
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**On relations between activity constant and activation
energy in chemical kinetics**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 57 (1974), n.6, p. 649–654.*
Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1974_8_57_6_649_0>

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica fisica. — *On relations between activity constant and activation energy in chemical kinetics* (*). Nota (**) del Socio Straniero HERMANN HARTMANN.

RIASSUNTO. — Viene discusso un modello molto semplice di processo bimolecolare e si dimostra che esso è particolarmente ben adatto a spiegare effetti cinetici compensativi.

The non specifically acid-catalysed hydrolysis of esters in aqueous solution has been since a long time a favourite object for studies on chemical kinetics in liquid phase.

Hinshelwood and Fairclough ⁽¹⁾ have assumed that all those reactions run over the same mechanism. For the velocity v the law holds

$$v = k [H^+] [E]$$

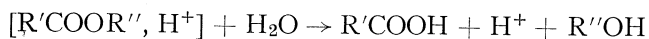
where $[H^+]$ and $[E]$ are the concentrations of hydrogen ions and ester. Normally to a good approximation the Arrhenius equation holds

$$k = A e^{-\frac{E}{RT}}$$

where A and E are the action constant and the activation energy.

Hinshelwood and Fairclough have shown, and Hartmann and Kleinpaul ⁽²⁾ have given further evidence, that a comparison of pairs of values of A and E for different reactions belonging to the class of reactions named, leads to the result, that within this class A seems to be a monotonically increasing (decreasing) "function" with increasing (decreasing) E . This statement has the character of a rule. But even the work of Hartmann and Kleinpaul has shown that the rule is exact enough to select reactions with very low action constants.

It is reasonable to assume that the bimolecular process



is at least practically the rate determining step and so there arises the problem of understanding how for bimolecular processes A which is determined by

(*) Dedicated to Prof. E. Wicke on occasion of his sixtieth birthday.

(**) Presentata nella seduta il 14 novembre 1974.

(1) R. A. FAIRCLOUGH and C. N. HINSHELWOOD (1938) — «J. Chem. Soc. [London]», 236.

(2) H. HARTMANN and W. KLEINPAUL (1960) — «Zeitschr. f. physik. Chem. Neue Folge», 25, 415.

some sort of collision number is related to E which is an internal quantity of the transition complex.

The purpose of this note is to show that already for a very simple model system allowing a bimolecular process there can be shown that it is possible to understand the postulated type of relation.

The model shall contain as a first part three masspoints all lying on a straight line. One of these bodies shall be fixed. The other two shall have equal masses (m) and their distances from the fixed body shall be described by x and y . A further part of the model shall be a harmonic oscillator with frequency ν and coordinate q .

The coordinate space (x, y, q) of the model is split into regions according to a splitting of the (x, y) -subspace.

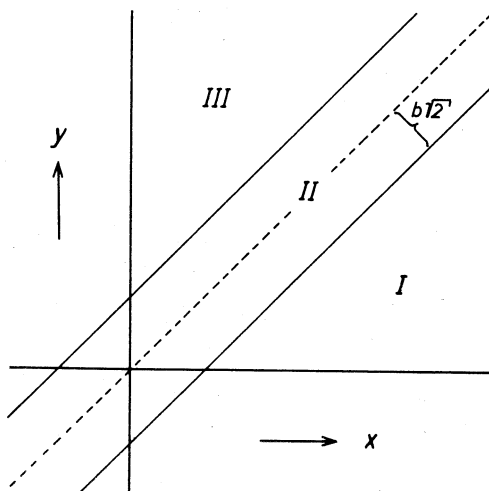


Fig. 1.

In fig. 1 there are shown the three regions I, II, III. For all configurations of the whole model belonging to the regions I and III, we assume the potential energy of the model to be of the separated form

$$V = M(x, y) + N(q).$$

Only for configurations belonging to the region II we assume a coupling between the 3 resp. 2-mass system and the oscillator, so that the general expression for the potential energy will be

$$V = M(x, y) + N(q) + W(x, y, q)$$

where W disappears outside II.

We introduce further assumptions on the function $M(x, y)$ for configurations lying inside II. First we define new coordinates ξ, η by

$$\xi = \frac{1}{\sqrt{2}} (x - y)$$

$$\eta = \frac{1}{\sqrt{2}} (x + y - 2a).$$

Then we assume

$$M(x, y) = E(b\sqrt{2} - \xi)/b\sqrt{2} + \frac{c}{2}\eta^2 \quad \text{for } 0 \leq \xi \leq b\sqrt{2}$$

and

$$M(x, y) = E(\xi - b\sqrt{2})/b\sqrt{2} + \frac{c}{2}\eta^2 \quad \text{for } -b\sqrt{2} \leq \xi \leq 0.$$

The contour map of the potential energy function M is represented in fig. 2.

M is a highly simplified, but typical reactive energy surface in the neighbourhood of the transition point.

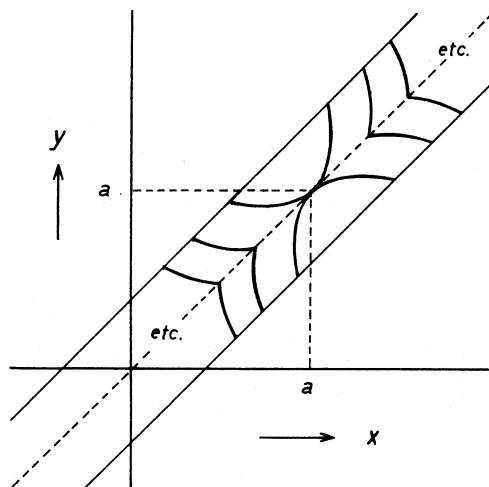


Fig. 2.

