Abstract – Modern experimental and theoretical advances in chemical kinetics are documenting an ample spectrum of phenomena on reactions occurring under conditions relevant for astrochemistry, from those of interest for formation of molecules in the early universe to those encountered in interstellar medium. Here, we present a set of exact, phenomenological and first-principles tools to describe temperature dependence of rate constants under extreme conditions, showing non-Arrhenius behavior, especially at low temperatures. We are mainly concerned with illustrating case studies on (i) super-Arrhenius kinetics, including treatment of diffusion and viscosity in supercooling and glass material; (ii) sub-Arrhenius kinetics, regarding quantum mechanics proton or atomic hydrogen transfer in chemical reactions of interest in astrochemistry, astrobiology, and also in atmospheric and industrial applications; and (iii) anti-Arrhenius kinetics, where processes with no energetic obstacles are rate-limited by molecular reorientation requirements, such as documented for OH + HX (X = Br and I) elementary chemical reaction.

1. INTRODUCTION

The understanding of the history, role and fate of molecules in the universe requires information of the kinetics of the involved elementary processes, particularly

1 Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy.
2 Grupo de Química Teórica e Estrutural de Anápolis, Ciências Exatas e Tecnológicas. Universidade Estadual de Goiás, CP 459, 75001-970 Anápolis, GO Brazil.
3 Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, 06100, Rome, Italy.
on their rates, and often in a wide range of conditions and specifically as a function of temperature. The temperature dependence of the rate constant of the primordial chemical reaction process is therefore crucial in order to establish the molecular abundances and the early universe evolution. The rate constants for most rate processes depend on absolute temperature according to the Arrhenius law: however, modern experimental progress in the age of nanotechnologies and computational progress, that are manifesting in a variety of approaches, has shown that when extended to low temperatures, deviations are observed even with no apparent changes in the chemical mechanism or in the physical nature of the moieties. Indeed, these advances have assisted to control the physical chemistry of materials in a large variety of environments and in the progress of new sciences, such as astrochemistry and astrobiology.

The deviations from linearity in Arrhenius plot leads to distinct regimes, denoted sub-Arrhenius, super-Arrhenius and anti-Arrhenius: the first two case correspond, respectively, to higher or lower reactivity as temperature decreases, and therefore to a decrease or increase of the apparent activation energy; the last and extreme case arises when the activation energy has negative value. To describe these behavior, recent systematic investigations lead to a simple formulation in terms of a single deformation parameter, denominated as deformed-Arrhenius (d-Arrhenius), which is inspired by Tsallis non-extensive statistical mechanics and exploits Euler’s expression of the exponential function as the limit of a succession.

Special attention requires the chemistry of the early Universe, which plays an important role in our understanding of the formation of the first cosmological objects. Molecular formation began in the recombination era, when the temperature was low enough for the newly formed atoms to survive and participate in further evolution. At the end of the era, atomic density was still too low for three body reactions to play any significant role; however, it was then that the first molecular species were postulated to be formed through radiative association. The formation of molecular species in the primordial Universe is extremely important, because roto-vibrational quantum states became available to participate in the cooling process, permitting the dissipation of the radiative energy and balancing the increase of the gravitational energy during the collapse of the first cosmological objects. Gas phase chemistry of formation and destruction of these molecules is therefore very important to get a good understanding of how galaxies and clusters came to be.

Accordingly, this paper aims to illustrate the recent advances in the understanding of chemical kinetics in extreme temperature conditions, mainly in astrophysical environment. In the Section 2 we show the new paradigms and the current state of kinetic theory for super-Arrhenius, sub-Arrhenius and anti-Arrhenius behavior. In sections 3 and 4 we present an exact quantum dynamics study of the F + HD and H + HeH+ reactions for ultra-cold collision energies with an emphasis on the application of the d-Arrhenius formula and of the relevance of these results in the early universe scenario. Concluding remarks follow in Section 4.
2. Low Temperature: Sub, Super and Anti-Arrhenius Behavior

