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Abstract

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On the Resonance Theory of the Rates of Chemical Reactions

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1. In recent years the problem of determining the rates of chemical reactions caused by hot atoms, ions, radicals, and molecules with kinetic energy of translational motion E, lying in the range from tenths of an electron-volt to the value of the first excitation potential of electronic terms, has become topical. Similar problems are also posed by the chemistry of new atoms and molecules (muonium, mu-mesonic molecules, positronium, etc.). An attempt to apply in this energy region the method of the equilibrium complex is not justified and raises objections ([1,2]). Experimental results ([2]) are also not in agreement with the model of direct knocking-out of atoms from a molecule by an incident hot atom, since from the point of view of this model reactions should predominate that are not accompanied by binding of the incident atom in one of the fragments of the molecule. In the present work, on the basis of a number of arguments, it is proposed that the scattering amplitude and the cross sections of the reactions under consideration are in a number of cases determined mainly by resonance terms and are described by the Breit-Wigner formula ([3–6]). This proposal also applies to certain other inelastic bimolecular processes. To substantiate this proposal we use some general concepts of the modern theory of scattering and nuclear reactions ([5–9]), based on the study of the analytic properties of the scattering amplitude. The considerations developed may also prove useful at low energies, when the method of the equilibrium complex is valid.

The resonances under consideration are formed if, in the course of collision, the interaction energy between the colliding systems becomes, owing to the overlap of their electronic wave functions, of the same order as the energy of chemical bonds. The state of the colliding systems that arises in this way can be visualized as the state of a certain unstable compound molecule. In the case of collision of two atoms, another visual interpretation can also be given, by associating resonances of elastic scattering with virtual transitions from a repulsive term to an attractive one and back in the vicinity of the point of intersection of the terms. In the case of collision of a hot atom with a polyatomic molecule that does not possess a system of conjugated bonds, a similar interpretation can be given if one takes into account that only one of the atoms composing the molecule participates in the formation of the complex.* The influence of the remaining atoms on the decomposition of the compound molecule should be taken into account only in those cases when its lifetime is comparable with the characteristic time of energy transfer through the molecule. In this case the transfer of energy to other degrees of freedom may be regarded as the addition of new channels for the decomposition of the complex. This makes it possible, in the limiting case, to pass from isolated resonances to the ordinary theory of the equilibrium complex. The local character of the strong interaction caused by overlap of the electronic wave functions makes it possible to—approximately represent the scattering amplitude $f(\theta)$ of an atom by a polyatomic molecule, as in the collision of two atoms, in the form of a series in symmetric-top functions ($^{3}, ^{14}$), depending, in particular, on the projection Λ of the orbital electronic angular momentum on the line joining the two nuclei. By studying the analytic properties of the S-matrix continued to complex values of Λ, one can develop a theory analogous to Regge theory ($^{8}, ^{9}$). For our further arguments it is sufficient to assume that, in this case, the principal conclusions of Regge theory ($^{8}, ^{9}$) remain valid for Λ. Then the following results may be expected. The complex energies $\mathcal{E}$ of bound states and resonances are continuous functions of the complex projection of electronic angular momentum λ. The observed bound states and resonances correspond only to points where $\operatorname{Re}\lambda = \Lambda$ (Λ an integer)*. In this case $\operatorname{Im}\mathcal{E}(\Lambda + \operatorname{Im}\lambda) \sim \operatorname{Im}\lambda \geq 0$, so that true bound states ($\operatorname{Im}\mathcal{E} = 0$) correspond to $\operatorname{Im}\lambda = 0$. The following features of pole trajectories will be important below. A pole first moves from left to right along the real axis; then, for some $\lambda = \lambda_0$, the trajectory goes into the upper half-plane. Its departure from the real axis is the slower, the larger λ_0 is. If there are no bound states on the trajectory, then there are no resonances either, and the trajectory rapidly goes into the region of large $\operatorname{Im}\lambda > 0$ and then bends toward $\operatorname{Re}\lambda < 0$. However, even for $\lambda_0 > 1$ the number of resonances is small; moreover, each successive resonance has a greater width than the preceding one, while the energy differences between them remain, in the initial part, approximately the same and correspond to the energy differences of neighboring bound states on the given trajectory**.

