilon_i$  and  $g_i$  is the degeneracy of that level. Since

$$N = \sum n_i = \text{const.} \times \sum g_i e^{-\epsilon_i/kT}$$

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} = \frac{g_i e^{-\epsilon_i/kT}}{q}$$

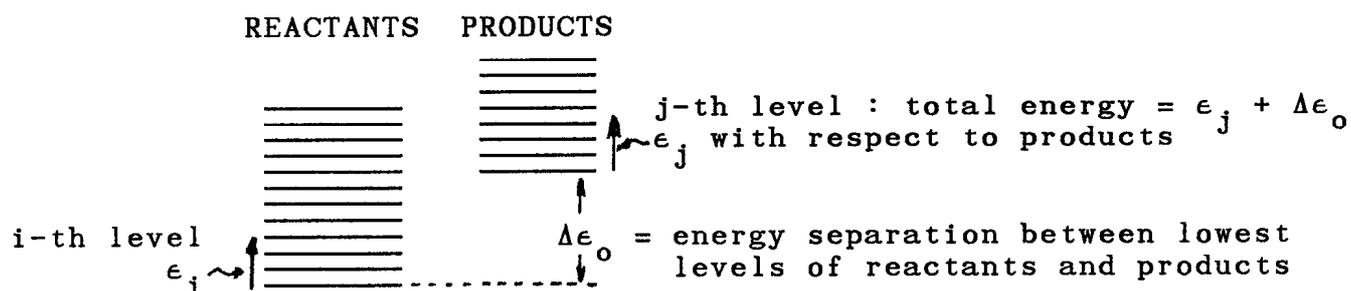
The quantity  $q = \sum g_i e^{-\epsilon_i/kT}$  is called the partition function, since it describes the partitioning of particles between the available levels. It may be evaluated from molecular constants obtained, for example, spectroscopically. Summation (or integration) of the explicit forms of  $\epsilon_i$  for translational, rotational and vibrational energy leads to the following formulae for  $q$  in a diatomic molecule

translation $(q_t)^3$	rotation $(q_r)^2$	vibration $(q_v)$
$(3 - D)$		

$\left[ \frac{2\pi mkT}{h^2} \right]^{3/2} v$	$\frac{8\pi^2 I kT}{h^2}$	$(1 - e^{-h\nu/kT})^{-1}$
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Given the Born-Oppenheimer approximation, the additivity of energies means that  $q_{\text{total}} = q_t q_r q_v$ .

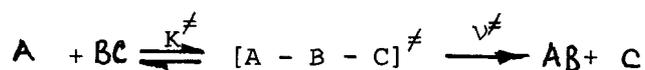
An expression can be derived for equilibrium constants in terms of partition functions in the following way. Let us consider the distribution of particles between the levels in the reactants and products: since there is chemical equilibrium there is also thermal equilibrium, so that the populations will be described by Boltzmann statistics. The diagram below illustrates the disposition of the levels



$$\frac{N_{\text{PRODUCTS}}}{N_{\text{REACTANTS}}} = \frac{\sum_j n_j}{\sum_i n_i} = \frac{\sum_j g_j e^{-(\epsilon_j + \Delta\epsilon_0)/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} = \frac{q_{\text{PRODUCTS}}}{q_{\text{REACTANTS}}} e^{-\Delta\epsilon_0/kT}$$

$$K_c = \frac{N_{\text{PRODUCTS}}/V}{N_{\text{REACTANTS}}/V} = \frac{q'_{\text{PRODUCTS}}}{q'_{\text{REACTANTS}}} e^{-\Delta\epsilon_0/kT}$$

where  $q' = q/V$ . Remember that the 3 - D translational partition function is proportional to  $V$ , so that  $q'$  has a simplified form.

Transition State Theory : Classical Thermodynamics

$$\text{Rate} = v^\ddagger [ABC^\ddagger]$$

Quasi-equilibrium assumption puts

$$[ABC^\ddagger] = K_C^\ddagger [A][BC]$$

Thus the second order rate constant,  $k_2$  ( $= \text{Rate}/[A][BC]$ ) is given by

$$k_2 = v^\ddagger K_C^\ddagger$$

Remembering the thermodynamic relation

$$\Delta G^\ddagger = -RT \ln K_p^\ddagger,$$

we may write, for the gas phase,

$$K_C^\ddagger = (T/298) e^{-\Delta G^\ddagger / RT}$$

if the standard state applies to  $1 \text{ mol dm}^{-3}$  at 298K.

Thus

$$k_2 = v^\ddagger (T/298) e^{-\Delta G^\ddagger / RT} \quad (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$$

or, since  $\Delta G = \Delta H - T\Delta S$

$$k_2 = v^\ddagger (T/298) e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

One way of obtaining a value for  $v^\ddagger$  assumes that the motion follows the equipartition law, i.e. it has two degrees of freedom, each of which contributes an energy  $\frac{1}{2}kT$ . That is

$$\epsilon = hv^\ddagger = kT$$

or  $v^\ddagger = kT/h$ .

Thus the complete expression for  $k_2$  is

$$k_2 = \frac{kT}{h} \frac{T}{298} e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

Comparison with the experimental Arrhenius expression

$$k_2 = A e^{-E_a / RT}$$

is achieved by taking logarithms of each and differentiating with respect to temperature

$$RT^2 \frac{d \ln k_2}{dT} = 2RT + \Delta H_{\ddagger}^{\ominus}$$

and  $= E_a$

$$\therefore \Delta H_{\ddagger}^{\ominus} = E_a - 2RT$$

$$\therefore k_2 = \left\{ \frac{kT}{h} \frac{T}{298} e^2 e^{\Delta S_{\ddagger}^{\ominus}/R} \right\} e^{-E_a/RT}$$

The bracketed terms correspond to the collision frequency factor in collision theory, numerically about  $5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ; since  $(kT/h)(T/298)e^2 \sim 4.7 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 298K, it follows that  $\Delta S_{\ddagger}^{\ominus} \sim -57 \text{ J K}^{-1} \text{ mol}^{-1}$  even for a "P-factor" of unity.

Transition State Theory: Statistical thermodynamics

The equilibrium constant,  $K_c^{\ddagger}$ , is written in terms of partition functions

$$K_c^{\ddagger} = \frac{N_{ABC}/V}{N_A/V \cdot N_{BC}/V} = \frac{q_{ABC}/V}{q_A/V \cdot q_{BC}/V} e^{-\Delta \epsilon_0/kT}$$

From the equation derived earlier

$$k_2 = \nu^{\ddagger} K_c^{\ddagger} = \nu^{\ddagger} \frac{q'_{ABC}}{q'_A q'_{BC}} e^{-\Delta \epsilon_0/kT}$$

$$q' = q/V$$

where  $q'$  represent volume independent partition functions. We now factorise from  $q'_{ABC}$  the one vibration, frequency  $\nu^{\ddagger}$ , that leads to reaction

$$q'_{ABC} = q''_{ABC} q_{ABC}^{\ddagger \text{vib}} = q''_{ABC} (1 - \exp(-h\nu^{\ddagger}/kT))^{-1}$$

Since  $\nu^{\ddagger}$  is small,  $h\nu^{\ddagger}/kT \ll 1$  and  $q_{ABC}^{\ddagger \text{vib}} = kT/h\nu^{\ddagger}$

$$q'' = q'/q^{\ddagger}$$

$$\therefore k_2 = \nu^{\ddagger} \cdot \frac{q''_{ABC} \cdot kT/h\nu^{\ddagger}}{q'_A q'_{BC}} e^{-\Delta \epsilon_0/kT}$$

$$= \frac{kT}{h} \frac{q''_{ABC}}{q'_A q'_{BC}} e^{-\Delta \epsilon_0/kT} = \frac{kT}{h} \frac{q''_{ABC}}{q'_A q'_{BC}} e^{-E_a/RT}$$

$$E_a = RT^2 \frac{d \ln k_2}{dT}$$

BY DEFINITION

$$= \Delta E_0 + RT + RT^2 \frac{d \ln q''_{ABC}}{dT} - RT^2 \frac{d \ln q'_A q'_{BC}}{dT}$$

T-dependence  $\rightarrow$  HOW  $q$ 's VARY WITH T  
 GENERALLY  $\frac{d \ln q''_{ABC}}{dT}$  INCREASES FASTER THAN  $\frac{d \ln q'_A q'_{BC}}{dT}$   $\therefore E_a \uparrow T \uparrow$



- ER IV 2 -

N.B. There is a handwritten page for suggested presentation: first, transcribe the degrees of freedom, and derive  $k_2$  in terms of Collision theory and TST. He makes a partition function substitution on  $q_{int}$  and  $h$ .

What does TST predict for hard sphere reactants?  
 Through basis of derivation: result as collision theory with  $Z'$   
 Note also identification of  $Z'$  with  $(kT/h) \times (q^{\ddagger}/q_R)_h$

ER4: View 5

Frequency factors for more complex reactions

First  $A + B$  First, assume all  $q_{tr}, q_{vib}, q_{rot}$   
 $A-B$  has  $3t, 2r,$  and  $1v$  which is  $\nu^{\ddagger}$  equal for  $A, BC,$  and  $ABC^{\ddagger}$   
 Leads to  $(q^{\ddagger}/q_R) = q_R^2/q_t^3$   
 Now co-linear  $A + BC$   
 $A-B-C$  has  $3t, 2r$  and  $4v$  one of which is  $\nu^{\ddagger}$   
 Leads to  $(q^{\ddagger}/q_R) = q_v^2/q_t^3$   
 Thus

$$\frac{k_2(A + BC)}{k_2(A + B)} = \text{"P factor"} = \frac{q_v^2}{q_r^2}$$

Given that  $q_v = 1 - 10$  and  $q_r = 10 - 10^3$ , P can be expected to be typically  $10^{-2}$ , in agreement with experimental findings

For two non-linear polyatomic reactants, the ratio of partition functions becomes

$$\frac{q_v^5}{q_r^5}$$

which is  $10^{-5}$  or less. This value is rather smaller than ordinary P factors: more like three orders of magnitude slower than  $A + B$  reaction. However, explained when it is realised that the "new" internal modes in  $^{\ddagger}$  are low frequency motions, such as free internal rotations, and unusually free bending vibrations

Adiabatic Selection

ER4: View 6

An attempt to avoid the quasi-equilibrium hypothesis  
 Assume that reaction is adiabatic: that is, no change in internal quantum numbers during reaction. Will describe calculation for vibrational adiabaticity - easily extended for rotations as well.  
 Write a rate constant for each vibrational level in collision theory form, and ultimately sum total rate over all levels

[Through derivation on handout]

(internal) → That is, same result as obtained in earlier derivations, but without any assumption of equilibrium. The partition functions are present in the expression

(i) for " because of the sum of activation energies, and

(ii) for reactants because of a thermally equilibrated population

Note, however, the tacit assumption that all reactant pairs reaching the transition state are on their way to become products

#### "Real Assumptions of TST"

1. All flux across critical dividing surface is reactive flux

2. Reactants are themselves thermally equilibrated

3. Born-Oppenheimer approximation is valid

Note that if both 1 and 2 are true, then the occupancy of levels at the dividing surface will be described by Boltzmann statistics.

Assumption 1 may be tested by dynamic (scattering) calculations confined to the barrier region

Reactants themselves usually are equilibrated, but might not be so for very fast reactions at low pressures (a situation which certainly applies in unimolecular reactions at low pressure)

A further assumption

4. Separability of motions at S\*

is not essential to the treatment, although it makes TST mathematically more accessible

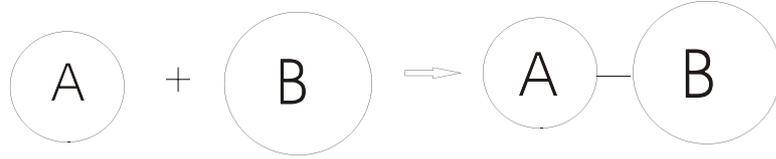
#### Quantum effects

Quantum treatments of TST give essentially the same results as the semiclassical approach used here. Sometimes essential to incorporate quantum effects: already seen tunnelling in the OH + H<sub>2</sub> reaction. Will discuss further in connection with condensed phase reactions

## **Handouts and overheads for Lecture IV**

# Collision Number and Partition Functions

## 1. To show that CT and TST give the same results for hard spheres



Degrees of freedom

translation (t)	3	3	3
rotation (r)	0	0	2
vibration (v)	0	0	$(1 - 1^\neq) = 0$

Partition functions

$$(q_t')^3 \quad \left( \frac{2\pi m_A kT}{h^2} \right)^{3/2} \quad \left( \frac{2\pi m_B kT}{h^2} \right)^{3/2} \quad \left( \frac{2\pi(m_A + m_B)kT}{h^2} \right)^{3/2}$$

$$(q_t)^2 \quad \frac{8\pi I kT}{h^2}$$

N.B.  $I = \frac{(m_A m_B)}{(m_A + m_B)} (r_A + r_B)^2 = \mu (r_A + r_B)^2$

$$q_v \quad (1 - \exp(-hv^\neq/kT))^{-1} \approx kT/hv^\neq \text{ for } v^\neq \rightarrow 0$$

Thus  $k_2 = \frac{kT}{h} \frac{q_{AB}''}{q_A' q_B'} \exp(-\Delta\epsilon_0/kT) = \frac{kT}{h} \frac{(q_{AB}')_t^3 (q_{AB}')_r^2}{(q_A')_t^3 (q_B')_t^3} \exp(-\Delta\epsilon_0/kT)$  (1)

Substituting the partition functions yields

$$k_2 = \frac{kT}{h} \cdot \frac{h}{kT} \cdot \pi (r_A + r_B)^2 \cdot \left( \frac{8kT}{\pi\mu} \right)^{1/2} \cdot \exp(-\Delta\epsilon_0/kT)$$

$$= Z'_{AB} \exp(-\Delta\epsilon_0/kT) \quad , \text{ as collision theory.}$$
(2)

Note also that

$$Z'_{AB} = \frac{kT}{h} \frac{(q_{AB}')_t^3 (q_{AB}')_r^2}{(q_A')_t^3 (q_B')_t^3} = \frac{kT}{h} \left( \frac{q''}{q_R} \right)_{\text{hard sphere}}$$
(3)

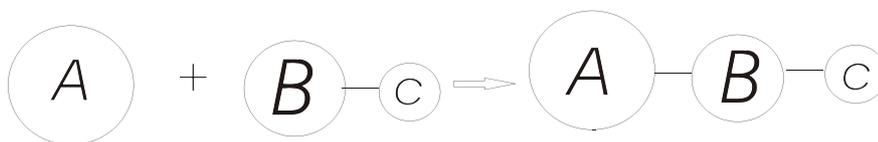
## 2. Estimation of $P$ -factors in CT

In what follows, an assumption is made that *for order of magnitude purposes*,  $q_t$  are the same for each of the reactants and for the transition state; that  $q_r$  are all the same as each other; and that  $q_v$  are all the same.

Equation (1) for the hard-sphere case thus be written out

$$k_2 = \frac{kT}{h} \frac{q_{AB}''}{q_A' q_B'} \exp(-\Delta\epsilon_0/kT) = \frac{kT}{h} \frac{(q')_t^3 (q')_r^2}{(q')_t^3 (q')_t^3} \exp(-\Delta\epsilon_0/kT) = \frac{kT}{h} \frac{(q')_r^2}{(q')_t^3} \exp(-\Delta\epsilon_0/kT) \quad (4)$$

Now we repeat the same type of analysis for a system that is more complex than the hard-sphere case. Let us consider a reaction between an atom and a diatomic molecule proceeding *via* a linear transition state.



