Revista Mexicana de Física 22 (1973) 351-373

THE MANY-BODY APPROACH TO CHEMICAL KINETICS

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(Recibido: enero 21, 1974)

ABSTRACT: In this review we approach the theory of chemical reactions emphasizing the N-body character of the process. The present status of the description of chemical kinetics as a transport phenomenon is critically assesed. This point of view should account for the irreversibility and non-linearity exhibited by the system. We review briefly the reduction from the many-body dynamics to fundamental two-body interactions by studying the reactive cross sections. Existing theories for unimolecular reactions are analyzed to emphasize how their vicissitudes have prevented a parallel development of this point of view. Several suggestions are given in different directions as to how to venture into a more fundamental de-

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scription of the problem. Extensions and corrections to the well known macroscopic equations are also indicated.

1. INTRODUCTION

The idea behind the elaboration of this review is to present chemical reactions as a many-body problem. It is not common to encounter this philosophy concerning reactive kinetics. We intend to establish a point of view which may be attractive to theoretical physicists interested in other N-body phenomena, as well as refreshing to specialists that all too often are faced with half-hearted and partial attempts at genuine statistical mechanical treatments of chemical reactions. This approach calls for a biased selection and evaluation of the enormous amount of material in the field. The orthodox theories have been the subject of many excellent books and reviews, some of which are included in the Bibliography at the end of the paper[I-IX].

Thermodynamics deals with chemical reactions by introducing the concept of chemical equilibrium, defined in terms of a minimal free energy. A partial description is thus achieved by computing the equilibrium constant.

The evolution of the system entails however, rate equations which in general are nonlinear as:

$$-dA/dt = kAB - k'CD \quad , \tag{1.1}$$

where A, B, C, D represent the chemical species densities, and k, k' are the rate constants for the following reaction:

$$A + B \underset{k'}{\overset{k}{\rightleftarrows}} C + D \quad . \tag{1.2}$$

In order to write (1.1), the law of mass actions for ideal systems is invoked.

The rate constants are considered to depend only on the temperature through the expression:

$$k(T) = a \ \exp\,(-E^{*}/k_B T) \tag{1.3}$$

known as Arrhenius' law. Here E^{*} is the activation energy and a is called the pre-exponential factor, which might also depend on T.

A rationale of Eq. (1.1) is given in Irreversible Thermodynamics[X]. Indeed we can describe the reaction in terms of the affinity $\mathcal{A}$. The rate of depletion J is, in the linear approximation:

$$J = - L(\mathcal{A}/T), \tag{1.4}$$

where L is a phenomenological coefficient. However, in contrast to other processes studied by Thermodynamics, the linear relationship is inadequate. In fact, a more general expression for J is given[1] by:

$$J = k' CD \left[\exp(-\mathcal{A}/k_B T) - 1 \right] . \tag{1.5}$$

Hence, the equations describing the reaction's evolution are also non-linear in $\mathcal{A}$ and (1.4) is just a linear approximation valid only when $\mathcal{A} << k_B T$

Most treatments of chemical kinetics are focused at the explanation of Eq. (1.3). Amomg these, the best known is perhaps Eyring's theory, which is indeed covered in many books, ranging from the 1930's to date[I-IV, VI]. This model relates E^* to the enthalphy, while the pre-exponential factor a in Eq. (1.3) is considered to contain quantum information such as tunneling effects. Thus a mixture of microscopic and macroscopic concepts results, whithout really analyzing the statistical N-body problem. It is for this reason that we shall not discuss this important aspect of reactions. Yet we shall give a brief description of the use of potential energy surfaces in Section 3

A historical viewpoint closer to ours is that of the early developments of collision theory[XI], Indeed in 1916, Trautz and later McLewis[2] gave a kinetic explanation of the factor a in (1.3) assuming hard sphere collisions. Similar treatments have been advanced directly from the reactive cross sections, mostly for bimolecular reactions. They are well summarized in Ref. 3.

A way to circumvent the many-body problem is by means of a stochastic description. This method has been applied to reactions,[XII-XIII] which in this context are looked upon as death-birth processes[4]. Starting from master equations, the empirical rates are reproduced, without involving the detailed dynamics.

As mentioned earlier, all of these theories attempt to reproduce either Arrhenius law or the empirical rate equation (1.1) . This shall not concern us here as a primary aim. Our purpose instead is to reduce the many-body problem, with its intrinsical irreversibility into the reversible few-body dynamics. Both the macroscopic rate equations and the phenomenological coefficients should appear as a natural consequence of the averaging process.

The plan of the article is as follows: in the next section we present the attempts to describe chemical reactions as a transport phenomenon, providing the searched link from the many-body description to few-body dynamics. The status of direct computations of two-particle interactions is analyzed in Section 3. The very special case of unimolecular decompositions is reviewed critically in Section 4, showing that the *N*-body approach is practically non-existent for these reactions. Finally a very personal appraisal of promising new developments is established in the Outlook, corresponding to Section 5.

