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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

THE KINETICS AND DYNAMICS OF GAS-SURFACE PROCESSES
(Lecture I)

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The Kinetics + Dynamics of Gas-Surface Processes.

L(i) Introduction. Potential energy surfaces, the Born-Oppenheimer approximation. Electronic representations. Transition state theory.

L(ii) Elementary surface processes. H_2/Cu, a prototype for adsorption/desorption. Activated processes: the Van Willigen model.

L(iii) Calculating desorption rates. Molecular dynamics of infrequent events. Crossing surfaces. Detailed balance + microscopic reversibility. Examples.

L(iv) Early + Late barriers and their influence on surface processes. Scattering. Sticking coefficients and beam properties. Precursor states. Normal vs. parallel energy scaling.

L(v) Multiple activation barriers: how are rates affected? Quantum effects in scattering. When is molecular dynamics not enough? Mode pumping and reactivity.

-Busta!

Introduction.

What do we want to understand?

Catalysis:
- Product formation
- Selectivity
- Poison / promotion

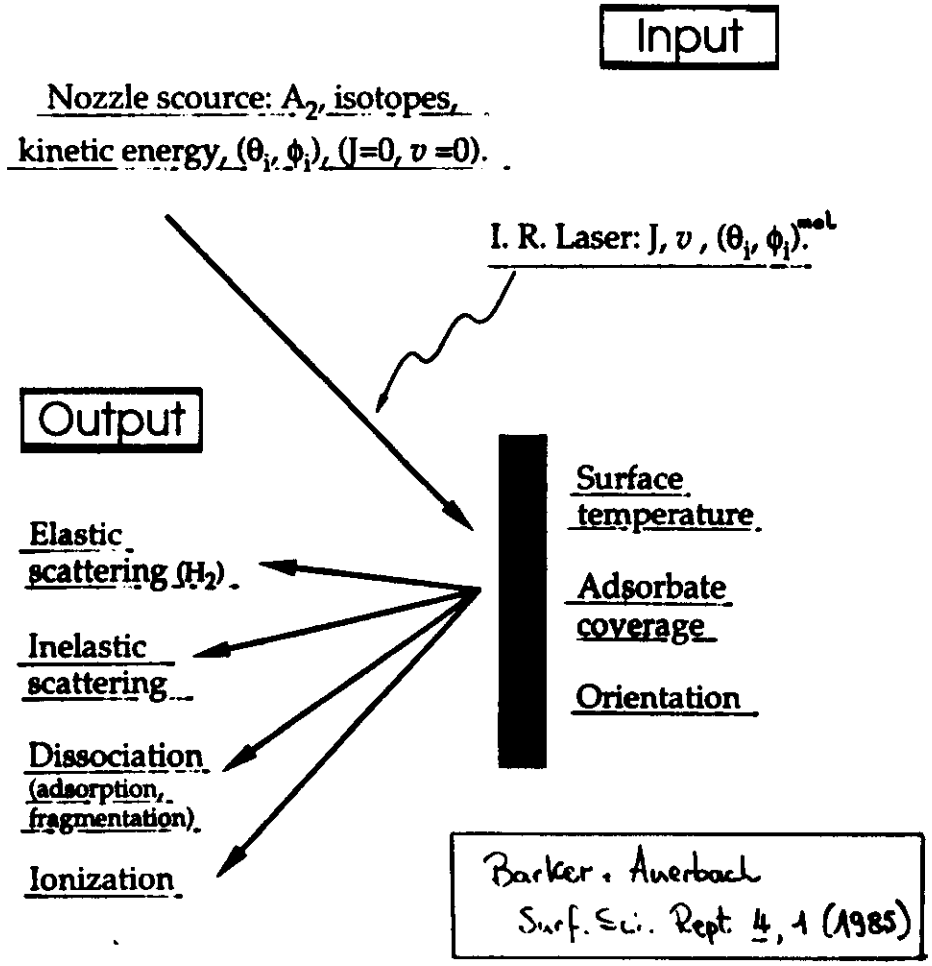
Growth Processes:
- Metal/semiconductor: MBE
- Feedstock
- Dopants
- Impurities