Degrees of freedom

translation (t)	3	3	3
rotation (r)	0	2	2
vibration (v)	0	1	$(4 - 1^{\neq}) = 3$

$$k_2 = \frac{kT}{h} \frac{q_{AB}''}{q_A' q_B'} \exp(-\Delta\epsilon_0/kT) = \frac{kT}{h} \frac{(q')_t^3 (q')_r^2 (q')_v^3}{(q')_t^3 (q')_t^3 (q')_r^2 (q')_v} \exp(-\Delta\epsilon_0/kT) = \frac{kT}{h} \frac{(q')_v^2}{(q')_t^3} \exp(-\Delta\epsilon_0/kT) \quad (5)$$

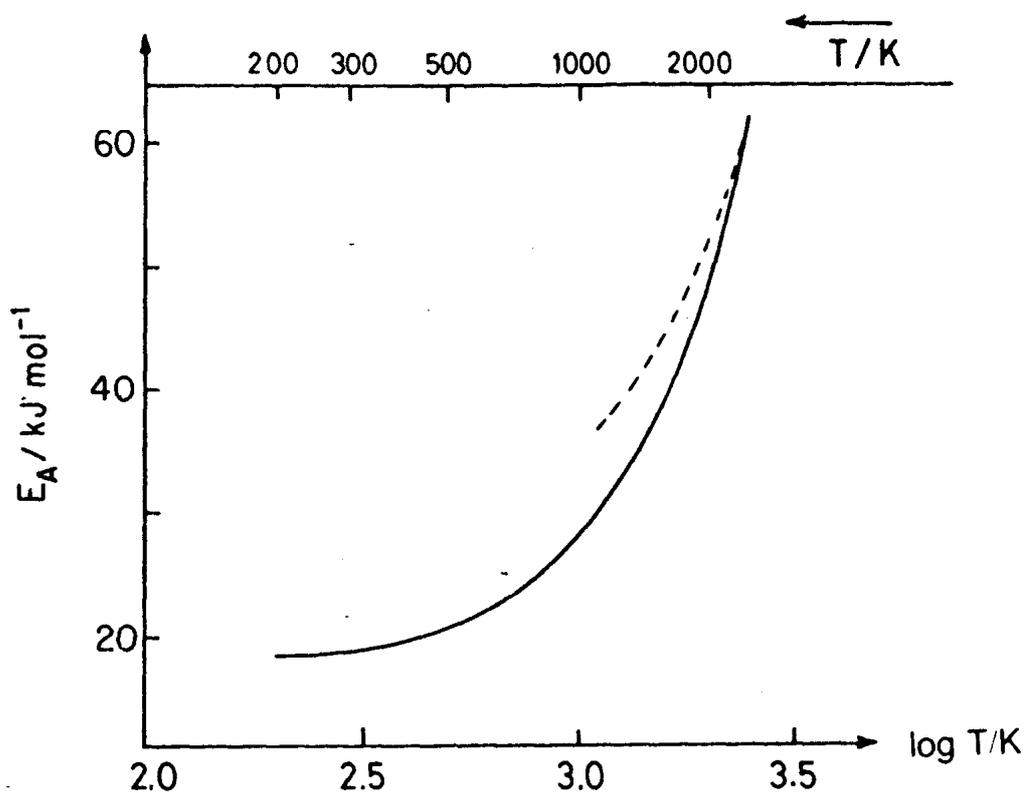
Thus, dividing equation (5) for  $k_{A+BC}$  by equation (4) for  $k_{A+B}$ , we obtain

$$\begin{aligned} \frac{k_{A+BC}}{k_{A+B}} &= \frac{(q')_v^2}{(q')_t^2} \\ &= P, \text{ by definition.} \end{aligned}$$

Since  $q_v$  are typically of the order of 1–10, and  $q_r$  are typically 100–1000, this equation suggests that the  $P$ -factor for the linear  $A + BC$  reaction will be, say,  $10^{-3}$  or  $10^{-4}$ .

Similar exercises can be carried out for a non-linear transition state and, of course, for yet more complex reactions involving polyatomic transition states. In general, the predicted  $P$ -factor is the ratio of vibrational partition functions for the transition state divided by rotational partition functions for the reactants, all raised to some power that depends on the complexity of the reaction. Because the ‘new’ internal modes in the transition state are low frequency motions (internal rotations and unusually free bending motions),  $q_v$  for the transition state is usually larger (order of 10–100) than for ‘ordinary’ molecules.

Bimolecular Reaction Rate Coefficients



Change of activation energy with temperature for  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  as calculated from Eq. (3.60). A nonlinear transition state with vibrational frequencies  $\omega_i/\text{cm}^{-1} = 3227, 2353, 939, 572, 453$ , and potential maximum  $V^* = 21$  kJ was assumed (Smith and Zellner, 1974). The dashed curve corresponds to the classical limit of fully excited vibrations.

**Table 2.** Calculated transition structure properties for HOHH.

	BEBO <sup>a</sup>	LEPS <sup>a</sup>	<i>ab initio</i> <sup>b</sup>
$r_{\text{H-O}}/\text{\AA}$	0.96	0.96	0.98
$r_{\text{O..H}}/\text{\AA}$	1.24 <sup>c</sup>	1.21	1.33
$r_{\text{H-H}}/\text{\AA}$	0.85 <sup>d</sup>	0.85	0.85
H-O-H angle	104.6	104.6	97.6
O-H-H angle	180	180	165
$V^*$	21	21	31(26) <sup>e</sup>
$\omega_i/\text{cm}^{-1}$	3727, 909i, 2354	3741, 1244i, 1936	3368, 1655i, 1945
	939, 453, 578	1036, 557, 758	1248, 440, 686
$E_A/\text{kJ (300 K)}^f$	20	19	23(19) <sup>g</sup>

<sup>a</sup> Smith and Zellner (1974).

<sup>b</sup> Walch and Dunning (1980); Schatz and Walch (1980).

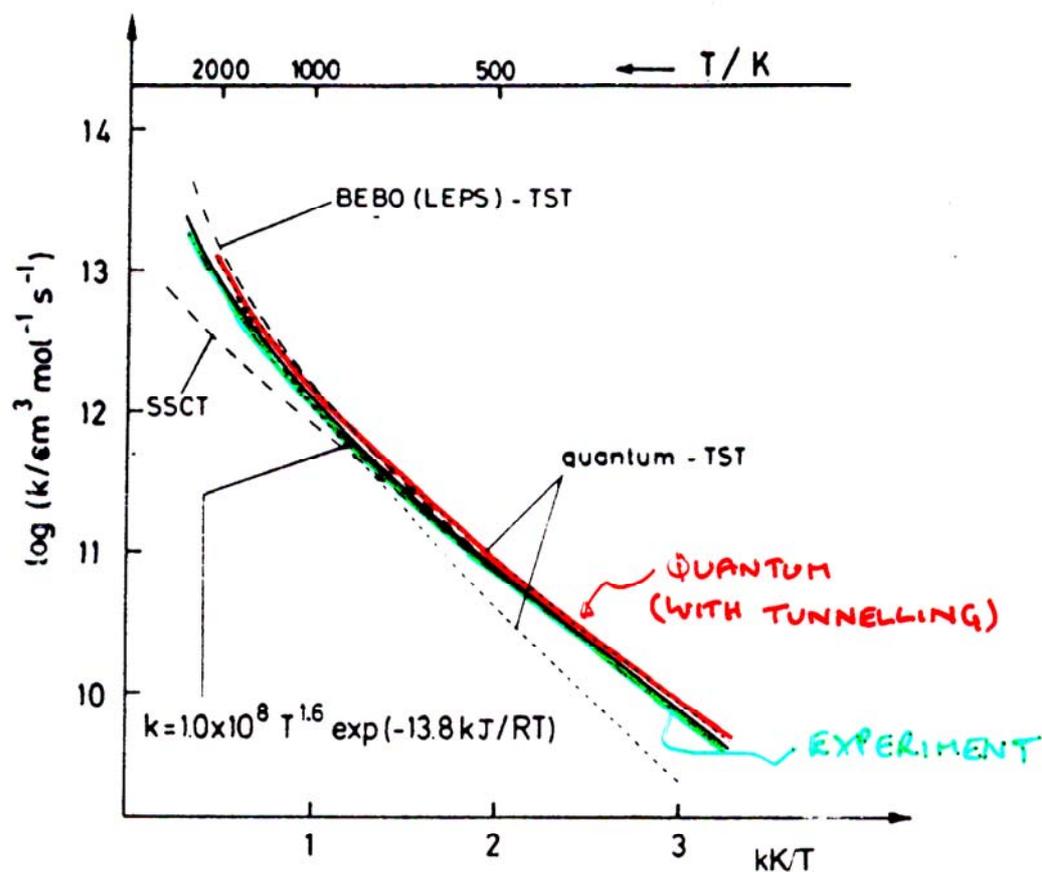
<sup>c</sup> Equilibrium bond length of OH is 0.98 Å.

<sup>d</sup> Equilibrium bond length of H<sub>2</sub> is 0.74 Å.

<sup>e</sup> The smaller barrier was obtained with a larger basis set.

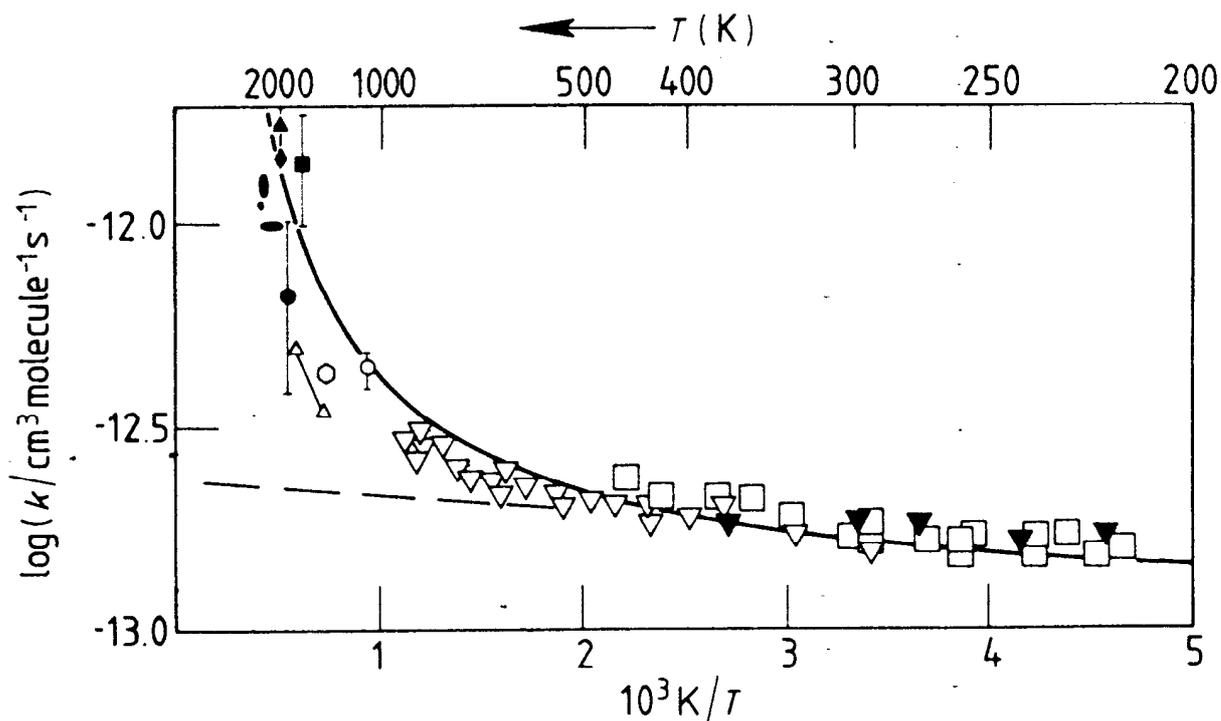
<sup>f</sup> Calculated from Eq. (3.60).

<sup>g</sup> Includes a tunneling correction.

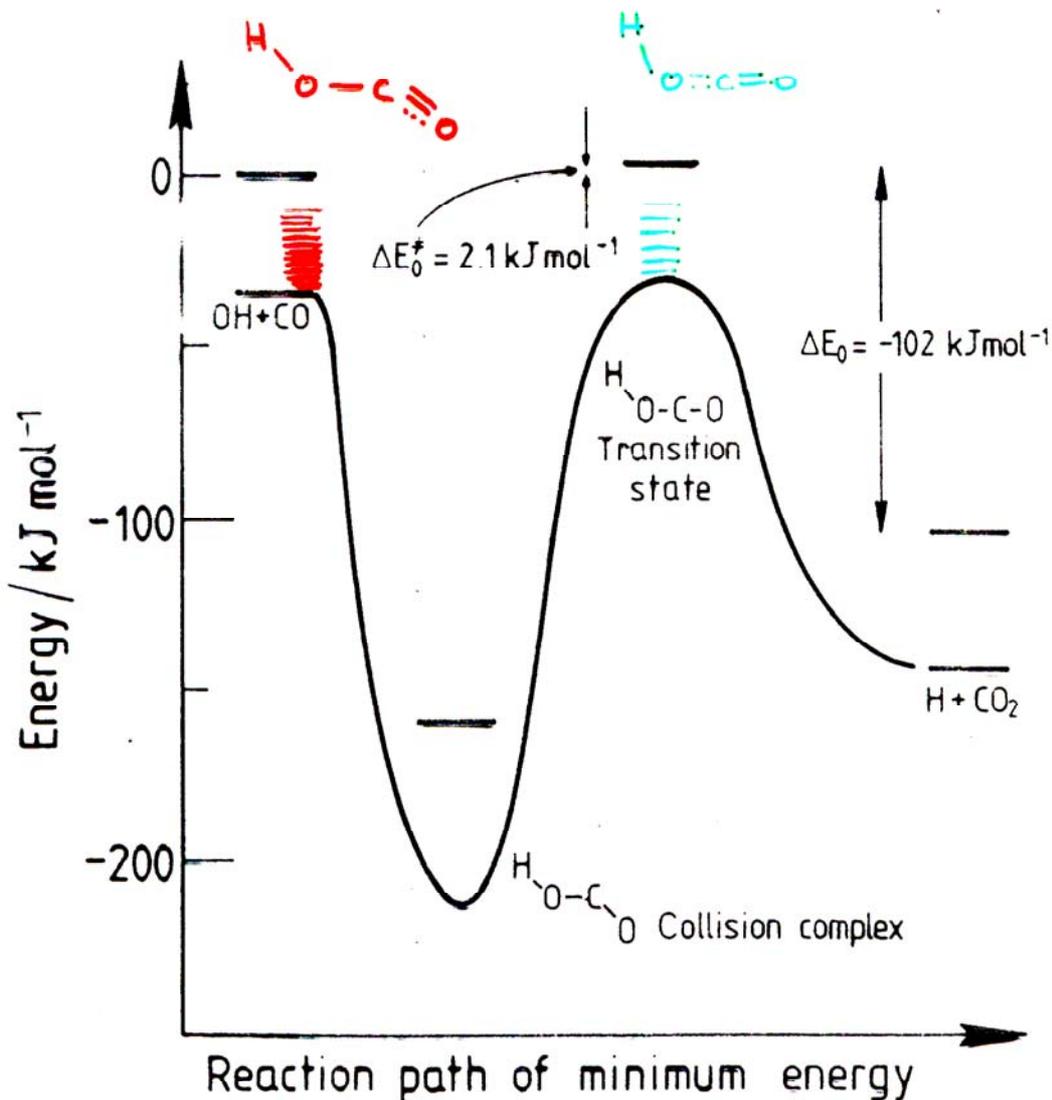


Arrhenius plot for  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . The heavy curve corresponds to the expression recommended by Zellner (1979). Theoretical results refer to: BEBO(LEPS)-TST, Smith and Zellner, (1974); quantum-TST, Schatz and Walch (1980) (the upper curve includes a tunneling correction); SSCT, Zellner and Steinert (1981).