2. THE TRANSPORT EQUATIONS

The most fundamental approach to chemical reactions implies the study of dynamical interactions among a very large number of molecules, where changes in their internal structures are involved. Furthermore, the large number of degrees of freedom is responsible for the irreversible character of the event. Typical irreversible processes are treated as transport phenomena, with linear causal relationships sufficing for their description, at least within a wide range of experimental conditions. As already pointed out, chemical reactions are in fact exceptional in this sense, since nonlinearity is here a primary feature.

The first attempt to explain rate theory starting from non-equilibrium statistical mechanics was made by Curtiss[5], and Prigogine *et al*[6]. Using an *ad hoc* Boltzmann-type of kinetic equation, they obtained a modified distribution function from which the rate constant was computed. Improvements of this version were made by Mahan[7] and Present[8]. The molecular internal degrees of freedom[9], as well as the chemical species labels[6, 10] have been included in this type of description. This in turn implies that the distribution function must contain this information besides the usual position and velocity variables. In a series of papers[11-14], Ross has developed further this approach based on a modified Boltzmann equation of the form:

$$\frac{\partial(n_{A_i} f_{A_i})}{\partial t} = \sum_{jlm} \iint v_{AB}\, \sigma^{\mathrm{reac}} \left({l\,m \atop i\,j}; v_{AB}\Omega \right) \cdot \left(n_{C_l} n_{D_m} f'_{C_l} f'_{D_m} - \right.$$

$$\left. - n_{A_i} n_{B_j} f_{A_i} f_{B_j} \right) d\Omega\, d\mathbf{p}_B + \text{inel. coll.} + \text{elast. coll.} \qquad (2.1)$$

where i, j, l, m refer to the internal quantum numbers and $\mathbf{v}_{AB}$, $\mathbf{p}_{AB}$, are the relative velocity and momentum. Its solution yields the distribution function f_{A_i} for species A. An integration over the momentum $\mathbf{p}_A$ and a summation of the internal quantum numbers i is then carried out, thus eliminating the elastic and inelastic (nonreactive) collision terms, from symmetry arguments[11]. We can hence identify the rate constant as a function of the reactive cross section and the relative concentrations[13] $x_{A_i} = n_{A_i}/n_A$ and x_{B_j}:

$$k(T) = \sum_{ijlm} x_{A_i} x_{B_j} \iint v_{AB}\, \sigma^{\mathrm{reac}} \left({l\,m \atop i\,j}; v_{AB}\Omega \right) f_{A_i} f_{B_j}\, d\mathbf{p}_A\, d\mathbf{p}_B\, d\Omega\,. \quad (2.2)$$

We have thus obtained an expression linking an empirical quantity - the rate constant - with a microscopical parameter - the reactive cross section - which in principle is computable directly from the intermolecular potential. As a by product, Arrhenius law can also be reproduced[6,13] using primitive models for this cross section, such as rigid spheres of radius d/2 with a minimal activation energy E^*:

$$\sigma^{\mathrm{reac}}(E) = \begin{cases} 0 & , E \leqslant E^* \\ \pi d^2 (1 - E^*/E), & E > E^*. \end{cases} \qquad (2.3)$$

This is evidently a gross oversimplification since rigid spheres cannot possibly give rise to reactive collisions. On the other hand, the introduction of an energy parameter as in (2.3) is foreign to the kinetic approach.

To obtain the rate constant from (2.3), the distribution function in (2.2) is approximated by a simple Maxwell-Boltzmann distribution. This, however, is not so restrictive as it seems. It has been proven that non-equilibrium effects change the rate constant only slightly[5-8, 15], by solving Boltzmann's equation to first order in the gradients.

The first sound and serious attempt to calculate the transport coefficient relating the chemical affinity with the chemical rate was performed by Yamamoto in 1960.[16] Instead of postulating a Boltzmann equation, he starts from linear response theory, as developed by the Japanese school of Kubo[17] and Mori[18]. The rate constant is expressed in terms of a time correlation function for the progress variable ξ:

$$k(T) = \Omega\,[\beta\langle n_A\rangle_0 \langle n_B\rangle_0]^{-1} \int_0^{\Delta t} dt \int_0^{\beta} d\lambda \langle \dot{\xi}\, \dot{\xi}(t + i\hbar\lambda)\rangle_0 \qquad (2.4)$$

where $\langle\,\rangle_0$ refers to the equilibrium values, and Ω is the volume.

To define microscopically the species' densities, Yamamoto used a projection operator which singles out the scattering channel containing the reaction products. By substituting this into the correlation function (2.4), he obtains a linear version of Eq. (2.1), where the rate constant is expressed as in Eq. (2.2).