Oxidation:
- Adsorption/absorption
- Critical coverages
- Specificity

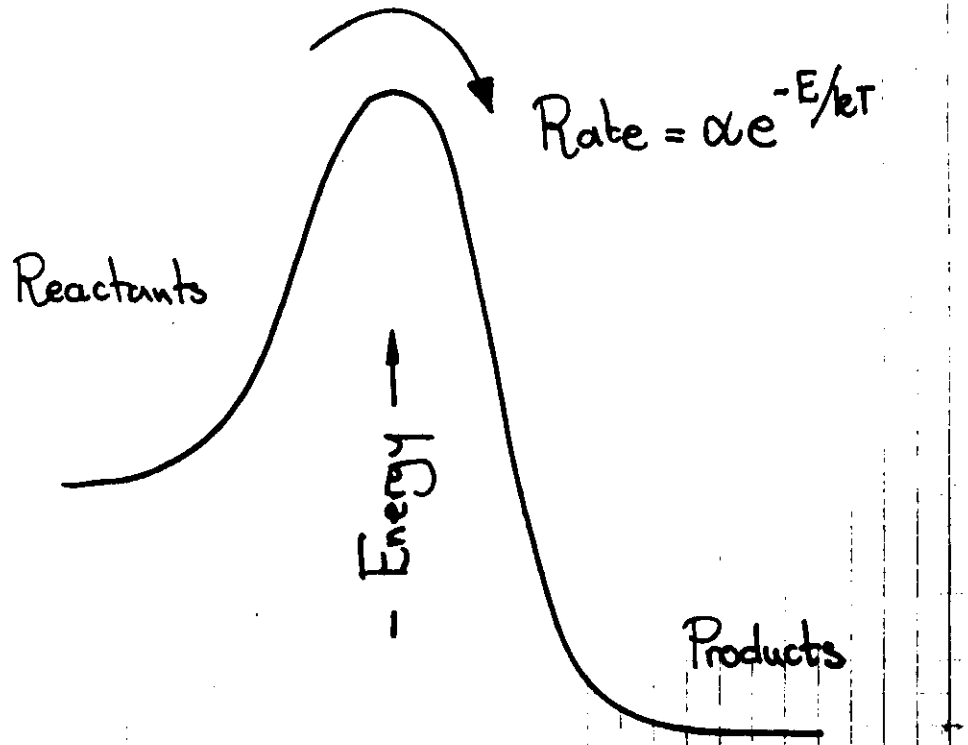
Electrochemistry:
- Liquid/solid interface
- Electric fields
- Screening
- Dipoles + free charges
- Reconstruction.

etc.. etc.. etc...

The Interaction of Molecules with Metal Surfaces



Kinetics

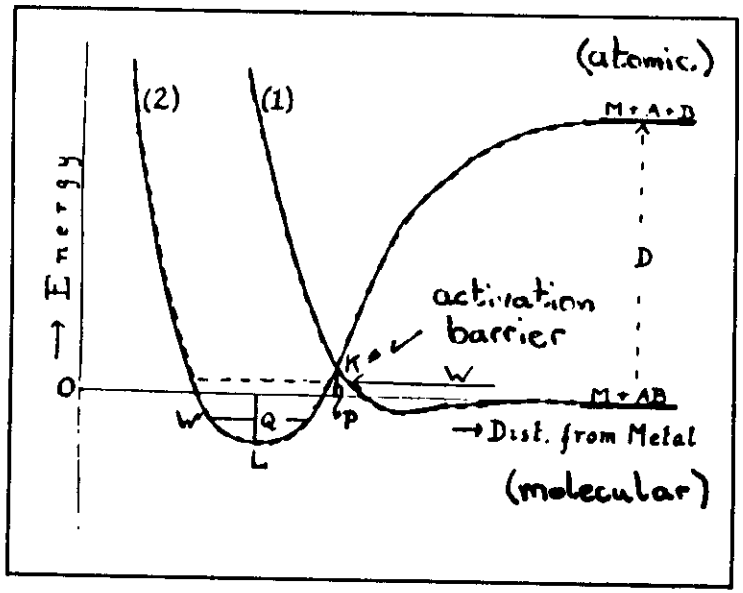


Q(i) What is the black line + where does it come from?

Q(ii) Where does the Arrhenius expression come from?