Thermal rate data



Arrhenius plot of the rate constants for the reaction  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ . The experimental data below 1000 K are those of Smith and Zellner<sup>33</sup> ( $\square$ ), Davis, Fischer and Schiff<sup>31</sup> ( $\blacktriangledown$ ), and Steinert and Zellner<sup>30</sup> ( $\triangle$ ). The points above 1000 K are taken from the review by Wilson<sup>29</sup>. The full line shows the result of TST calculations based on the model of reaction illustrated in Figure 5.6. The dashed line shows an extrapolation of the Arrhenius expression chosen by Davis et al. to represent their low-temperature ( $220 \leq T \leq 373 \text{ K}$ ) data

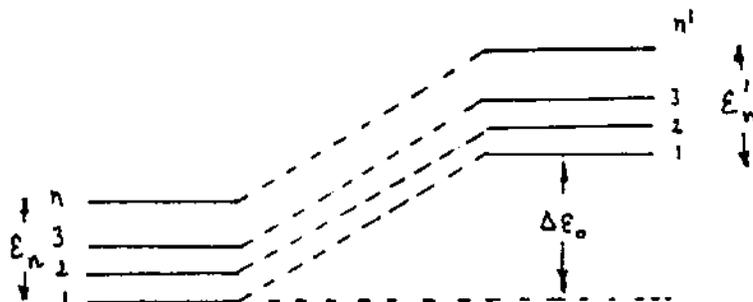


Transition states for 2 processes needed.  
(different forms of HOCO)

$q_{\ddagger}$  depends crucially on  $T$

particularly in this case  $q_{\ddagger}(\text{vib})$

## Adiabatic Selection from Boltzmann Population



Difference of energy between  $n$ th state in reactant and  $n$ th state in "transition state" is

$$\Delta\epsilon_n = \Delta\epsilon_0 + \epsilon'_n - \epsilon_n$$

Rate constant for each  $n$ th state is written in collision theory form

$$k_n = Z' e^{-\Delta\epsilon_n/kT} = Z' e^{-\Delta\epsilon_0/kT} e^{-\epsilon'_n/kT} e^{\epsilon_n/kT}$$

Concentration of  $n$ th state,  $[R_n]$ , in reactant R is given by Boltzmann distribution

$$[R_n]/[R] = e^{-\epsilon_n/kT} / \sum e^{-\epsilon_n/kT}$$

By definition,  $\sum e^{-\epsilon_n/kT}$  is the (internal vibrational) partition function for the reactant,  $q_R$ , so that

$$\text{Rate} = \sum k_n [R_n] = Z' \frac{e^{-\Delta\epsilon_0/kT} \sum e^{-\epsilon'_n/kT}}{q_R} [R] = Z' \left[ \frac{q^\ddagger}{q_R} \right]_{\text{int}} e^{-\Delta\epsilon_0/kT} [R]$$

where  $(q^\ddagger/q_R)_{\text{int}}$  is the ratio of internal (i.e. vibrational [rotational]) partition functions of the transition state and reactants.

Thus

$$k_2 = Z' \left[ \frac{q^\ddagger}{q_R} \right]_{\text{int}} e^{-\Delta\epsilon_0/kT}$$

But we have shown ("Collision number and partition function") that

$$Z' = \frac{kT}{h} \left[ \frac{q''^\ddagger}{q_R} \right]_{\text{hard sphere}} \quad \text{so that}$$

$$k_2 = \frac{kT}{h} \left[ \frac{q''^\ddagger}{q_R} \right]_{\text{total}} e^{-\Delta\epsilon_0/kT}$$

## Elementary Reactions V

### Unimolecular Reactions

"At first sight"

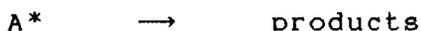
Unimolecular reaction simplest kind of elementary reaction, since it involves isomerization or decomposition of a single isolated reactant molecule



e.g.



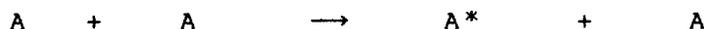
An energy barrier must be overcome, so process must really be



What is A\*?

radioactive species  
photochemically excited  
e.g.  $\text{CH}_2\text{N}_2 + h\nu$   
chemically activated  
e.g.  $\text{CH}_3 + \text{CH}_2\text{Cl}$

But also THERMAL activation



or

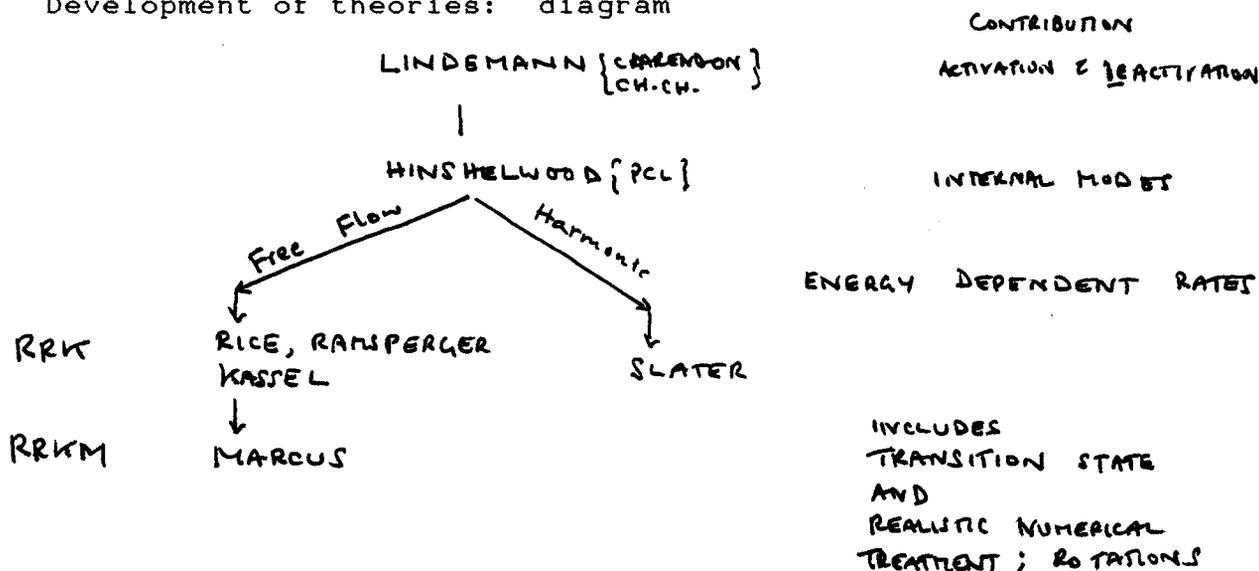


(i.e. activating collisions with a non-reacting partner).

(At beginning of 20th century, many reactions known to be 1st order and assumed unimolecular, and unimolecular reactions thought to be 1st order under all conditions.) However, if bimolecular collisions activate the molecules, process might be expected to be second order.

Explanation proposed by Lindemann - still essentially basis of modern theories

Development of theories: diagram



NB: If product and reactant are distinct entities, there has to be a barrier separating them.

Lindemann mechanism

H/O 1  
 (p11) Variable order: 2<sup>nd</sup> order at low p (- Point out equivalence of P and [A].)  
 Dominant pathways at high and low pressures  
 VIEW Define  $k_{uni}$  (Rate/[A])  
 ERG/1 (TOP) Fall off graphs  
 Idea of limiting high pressure k:  $k_{\infty}$  (1st order) and low p ( $k_0$ , 2<sup>nd</sup> order)  
 (= Fig 1 on H/O)  
 Quantitative detail

H/O 1 (p11) Invert Eq.(5) → Eq.(7)  
 Expectations  
 VIEW ERG/1 (1) linear → actually curved  
 (BOTTOM) (ii)  $k_1 = Z' \exp(-E_c/RT)$  → actually greatly exceeded

(= Fig 2 on H/O) Start with (ii) as rather easier to explain  
 Problem can be expressed another way  
Transition pressure taken as point where  $k_{uni} = \frac{1}{2} k_{\infty}$   
 (i.e. half way to limiting rate constant): can be seen  
 from second form of Eq.(5) to be =  $k_{\infty}/k_1$ . Experimental  
 values of transition pressure are far lower than those  
 calculated.  
 E.g. for cis- to trans-but-2-ene at 469°C the  
 experimental value is 0.04 Torr, and the calculated  
 $9 \times 10^6$  Torr.  
 Once again evidence for  $k_1$  being far larger than simple  
 calculation indicates.

SHOWN IN  
 BLUE ON H/O VI

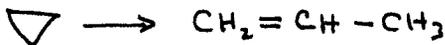
Hinshelwood Modification

Internal energy, as well as the collisional energy, can contribute to the breaking (or isomerization) of the critical bond. Thus the activation energy term  $\exp(-E_c/RT)$  has to be modified:

Equation (8) from statistical thermodynamics

N.B. About 1/3 to 1/2 of the available vibrations need to be used.

For example



$3 \times 9 - 6 = 21; s \approx 7$

Note that increased complexity leads to larger rates (contrast with bimolecular kinetics). Time delay between activation and deactivation and/or reaction allows energy to flow into critical bond

Energy Flow

Is there evidence that energy flows in this way?

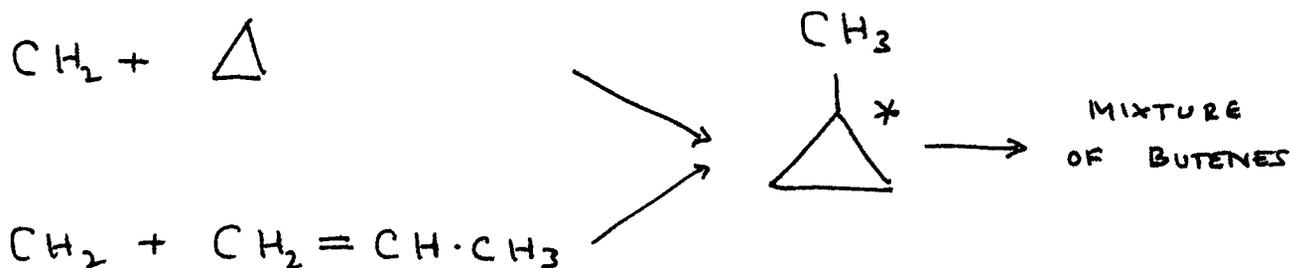
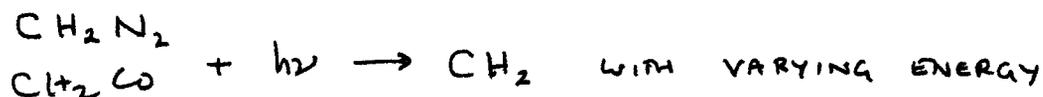
Theoretical considerations show that flow can ONLY occur with ANHARMONIC oscillators. However, since we are discussing systems near their dissociation limits, the vibrations will be highly anharmonic.

5: in formula is number of vibrational modes (degrees of freedom = 2s)

Chemical Activation

Some of best experimental tests use technique of "chemical activation"

Examples

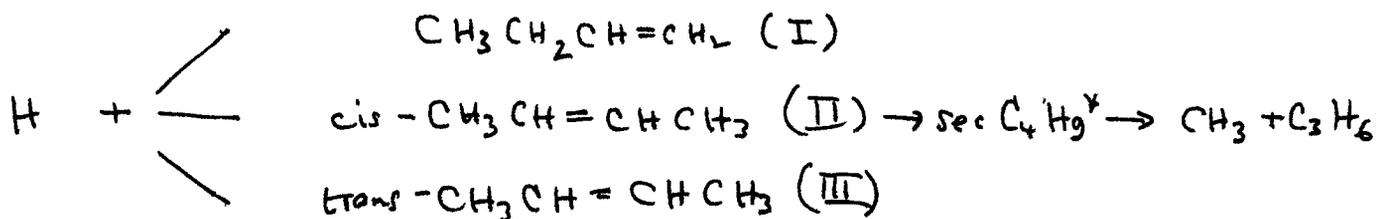


② Lifetime of hot methylcyclopropane depends on its source  
 ① Composition of the product butenes does not depend on source

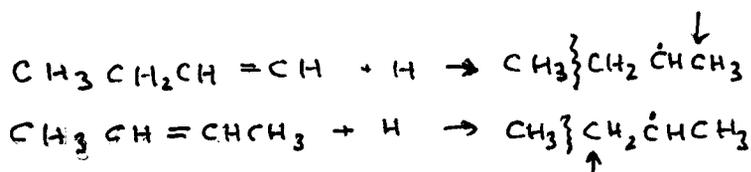
Two conclusions:

- ① Redistribution of energy before decomposition (energy in CH<sub>3</sub>-ring bond in first case, within the ring in the second)
- ② Rate of reaction of activated A\* is greater for greater excess energy. That is k<sub>3</sub> in scheme is a function of energy, k<sub>3</sub>(ε). It is this feature that leads to the curvature in the 1/k<sub>uni</sub> vs 1/[A] plots mentioned earlier, and it plays an important part in the more sophisticated theories of unimolecular kinetics.

Another chemical activation example

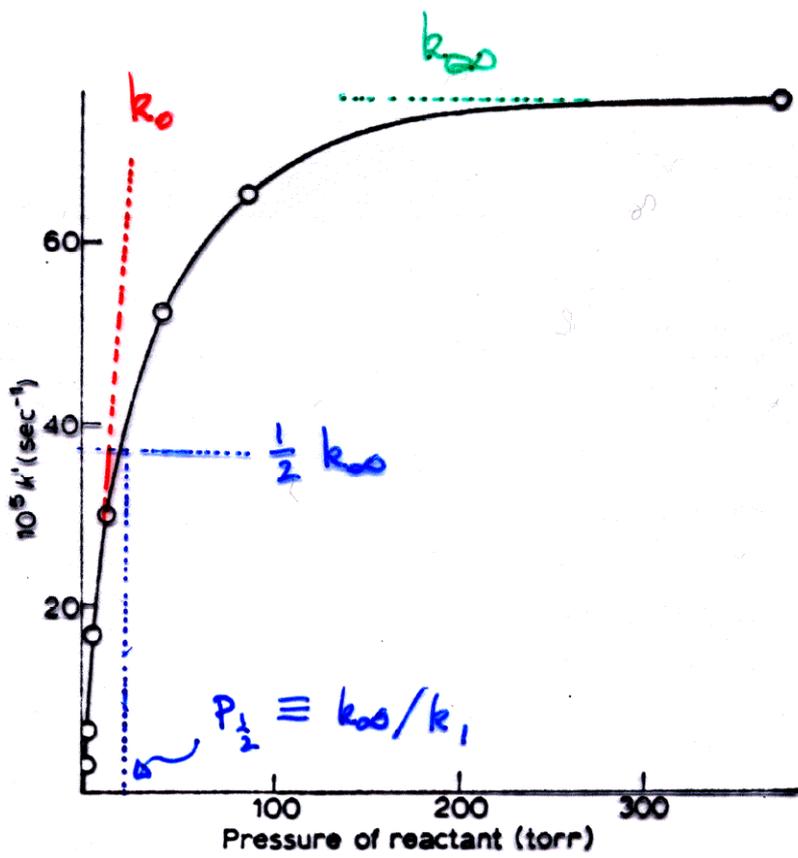


Energies comparable for all three processes, and the rates are comparable. But in I the C-C bond ruptured is furthest from the point from point of H addition, while in II and III the ruptured bond is attached to the C to which H adds.