There are two criticisms to be made at Yamamoto's approach: Firstly the introduction of a channel projector, which is a two-body operator, enters in conflict with linear response theory. This unduly incorporates the low-density limit in the definition of the progress variable itself. Secondly linear response theory is too restrictive since linearisation of the rate equations does not yield a realistic picture of chemical reactions as emphasized above.

Amongst the kinetic processes, chemical relaxation is distinctive in the sense that the linearized equation suffices. The method of relaxation was introduced by Eigen[19] to measure fast reaction rates (with relaxation times of $\sim 10^{-6}$ sec). The experimental device consists in perturbing chemical equilibrium and then allowing the system to relax into a (new) state of equilibrium. Once the relaxation time is measured, we can compute the rate constants with the aid of the equilibrium constant. As just mentioned, for this case the linear response method is fully justified.

The corresponding theoretical analysis has been worked out by Berrondo[20], by computing the relaxation time from the density-density spectral function. The density operator refers there to the progress variable, and this is indeed a one-body operator in contrast to Yamamoto's. The low density limit is introduced explicitly as an approximation, by considering only two body collisions. The resulting transport equation corresponds to a linear Boltzmann equation including reaction. The inverse relaxation time is given as:

$$k = 2\pi \sum_{\alpha\xi} \left| <\alpha|\tau|\xi> \right|^2 \left[<n_A + n_B>_0 f_A f_B + \right.$$

$$\left. + <n_C + n_D>_0 f_C f_D \right] \delta(E_\alpha - E_\xi) \qquad (2.5)$$

summed over the initial and final reactive channels α and ξ, and where the delta function assures energy conservation. From it, the rate constant is obtained in terms of the reactive τ-matrix as:

$$k(T) = 2\pi \sum_{\alpha\xi} \left| <\alpha| \tau |\xi> \right|^2 f_A f_B \; \delta(E_\alpha - E_\xi). \qquad (2.6)$$

In this way we have achieved a description of chemical kinetics as a transport process. Cross-effects with other transport phenomena are expected to arise. In order to include them, we set aside the strictly microscopic viewpoint and start instead from the hydrodynamical equations for the chemical species. The link with linear response theory was given by Kadanoff and Martin[21], exploiting only general properties of the correlation functions, such as dispersion relations and sum rules.

A full account of this approach for the case of chemical reactions is found in Ref. 22. The behaviour of the various correlation functions in a binary reactive system is studied. All the hydrodynamical modes are taken into account, but the validity of the linearized hydrodynamical equations is assumed.

We have described above several attempts to reduce the original many-body problem into a few-body problem, albeit valid only for bimolecular reactions in the low density limit. A remarkable feature here is that two-body properties appear to be sufficient to describe the phenomena. In this sense, we can assert that additivity of intermolecular forces may be assumed for bimolecular chemical reactions. Thus we are justified in studying in detail the bare molecular interactions.

3. THE CROSS SECTIONS

Once the statistical problem has been presented, we shall review some aspects of dynamical interactions between two reacting molecules. The obtention of the reactive cross section is here the ultimate goal, thus serving as a bridge towards the many-body description through its use in the transport equation.

The two-body collisions related to these cross section are indeed reversible, in the sense that the transition probabilities w from initial to final states and back, are related through:

$$w(i \to f) = w(\bar{f} \to \bar{i}), \tag{3.1}$$

where $|\bar{f}>$ is the initial state in the time-reversed system, and corresponds to the final state $|f>$ in the original system. Provided there is no degeneracy, $|\bar{f}>$ coincides with $|f>$.

It is clear that cross sections must be computed quantum-mechanically. So, in principle, we have to solve the time-dependent Schrödinger equation to determine whether the collision is reactive or not. In order to describe the collisions between molecules however, it is convenient to introduce an "intermolecular potential". This is defined as the average effect between the composite particles, stemming from the complex interplay of Coulomb forces acting among nuclei and electrons.

Towards this end, we first separate the nuclear and electronic motions[23], by expanding the exact stationary wave function $\Psi\ (\mathbf{r}, \mathbf{R})$ in terms of a basis $\Phi_{m}(\mathbf{r}\,|\,\mathbf{R})$ with respect to the electronic coordinates $\mathbf{r}$, and depending parametrically on the nuclear coordinates $\mathbf{R}$:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{m} \chi_{m}(\mathbf{R}) \ \ \Phi_{m}(\mathbf{r}|\mathbf{R}). \tag{3.2}$$

The coefficients $\chi_{m}(\mathbf{R})$ turn out to be the nuclear wave functions, satisfying a set of coupled equations:

$$[E - T_{\mathbf{R}} - V_{m}(\mathbf{R})] \ \chi_{m}(\mathbf{R}) = \sum_{n \neq m} C_{mn}\, \chi_{n}(\mathbf{R}), \tag{3.3}$$

where $V_{m}(\mathbf{R})$ is the intermolecular potential, E and $T_{\mathbf{R}}$ are the total and nuclear kinetic energies, and C_{mn} represent the coupling terms, arising from the momentum transition values.

