A relativistic approach to macroscopic chemical kinetics

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Abstract: Theoretical research has paid little attention to the influence on chemical kinetics of the motion of reference frames where chemical reactions are carried on. In order to improve this situation, in this paper the main chemical-kinetics relations with regards to inertial and gravitational frames in the relativistic range are developed, and also some simple experiments designed to test their scope are suggested.

Keywords: Chemical, kinetics, relativistic, rate, reaction.

Introduction

The impact of quantum physics on modern chemistry can be hardly exaggerated. Only a few of its consequences, among many other progresses, are the theory of chemical bonds, the rules for electronic configuration, the theory of hybrid orbitals, the notion of free radical, the resonant structures in certain molecules, or the spectroscopic determination of the chemical species in ongoing reaction. However, the theory of relativity –almost contemporary of the quantum revolution in the early XXth century– does not seem to have exercised an equivalent influence on chemistry.

Most of the references on this subject in the chemical bibliography only discuss the relativistic energy corrections to the electrons in interatomic bonds [1] and to the spectroscopic derived data [2]. In other cases statistical mechanics is studied in the relativistic-energy range, with the purpose of providing better estimates for the activation energy [3,4], chemical potentials [5], or the ions excitated by relativistic collisions [6].

The few authors who managed to get a relativistic version of macroscopic chemical processes –reaction rates, for instance– regarded their own efforts as sofisticated refinements of the well-known non-relativistic situations, and they also restricted their results to specific purposes, either their influence on enzimatic activity [7] or on coloidal reactions [8]. And there are some authors who claim –against the orthodox interpretation of relativistic physics– that the time-dilation associated with speeds close to the light speed, c, will slow down biological processes causing the death of every living-being in such conditions [9]. Moreover, none of the aforementioned approaches took advantage of the four-dimensional formalism in the original spirit of the einsteinian relativistic theory.

The aim of the present work is to present an elementary treatment of chemical kinetics taking on from the beginning the requirements of the four-dimensional relativistic formalism, so that the usual chemical-kinetic equations will be obtained as an acceptable approximation for low speeds and weak fields. Anyway, in order to get simpler algebraic expressions, it will be assumed that chemical-kinetics constants and reaction orders remain invariant under changes of reference frame, or that we can express their modifications exchanging the constant K_v for K'_v.

The classic kinetic law was certainly formulated for ordinary temperatures, and this paper does not intend to discuss the modification of the chemical rates when the internal energy of the system becomes very high (energetic or thermal view) but the relationship between the descriptions given by two mutually inertial observers of the kinetics of a unique chemical system, with no regards to its internal energy (kinematic view).

Anyway, the study of quantum-relativistic corrections that would affect without a doubt to the reaction-rate constants –considered in microscopic terms– and the problem associated with the relativistic change of thermodynamic magnitudes, like temperature, lie outside the scope of this

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work. The controversy on the proper relativistic trmsformation for abolute temperture began when Planck [10] carried out the modification of thermodynamics in agreement with Einstein's relativity theory, and he concluded the relativistic invariance of entropy. Fon this starting point, Einstein deduced the relativistic transformations for heat and temperature [11]. Their results, nevertheless, received a negative answer [12] that generated in turn a debate whose derivations seem still far from having been extinguished.

Relativistic reaction rates

Let there be a quantity N of corpuscles (atoms or molecules) dissolved in a certain spatial volume V. Then we will have an initial concentration $n = N/V$ as measured in an inertial frame O regarded at rest for our convenience. That very concentration located in a system O' in relative motion with respect to O, will be perceived as greater in O because of the relativistic contraction of the spatial dimension parallel to the speed (that we can arbitrarily take parallel to the X-axis, $v_x = v$) and the subsequent volumetric contraction (Fig. 1).

Taking the speed of the light $c = 1$, and denoting $\gamma = (1 - v^2)^{-1/2}$, if the concentration in O' is n, for O it will be γn. Moreover, for the observer O all the corpuscles of the chemical system in O' shares the relative speed v. Therefore, with regard to O a flow-density exists given by $\gamma n v$. With these two expressions it is now possible to build a flux-density vector [13] for the corpuscles of the chemical system that will later undergo the chemical reaction and will be subject to kinetic study. In our example, this 4-vector defined for the flow of corpuscular concentration will be given by $N = [\gamma n, \gamma n v, 0, 0]$. In brief, the relativistic contraction of the length causes that the density of particles would depend on the reference frame from which it is is measured.