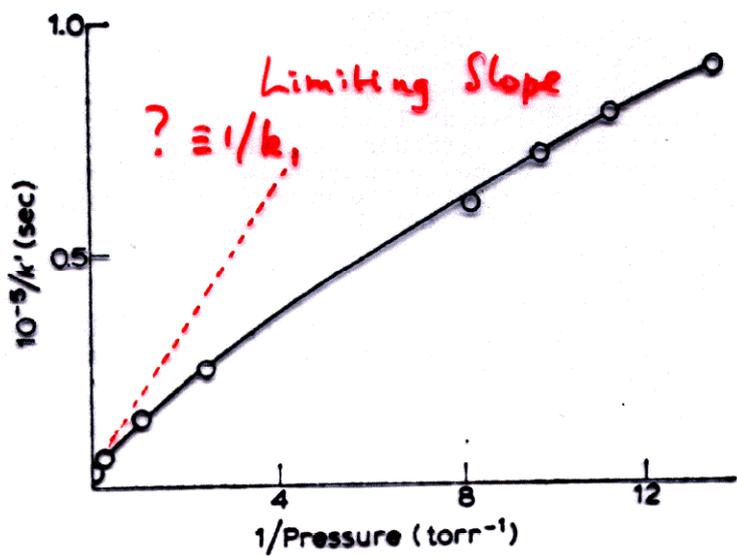




ERS  
VI



The variation of  $k'$  with pressure in the isomerization of  $\text{CD}_3\text{NC}$  to  $\text{CD}_3\text{CN}$



Plot of  $1/k'$  against inverse pressure for the isomerization of  $\text{CD}_3\text{NC}$

Elementary Reactions VI

Energy-dependent Reaction Rates

This lecture provides an outline of the major conclusions from free-flow theories, rather than going through detailed derivations.

*Position at the end of lecture V: write L-H scheme on board, but leave space for  $A^* \rightarrow A^\ddagger$ .*

Equation (5) from LV

$$k_{\text{uni}} = \frac{k_3 k_1 [A]}{k_2 [A] + k_3}$$

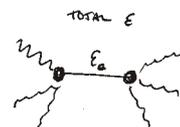
Additional conclusions

Internal energy counts

It flows more or less freely

Thus  $k_3$  may be a function of  $\epsilon$

(i.e.  $k_3(\epsilon)$ )



Recognition that  $k_3$  may be a function of energy means that we must also consider the rate of activation of specific energy levels: that is, we must allow for  $k_1$  being a function of energy as well as  $k_3$ . We return shortly to the question of how  $k_2$  is treated.

$$k_{\text{uni}} = \frac{k_3 (k_1/k_2)}{1 + \frac{k_3}{k_2 [A]}} = \frac{k_3 P}{1 + \frac{k_3}{k_2 [A]}} \quad (9)$$

Divide equation (5) by  $k_2 [A]$  to rewrite in the form  $P$  is the fraction, or probability, of  $A$  that are excited to  $A^*$  **in the absence of decomposition.**

Thus if  $k_1$  is a function of energy,  $P$  is also: it is the probability distribution function  $P(\epsilon)d\epsilon$  of finding a molecule at energy  $\epsilon$  so long as there is thermal equilibrium.

Equation (9) now has to be rewritten for a specific energy,  $\epsilon$ . That is,  $k_3(\epsilon)$  and  $P(\epsilon)d\epsilon$  replace  $k_3$  and  $P$ , and the result must be integrated from the threshold energy to infinity to yield  $k_{uni}$ .

We shall consider purely statistical theories. Thus

$$k_{uni} = \int_{\epsilon_c}^{\infty} \frac{k_3(\epsilon) P(\epsilon) d\epsilon}{(1 + k_3(\epsilon)/k_2[A])} \quad \begin{array}{l} \text{EQUATION (10)} \\ \text{OF HANDOUT} \end{array} \quad (10)$$

Free Flow theories: RRK

Coupling is assumed sufficient for free flow, but weak enough for independence of oscillators

Critical energy  $\epsilon_c$  must be concentrated in one particular part of molecule: total energy  $\epsilon$  is assumed to be rapidly redistributed around molecule

$P(\epsilon)d\epsilon$  is given by the Boltzmann distribution (this is coming later - see equation (13) of the handout). We now turn to simple probability arguments about the numbers of ways of arranging a certain number of quanta, equivalent to  $\epsilon$ , amongst a different number of oscillators,  $s$ , so that a number of quanta equivalent to  $\epsilon_c$  is in one particular oscillator.

First approximation: **Rice-Ramsperger-Kassel (RRK)** theory

Assumes all oscillators of same frequency,  $\nu$

Assumes strictly harmonic oscillators, so that  $\epsilon_i = i h \nu$  (despite 'free flow'!!!!)

It can be shown, from simple statistical arguments about the numbers of ways of selecting numbers of quanta that

$$r(\epsilon) = \left( \frac{\epsilon - \epsilon_c}{\epsilon} \right)^{s-1}$$

so that

$$k_3(\epsilon) = \nu^* \left( \frac{\epsilon - \epsilon_c}{\epsilon} \right)^{s-1}$$

**Note:** this expression implies that  $k_3$  increases the more that  $\epsilon$  exceeds the threshold,  $\epsilon_c$ , and that it also increases with the number of oscillators,  $s$ .

### Comparison with experiment

This result for  $k_3(\epsilon)$  leads to the conclusion that

$$k_{\infty} = \nu^* \exp(-\epsilon_c/kT)$$

which is to be compared with the experimental Arrhenius form

$$k_{\infty} = A \exp(-E_a/RT)$$

$A$  ought therefore to correspond to the vibrational frequency of the dissociating bond

Figure 3 shows measured pre-exponential factors: although many  $A$ -factors are  $\approx 10^{13} \text{ s}^{-1}$ , some are much bigger and some much smaller

### RRKM Theory

Although part of the problem with RRK theory is that the vibrations are not treated realistically, a more serious problem is that the effects of molecular rotation are neglected

RRKM theory is a "quantum statistical" one, in which the activated molecule,  $A^*$ , and the transition state,  $A^\ddagger$ , are expressly distinguished.

Reaction scheme

[Add to Lindemann-Hinshelwood scheme on board. replacing  $A^* \rightarrow$  products by  $A^* \rightarrow A^\ddagger$  and adding  $A^\ddagger \rightarrow$  products].

Point about counting can be made by reference to the  $P(\epsilon)d\epsilon$  term needed: densities of states directly assessed from vibrational frequencies. Explain how  $P(\epsilon)d\epsilon$  is

Improvements over RRK are

- (i) account taken of molecular rotation (and related centrifugal effects)
- (ii) active internal states are counted with due regard for actual molecular frequencies

related to  $P_j$ , and explain about  $G(\epsilon)d\epsilon$ .

Now discuss  $k_3(\epsilon)$ . From reaction scheme:

VIEW 1  
(REVERSE OF  
H/O)

(BOTTOM OF  
P10, H/O)

H/O eqn (13)  
Boltzmann in  
continuous form

( Rate of prod<sup>n</sup> of A\* = Rate of loss of A\* )

$$k_3(\epsilon) [A^*] = \nu^*(\epsilon) [A^*]$$

and from statistical mechanics

$$\frac{[A^*]}{[A^*]} = \frac{Q_{rot}^{\ddagger} G(\epsilon^{\ddagger}) d\epsilon}{Q_{rot}^* G(\epsilon) d\epsilon}$$

since A<sup>‡</sup>, A\* are at the same energy

Thus

$$k_3(\epsilon) = \nu^*(\epsilon) \frac{Q_{rot}^{\ddagger} G(\epsilon^{\ddagger}) d\epsilon}{Q_{rot}^* G(\epsilon) d\epsilon}$$

As in bimolecular TST,  $\nu^*$  is evaluated by factorizing out the reaction coordinate vibration from  $G(\epsilon)d\epsilon$ , and the final result is

Equation (14)  
on H/O

$$k_3(\epsilon) = \frac{1}{h} \frac{Q_r^{\ddagger}}{Q_r^*} \frac{\int_0^{\epsilon^{\ddagger}} Q(\epsilon_n^{\ddagger}) d\epsilon_n^{\ddagger}}{Q(\epsilon)}$$

$\epsilon_n$  is analogous to states involved in  $q^{\ddagger}$  for bimolecular reaction.

$Q_R^{\ddagger} = Q_R^*$   
and classical form for  $Q_V$

$$k_3(\epsilon) \cdot \nu^* \left[ \frac{\epsilon - \epsilon_c}{\epsilon} \right]^{-1}$$

$$+ \nu^* \exp(-\epsilon/kT)$$

Note that this equation can be shown to reduce to the RRK form [Handout equation (15)] if the two rotational partition functions are the same: that is, if differences between the activated molecule and the transition state are not considered. (and classical  $Q_V$ s are used)

The differences between the RRK and RRKM forms for  $k_{\infty}$  should now be emphasized

RRK  $k_{\infty} = \nu^* \exp(-\epsilon_c/kT)$

(RRM (simp. form RRKM)  $k_{\infty} = \nu^* \exp(-\epsilon_c/kT)$ )

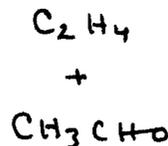
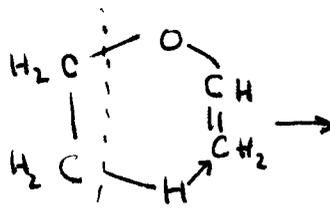
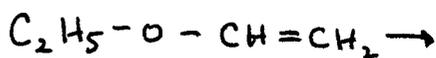
RRKM  $k_{\infty} = \frac{kT}{h} \frac{Q_r^{\ddagger} Q_v^{\ddagger}}{Q_r^* Q_v^*} \exp(-\epsilon_c/kT)$

Since  $kT/h$  is comparable with vibration frequencies  $\nu^*$ , the A-factors  $\gg$  or  $\ll 10^{13} \text{ s}^{-1}$  must be ascribed to the ratio of partition functions.

For example, conversion of vibration (small  $Q$ ) in  $A^*$  to rotation (large  $Q$ ) in  $A^{\ddagger}$  will lead to a large pre-exponential factor, as in fission of polyatomics.

Conversely, if essentially free rotations in  $A^*$  become locked up as internal vibrations in  $A^{\ddagger}$ , then the pre-exponential factor will be anomalously small: e.g.:

$A \sim 10^{14} \text{ s}^{-1}$



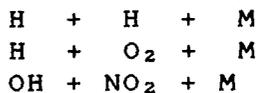
Fall-off Tests

Final test of theory is in fitting pressure dependence of rates ( $k_{uni}$ )

Some results for isomerization of methylcyclopropane (Approx curve is RRK: calc.  $\lambda=0.22$  is "best" RRKM)

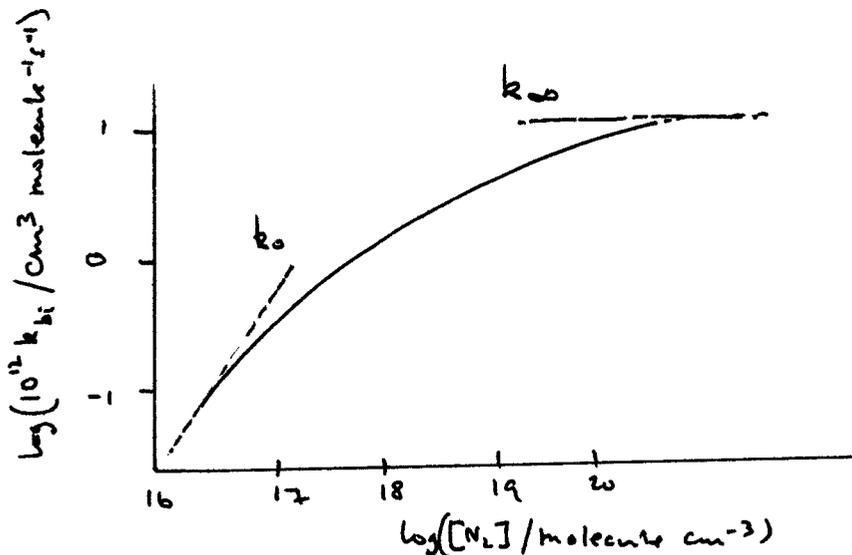
Termolecular Reactions

Some termolecular reactions extremely important: especially recombination reactions such as



Can be third order, but can also be variable order as are unimolecular reactions, and for the same reasons. That is, a hypothetical  $k_{bi}$  (to replace  $k_{uni}$ ) may be independent of P at high P, but proportional to P at lower P.

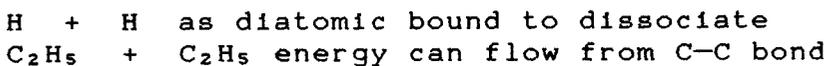
Diagram to show results for OH + NO<sub>2</sub>



Particularly evident for atom + atom, and for small radical reactions

Ideas follow naturally from concept of chemical activation

Explain



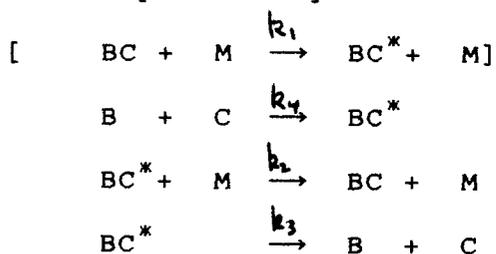
VIEW 2  
FIGURE 4, H<sub>6</sub>

Write  $B+C+M \rightarrow BC+M$   
 $k_{bi} = \frac{\text{Rate}}{[B][C]}$

VIEW 3

Better draw a sketch of  $k$  vs  $[M]$  so that the limiting slopes rather are better

Scheme: consider a molecule BC, to stand in the place of A used previously



write on board as unimolecular scheme for BC omitting second line as for (but with space left)

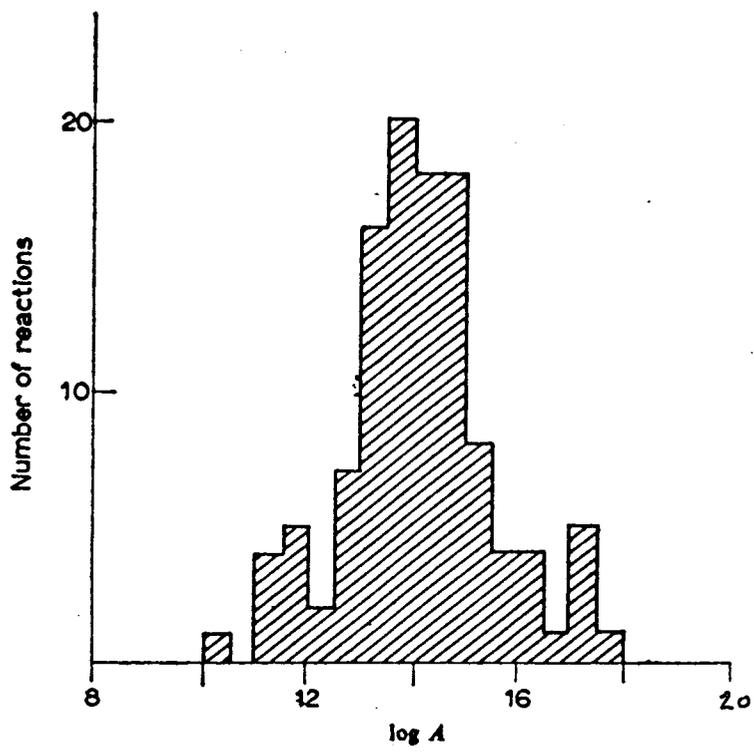
$$\text{Rate} = \frac{k_4 k_2 [B][C][M]}{k_3 + k_2 [M]}$$

The scheme thus predicts that reaction is third order at low pressure, but might become second order at high enough pressures where stabilization is not rate determining. Turnover pressure will depend on relative magnitudes of  $k_3$  and  $k_2$ . Stabilization rate ( $k_2[M]$ ) cannot exceed gas kinetic collision frequency, while  $k_3$  will depend on complexity of molecule (flow of energy into bonds other than the newly formed one).