In the stationary case, as for molecular vibrations and rotations, the adiabatic approximation is usually quite adequate. This approximation consists in neglecting the coupling terms C_{mn}[23]. The functions $V_{m}(\mathbf{R})$ hence act as potential energy surfaces over which the nuclei move. It has been a common practice to apply this restrictive treatment also to the case of reactive collisions between molecules. Furthermore, a semiclassical approximation for the nuclear rearrangements during the reactions is ussually assumed. In fact, classical equations for the nuclei's trajectories are derived and solved^{IX}.

Within these approximations, the reaction is pictured as the motion of a representative mass point on the potential hypersurface^{I-II}. This surface presents a number of minima, corresponding to stable and metastable states. The two essential minima correspond to the reactants' and products' stages of the reaction. The optimal energy trajectory connecting these two minima defines the so-called reaction coordinate^{II}. The representative mass point not only vibrates as for the case of stable molecules, but also undergoes a translation along this reaction coordinate. In fact, there is often an interconversion of relative kinetic energy to intramolecular excitations, and vice versa$^{24-25}$. This is depicted in Fig. 1.

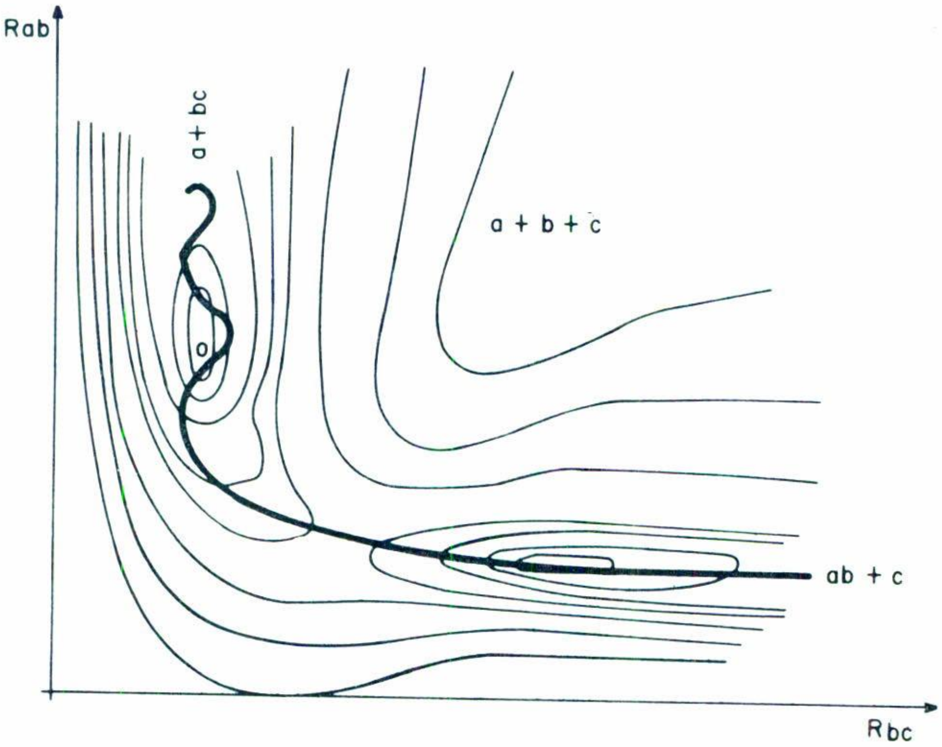

Fig. 1. Trajectory of the mass point on the potential surface as it traverses the saddle point separating the reactants' and products' valleys. The translational energy is converted into vibrational energy in the products valley due to the energy-momentum conservation law. Notice the displacement of the saddle point towards the reactants' valley. In the reverse reaction, the most efficinet trajectory starts with an excited vibration following the same trajectory in the opposite sense.

Once the reactive trajectory is determined, the differential cross section is obtained from the classical expression in terms of the impact parameter. A practical way to integrate these equations is by means of the well-known Monte Carlo Technique^{VII}.

This is very far indeed from solving the time-dependent quantum equations. Instead one solves the stationary Schrödinger equation only for the electronic motion, while for the nuclei, classical equations are used. Besides it is difficult to believe that the reaction proceeds adiabatically in all instances. Energy transfer from nuclear to electronic states is expected to play a role, except in the low velocity limit.