1.5

Lennard-Jones Potential Energy Surface

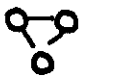


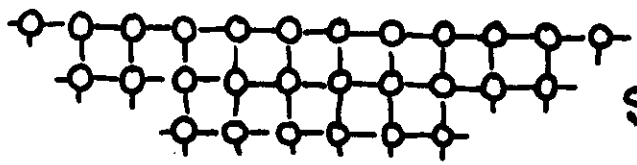
J.E. Lennard-Jones, Trans. Faraday Soc. 28, 333 (1932)

1.6

Potential Energy Surfaces.

(1) Separation of Electronic & Nuclear Motion


Gas-species


Surface

electrons $\underline{r} = (\underline{r}_1, \underline{r}_2, \underline{r}_3 \ldots \underline{r}_n)$

nuclei $\underline{R} = (\underline{R}_1, \underline{R}_2, \underline{R}_3 \ldots \underline{R}_M)$

Hamiltonian

$$\mathcal{H} = T_R + \mathcal{H}_0 \qquad (1)$$

$$T_R = \sum_{M=1}^{M} -\frac{\hbar^2}{2\mu_M} \nabla_M^2$$ { nuclear kinetic energy operator

$$\mathcal{H}_0 = \sum_{i=1}^{n} -\frac{\hbar^2}{2} \nabla_i^2 + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|\underline{r}_i - \underline{r}_j|} - \sum_{i=1}^{n} \sum_{M=1}^{M} \frac{Z_M}{|\underline{r}_i - \underline{R}_M|} + \sum_{M=1}^{M} \sum_{N>M}^{M} \frac{Z_M Z_N}{|\underline{R}_M - \underline{R}_N|}$$

electronic Hamiltonian for FIXED nuclear positions

Basis set of electronic wavefunctions $\phi_k(\underline{r};\underline{R})$ depending parametrically on $\underline{R}$. $\phi_k(\underline{r};\underline{R})$ orthonormal + complete. If $\Xi(\underline{r},\underline{R})$ is the total wave function, then

$$\Xi(\underline{r},\underline{R}) = \sum_k \phi_k(\underline{r};\underline{R})\,\chi_k(\underline{R}) \quad (2)$$

Nuclear wave function describing the motion on electronic state k.

S.E. $$(\mathcal{H} - \mathcal{E})\Xi(\underline{r},\underline{R}) = 0 \quad (3)$$

describes the complete motion of all particles with restrictions on the (prepared) asymptotic initial states

Substitute (1) and (2) into (3) gives:-

$$\left[T_R + T'_{kk} + U_{kk} - \mathcal{E}\right]\chi_k = -\sum_{k'\neq k}\left[T'_{kk'} + T''_{kk'} + U_{kk'}\right]\chi_{k'}$$

Infinite set of coupled equations for the nuclear motion $\chi_k(\underline{R})$

$U_{kk}(R) = \langle \phi_k | \mathcal{H}_0 | \phi_k \rangle$

Potential Energy Surface for electronic state k

$$\Rightarrow T'_{kk'} = \sum_{n=1}^{N-1}\left(\frac{-\hbar^2}{2\mu_n}\right)\underline{d}^{(n)}_{kk'}\cdot\underline{\nabla}_n \Leftarrow \text{velocity dependent.}$$

where $\underline{d}^{(n)}_{kk'} = \langle \phi_k | \underline{\nabla}_n | \phi_{k'} \rangle$

$$\Rightarrow T''_{kk'} = \sum_{n=1}^{N-1}\left(\frac{-\hbar^2}{2\mu_n}\right)D^{(n)}_{kk'}$$

where $D^{(n)}_{kk'} = \langle \phi_k | \nabla_n^2 | \phi_{k'} \rangle$

$$\Rightarrow U_{kk'} = \langle \phi_k | \mathcal{H}_0 | \phi_{k'} \rangle$$

These are the non-adiabatic interactions which promote transitions between potential energy surfaces.

Procedure.

Electronic ⇒ Select electronic basis functions $\phi_k(r)$

Electronic ⇒ Obtain potential energy surfaces U_{kk} and off-diagonal coupling terms

Nuclear ⇒ Solve (sic) the infinite set of coupled equations for $\chi_k(R)$.