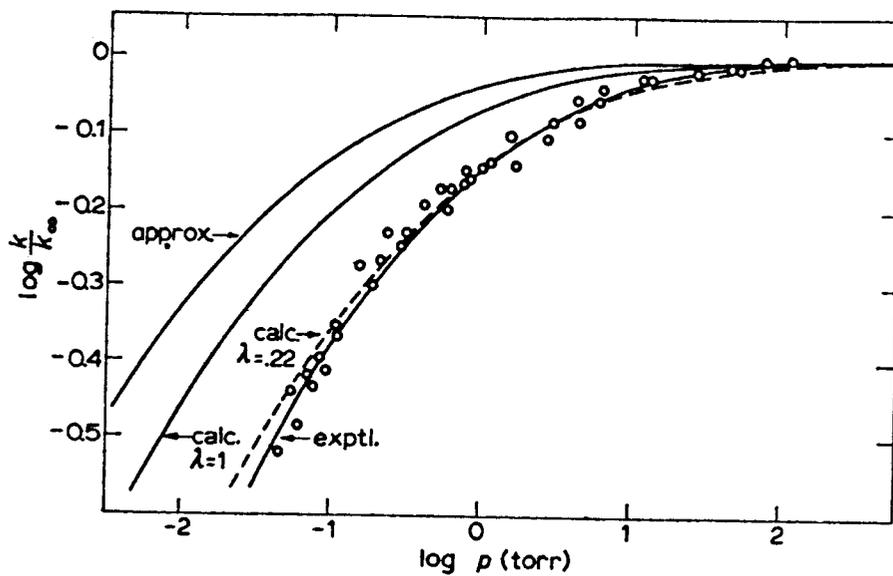
For atom + atom reactions,  $k_3 \approx 10^{13} \text{ s}^{-1}$ , and the "half pressure" would be  $2 \times 10^4 \text{ Atm}$ .

For  $\text{CH}_3 + \text{CH}_3$ , half pressure\* is around 5 Torr, so that  $k_3$  must be about  $2.5 \times 10^7 \text{ s}^{-1}$ . That is,  $10^5$  to  $10^6$  vibrations occur before redissociation of the newly formed (and activated) molecule.

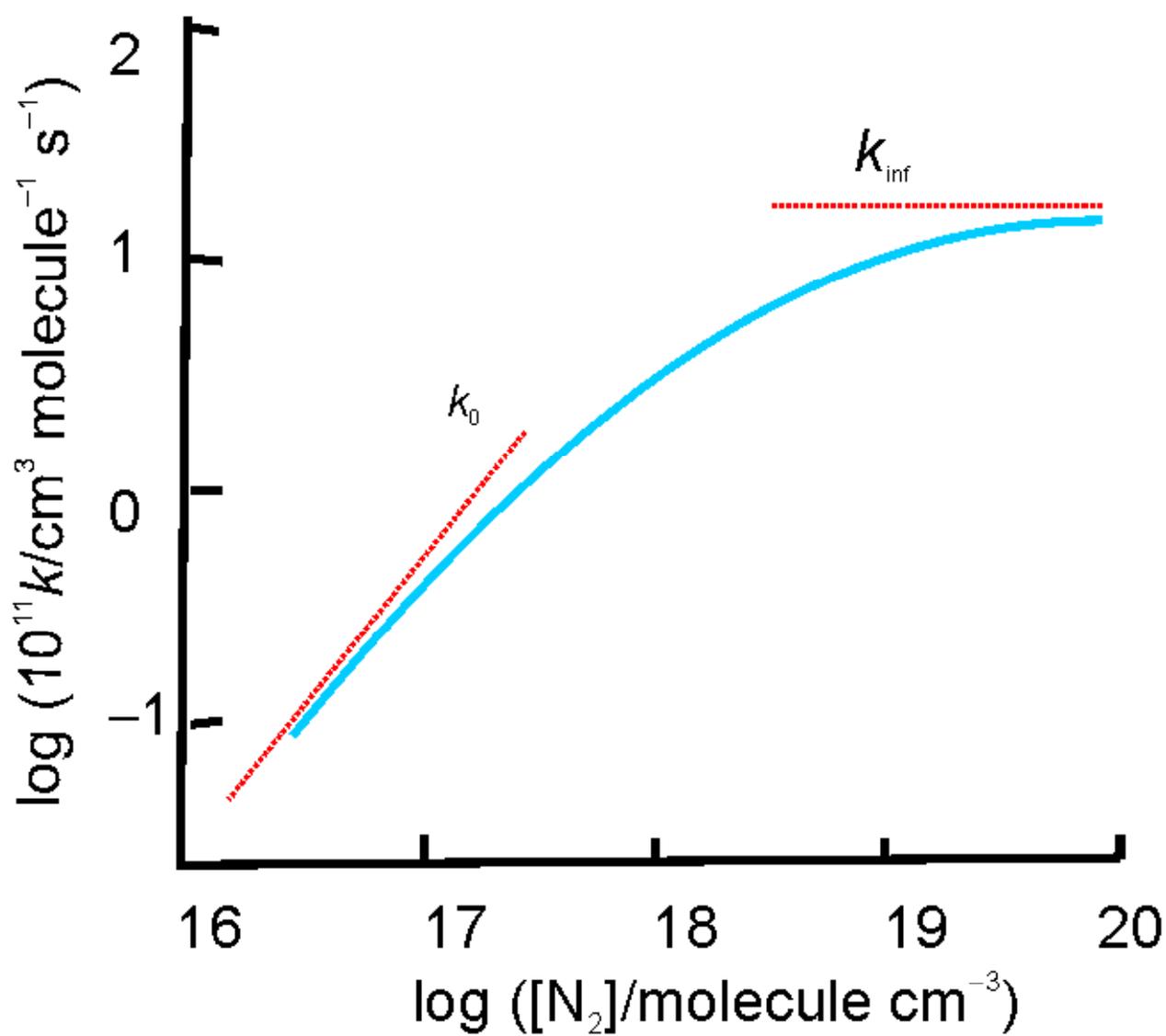
\* (determined experimentally)



Histogram of numbers of unimolecular reactions having given pre-exponential factors.



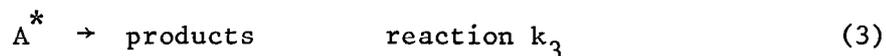
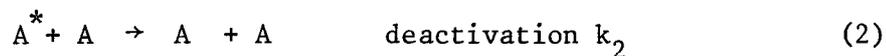
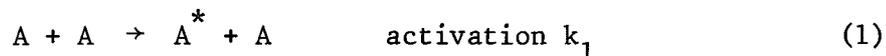
Fall-off test of the thermal isomerization of methylcyclopropane Wieder and Marcus



**Handouts for Lectures V and VI**  
**(Unimolecular Reactions)**

UNIMOLECULAR REACTIONS I

1. Lindemann Scheme



Steady state analysis yields the result:

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} \quad (4)$$

If  $k_3 \ll k_2 [A]$  (high pressure),  $\text{Rate} = \frac{k_3 k_1}{k_2} [A]$ ; i.e. first order.

If  $k_2 [A] \ll k_3$  (low pressure),  $\text{Rate} = k_1 [A]^2$ ; i.e. second order.

We may define an effective first order rate "constant"  $k_{\text{uni}}$  as  $\text{Rate}/[A]$ , which gives, from equation (4),

$$k_{\text{uni}} = \frac{k_3 k_1 [A]}{k_2 [A] + k_3} = \frac{k_{\infty}}{1 + \frac{k_{\infty}}{k_1 [A]}} \quad (5)$$

where for high pressures

$$k_{\text{uni}} \rightarrow k_{\infty} = \frac{k_1}{k_2} k_3 \quad (6)$$

The rate "constant"  $k_{\text{uni}}$  at low pressures decreases with  $[A]$ , and eventually  $k_{\text{uni}} = k_1 [A]$ .

Rearrangement of equation (5) yields the result

$$\frac{1}{k_{\text{uni}}} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1 [A]} \quad (7)$$

so that a plot of  $1/k_{\text{uni}}$  against  $1/[A]$  should

(i) be linear

(ii) have a slope =  $1/k_1$ .

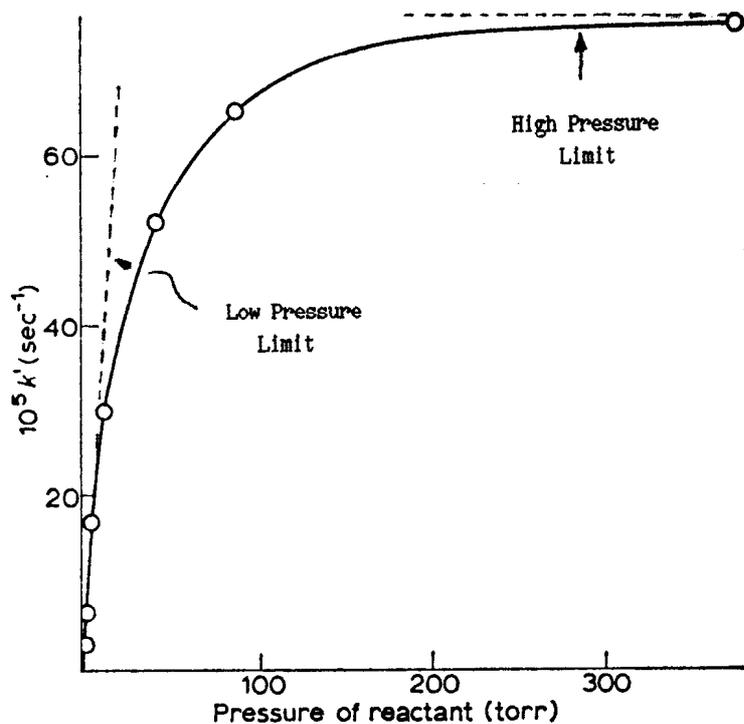


Figure 1 The variation of  $k'$  with pressure in the isomerization of  $\text{CD}_3\text{NC}$  to  $\text{CD}_3\text{CN}$

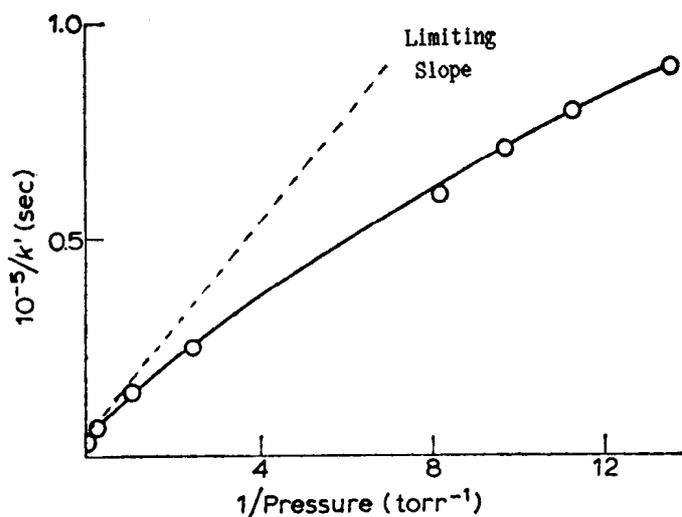


Figure 2 Plot of  $1/k'$  against inverse pressure for the isomerization of  $\text{CD}_3\text{NC}$

## 2. Hinshelwood Modification

Effective activation energy for many degrees of freedom given by

$$\frac{(E_c/RT)^{s-1} \exp(-E_c/RT)}{(s-1)!} \quad (8)$$

where  $s$  is the number of vibrational modes, instead of the form  $\exp(-E_c/RT)$  for hard spheres

Note that  $E_c/R = \epsilon_c/k$  where  $E_c$  and  $\epsilon_c$  are the critical energies expressed per mole and per molecule respectively.

UNIMOLECULAR REACTIONS II

Equation (5) (of "Unimolecular Reactions I") can be rewritten

$$\begin{aligned}
 k_{\text{uni}} &= \frac{k_3 k_1 [A]}{k_2 [A] + k_3} = \frac{k_3 (k_1/k_2)}{1 + (k_3/k_2 [A])} \\
 &= \frac{k_3 P}{1 + (k_3/k_2 [A])} \quad (9)
 \end{aligned}$$

Now we allow that both  $k_3$  and  $P$  are a function of energy (but suppose that  $k_2$  is not)

Then

$$k_{\text{uni}} = \int_{\epsilon_0}^{\infty} \frac{k_3(\epsilon) P(\epsilon) d\epsilon}{1 + (k_3(\epsilon)/k_2 [A])} \quad (10)$$

$k_2 [A]$  is often taken to be a constant fraction of the collision rate (i.e. =  $\lambda Z' [A]$ ).

Thus the basic problems are of finding  $P(\epsilon) d\epsilon$  and  $k_3(\epsilon)$ .

Rice - Ramsperger - Kassel - Marcus Theory (RRKM)

Adds transition state ideas to the Lindemann - Hinshelwood scheme :



In this treatment,  $P(\epsilon)d\epsilon$  is taken to be given by statistics

$$P(\epsilon)d\epsilon = \frac{G(\epsilon)\exp(-\epsilon/kT)d\epsilon}{\int_0^{\infty} G(\epsilon)\exp(-\epsilon/kT)d\epsilon} \quad (13)$$

and the transition state treatment yields the result

$$k_3(\epsilon) = \frac{1}{h} \frac{Q_r^\ddagger}{Q_r^*} \frac{\int_0^{\epsilon^\ddagger} G(\epsilon_n^\ddagger) d\epsilon_n^\ddagger}{G(\epsilon)} \quad (14)$$

where the subscript  $n$  indicates that only modes not leading to reaction are to be included.  $Q_r^*$ ,  $Q_r^\ddagger$  are the rotational partition functions for activated molecule and transition state respectively.

Classically ("RRK" theory) for  $s$  oscillators, and

$$\text{if } Q_r^\ddagger = Q_r^*$$

$$k_3(\epsilon) = \nu^\ddagger \left[ \frac{\epsilon - \epsilon_c}{\epsilon} \right]^{s-1} \quad (15)$$

and this result leads on substitution in eq. (10) to

$$k_\infty = \nu^\ddagger \exp(-\epsilon_c/kT) \quad (16)$$

Full RRKM treatment gives

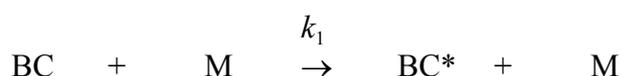
$$k_\infty = \frac{kT}{h} \frac{Q_r^\ddagger Q_v^\ddagger}{Q_r^* Q_v^*} \exp(-\epsilon_c/kT) \quad (17)$$

N.B. Figures appear overleaf

## Termolecular recombination reactions

Recombination places energy (i.e. the bond energy) into the newly-formed bond. If a diatomic molecule is the product (from two atoms), it has enough energy to fall apart again on the first vibration unless it is stabilized — some energy removed — within the vibrational period. If polyatomic molecules are produced from the recombination of atom + radical or radical + radical, then the energy of the newly-formed bond can flow into the other bonds, and it may no longer be necessary to stabilize the molecule within the first vibrational period. However, the ideas of unimolecular reaction theory suggest that the energy will be able eventually to flow back to the critical bond, so that decomposition must ultimately occur unless the newly-formed molecule is collisionally stabilized. Obviously, the more complex the species involved, the longer the lifetime of the activated molecules. The newly-formed molecules are 'chemically activated', and their decomposition and stabilization may be treated in the same way as collisionally-activated molecules are in ordinary unimolecular reaction theory.