An evident breakdown of the adiabatic approximation appears when two potential energy surfaces lie close to each other. The transition probability from one surface to the other is enhanced near the avoided crossing point (see Fig. 2). It is for this reason that the diabatic picture was developed[26]. In this representation, we select a different set of basis functions $\Phi'_m(r|\mathbf{R})$ in Eq. (3.2). This new set is chosen[27] in such a way that it diagonalizes the radial momentum matrix*:

$$\mathcal{P}_{mn}(\mathbf{R}) = \int \Phi'_m(r|\mathbf{R})(\hbar/i)\,\nabla_{\mathbf{R}}\,\Phi'_n(r|\mathbf{R})\,dr. \tag{3.4}$$

Contrary to the adiabatic case, the coupling terms C_{mn} in Eq. (3.3) cannot be neglected. Thus a non-diagonal potential matrix $V_{mn}(\mathbf{R})$ results. The non-crossing rule[28] does not apply in this case, so the surfaces are degenerate at a certain point R_0, as depicted in Fig. 2.

The transition probability from one surface to the other is given by the well-known Landau-Zener expression[29-30]:

$$P_{12} = \exp\left[-2\pi\left|V_{12}(R_0)\right|^2/\hbar v\cdot\Delta F\right] \tag{3.5}$$

where v is the mass point velocity and ΔF measures the difference between the slopes of the adiabatic surfaces, both evaluated at the crossing point R_0 (see Fig. 2). The cross section corresponding to this case is relevant to several types of reactions such as charge-transfer[31], electronic recombination[32], and predissociation[33].

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[*] The diabatic representation is not unique as defined. We further require (Ref. 27) that, asymptotically, the potential surfaces coincide with the adiabatic ones.

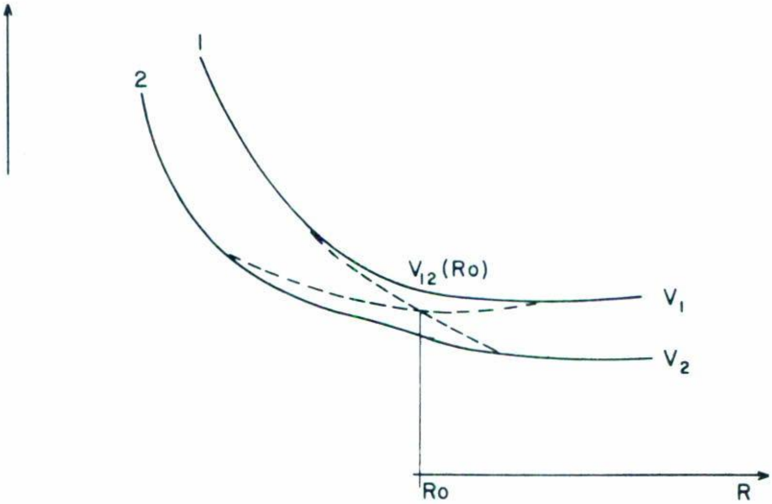

Fig. 2. Adiabatic (——) and diabatic (---) potential curves at the crossing point. Notice that adiabatic curves repel each other because of the non-crossing rule.

A way to go beyond the classical trajectory description is to invoke the WKB approximation. The *S*-matrix may be computed by using action-angle variables[34-35], or alternatively, via the path integral method[36]. An advantage here is that it is no longer necessary to calculate the complicated potential energy surfaces for the process. The computations are usually limited however, by the introduction of oversimplifying models[34].

Instead of producing particular models, we can also calculate the cross sections by introducing statistical assumptions[37] with respect to the two-body reactive collisions. This involves the use of microscopic reversibility, Eq. (3-1), and the assumption of the existence of a collision complex. This in turn implies a two-stage process which consists in the formation of the complex and its subsequent decay. The transition rate is hence factorized into the probability of formation times the decay rate[38]. Furthermore it is usually assumed[38] that the probability of appearence of the intermediate state is independent of the corresponding incoming channel.

A more fundamental justification[39] for this statistical rate theory follows from the introduction of an optical potential[40]. As is well known, an average of the *S* matrix is made over an energy interval ΔE:

$$\langle S_{fi} \rangle = -2\pi i \sum_s (\Delta E)^{-1} \int_E^{E+\Delta E} A^s_{fi} / (E' - \lambda_s)\, dE' \qquad (3.6)$$

where A_{fi}^{s} is the transition amplitude associated to the resonance λ_s. This theory is specially adequate for multichannel collision processes, where a great number of resonances play a role, so that a statistical average over them yields a good description[40] in terms of $<|S_{fi}|^2>$.