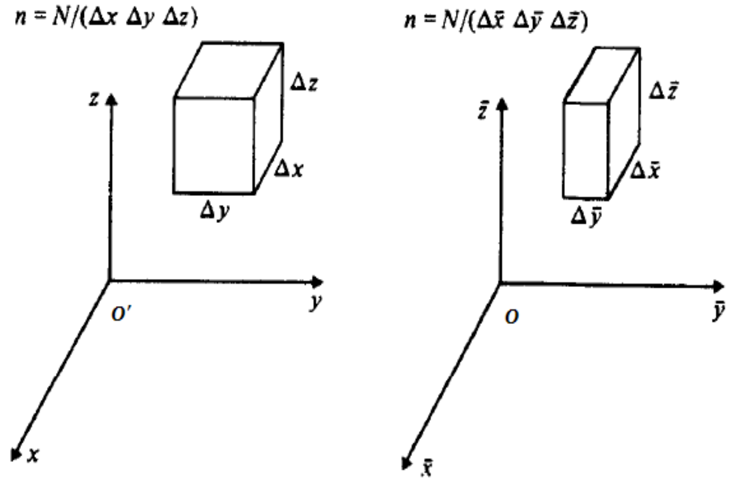

Fig. 1

Macroscopic chemical kinetics defines a reaction rate from the reagent decrease according to the equality $v_R = -dn/dt$. The fact of having now a 4-vector in space-time suggests the convenience of a derivative with regard to the proper-time [14] for the definition of the relativistic reaction-rate, $v_R = -dN/d\tau$. As a consequence it will be that

$$dN/d\tau = (dN/dt)(dt/d\tau) = \gamma(dN/dt). \tag{1}$$

In components,

$$\gamma(dN/dt) = \gamma[d(\gamma n)/dt, d(\gamma n v)/dt, 0, 0] = \gamma^2[dn/dt, v(dn/dt) + n(dv/dt), 0, 0]. \tag{2}$$

As in a relative inertial motion $v = 0$, $v_R = -\gamma^2[dn/dt, v(dn/dt), 0, 0]$, if $v << c$, the term $v(dn/dt)$ is negligible, and then $v_R = -\gamma^2 dn/dt$. With this we can regain the typical expression for the reaction rate in frame in relative rest $v_R = -dn/dt$, where $v = 0$ and $\gamma = 1$.

It is generally possible to establish proportionality between the reaction rate and the reagent concentrations. This expression has been traditionally given [15] by

$$v_R = \mathrm{K}_v \Pi_i (n_i)^{\alpha_i}, \qquad (3)$$

where n_i symbolize the concentrations, α_i the reaction orders, and K_v is the reaction-rate constant. Our purpose now will be to search for a relativistic extension of this reaction-rate law that would give us back the usual non-relativistic form under the proper conditions.

The transition from the usual concentration n in the chemical kinetics to the relativistic formalism (note that $c = 1$) has been obtained multiplying n for the relativistic 4-speed [16] $U = [\gamma, \gamma v, 0, 0]$. Then, the most natural generalization for the reaction-rate law seems to be

$$v_R = \mathrm{K}_v \Pi_i (\gamma n_i)^{\alpha_i} U. \qquad (5)$$

It obviously follows from this that in a frame in relative rest where $v = 0$, we will have $\gamma = 1$ and $U = [1, 0, 0, 0]$.

Starting from an approximate situation as the one described in one of the previous paragraphs, where we only retain the first component of the 4-vectorial relativistic reaction-rate, we will analyze those situations in which it is simple to integrate the reaction-rate equations with the expected relativistic corrections.

Zero-order equation

Let us consider for instance a zero-order reaction in the frame O' in rest with regard to it. If so, the reaction will be ruled by the ordinary equation $-dn'/dt' = \mathrm{K}_v$. But O' is in motion with regard to O that we have considered in rest for convenience. For that reason, the observer in O should apply the relativistic transformations of lengths and times.

Therefore, in the aforesaidd range of approach, which is limited to the first component of the four-vector N, we would obtain the relation

$$-dn'/dt' = -\gamma^2 dn/dt = \mathrm{K}_v \qquad (6)$$

Recalling that the relative speed between both frames, v, is constant in time, an elementary integration provides

$$-\Delta n = \gamma^{-2}\,\mathrm{K}_v\,\Delta t \qquad (7)$$

This one would be the transformation between the inertial frames O and O' for the integrated equation of the reaction rate. As expected, the reaction rate is slower in O than in O', since the latter is in relative rest with regard to the reacting chemical system.