About $N(q)$ we assume

$$N(q) = \frac{k}{2}q^2.$$

$N(q)$ is the potential energy of an harmonic oscillator, which in our model resembles a molecular vibration located a bit more distant from the reactive region.

If at first we neglect the coupling function W , a reactive trajectory enters the region II at some point on the straight line $\xi = b\sqrt{2}$ and after a time interval of length τ crosses the line $\xi = 0$. In the domain between $\xi = b\sqrt{2}$ and $\xi = 0$ the Lagrangian equations are

$$m\ddot{\xi} - E/b\sqrt{2} = 0$$

$$m\ddot{\eta} + c\eta = 0.$$

The problem is separated in the coordinates we have chosen. There is no energy exchange between the ξ - and the η -degree of freedom during the

motion. With respect to realistic conditions in chemical kinetics we are essentially interested in trajectories which just reach the line $\xi = 0$ with the corresponding velocity $\dot{\xi} = 0$. So we are only interested in the first Lagrangian equation and in the special solution of it:

$$(1) \quad \xi = b\sqrt{2} \left(1 - \frac{t}{\tau}\right)^2$$

with

$$(2) \quad \tau = 2b\sqrt{\frac{m}{E}}.$$

The zero of the time scale corresponds to the position $\xi = b\sqrt{2}$.

The next step in our treatment is to introduce the coupling between the q -oscillator and the motion in the x, y - resp. ξ, η -system. As already stated we assume that such coupling will happen only in region II and with regard to continuity conditions at $\xi = b\sqrt{2}$ the most simple function W is

$$(3) \quad W = K(b\sqrt{2} - \xi)q.$$

If we treat the q -oscillator as a quantized system the coupling executed by W may have the consequence that within the time interval $t = 0 \rightarrow t = \tau$, energy originally present in the ξ -degree of freedom may go over to the q -degree of freedom. That means that only a fraction of processes which started with a sufficient amount of energy in the ξ -degree of freedom finally will become really reactive, while in some cases the remaining energy in the ξ -degree of freedom does not suffice to overcome the barrier at $\xi = 0$.

This is the essential point of our proposal and we can now try to calculate the probability for the excitation of the q -oscillator using Dirac's perturbation theory. Substitution of (1) into W (3) leads to

$$W = b\sqrt{2}Kq \frac{t}{\tau} \left(2 - \frac{t}{\tau}\right).$$

The action of this perturbing potential can only lead to changes of the q -oscillators quantum number by one unit. It is reasonable to assume that this quantum-number at the time $t = 0$ has the value $n = 0$. So we have to think about the excitation process $n = 0 \rightarrow n = 1$. According to Dirac's theory the statistical amplitude of the state $n = 1$ at the time $t = \tau$ is

$$a_{10}(\tau) = -\frac{i}{\hbar} \int_0^\tau U_{10} dt$$

with

$$U_{10} = \int_{-\infty}^{\infty} e^{2\pi i \nu t} \psi_1(q) W \psi_0(q) dq.$$

We introduce the abbreviation

$$q_{10} = \int_{-\infty}^{\infty} \psi_1(q) q \psi_0(q) dq$$

so that we have

$$a_{10}(\tau) = \frac{ibK\sqrt{2}}{\hbar} q_{10} \int_0^{\tau} e^{2\pi i \nu k} \frac{t(t-2\tau)}{\tau^2} dt.$$

For reactions which are slow enough so that their velocity can be easily measured, the period $\tau_v = 1/\nu$ is probably small against τ and that means that in the last integral we can substitute unity for $\exp(2\pi i \nu t)$. So we get

$$\begin{aligned} a_{10}(\tau) &\approx \frac{ibK\sqrt{2}}{\hbar} q_{10} \int_0^{\tau} \frac{t(t-2\tau)}{\tau^2} dt \\ &= -\frac{ibK}{\hbar} \frac{2\sqrt{2}}{3} \tau = -\frac{4}{3} \frac{ib^2K}{\hbar} q_{10} \sqrt{\frac{2m}{E}}. \end{aligned}$$

The probability for the ξ -degree of freedom not having lost energy during the essential phase of the reactive process is

$$w = 1 - a_{10}^* a_{10} = 1 - \frac{\gamma}{E}$$

with

$$\gamma = \frac{32}{9} \frac{K^2 q_{10}^2}{\hbar^2} b^4.$$

The action constant A contains the quantity w as a factor and so we have

$$\ln A = \text{const.} + \ln \left(1 - \frac{\gamma}{E} \right)$$

or

$$(4) \quad \ln A = \text{const.} - \frac{\gamma}{E}$$

if γ/E is small compared with unity.

If we compare reactions of the same type, it is reasonable to assume the same value for the breadth b of the reaction zone in the coordinate space. Then (4) with constant γ describes the relation between A and E and from that equation one can see how A increases with increasing E .

A more elaborate treatment ought to have included transitions with initial energies $> E$ in the ξ -degree of freedom. The abundance of such transitions should be assumed to decrease exponentially with increasing energy. It is easy to see how our result would be modified by the inclu-

sion of such transitions. Certainly the increase of an A with increasing E would become slower than according to formula (4).

Hinshelwood and Fairclough have given the empirical equation

$$(5) \quad \ln A = \text{const.} - \frac{\gamma'}{E^{1/2}}$$

where γ' is a constant. But the known empirical data coincide with equation (4) nearly as well as with equation (5).

In fact the goal of this note has certainly not been to reach quantitative coincidence. Our aim has been to show that already an extremely simple model can in principle lead to a qualitative explanation of the Hinshelwood-Fairclough-relation, which so far in chemical kinetics has been visualized as a very strange fact.