Quite aside from the above-mentioned theories, some experimental techniques have been developed during the last few years. The most popular one consists in direct measurements of the cross sections using crossed molecular beams[XV, XVI]. Although the most interesting information evidently comes from reactive collisions, it has proven instructive to analyze also elastic scattering of reactive systems[41]. Rather detailed information about the dependence of the cross section on the energy and the angular distribution has been achieved through velocity selectors and angle scanning devices[42].

For simple compounds involving alkali and halogen atoms, for instance, a rather neat image of the molecular rearrangements during reactive collisions has evolved. This permits a discrimination between complex formation and direct reactions. For the former case, we fall under the assumptions of the statistical rate theory, while for direct processes, a further subdivision into two limiting cases known as stripping and rebound reactions is made[43]. The reader is referred to the excellent available reviews[XV – XVII], for further information.

In any event, it should be remarked that no matter how refined these techniques might become, a beam collision is *not* a chemical reaction as those the chemist faces in the laboratory. We already pointed out in Section 2 that essential features such as irreversibility and nonlinearity, stem directly from the many-body character of the chemical processes.

Before closing this section, we want to forward an enticing possibility, namely the description of reaction kinetics in entirely microscopic terms. If we are able to determine the intermolecular potential, we can study the evolution of the N-body reacting system via Liouville's equation. This is far from being trivial indeed. In the last section we shall present some possible pathways to implement this program.

4. UNIMOLECULAR REACTIONS

Hitherto we have described reactive processes in which several molecular species act as reactants. A different situation arises in the case of molecular decompositions such as dissociative breakdowns or in isomerizations[XVIII]. This case can be represented schematically as:

$$A \rightarrow \text{Products.} \tag{4.1}$$

This looks like a fundamental decay and one would be tempted to describe it as an isolated (microscopic) process. However, this simple image is contradicted by experiment since an important pressure dependence is observed. While the high-pressure behaviour is formally described by (4.1), in the low-pressure limit unimolecular reactions behave in such a way as if there were two reactants involved[44]. In fact, this pressure dependence is the essential characteristic of unimolecular processes.

This behaviour is usually explained via Hinshelwood-Lindemann's (LH) two-step mechanism[45]:

$$A + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} A^* + M' \tag{4.2 a}$$

$$A^* \overset{k_3}{\rightleftarrows} \text{Products.} \tag{4.2 b}$$

The molecule M (whether from species A or not) excites A into an unstable state A^* which decomposes subsequently. The inverse process of deexcitation through collisions with M and recombination of the products to form A^* are also considered. It is evident that this scheme is more realistic than (4.1) for the simple reason that A represents in principle a stable molecular state.

Interpreting now Eq. (4.2 a) as the excitation of internal states of molecule A, we have to explain the time lag between the formation of the excited state A^* and its decomposition, Eq. (4.2). This is achieved in a phenomenological way considering[46] an additional step in the decay of A^*. Marcus identifies this step as the formation and decay of an activated complex $A^\dagger$ following Eyring's ideas[II, VI]. This is the so-called RRKM theory[46,47] which describes the above-mentioned delay as the time spent in interconversions among the internal modes, until the energy is concentrated in a particular dissociative vibration of the activated complex $A^\dagger$. The overall reaction constant is thence computed by considering that the reaction constants in the L-H mechanism depend explicitly on the energies and then intergrating over them.

An alternative to the RRKM formulation, still within the phenomenological framework, is given by Slater's theory[XIX]. Here one starts from the detailed analysis of the molecular vibrations and their normal modes. Thence an internal coordinate is chosen as a superposition of harmonic modes. The rate constant is computed in the high-pressure limit by postulating an ***ad hoc*** critical value to provide for disruptive vibrations. Next, an average over these vibration weighted by a Boltzmann distribution is performed. The obtained value is henceforth extended to all pressures.

A stochastic description related to Slater's, was developed by Montroll and Shuler[48] to account for dissociation. As in all stochastic models, these is no attempt here to explain the explicit mechanisms of interaction. This model consists merely in the description of a single vibrational mode approximated by a truncated harmonic oscillator. Dissociation is viewed as the transition from the last bound oscillator state into the next one. From the knowledge of this passage time $\bar{t}$, the reaction rate is computed as:

$$k = (N^* \bar{t})^{-1} \tag{4.3}$$

where N^* is the heat bath molecule concentration. When the explicit form of the equilibrium value of $\bar{t}$ is substituted, an Arrhenius-type of expression is recovered.

Notice should be made of the difference between the present theory and other stochastic approaches[49] such as those of Refs. XII and XIII mentioned in the Introduction. In those, the stochastic assumption referred to the chemical changes of the species, rather than to individual dissociations. The use of a master equation was also distinctive of these theories. In spite of these differences, a limitation, common to both approaches for the dissociative case[50], is the fact that they are Markoffian. We shall come back to this point later.