The Born Oppenheimer separation (above) leads to a tremendous simplification in calculation. It (invariably) is possible to select a set of $\phi_k(r)$ which reduces the infinite set of coupled equations to a few.

(2) Electronic Representations.

The basis functions ϕ_k should be chosen to incorporate distortions when the gas-phase species nears the surface. the two most common are:

(i) Adiabatic

$$[\mathcal{H}_0 - E_k]\phi_k = 0$$

ϕ_k are eigenfunctions of the electronic Hamiltonian $\mathcal{H}_0$, and the potential energy surfaces

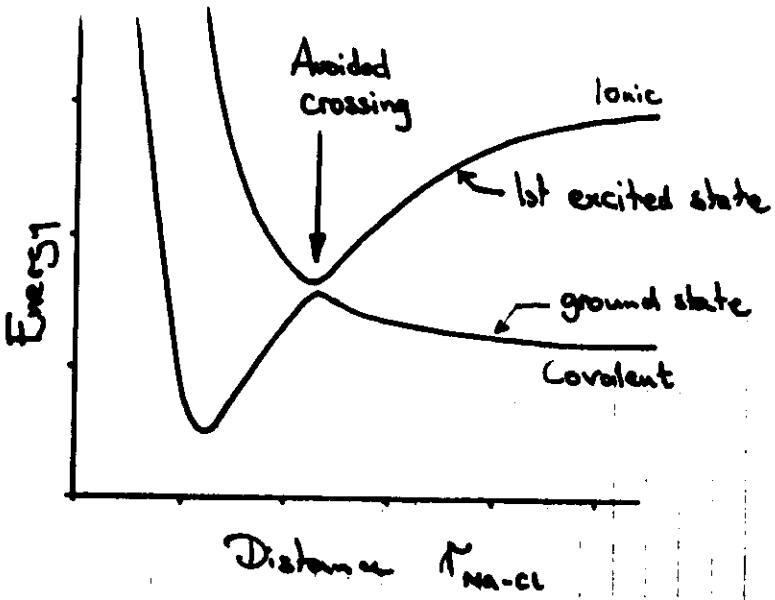
$$U_{kk}(\underline{R}) = E_k(\underline{R})$$

[c.f. Bernt Lindquist]

$T'_{kk'} \neq 0$, $T''_{kk'} \neq 0$ } Non-adiabatic coupling

Most frequently encountered since ϕ_k obey a variational principle.

example Na+Cl



For low energy collisions $T_{kk'} + T_{kk'}$ are large only when pes approach one another. Frequently occurs near regions when an electronic transition occurs (state switch). Near surfaces, the additional dimensionality gives rise to a seam which is the N-dimensional locus of an avoided crossing.

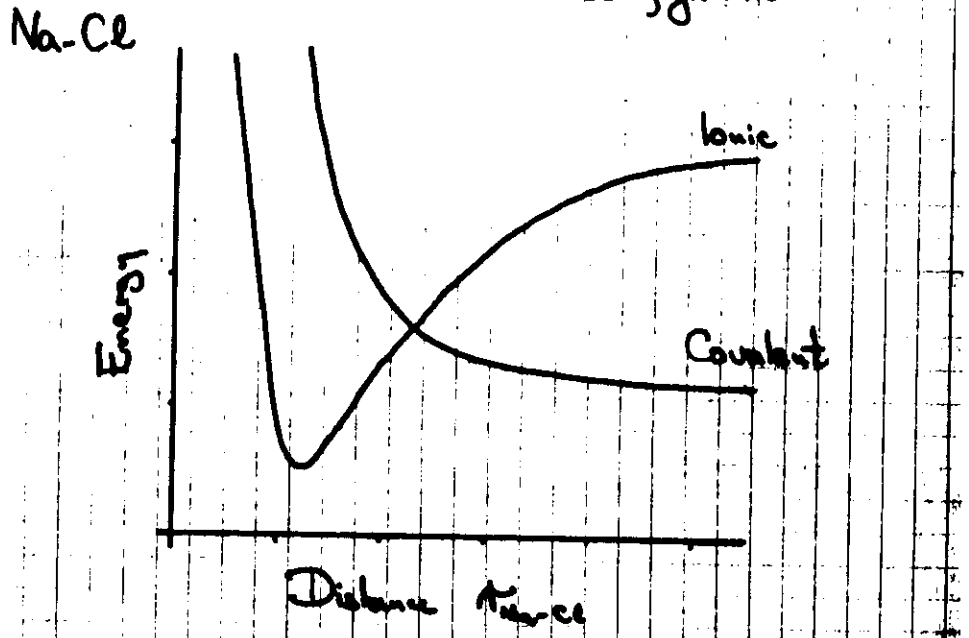
⇒ At low energies, motion will evolve on a single adiabatic hypersurface