First-order equation

Let it be a reaction of first order whose kinetics is expressed by the equation $-dn'/dt' = \mathrm{K}_v n'$ (where the stequiometric coefficients are supposed to be included in the rate-constant value) in the frame O'. The proper relativistic transformation would give for O the relation

$$-\gamma^2 dn/dt = \mathrm{K}_v\,\gamma n, \qquad (8)$$

what lead us to $-\gamma dn/dt = K_v\, n$. A simple integration would give us the equality

$$-\ln n = \gamma^{-1} K_v\, \Delta t \qquad (9)$$

Although with another functional form there also remains in this case the disparity in the reaction rates velocities either with regard to O or to O'.

Second order equation

We will discuss here a second order equation for a single reagent. It is very simple to notice that in this case for O' the equation would be written

$$-\,dn'/dt' = K'_v\, (n')^2. \qquad (10)$$

But in O the chemical-kinetic law would acquire a different form, as

$$-\,\gamma^2 dn/dt = K_v(\gamma n)^2. \qquad (11)$$

When simplifying it would be merely,

$$-dn/dt = K_v\, n^2, \qquad (12)$$

that is to say, the same expression as in the non-relativistic range or, in other words, the one that we would have in a frame in relative rest with regard to the reacting system.

Surprisingly, the measures of the reaction rate obtained by means of the coordinates in O coincide with the value calculated by means of the coordinates in O'. Nevertheless, it should be stressed that we arrive at this result beacuse of our strategy of rejecting all the components of the four-vector N just saving the first one.

Equation of arbitrary order

We will conclude this series of concrete examples of kinetic equations explicitly outlined with a general treatment –always inside the repeatedly aforementioned approach– of those reactions whose rate depends on the concentrations of several reagents and its different partial orders of reaction.

Let us have for the reagent n_i in the system O' a chemical-kinetics equation which is function of several concentrations such as

$$-\,dn_i'/dt' = K'_v\; n_1'^{\alpha_1}\cdot n_2'^{\alpha_2}\cdot n_3'^{\alpha_3}\ldots n_m'^{\alpha_m}\,. \qquad (13)$$

When passing to the frame O the equation is,

$$-\gamma^2 dn_i/dt = K_v(\gamma n_1)^{\alpha_1}\cdot(\gamma n_2)^{\alpha_2}\cdot(\gamma n_3)^{\alpha_3}\ldots(\gamma n_m)^{\alpha_m} = \gamma^{(\alpha_1+\alpha_2+\alpha_3+\ldots+\alpha_m)}(n_1)^{\alpha_1}\cdot(n_2)^{\alpha_2}\cdot(n_3)^{\alpha_3}\ldots(n_m)^{\alpha_m} \qquad (14).$$

Rearranging terms we will get at the end an expression just as,

$$-\,dn_i/dt = K_v\; \gamma^{\{(\Sigma\alpha_i)-2\}}\prod_{i=1}^{m} n_i^{\alpha_i}\,. \qquad (15)$$

Chemical kinetics and equilibrium

Although it is not the most general situation, we know that in reversible reactions, it is possible to distinguish between the forward reaction and the reverse reaction. When the rates of these two reactions are equal, a constant of chemical equilibrium can be defined. For a generic reaction $aA + bB \leftrightarrow cC + dD$ whose kinetic rates, in frame O in relative rest, are respectively, $v'_+ = \mathrm{k}_+[A']^a[B']^b$ y $v'_- = \mathrm{k}_-[C']^c[D']^d$. The equilibrium constant would be then,

$$K' = \frac{v'_+}{v'_-} = \frac{[C']^c[D']^d}{[A']^a[B']^b} \qquad (16)$$

As the concentrations measured in O (where an observer is considered in rest while O' is considered in motion) are $[A] = \gamma\,[A']$ we have that the equilibrium constant in O will be

$$K = \{\gamma^{\,(c+d-a-b)}\}\,K'. \qquad (17)$$

The equilibrium constant written in function of the pressures –since the relativistic transformation of pressures is still under a remarkable controversy– remains as a matter subject to further theoretical discussions inside a wider debate on the proper formulation of a consistent relativistic thermodynamics mentioned before.

Anyway, chemical reactions are multicomponent systems whose specific behavior very often depends on the specific details of the situation, in which also intervene a great number of factors (pressure, temperature, radiations, catalysts, state of aggregation of the chemical species, etc.). Therefore, even although the laws of equilibrium and chemical kinetics in any frame can be exactly deduced from the foundational quantum and relativistic principles –a porpouse that is quite far away from the scope of this paper– the resulting equations would exhibit such a degree of complexity that they would not possess exact analytic solutions and they must be solved by means of numeric approaches. It is even more likely that in the very attempt of stipulating such laws an amount of experimental peculiarities plays a decisive role in such an extent that perhaps overcome the limits of theoretical inference.