In order to introduce the detailed kinetics of the reaction it is necessary to go back to the L-H mechanism. In Levine's theory[51] (4.2 b) is interpreted as if it were valid for each molecule. Consequently unimolecular breakdown is described as the decay of a state prepared at a certain initial time and whose evolution is given by Schrödinger's equation. The probability of finding the molecule in the initial unstable state s at time t is shown to be given as an exponential decay law:

$$P_S(t) = \exp(-2\Gamma_S\, t/\hbar) \tag{4.4}$$

with lifetime proportional $t_0 \;\; \Gamma_S^{-1}$.

The excitation stage (4.2 a), on the other hand, is not considered individually[51]. Levine elaborates on the discussion of rate processes in an ensemble by introducing a reduced density operator ρ_{AM} for the pair (A,M) in the binary collision approximation. This is interpreted to imply that ρ_{AM}

obeys[51] a two-body Liouville equation. From it, a reduced one-body density is defined as $\rho_A = \mathrm{Tr}_M\ \rho_{AM}$ which in turn obeys the following equation:

$$i\hbar(d\rho_A/dt) = [H_A, \rho_A] + \mathrm{Tr}_M\,[U, \rho_{AM}]\,, \tag{4.5}$$

where U represents the interaction between A and M. Eq. (4.5) is the fundamental equation in Levine's theory of unimolecular reactions.

From the tenet established in this review, we must distinguish the above approach from a genuine N-body treatment. The main drawback comes from the use of a *reversible* two-body equation which does not contain many-body effects whatever. Irreversibility is artificially introduced by merely taking the trace over the variables of a single molecule M.

In this context, we conclude that there is no *bona fide* N-body treatment in the unimolecular case. A description similar to the one found in Section 2 for bimolecular processes is lacking. Indeed, our programme in both cases should be the reduction of the statistical many-body problem to few-body dynamics. In the Outlook we shall discuss this viewpoint for dissociation.

A word should be added here about unimolecular dynamics: instead of concentrating on cross sections as in the bimolecular case, we should aim at the information about lifetimes in this case. This difference arises from the fact that there appears a new time besides the lapse between two exciting collisions, namely the decay time of the excited state A^*. In the event that these two times are comparable, we are not allowed to study the two steps in (4.2) as independent of each other. This situation contrasts with the bimolecular case at low densities, where the two time scales involved — the time between collisions and the duration of a collision — are well separated. In fact this is the reason for the strong pressure-dependence mentioned above. When the frequency of collisions augments, the decompositon is regarded as a first order rate process, contradicting our common sense. This is only a delusion however, since we are introducing an *effective* rate constant k_∞ as an averaged contribution from the medium. The net result of the frequent collisions is the apparent constancy of the concentration of A^*. Many-body effects become drastic in this case since they modify the rate constant itself.

5. OUTLOOK

As a general conclusion from this review we can state that the present understading of chemical reactions is far from satisfactory. We have particularly emphasized the N-body aspects of a reaction which are frequently overlooked or masked in the orthodox theories. Partly from the misconceptions about chemical processes introduced by the latter, but also from the intrinsical difficulties of more fundamental approaches, no complete kinetic or statistical mechanical theory exists. Thus the corresponding phenomenological or hydrodynamic description of the system both in the linearized version and the non-linear case, are lacking. It is not surprising then that some macroscopic phenomena such as sound propagation or light scattering still pose unanswered questions. We shall now discuss a number of promising new ideas and developments regarding some of these matters.

The kinetic approach to chemical reactions has been centred around the description of the system via a Boltzmann-like equation. The main objection to this approach is that it limits us to a classical description of a situation which is intrinsically a quantum mechanical one. Thus the use of an equation for either a Wigner distribution function or a reduced density matrix is crucial. Although there exist many attempts of deriving quantum mechanical kinetic equations for systems composed of particles having internal degrees of freedom[52-59], the inclusion of attractive forces allowing for the formation of bound states has never been successfully accomplished[59]. Moreover a third limitation is implied in this scheme, namely the restriction to a low-density limit, which is common to both the theoretical and phenomenological descriptions, where it is always assumed that the rate is directly proportional to the species density. Within the Boltzmann like approach it is difficult to see how these limitations will be overcome.

As far as the problem of the molecules distinguishability is concerned, let us recall that the basic statistics involved are those of bosons and fermions. This refers only to the electrons and nuclei composing the molecules, while the latter do not obey either statistics due to electron exchange among different species. A method for dealing simultaneously with pure and mixed statistics has been developed by Girardeau[60]. This opens the possibility for implementing it for reactive systems.