⇒ At high energies, transitions will occur near avoided crossings

(ii) Diabatic

If motion through an avoided crossing is large, then a "surface switch" will occur with high probability

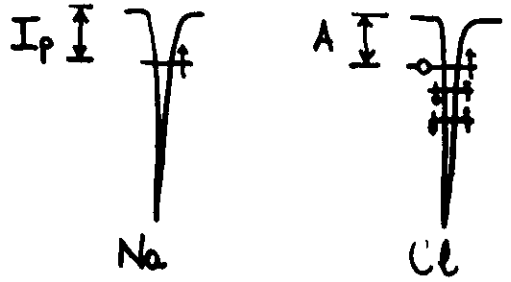
↳ choose ϕ_k to be that of the electronic configuration



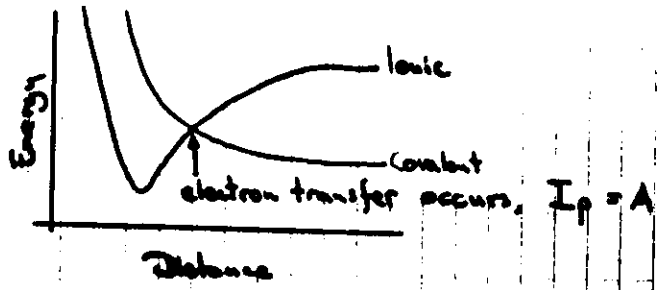
Thus the ionic and covalent pes are the diabatic states of interest

NB ⇒ There is no formal method for constructing diabatic ϕ_k

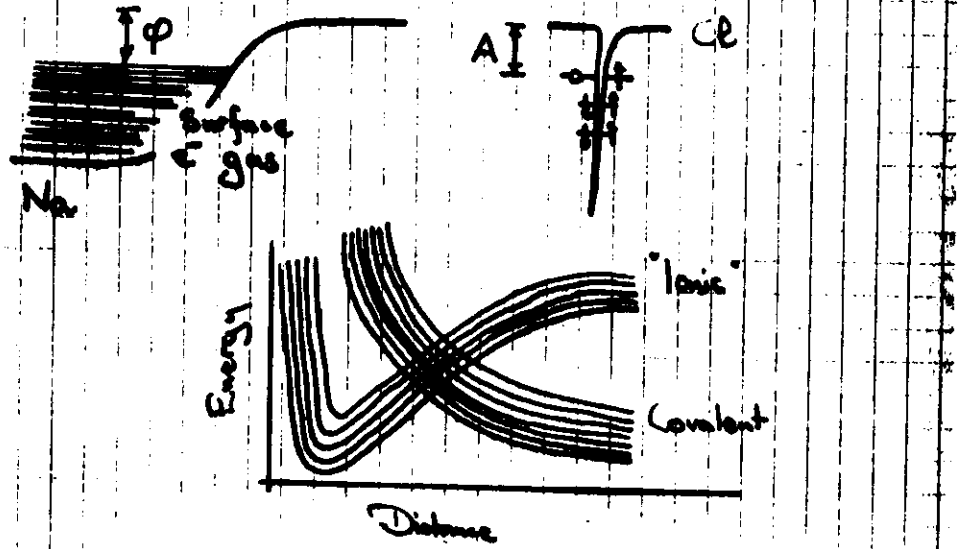
Gas-phase scattering.