As follows from the preceding, when a hot atom collides with a molecule, scattering in the electron-volt region will in most cases be determined by a single resonance term. Then, according to the Breit–Wigner formula (^{4}), for the cross section we have the general expression

$$\sigma_{fi}(E) = \sum_{\alpha} g_i^{C_\alpha} \pi \lambda_i^2 \Gamma_i^{C_\alpha} \Gamma_f^{C_\alpha} / \left[\left(E - E'_{C_\alpha}\right)^2 + \left(\frac{1}{2}\Gamma^{C_\alpha}\right)^2 \right], \qquad (1)$$

where λ is the de Broglie wavelength corresponding to the relative motion of the

* Strict fulfillment of this condition is not necessary, and in the general case it may be discarded (for example, in "bond attack" (^{2})). Then one must first decompose the scattering amplitude into components corresponding to different axes of symmetry.

colliding systems, $\Gamma_i^{C_\alpha}$ and $\Gamma_f^{C_\alpha}$ are the partial widths of the entrance and exit channels, Γ^{C_α} is the total width, E'_{C_α} is a quantity close to the resonance level E_{C_α} (^{9}), and $g_i^{C_\alpha}$ is the statistical weight of the state with a definite projection Λ, definite total spin, and parity. The summation over α is a summation over all atoms of the molecule, or, more precisely, over all geometrically possible ways of forming the complex. It is assumed here that an averaging over the different directions of collision has been carried out. Including among the partial widths the widths $\Gamma^{C_\alpha}_{f\rho\varepsilon}$, corresponding to transfer of energy to various degrees of freedom of the molecule, the cross section of the chemical reaction $\sigma^R_{fi}(E)$ can be written as

$$\sigma^R_{fi}(E) = \sum_{\alpha,\varepsilon,\rho} g_i^{C_\alpha}\pi\lambda_i^2\Gamma^{C_\alpha}_{f\rho\varepsilon}\Gamma_i^{C_\alpha}\varkappa_{\varepsilon\rho f}/\left[\left(E-E'_{C_\alpha}\right)^2+\left(\frac{1}{2}\Gamma^{C_\alpha}\right)^2\right], \qquad (2)$$

where $\varkappa_{\varepsilon\rho f}$ is the probability of reaction through channel f, if the degree of freedom ρ has energy ε. In its meaning this quantity is analogous to the so-called to the transmission coefficient in the activated-complex theory. The quantities $\Gamma^{C_\alpha}_{f\rho}$ can, in principle, be calculated with the aid of the pair-correlation function of Van Hove (^{10}). In an analogous way one can also consider the transfer of energy from excited molecules to other molecules by collisions and by means of direct electromagnetic interaction of the type (^{11}). Let us note that formula (2), without further qualifications, is suitable only for such reactions as have time to occur before the process of multiple transfer of excitation energy from some degrees of freedom to others begins.

2. The rate J_{fi} of a bimolecular reaction in the gas phase may be written in the form

$$J_{fi}(t) = \sum_{A,B} n_A(t)n_B(t)\int dp\,|\mathbf{v}|\,\sigma^{AB}_{fi}(E)\,F(\mathbf{p}), \qquad (3)$$

where $\mathbf{p}$, $\mathbf{v}$, and E are the momentum, velocity, and energy of the colliding molecules of components A and B in the c-system, n_A and n_B are the numbers of molecules of these components per unit volume,

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* In the case of exchange interaction, certain complications arise, not of a fundamental nature, connected with the necessity of separately considering states of different parity.

** Thus the system of colliding particles as it were "senses" the presence of bound states existing in this system at negative energies.

$$F(\mathbf{p}) = \iint d\mathbf{p}_A \, d\mathbf{p}_B \, f_{AB}(\mathbf{p}_A, \mathbf{p}_B) \, \delta(\mathbf{p}_A - \mathbf{p}_B - \mathbf{p}),$$

$\mathbf{p}_A$ and $\mathbf{p}_B$ are the momenta in the l-system, and $f_{AB}(\mathbf{p}_A, \mathbf{p}_B)$ is the binary distribution function. In the case where the deviation from the equilibrium distribution is so small that it may be neglected in calculating reaction rates, f_{AB} is calculated from the grand canonical distribution. Formula (3) is obviously simplified when considering reactions of hot atoms, the kinetic energy of whose translational motion substantially exceeds the average energy of thermal motion at a given gas temperature T, since then the molecules of the medium may be regarded as immobile.