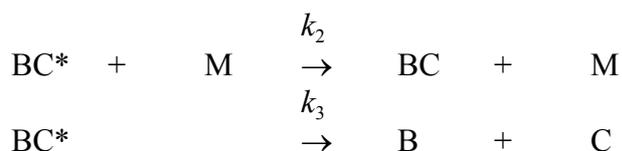
The overall recombination reaction is, in fact, the reverse of a unimolecular decomposition. With a molecule BC as the reactant, the first, activating step in a thermal unimolecular reaction is



Recombination of B and C can also yield BC\* in the reaction



The subsequent fates of BC\* are stabilization or decomposition



Solution of the steady-state equations for [BC\*] leads to the result

$$\text{Rate} = \frac{k_4 k_2 [\text{B}][\text{C}][\text{M}]}{k_3 + k_2 [\text{M}]}$$

The scheme thus predicts that reaction is third order at low pressure, but might become second order at high enough pressures where stabilization is not rate determining. The turnover pressure will depend on relative magnitudes of  $k_3$  and  $k_2$ . The stabilization rate ( $k_2[\text{M}]$ ) cannot exceed the gas-kinetic collision frequency, while  $k_3$  will depend on the complexity of the molecule (flow of energy into bonds other than the newly formed one). For atom + atom reactions,  $k_3 = 10^{13} \text{ s}^{-1}$ , and the "half pressure" would be  $2 \times 10^4 \text{ atm}$ . For  $\text{CH}_3 + \text{CH}_3$ , the 'half pressure' is around 5 Torr, so that  $k_3$  must be about  $2.5 \times 10^7 \text{ s}^{-1}$ . That is,  $10^5$  to  $10^6$  vibrations occur before redissociation of the newly formed (and activated) molecule.

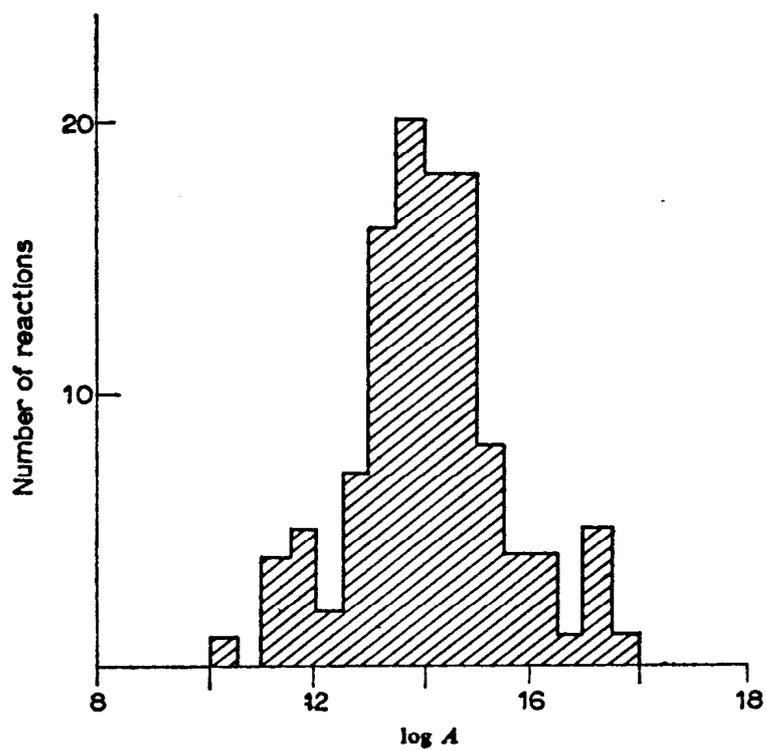


Figure 3 Histogram of numbers of unimolecular reactions having given pre-exponential factors.

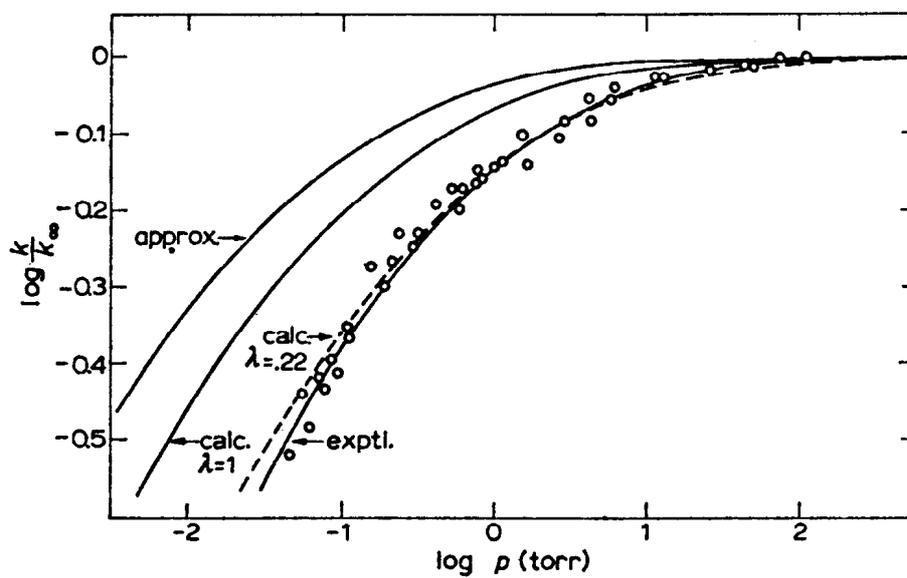


Figure 4 Fall-off test of the thermal isomerization of methylocyclopropane Wieder and Marcus

## Elementary Reactions VII

### Reactions in Solution - I

#### Effects of the solvent

##### A Mechanical constraints

Virtually unhindered motion in gases becomes much more constrained in liquids

##### B1 Direct: Solvent affects A, B ↔ S interactions

Solvent may interact with solute directly - solvation

##### B2 Indirect: Solvent affects A ↔ B interactions

Solvent may play a part in affecting interactions between solute molecules

n.b. charged species may be particularly affected (ions favoured because of permittivity considerations)

#### Cage Effects

Molecules occupy 0.2% of total volume in gases  
>50% in liquids

Molecules have to squeeze past each other in liquid

Motion consists of repeated vibrations in a "cage" (100 - 1000 vibrations, typically) before escape.

Then trapped in new cage: No memory of original approach

I<sub>2</sub> dissociation example:  $\phi = 1$  in gas

At  $\lambda = 436$  nm,  $\phi = 0.66$  in hexane,  $\phi = 0.075$  in hexachlorobutadiene. Note viscosity effect: quantify later.

#### Cage effects and recombination

e.g.  $I + I + M \rightarrow I_2 + M$

termolecular in gas phase (as discussed in previous lecture); always second order in solution, but  $k \ll k^\infty$  in gas.

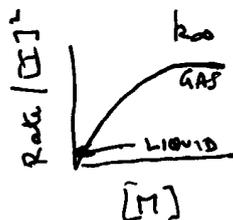
Similarly,



$$k_{\text{gas}}^\infty = 2.5 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{\text{liq}} = 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Solvent a) inhibits approach, but  
b) acts as energy sink

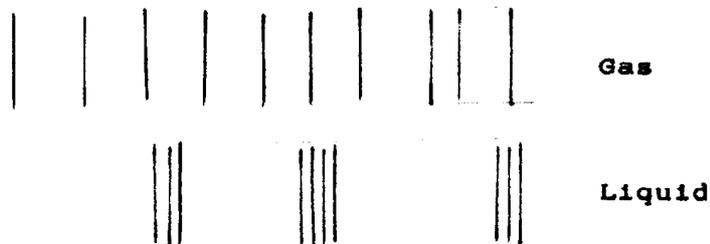


Reaction

Incidence of collisions

Different in solution and in gas

A and B must share a cage to react ("Encounter Pair").  
Have to get inside cage, but once there undergo many collisions.



General Scheme for Solution Reactions

Derivation, leading to two limiting cases:

VIEW 1  
H/O p14

- a)  $k_c \gg k_d$       DIFFUSION CONTROL ( $k_2 = k_d$ )
- b)  $k_d \gg k_c$       ACTIVATION CONTROL ( $k_2 = k_c K_d$ )

Diffusion Controlled Reactions

VIEW 2  
H/O p15

Derivation of model for DCRs

Fick's First Law:

Flux ( $J$ ) = Conc. gradient x Area x Diffusion coeff.

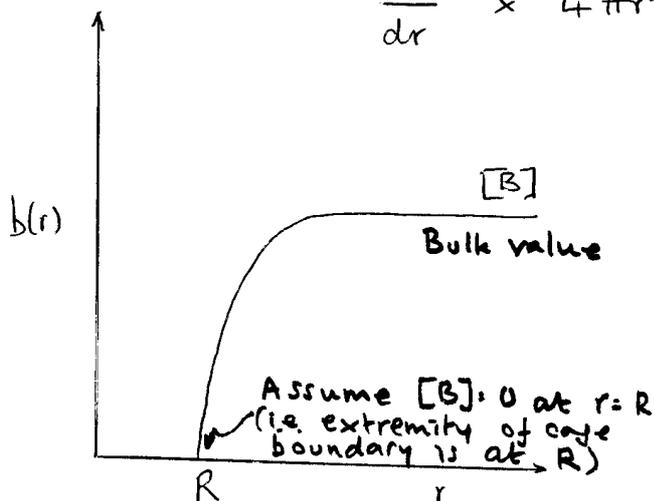
$$= \frac{db(r)}{dr} \times 4\pi r^2 \times D_{AB}$$

$$\therefore \int_0^b db(r) = \int_R^\infty \frac{\overleftarrow{J}}{4\pi r^2 D} dr$$

$$[B] = \frac{\overleftarrow{J}}{4\pi R D}$$

$$\text{Rate} = k_2 [A][B] = \overleftarrow{J} [A]$$

$$\therefore \boxed{k_2 = 4\pi R D}$$



For H<sub>2</sub>O solvent ( $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ), and with  $R = 0.5 \text{ nm}$ ,  
 $k_2$  is thus  $\approx 6.3 \times 10^{-18} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , or  
 $\approx 4 \times 10^9 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$

Thus a value of  $k_2 \geq 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is usually indicative of a diffusion controlled reaction

Effects of solvent viscosity

Reminder of viscosity effects in I<sub>2</sub> photolysis

Stokes-Einstein equation relates D to η

$$\text{Bulk: } D = \frac{kT}{6\pi\eta r_g} \quad \text{Molecular: } D = \frac{kT}{4\pi\eta r_g} \quad (\text{suspect})$$

where r<sub>g</sub> is the radius of the diffusing species (>> r<sub>solvent</sub>)

Hydrodynamic radius, r<sub>g</sub>, may differ from encounter radius, R:

r<sub>g</sub> depends on A or B + solvent interaction, R on A + B interaction

Temperature dependence

Viscosity decreases with increasing temperature, and the effect is a result of molecules overcoming energy barriers in order to squeeze past each other.

BOARD:

$$k \propto D \\ D \propto 1/\eta$$

Leads to exponential form:  $\eta \propto e^{E/RT}$ , so that

$$k_2 = A e^{-E/RT} \quad ; \quad \text{"Arrhenius" form}$$

Energy barriers in water are ≈ 15kJ mol<sup>-1</sup>, so that E<sub>a</sub> also ≈ 15kJ mol<sup>-1</sup> for diffusion-controlled reactions. A ≈ 10<sup>12</sup> dm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> in H<sub>2</sub>O (rather larger than Z' in gas phase)

Diffusion coefficients of ions

VIEW 3A

Table (viewgraph)

Note enormous value of D for H<sup>+</sup> and OH<sup>-</sup>



is ≈ 1.4 x 10<sup>11</sup> dm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup>, one of the fastest solution reactions known

But D alone does not explain k<sub>2</sub>: note additional effect of CHARGE.  
Leads to next topic

Effects of charge

Long range attraction or repulsion depending on

- 1) whether signs on A and B are same or different
- ii) relative permittivity of solvent

Relative motion can no longer be described as random (walk)

Probability of an effective encounter is thus altered, the effective radius,  $r_{eff}$ , being different from R

Charges same sign,  $r_{eff} < R$ ; opposite sign,  $r_{eff} > R$

Coulombic interaction energy

$$V(r) = \frac{z_A z_B e^2}{4\pi\epsilon_0 \epsilon r}$$

so that the effects are most pronounced for small  $\epsilon$

We write

$$k_2 = 4\pi r_{eff} D$$

It may be shown that

$$r_{eff} = R \times \frac{V}{kT} \left[ \exp\left\{ \frac{V}{kT} \right\} - 1 \right]^{-1}$$

VIEW 3B  
 $\eta, \epsilon$  and  $r_{eff}$

Dielectric Saturation

Complication, especially for high  $\epsilon$  solvents (e.g. H<sub>2</sub>O)

Solvation effect: First shell highly ordered; unable to reorient to reduce interionic field on approach of second ion. Thus local  $\epsilon$  decreases (as r decreases)

Value of  $\epsilon \rightarrow 6$ , which is characteristic of non-polar solvents

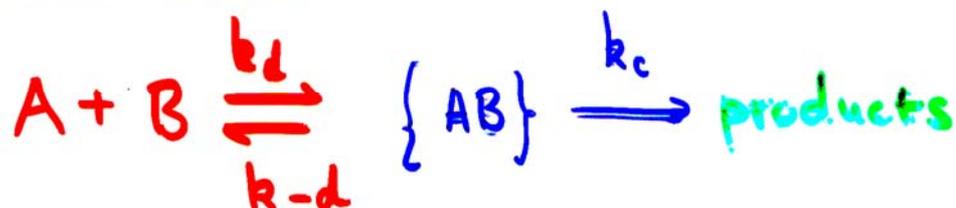
Phenomenon called "Dielectric Saturation", and illustrates the problem of applying a bulk property to a molecular process

## **Handouts and overheads for Lecture VII**

ER7  
VI

## REACTIONS IN SOLUTION

GENERALIZED SCHEME



STEADY STATE KINETICS FOR [AB]

$$\frac{d[AB]}{dt} = 0 = k_d[A][B] - (k_{-d} + k_c)[AB]$$

$$\therefore [AB] = \frac{k_d[A][B]}{k_{-d} + k_c}$$

$$\text{RATE} = k_c[AB] = k_2[A][B]$$

$$\therefore k_2 = \frac{k_d k_c}{k_{-d} + k_c}$$

LIMITS

$$k_c \gg k_{-d}$$

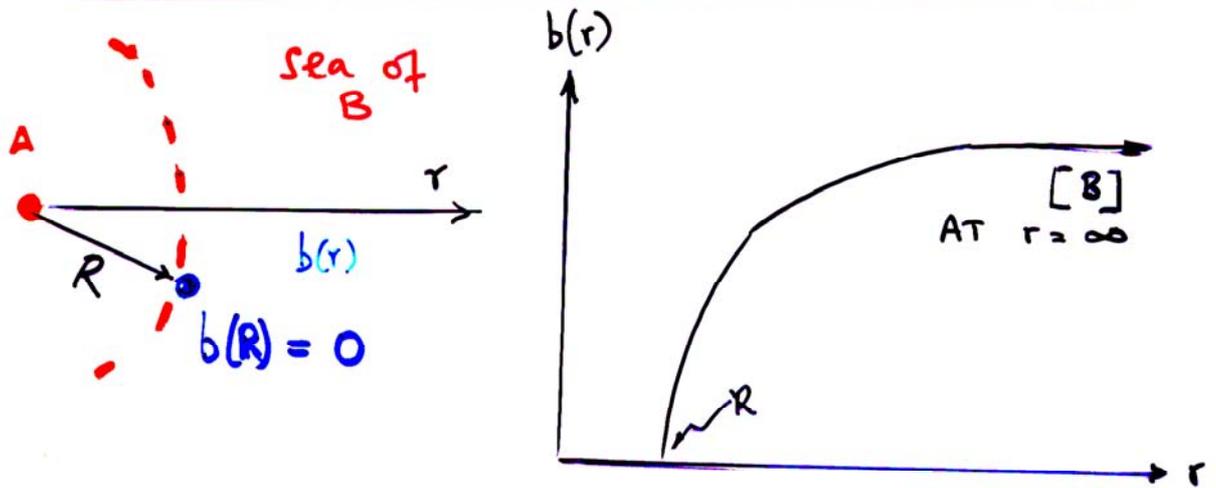
$$k_2 = k_d \quad \text{DIFFUSION CONTROL}$$

$$k_c \ll k_{-d}$$

$$k_2 = k_c \left( \frac{k_d}{k_{-d}} \right) = k_c K_D \quad \text{ACTIVATION CONTROL}$$