Harpooning reaction



Gas-surface scattering

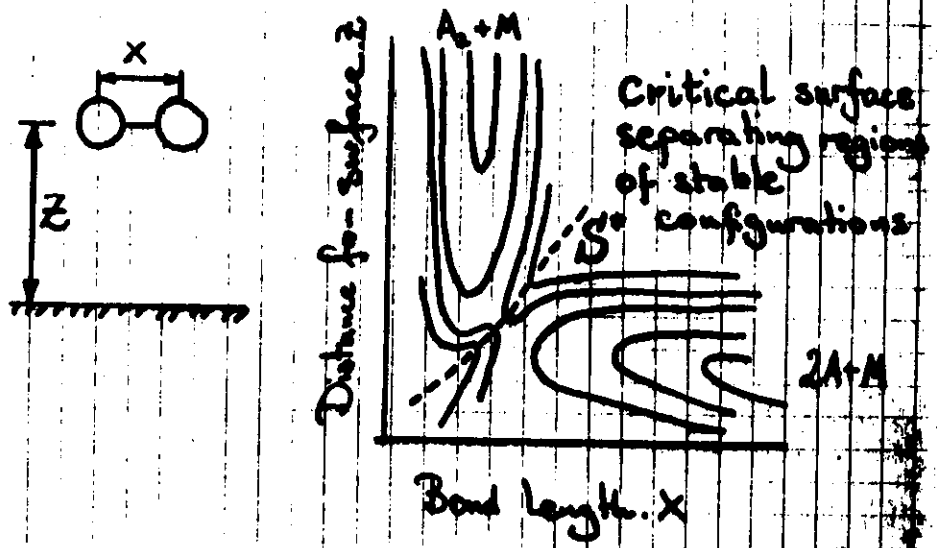


Transition state theory

H. Eyring J. Chem. Phys. 3 (1935) 107

TST (absolute rate theory) avoids all complex dynamics and averaging. It is based upon properties of the Maxwell-Boltzmann distribution function.

Rate of reaction for associative desorption



$$2A(ads) + Metal \rightarrow A_2(gas) + Metal$$

ASSUME

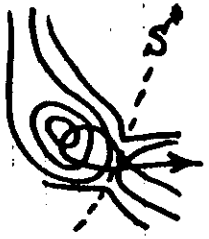
① There exists an adiabatic pes, $U(\underline{R})$ which determines the motion near the critical surface $S^{\ddagger}$.

⇒ well separated electronic states although $S^{\ddagger}$ frequently chosen to be near a seam!!

② The distribution function for representative points intersecting $S^{\ddagger}$ towards products, is the equilibrium distribution function for the reactants.

⇒ there are no fundamental reasons to believe this. Were it rigorously true, then the forward + backward rates would be the same.

③ The reaction rate is given by the velocity of representative points across $S^{\ddagger}$



⇒ Recrossing diminishes the rate of reaction. TST is an upper limit.

Example.

$$2A + M \rightleftharpoons \ddagger \rightarrow A_2 + M$$

↑ "activated complex"

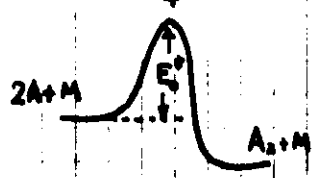
Rate = [conc ‡] × decomposition rate of ‡

= $[\ddagger] \cdot f$

equilibrium constant $\tilde{K} = \dfrac{[\ddagger]}{[2A][M]}$

↳ $\underline{\text{Rate} = f \tilde{K} [2A][M]}$

In general $\tilde{K} = \dfrac{Q^{\ddagger}}{Q_{2A} Q_M} e^{-E_0^{\ddagger}/kT}$ ← partition function



$$Q = \prod_i q_t^i q_r^i q_v^i$$

In passing from reactants → products one mode of vibration [along reaction coordinate, $\nu^{\ddagger}$] softens. Then

$f = \nu^{\ddagger}$ · rate of crossing ‡

For the activated complex $Q^{\ddagger} = Q^{\ddagger\prime} q_{\nu^{\ddagger}}$

$$q_{\nu^{\ddagger}} = \frac{1}{1 - e^{-h\nu^{\ddagger}/kT}} \approx \frac{kT}{h\nu^{\ddagger}}$$

⇒ $\boxed{\text{Rate} = \dfrac{kT}{h} \dfrac{Q^{\ddagger\prime}}{Q_{2A} Q_M} e^{-E_0^{\ddagger}/kT}}$