Substitution into (3) of expression (1) for $\sigma_{fi}^{AB}(E)$ leads, in the equilibrium case, to a rather peculiar dependence of J_{fi} on temperature, with a certain maximum against the background of an almost Arrhenius curve. For $kT \ll E_{C_\alpha}$, an Arrhenius curve is obtained with activation energy $E_{C_\alpha} + (1/2)\Gamma^{C_\alpha}$.* For $kT > E_{C_\alpha}$, the reaction rate over a certain interval will decrease according to the law $T^{-3/2}$. In particular, this should occur already at moderate temperatures in the case where E_{C_α} is close to zero or even less than zero, for example in recombination and disproportionation reactions. The indicated phenomenon has been observed experimentally (see, for example, ([12])). An analogous effect should also be observed for the dependence of the rates of reactions of hot atoms on their initial energy, if the medium is an energetic moderator. From (1) and (3) it follows that for any two reactions $i \to f$ and $i \to f'$ of components A and B (or χ and A) the relation

$$J_{fi}^{\alpha,AB} / J_{f'i}^{\alpha,AB} = \Gamma_f^{C_\alpha} / \Gamma_{f'}^{C_\alpha} = \text{const},$$

must hold if both reactions proceed through a compound molecule with one quasistationary state.** If one takes into account what was said above about the local character of the complex, then from this relation one can obtain interesting consequences pertaining already to reactions of different pairs

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* We emphasize that the physical meaning of the activation energy when the Breit-Wigner formula is used is substantially different from that in the transition-state method.

** This consequence of the assumption concerning the resonance character of the reactions can be tested experimentally by varying $n_\chi(E,t)$ (by introducing different concentrations of inert atoms) or by varying the temperature (in high-temperature chemistry and in plasma chemistry). Fulfillment of this relation is a criterion that the corresponding reactions proceed through one quasistationary level. Experiment apparently indicates the independence from temperature of the ratio of the rates of recombination and disproportionation of methyl radicals

(^{13}), although, according to the usual interpretation, the latter reaction should have a nonzero activation energy.

components and with different a, for example, to reactions of hot hydrogen atoms with molecules having different numbers of identical C or H atoms.

3. In the chemistry of hot atoms, $n_\chi(E, t)$ is the solution of a kinetic equation; to write this equation it is necessary to know the form of $\sigma_{fi}(E)$ and the effective cross section $\sigma_{s\chi A}(E)$ for collisions of the hot particle with gas molecules that lead to loss of energy by this particle. We have considered the case in which the energy loss in a single collision is small compared with E. In the stationary case, for a one-component gas A, in which hot atoms of one type χ propagate, we obtain the equation

$$\frac{|v|}{\lambda(E)} n_\chi(E) = \int_E^{E_0} dE' \, \frac{|v'|}{\lambda_s(E')} K(E, E') n_\chi(E') + Q(E), \tag{4}$$

$$\lambda(E) = \left\{ \left[\sigma_s(E) + \sum_f \sigma_{fi}(E) \right] n_A \right\}^{-1}, \qquad \lambda_s(E) = [\sigma_s(E) n_A]^{-1}, \quad K(E, E')\, dE\, dE'$$

is the probability, normalized to unity, of a change in energy upon collision of a hot atom with a molecule from a value $\tilde{E} \in (E', E' + dE')$ to a value $\tilde{E} \in (E, E + dE)$. Solving (4) by reduction to a differential equation, restricting ourselves to the case $Q(E) = D\delta(E - E_0)$ $(E_0 > E_c)$, and finding J_{fi}, we obtain*, that

$$J_{fi} = \frac{D\hbar^2 \pi g_i^C (1-p) q}{m\sigma_A \ln(1/p) r} \frac{\Gamma_i \Gamma_f}{\Gamma^2} \frac{n}{E_c' + \Gamma/2} \times \{1 - \exp\left[-(r/q)\Gamma\right]\}, \tag{5}$$

where $q \ll 1$ is the mean value of the relative energy loss in one collision, $r = (\sum_f I_f)/\Gamma_i$, $p = [(M - m)/(M + m)]^2$, M and m are the masses of the gas molecule and the hot atom, and $\sigma_A = \text{const}$ is the geometrical cross section of the gas molecule.

We have retained only the principal term in the expression for the reaction rate, taking into account only reactions occurring in the resonance region of width Γ. Allowance for the influence of the “tails”of the resonance formula (1) only slightly refines expression (5), without introducing any qualitative changes. According to (5), the rates of reactions of the type under consideration do not depend on E_0. This is not the case if $q \sim 1$.

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* In this, all cross sections entering into (3) and (4), with the exception of the nonresonant part σ'_s of the cross section σ_s, were determined by formula (1).

The slowing down was attributed entirely to elastic scattering of hot atoms on molecules. σ_s' was determined as the collision cross section of elastic spheres.

Note: Figure translations are in progress. See original paper for figures.

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