The general relativistic case

When passing from special relativity to general relativity, we can appeal to the method of mínimal coupling [17] substituting the ordinary derivatives by covariant derivatives. Then we would have that the ν-th component of the reaction-rate vector v would be written $v^\nu = -\{dN^\nu/d\tau + \Gamma^\nu{}_{\mu\sigma}N^\mu N^\sigma\}$, where, as usual, τ is the proper time of an observer in rest with regard to the chemical system and the Christoffel symbols are $\Gamma^\sigma{}_{\mu\nu}$.

To specify a law that relates the reaction rate with the reagent concentrations is much more difficult in general relativistic that in special relativity. The peculiar characteristics of curved space-time that affect us in these circumstances make our work much harder. For simplicity we will consider a system that moves radially in a gravitational field and an external observer in rest (their coordinates r, θ, φ are constant) with regard to the mass that creates the field. The motion of the frame where the chemical reaction occurs (whose size is negligible compared with the distance that separates it from the field source) is described by means of Schwarzschild coordinates system in which the space-time interval takes the usual form [18, 19, 20],

$$ds^2 = (1 - 2m/r)dt^2 - (1 - 2m/r)^{-1}dr^2 - r^2(d\theta^2 + \mathrm{sen}^2\theta d\varphi^2) \qquad (18)$$

where for our convenience we keep on using geometric units ($c = G = 1$).

If the chemical system is in free fall radially inside a Schwarzschild gravitational field, the module of its vectorial 4-speed U^ν will be given [21] by $|U| = (g_{11}/|g_{00}|)^{1/2}\,dr/dt$. Their components will satisfy the relations $U^{\nu} U_{\nu} = -1$, with $U_{\nu} = (-g_{00})^{-½} g_{\nu 0}$. Therefore, generalizing the reaction-rate law obtained by means of the arguments developed in the previous epigraph on special relativity, we would have $v_R = \mathrm{K}_{\nu}\Pi_i (n_i^*)^{\alpha_i} U$. Here n_i^* stands for the corpuscular concentration of the i-th component calculated for a three-dimensional volume affected by the contraction that the general relativity establishes for the lengths radially located along the gravitational field. In the Schwarzschild geometry this space 3-volume would be $(1 - 2m/r)^{½} dr(rd\theta)(r\mathrm{sen}\theta d\varphi)$.

As for the special-relativistic case, under a weak and/or slowly variable gravitational interaction, we can reject the spatial components of the 4-vectors retaining only the time component. That is to say,

$$v_R \approx v^0 \approx (1 - 2m/r)^{-1} dn/dt. \qquad (19)$$

Invariants in relativistic chemical kinetics

As in any other theory compelled to satisfy relativistic requirements, also in this relativistic formalism for chemical kinetics we can find magnitudes taht are invariant. In other words, quantities whose value is independent of the mechanical state of the observer that computes it, and by this reason they are regarded as physically objective.

One of such invariants, obviously, is the module of the 4-vectorial corpuscular concentration, $N^{\mu} N_{\mu} = N^2 = n^2$. The square of the module of N express the value of the concentration n as measured by an observer in rest with regard to the chemical system in question. However, maybe the most characteristic invariant in this whole treatment –the one that we could regard as a true kinetic-chemical invariant– concerns to the product of the spatial volume inside which the chemical reaction occurs and a characteristic time duration of this reaction.

Let $dx_R dy_R dz_R$ be the spatial volume associated with the aforesaid reaction, and dt_R a characteristic time of the process (a semi-reaction time, the period of a oscillating reaction, etc.). We define the 4-volume of reaction Q, or chemical-kinetic invariant, as the four-dimensional scalar formed by the product

$$Q = (-g)^{½} dt_R\, dx_R\, dy_R\, dz_R, \qquad (20)$$

where g is the determinant of the space-time metrics.

Different observers will differ in the specific values of the spatial volume $dx_R dy_R dz_R$ and the lapse dt_R, but they all will coincide in the value of Q whose nature of space-time magnitude guarantees its independence of frame's motion.

Experimental applications

In the previous section a characteristic time for a generic chemical reaction, dt_R, was mentioned. This idea leads us to a possible experimental test for the theoretical developments sketched before. So far, all the experiences designed to test the relativistic predictions about the distortion of time in frames with speeds next to c or subjected to intense gravitational fields, have been carried out by means of physical clocks, thats is, periodic physical processes –generally related to the constitution of atomic clocks– whose high precision granted to the results a degree of equally remarkable reliability.