From the statistical mechanical point of view two directions may be taken to deal with the problem. One is the possibility of deriving kinetic equations from the BBGKY hierarchy for reactive systems, provided we allow for different intermolecular potentials for the various interacting species. However one may include the contribution of three body collisions which could lead to a description for termolecular chemical reactions or bimolecular reactions at higher densities. Besides, the density dependence of the macroscopic quantities in reactive systems is still to be clarified, but it is unlikely that it will be described by virial-type expansions. Also the presence of a third partner during a reactive collision might play a fundamental role as an energy quencher in many instances, stressing the importance of three body collisions. In this connection an additional question arises: whether this introduces non-additive corrections whose very existence may alter the whole picture in a qualitative fashion.

The second possiblity is to circumvent the use of kinetic equations for the distribution function. This is achieved through the local equilibrium hypothesis and postulating a functional form for the initial density matrix in terms of thermodynamical quantities locally dependent on position and time. To describe a chemical reaction in this picture[61] the species densities have to be included in the initial density matrix. Its time evolution is governed by Liouville's equation and the relevant physical information about the system can be extracted through the corresponding averages. In the linear regime this has been accomplished by linear response theory as described in Section 2. The generalization to non-linear regimes is now in progress[62].

The study of the hydrodynamical stage, both in the low-density or Boltzmann-like context and in the distribution function method, has not been thoroughly undertaken. Thus the phenomenological equations for the various local macroscopic variables have never been derived. In the linear approximations, as remarked in Section 2, the phenomenological rate equation for bimolecular reactions may be obtained. However the full rate equations which are highly non-linear, including those for unimolecular reactions, are still awaiting a microscopic explantion. Furthermore the cross effects which are characteristic of chemically reactive systems such as the viscoreactive coefficient[63] have never been studied at all. This coefficient is deeply associated with the so-called *effective bulk viscosity*. This term is meant to account for those dissipative mechanisms responsible for the sound attenuation in chemically reactive systems associated with the relaxation of various internal degrees of freedom. Such a picture has been recently questioned[64] but it is impossible to foresee what scheme holds for such phenomenon without resorting to microscopic equations. Indeed if one could calculate the viscoreactive coefficient from first principles most of the difficulties would be surpassed[65]. Finally, it is important to remark that if the derivation of the hydrodynamic equations proposed above is achieved including three body collisions, we would be led to *new* macroscopic equations beyond the presently known phenomenological descriptions.

Unimolecular reactions deserve a separate treatment due to their very singular nature. As mentioned in Section 4, no satisfactory N-body treatment has been developed for their understanding. The fact that the life-time of the excited states must be of the order of a mean free time necessarily introduces an intrinsic memory effect which at present is not clear how to take into account in a collisional description.

For this problem, at least in the case of equilibrium, there exists a very attractive fromulation by Blatt which stems from the study of superconducting systems[66]. Here the molecules are simply viewed as correlated clusters which are stable for a sufficiently long period of time as compared with the collision time. Dissociation and recombination correspond to the breakdown and formation of these persistent clusters. Thus Blatt's theory is not really dynamical but purely descriptive and does not discriminate among the different types of interactions.

One way to generalize this description to obtain reaction rates is invoking once more the local equilibrium hypothesis. Indeed, it would seem most appropriate[67] to take into account these linked clusters by expanding the density expectation values in powers of the activity[68]. Keeping terms only up to second order in this expansion should be enough for a two component recombination since this corresponds to chemical saturation. However, care must be excercised in separating *dynamical* from *statistical* correlations. These ones should be obviously kept to all orders in the expansion as they determine the correct equation of state.

We would like to add two concluding remarks to this review. Firstly, in spite of the tremendous amount of work that has been done in the past in order to obtain a microscopic description of chemical rate equations, their main features from the many-body point of view still remain far from being understood. Efforts have been focused via two-body techniques, which is only the first approximation to their dynamical aspect. Secondly, chemical rate equations are nonlinear and our ultimate goal should be to derive them from a microscopic approach. This cannot be accomplished if the many-body effects are not taken into account. Nonlinear problems in Science are now in the frontiers of research. Chemical kinetics should consequently regain its lure as a field of central interest for the physicist.

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RESUMEN

Este artículo constituye una revisión de la teoría de las reacciones químicas donde se subraya el caracter de N-cuerpos del proceso. La situación actual de la descripción de la cinética química como un fenómeno de transporte se analiza críticamente. Este punto de vista debería justificar la irreversibilidad y la no-linearidad inherente en el sistema. Revisamos brevemente la reducción de la dinámica de muchos cuerpos a interacciones fundamentales de dos cuerpos al estudiar las secciones de colisión reactiva. Analizamos las teorías existentes para reacciones unimoleculares para enfatizar como es que sus vicisitudes han evitado un desarrollo paralelo de este punto de vista. Se hacen varias sugerencias sobre como introducirse a una descripción más fundamental del problema siguiendo varios caminos. También se indican extensiones y correcciones a las ecuaciones macroscópicas conocidas.