ER7  
V2

## DIFFUSION CONTROLLED REACTIONS



FICK'S FIRST LAW OF DIFFUSION

NUMBER OF MOLECULES PASSING UNIT AREA IN UNIT TIME =

-(CONCENTRATION GRADIENT)  $\times$  DIFFUSION COEFFICIENT

$$\therefore \text{FLUX, } \vec{J} = \frac{db(r)}{dr} \cdot 4\pi r^2 \cdot D$$

$$\therefore \int_0^{[B]} db(r) = \int_R^{\infty} \frac{\vec{J}}{D} \cdot \frac{dr}{4\pi r^2}$$

INTEGRATE  $\Rightarrow$   $[B] = \frac{\vec{J}}{4\pi R D}$  OR  $\vec{J} = 4\pi R D [B]$

$$\text{RATE} = k_2 [A][B] = \vec{J} [A]$$

$$\therefore k_2 = \vec{J} / [B] = 4\pi R D$$

ER7  
V3

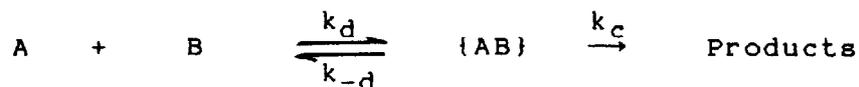
A. DIFFUSION COEFFICIENTS FOR IONS  
IN AQUEOUS SOLUTION (25°C)

ION	$D/m^2 s^{-1}$	ION	$D/m^2 s^{-1}$
$H^+$	$9.1 \times 10^{-9}$	$OH^-$	$5.2 \times 10^{-9}$
$Li^+$	$1.0 \times 10^{-9}$	$Cl^-$	$2.0 \times 10^{-9}$
$Na^+$	$1.3 \times 10^{-9}$	$Br^-$	$2.1 \times 10^{-9}$

B. PHYSICAL PROPERTIES OF SOME  
COMMON SOLVENTS

SOLVENT	VISCOSITY $kg\ m^{-1}\ s^{-1}$	RELATIVE PERMITTIVITY	EFFECTIVE † ENCOUNTER DISTANCE (nm)	
			$z_A = z_B$	$z_A = -z_B$
WATER	$1.00 \times 10^{-3}$	78.5	0.2	0.9
ETHANOL	$1.20 \times 10^{-3}$	24.3	0.02	2.3
HEXANE	$0.33 \times 10^{-3}$	1.89	$10^{-25}$	29

† Assumes  $R \sim 0.5\ nm$  for  $z = 0$ ;  $|z_A| = |z_B| = 1$

Reactions in SolutionGeneralized scheme

where  $\{AB\}$  is an encounter pair,  $k_d$  and  $k_{-d}$  are the rate constants for diffusive approach and separation of A and B, and  $k_c$  is the rate constant for reaction of the encounter pair. Both  $k_c$  and  $k_{-d}$  are first order rate constants, while  $k_d$  is second order.

Since  $\{AB\}$  is short-lived, the Steady State Hypothesis is applicable

$$\frac{d[\{AB\}]}{dt} = k_d[A][B] - (k_{-d} + k_c)[\{AB\}] = 0$$

$$[\{AB\}] = k_d[A][B]/(k_{-d} + k_c)$$

The rate of formation of the products

$$= k_c[\{AB\}] = k_2[A][B]$$

where  $k_2$  is the phenomenological second order rate constant

$$k_2 = \frac{k_d k_c}{k_{-d} + k_c}$$

We can distinguish two limiting cases:-

a)  $\underline{k_c \gg k_{-d}}$

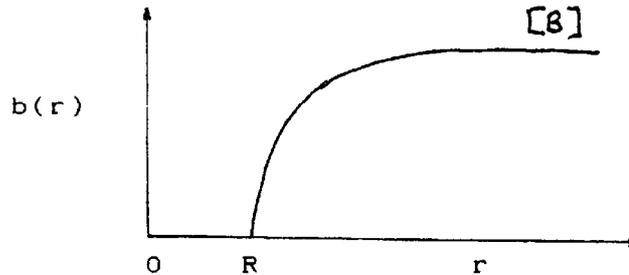
$$k_2 = k_d \quad \text{DIFFUSION CONTROL}$$

b)  $\underline{k_{-d} \gg k_c}$

$$k_2 = k_c(k_d/k_{-d}) \quad \text{ACTIVATION CONTROL}$$

Model for Diffusion Controlled reactions

Imagine an ensemble of systems, each system consisting of a central A molecule, surrounded by B molecules in a solvent. Let the concentration of B molecules, at distance  $r$  from the central A molecule, be  $b(r)$ . Assume that A and B react instantaneously when they reach a critical separation  $R$  (so that  $b(R) = 0$ ), and that the reaction does not deplete the bulk concentration of B (so that  $b(\infty) = [B]$ ). Thus the reaction sets up a concentration gradient centred on A:



The rate of reaction depends on the diffusive flux of B particles into A, and may be evaluated from Fick's first law. At any given  $r$ ,

$$\text{Flux} = \bar{J} = \frac{db(r)}{dr} \cdot 4\pi r^2 D_{AB}$$

where  $D_{AB}$  is the relative diffusion coefficient ( $= D_A + D_B$ ). Note that the flux is in the direction of decreasing concentration (i.e. decreasing  $r$ ).

$$\int_0^{[B]} db(r) = \int_R^\infty \frac{\bar{J}}{4\pi r^2} \cdot \frac{dr}{D_{AB}}$$

$$[B] = \frac{\bar{J}}{4\pi R D_{AB}}$$

and  $\bar{J} = 4\pi R D_{AB} [B]$

The total rate is given by the flux into A multiplied by the total concentration of A

$$\text{Rate} = \bar{J}[A] = k_2 [A][B]$$

where  $k_2$  is the phenomenological second order rate constant, so that

$$k_2 = \bar{J}/[B] = 4\pi R D_{AB}$$

(N.B. In this limit,  $k_2 = k_d$ ).

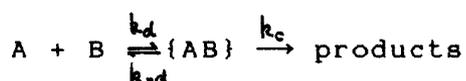
## Elementary Reactions VIII

### Reactions in Solution - II

#### Activation controlled reactions

Note concentration distribution differences between diffusion and activation controlled reactions

Remember that for scheme



$$k_2 = k_c K_d$$

=  $k_c e^{-\Delta G_d/RT}$  from thermodynamics

$$\text{or } \ln k_2 = \ln k_c - \Delta G_d/RT$$

#### Ionic reactions

Concentration of encounter pairs now depends on charges on reactants, and on solvent permittivity

$$\text{Since } \Delta G_d = \Delta G_d^\ddagger + V(r)$$

$$\ln k_2 = \ln k_2 - \Delta G_d/RT - V(r)/RT$$

$$\text{where } V(r) = \frac{z_A z_B e^2}{4\pi\epsilon_0 \epsilon r}$$

$$= 3.5 z_A z_B \text{ at } R = 0.5 \text{ nm for } H_2O (\epsilon = 78)$$

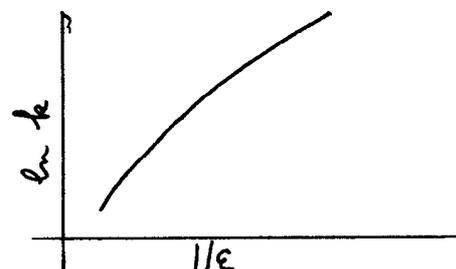
Thus expect

$$\ln(k_2/k_2^0) = - \frac{z_A z_B e^2}{4\pi\epsilon_0 \epsilon r kT}$$

$$\text{(n.b. } V'(r) \text{ per molecule} = V(r)/N_A)$$

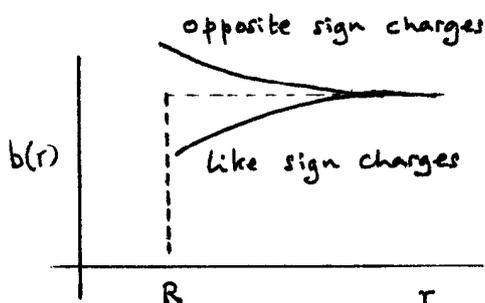
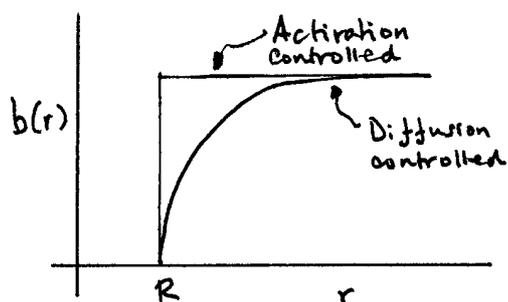
#### Experiment:

reaction of azodicarboxylate ion  $[(CO_2)_2N_2^-]$  with  $H_3O^+$  in dioxan - water mixtures of varying  $\epsilon$  varies in correct sense although plot is curved



#### Kinetic Salt Effects

So far, considered interactions only between reactant pairs; but approximation may be invalid when non-reactive ions are present. Many reactions are studied in buffer solution, so that non-reacting salts may be present in relatively high concentration, and the problem needs to be examined



Solvation effects lead to non-ideality, so that activities rather than concentrations should be used in computing  $K_d$  :viz.:-

$$K_d = \frac{a_{AB}}{a_A a_B} = \frac{\gamma_{AB}[AB]}{\gamma_A[A]\gamma_B[B]}$$

$$\therefore \frac{[AB]}{[A][B]} = K_d \frac{\gamma_A \gamma_B}{\gamma_{AB}}$$

Thus Rate =  $k_2[AB]$ ; or  $k_2 = \text{Rate}/([A][B])$

(Note that **concentrations**, not activities are used here because the process depends on the **numbers** of {AB} encounter pairs).

$$k_2 = \frac{k_c[AB]}{[A][B]} = \frac{\gamma_A \gamma_B}{\gamma_{AB}} k_c K_d = \frac{\gamma_A \gamma_B}{\gamma_{AB}} k_2^0$$

where  $k_2^0$  is the extrapolated rate constant at "zero" salt concentration

Limiting Debye-Huckel:

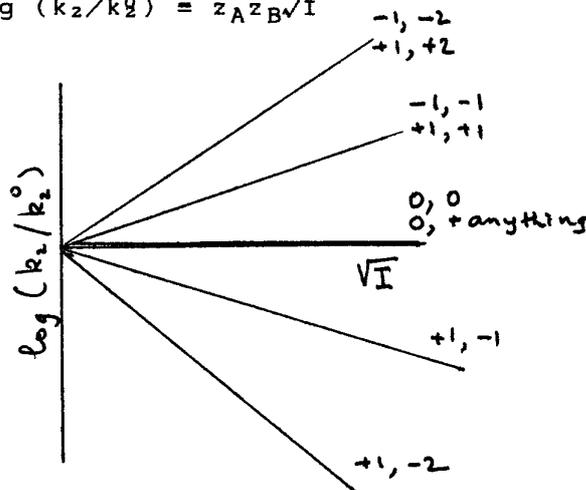
$$\ln \gamma = -Az^2/I$$

so that

$$\begin{aligned} \ln k_2 &= \ln k_2^0 - A\sqrt{I}(z_A^2 + z_B^2 - (z_A + z_B)^2) \\ &= \ln k_2^0 + 2Az_a z_b \sqrt{I} \end{aligned}$$

Since  $A=0.51$  for  $\log \gamma$  in  $H_2O$  at  $25^\circ C$

$$\log (k_2/k_2^0) = z_A z_B \sqrt{I}$$



KIE is a tool for determining **mechanism**: gain knowledge of ions involved in rate-determining step.

Kinetic Isotope Effect

More subtle tool for studying detail of reactions involving H and D is the kinetic isotope effect

Will examine pre-exponential (A) and activation energy ( $E_a$ ) terms in turn. Using  $m_H/m_D = 1/2$  in all partition functions, can show that  $A_H/A_D$  must lie in range  $1/2$  to  $\sqrt{2}/1$ . Larger isotope effects must therefore be a result of changes in  $E_a$ .

Substitution of D for H makes no difference to electronic distribution, but does alter the zero point energy

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

and z.p.e. is  $1/2(h\nu)$

Example:

HCl  $\mu = 0.97$

DCl  $\mu = 1.89$

and ratio is 1.95

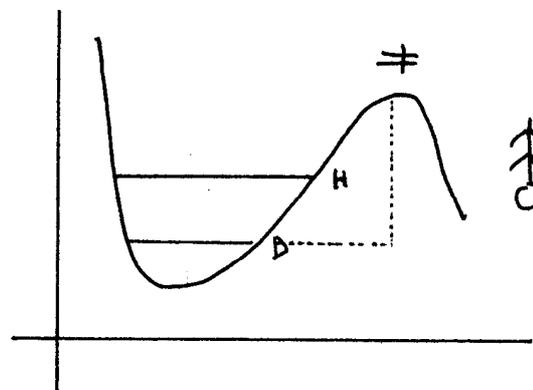
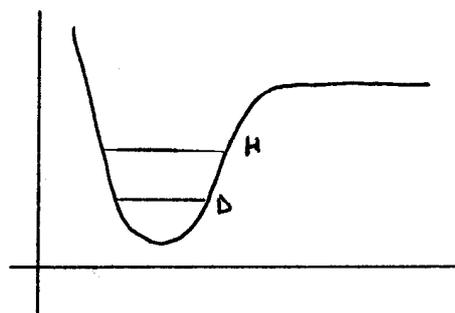
I.e.

$$\frac{\mu_{RH}}{\mu_{RD}} \approx \frac{1}{2}$$

or

$$\frac{\nu_{RH}}{\nu_{RD}} \approx \sqrt{2}$$

In proton transfer reactions, D or H is flying through the air, so that  $E_D > E_H$  and  $k_H > k_D$ . From stretching frequencies we find  $\Delta U_{zpe} \approx 5 \text{ kJ mol}^{-1}$ .