One of the well-known corroborations of relativity was the Hafele-Keating experience [21] in 1971. It consisted in taking four cesium atomic clocks, and to place them on commercial airplanes in flight around the world. Under such conditions the clocks turned twice around our planet –first toward the east and later toward the west– and they were compared afterwards with the clocks of the American Naval Observatory that had remained on earth.

In the data analysis there were taken into account the relativistic time delay caused by the relative speed of the clocks in flight with regard to an observer in rest on the Earth surface, together with an typical effect from General Relativity due to the changes of the gravitational potential with the height of the airplanes in flight. Of course, a decrease of gravitation implies an increase in the time lapses when compared with that of an observer located in a place with a more intense gravitation. The results happened to be in total agreement with the relativistic predictions.

Nevertheless, without aiming to so refined precisions as those of the atomic clocks, in chemistry there also exist reactions whose rhythmic behaviours allow us to use them as a natural clock [18], in this case a "chemical clock". From the middle of the XXth century oscillating reactions have bee studied with an increasing interest (although they were already known long before). Their periods of oscillation act as the characteristic time dt_R mentioned in the previous epigraph. An oscillating reaction exhibits a periodic alternation between the increase and the decrease in the concentration of the participant substances. As a consequence of it, these reactions can be taken as true chemical clocks [19, 20, 21, 22]. Whenever the external conditions remain constant, the oscillation periods will also remain without changes. Celebrated examples of this class of phenomena are the Belousov-Zhabotinsky reaction [23], or the Briggs-Rauscher reaction [29], among many others.

Certainly the particular mechanisms of these chemical reactions are still largely ignored, and it can darken the interpretation of the results in a hypothetical realization of relativistic experiments with chemical clocks. But it is not less true that this class of experiments with a new modality of material systems –oscillating chemical reactions– as well as the development of explanatory theoretical models for them open up toward the future a vast and practically unexplored field of research.

Anyway, we could also look for those best-known chemical reactions whose reaction times makes them good candidates for experiences as those carried out up to now by physical methods. Of course, the accuracy of the data would not be the same, although we can expect these experiences not to not lack of interest since they would be the pioneer studies in a new research trend.

If we want realist situations where these experiences could be implemented, there are some of them:

- Chemical clocks as those suggested before. That is to say, periodic reactions in frames with high speed motion but with different relative speeds, what means in fact a chemical version of the twin paradox.
- Chemical reactions that occur in space shuttles or orbital stations, whose rates would be influenced as much by the special-relativistic effects (orbital speed) as the general-relativistic effects (reduction of the Earth gravitation).
- Relativistic corrections to the hypothetical chemical reactions eventually discovered in the atmospheres of other celestial bodies and spectroscopically scanned.
- The biochemistry of hypothetical astronauts in journeys with relativistic speeds would be surely affected in its kinetic aspects.

Conclusions

The fact that the most usual chemical systems –those in equilibrium– do not depend explicitly on space and time coordinates has largely prevented chemistry from incorporating the principles of relativistic physics as well as designing experimental situations to contrast them. It has specifically happened in the kinetics of chemical reactions, the area of chemistry that is most explicitly time-dependent and that perhaps could accept such modifications in a best way.

In this paper some relativistic extensions –both special-relativistic and general-relativistic ones– of chemical kinetics have been attempted for the reaction-rate law, provided that it was subjected to the aforementioned initial simplifications whose transition to the usual equations for small speeds and weak fields invites us to think that they are not completely incorrect. The expectations of further theoretical progress and experimental confirmation generated by research lines as those presented here are numerous and promising:

- Application of new mathematical operators (scalar or tensorial densities, etc.) to the description of chemical-kinetic processes under relativistic conditions.
- Enquiry into a possible dependence of the rate constants and reaction orders with the frame motion or with the presence of gravitational fields.
- Exploration of more complex and realist conditions in the studied chemical systems: space and time gradients of concentration of chemical species inside the reaction volume, strongly non-linear reactive processes, situations very far from reversibility, etc.
- Justification of the theoretical link between macroscopic and microscopic levels in the relativistic descriptions of chemical kinetics.
- Search for the influence of diverse kinds of tracks inside a gravitational field, not necessarily with the Schwarzschild structure.

Whatever it was finally, considerations as those exposed here demonstrate that beyond the refinement of the quantum calculations for bond energies, or the design and analysis of molecular structures by means of computer programs, in the XXIth century chemistry has before itself a wide horizon of fascinating theoretical and experimental possibilities.

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