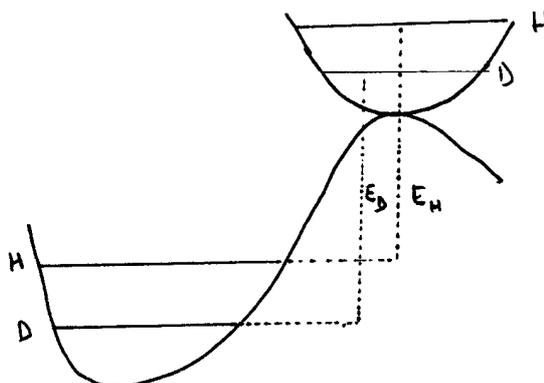
observed spectroscopically, we would thus expect

$$k_H/k_D = e^{\Delta U/RT} \approx 7.4.$$

In fact, measured value in most cases lies between 1 and 7.

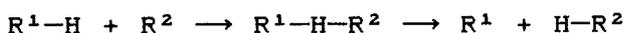
Values lower than the limit of 7.4 arise because of the involvement of H atom in vibrations of the activated complex

If H atom involved in oscillations not along reaction co-ordinate, then have to redraw PE diagram in order to represent the effect of isotopic substitution on frequencies of the activated complex. Thus,



$E_H = E_D$ , and  $k_H/k_D = 1$

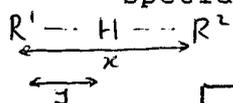
Consider



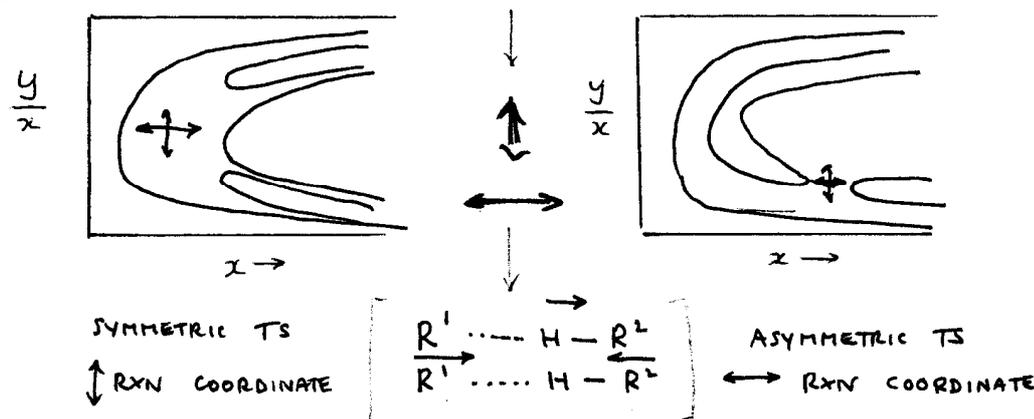
Situation we have discussed so far corresponds to  $R^1-H$  fission without concomitant formation of  $H-R^2$

Special PE curves will illustrate the point

Draw



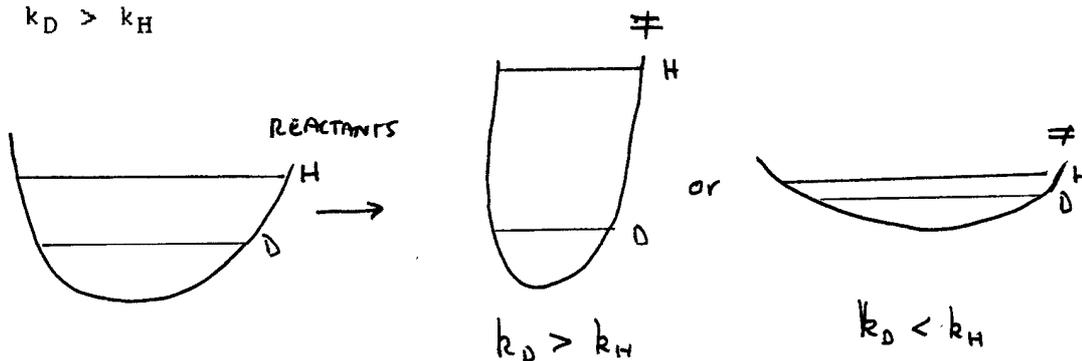
Then explain 'red', 'blue' motions ('vertical', 'horizontal')



RED: H involved: large change in zpe of TS  
 BLUE: H not involved: small change in zpe of TS

But in symmetric case, the RED vibration is dissociative, so that  $k_H/k_D$  tends to its maximum value of  $\approx 7.4$ . In asymmetric case, reaction coordinate does not involve H oscillation, which thus contributes fully to zpe of TS, and  $k_H/k_D = 1$

This result suggests that there might even be cases where  $k_D > k_H$



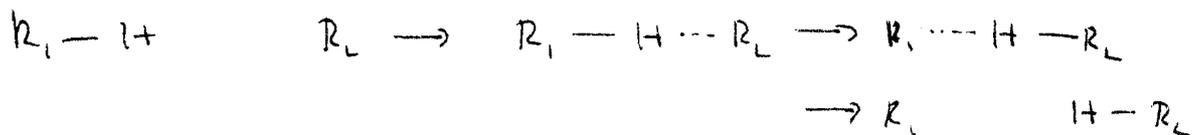
Can replace by more qualitative argument instead.

Can envisage two alternatives:

- (i) hydrogen moves from  $R_1$  to  $R_2$ , while the  $R_1$  and  $R_2$  remain relatively immobile



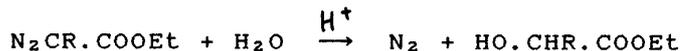
- (ii) hydrogen remains relatively immobile while  $R_2$  comes in and removes it from  $R_1$ ,



In case (i), hydrogen vibration is the reaction coordinate, so full contribution of isotope effect

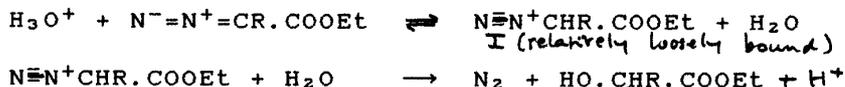
In case (ii), hydrogen vibrations contribute to transition state and  $k_H/k_D \rightarrow 1$

Good examples - acid catalysed decomposition of esters of diazocarboxylic acids: ethyl diazoacetate and ethyl diazopropionate

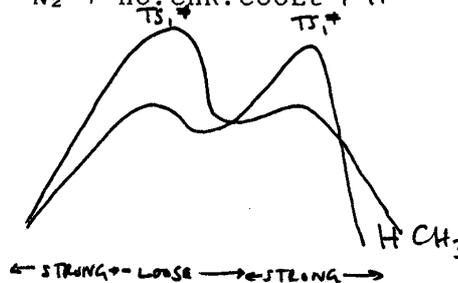


For R = CH<sub>3</sub>, k<sub>H</sub>/k<sub>D</sub> = 4 "normal"  
 R = H, k<sub>D</sub>/k<sub>H</sub> = 3 "inverse"

( Explanation: two step mechanism



For R = H, second step is R.D.S., TS more tightly bound than I, so that k<sub>D</sub> > k<sub>H</sub>. For R = CH<sub>3</sub>, I is effectively the TS, more loosely bound than the reactants, so that k<sub>H</sub> > k<sub>D</sub>

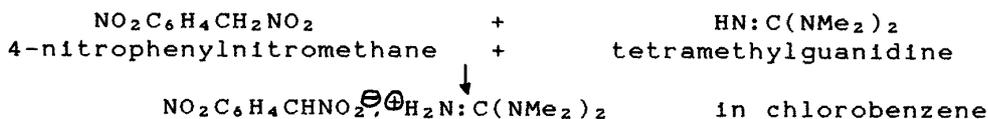


All these numbers near unity rather boring!

Something more spectacular

Tunnelling

Caldin's results



k<sub>H</sub>/k<sub>D</sub> = 50, far greater than semiclassical theory given so far

VIEW 1

A<sub>H</sub>/A<sub>D</sub> = 0.1 — semiclassical lower limit 0.5

ΔE<sub>a</sub> = 15.5 kJ mol<sup>-1</sup> — semiclassical upper limit 5 kJ mol<sup>-1</sup>

Also note that E<sub>A,H</sub> is strikingly low (8.8 kJ mol<sup>-1</sup>), and that plot is curved

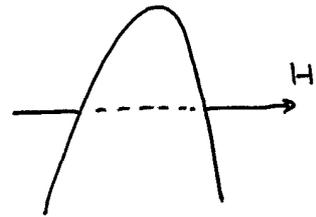
==> Quantum mechanical tunnelling

Interesting result of wave behaviour of particles that has no analogue in classical mechanics

Decay of wave in barrier <==> diffraction effect

	Classical	Observed
k <sub>H</sub> /k <sub>D</sub>	≤ 7.4	5.0
A <sub>H</sub> /A <sub>D</sub>	≥ 0.5	0.1
E <sub>D</sub> - E <sub>H</sub>	~ 5 kJ mol <sup>-1</sup>	15.5 kJ mol <sup>-1</sup>
E <sub>H</sub>	20-100 kJ mol <sup>-1</sup>	8.8 kJ mol <sup>-1</sup> at low T
Arrhenius plot	straight	curved

For kinetics, consequence is that reactants find themselves on the other side of activation barrier, even though they do not have the energy to surmount it.



Whatever way we describe barrier penetration, it is clear that the effect will only arise if the barrier width is comparable with, or less than, the de Broglie wavelength, given by  $\lambda = h/p$ . For fixed E of  $80 \text{ kJ mol}^{-1}$ ,

Atom mass:	1	2	5	10
$\lambda/\text{nm}$ :	0.031	0.022	0.014	0.009

Barriers typically  $0.05 \text{ nm}$  wide, so tunnelling only (marginally) important for H and D (and, of course,  $\epsilon$ ), and even for these, actual contribution very sensitive to mass ( $\gg$  for H than for D)

Return to Caldin's results:

VIEW 1

Curved Arrhenius plots, because tunnelling dominates reaction at low T

Therefore, extrapolation makes it appear that  $A_D > A_H$  and that  $E_{a,H} = 0$

#### Gas phase tunnelling

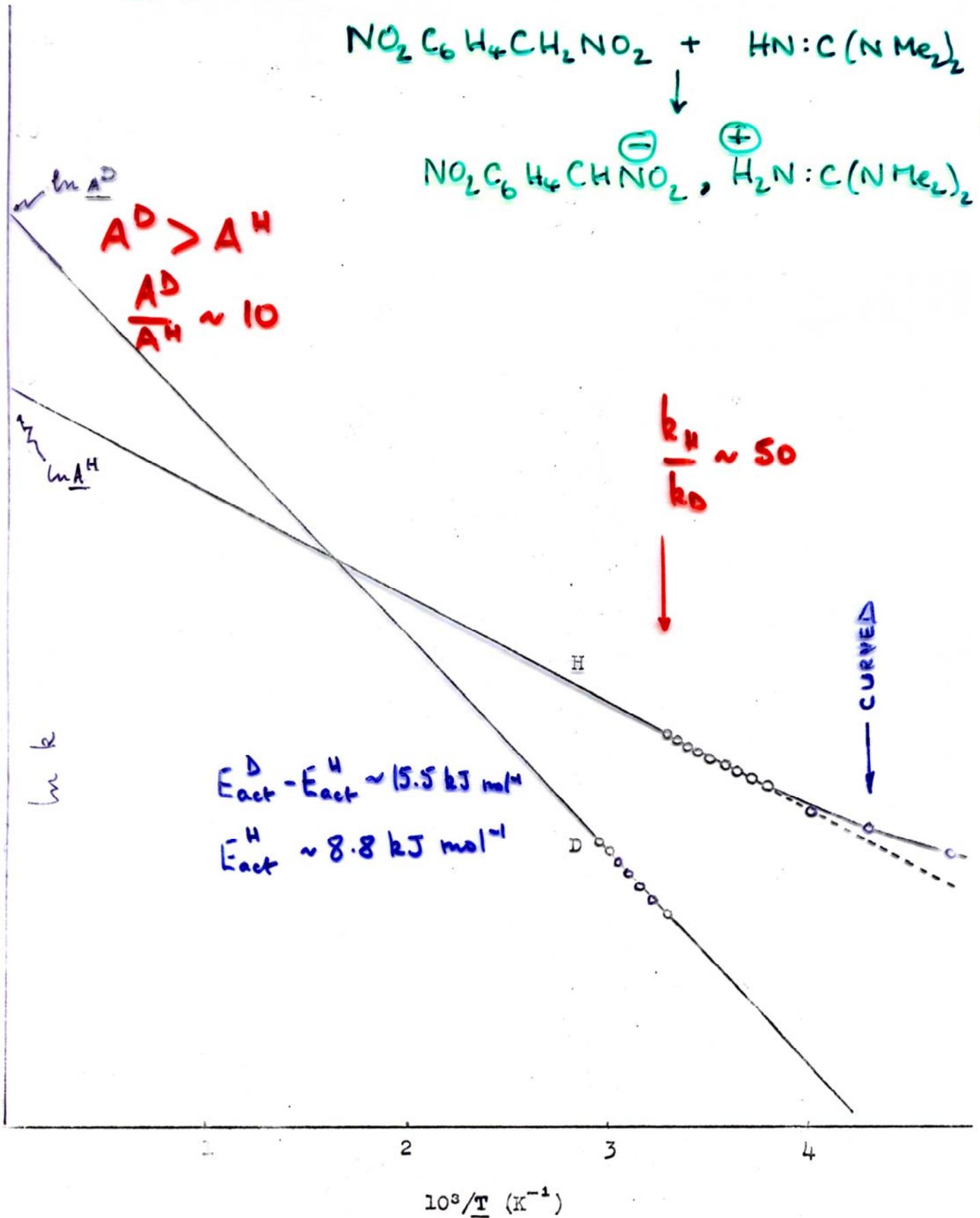
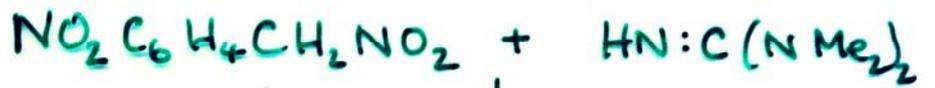
VIEW 2

Results for  $\text{H} + \text{H}_2$  reaction and its analogues with D

## **Overheads for Lecture VIII**

ER8  
V-1

# CALDIN :



ER8  
V-2

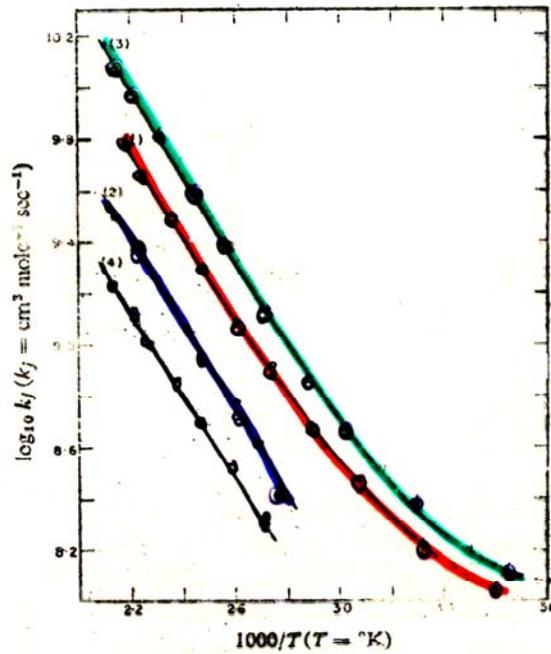


FIG. 2.—Rate constants for the reactions  $H+H_2 = H_2+H$  (1) (●),  $D_2 = D_2+D$  (2),  $D+H_2 = DH+H$  (3) and  $H+D_2 = HD+D$  (4). The curves for (1) and (3) are based on the  $\Gamma_{\text{exp}}$  method, using the parameters of table 2; those for (2) and (4) are given by eqn. (5) and (42), respectively.