The rate constant $k$ for the most rate processes depend on absolute temperature according to the well-known Arrhenius law [1]:

$$k(\beta) = Ae^{-Ea/\beta}$$

where $A$ is the pre-exponential factor, $Ea$ the apparent activation energy and $\beta = \frac{1}{kBT}$, where $k_B$ is the Boltzmann constant. However, modern experimental techniques and theoretical approaches are providing an ample phenomenology of deviations from Arrhenius behavior, especially at low temperatures. In order to provide a description of non-Arrhenius behavior, recent systematic investigations led to a simple formalism in terms of a single parameter, $d$. The use of the deformed Arrhenius law [2, 3]:

$$k(\beta) = A(1 - de\beta)^{\frac{1}{d}}$$

known as the Aquilanti-Mundim formula, permitting one to evaluate prototypical systems where the temperature dependence of the rate constant according to this equation is described by $\varepsilon > 0$ and $d > 0$ or $d < 0$, corresponding to convex (super-Arrhenius), concave (sub-Arrhenius) in the semi-log plots against reciprocal temperature (see figure 1). In the limit $d \rightarrow 0$, the term $(1 - de\beta)^{\frac{1}{d}}$ can be identified with the Arrhenius exponential law (Eq. (1)). Other case for $\varepsilon < 0$ will also be documented and indicated as anti-Arrhenius.

In the next section the recent paradigm and the current state are illustrated for: (i) super-Arrhenius kinetics, for example cases where transport mechanisms accelerate processes when increasing temperature; (ii) sub-Arrhenius kinetics, where quan-

![Fig. 1. Experimental, theoretical and simulation data are universally analyzed by an Arrhenius plot, where $k$ is reported against $T$. Deviations from linearity at low temperatures can be observed in the plot as showing either a «concave» behavior (sub-Arrhenius), i.e., higher than expected rates as temperature decreases, or a «convex» curve (super-Arrhenius), i.e., lower than expected rates as temperature decreases.](image)
2.1. The super-Arrhenius case

Super-Arrhenius behavior is one that deserves particular attention, and its occurrence is varied and demanding. It often manifests because of collective phenomena, such as those amenable to treatment by the non-extensive thermodynamics of Tsallis, and covers on ample set of phenomena: rates of enzymatic catalysis promoted processes [4–6], food preservation processes [7, 8], basic features of the dynamics of complex or glass-forming liquids and solids [9-14] and geochemistry [15]. A significant number of studies in the temperature-dependence of rates of enzymatic catalysis reactions has inspired several formulations for the description of the mechanism involved in these processes [16-19]. Results in the kinetics of catalytic reactions of the dehydrogenase and oxidase enzymes has shown an unequivocal super-Arrhenius behaviour [4, 5, 20, 21].

A similar behavior is found in the temperature dependence of food processes. We propose in Ref. [7] the use of Equation 1 to describe the non-Arrhenius behavior in these processes, showing that the $d$-Arrhenius formula is suitable for describing the effect of temperature on non-enzymatic browning of onion and on the rate of growth of several species of bacteria. The $d$-Arrhenius rate law provides a means to account for convex curvature. Such factors include particle diffusion and constraints on proposed microscopic model, in particular requiring that any successful approach to super-Arrhenius processes should be consistent with the microcanonical rate constant [7, 21].

A most fundamental case of super-Arrhenius temperature-dependence occurs for the diffusion in supercooled systems near the glass transition temperature, $T_g$. An interesting example is the diffusion of krypton in methanol and ethanol mixtures at low temperature near their glass transition temperatures [22-24]. Furthermore, in the vicinity of the glass transition temperature the viscosity and diffusion coefficients of polymers and other glass forming liquids are strong functions of temperature, and it is a frequently occurring observation that materials exhibit deviation from Arrhenius behavior. Non-Arrhenius relaxation rates in glassy materials can be associated with thermally activated rearrangements of increasing numbers of molecules as temperature decreases.

To account for the super-Arrhenius behavior in classical collective phenomena, it is shown that is inversely proportional to the barrier height, $\varepsilon$, and directly proportional to a limit critical temperature, $T^+$, which can be related to freezing in the degree of freedom of the system:

$$d = \frac{k_B T^+}{\varepsilon}$$  \hspace{1cm} (3)
2.2. The sub-Arrhenius cases

There are uncountable cases of concave deviation on the temperature rate constants for the elementary chemical reactions that can be classified as exhibiting a sub-Arrhenius behavior. In systems with no apparent changes in the chemical mechanism, this behavior can be attributed in most cases to quantum mechanical tunneling [2, 25]. Several investigations have provided examples of chemical reactions within this regime. A series of experimental kinetic data and of benchmark theoretical calculations [26-33] has established that, for example, the prototypical quantum mechanically investigated reaction of a fluorine atom with molecular hydrogen represents (See Section 3) an archetypical case of sub-Arrhenius behavior [34, 35], as has been experimentally confirmed [36].

To account for the sub-Arrhenius behavior in elementary chemical reactions, it has been shown that can be considered as inversely proportional to the square of the barrier height (ε) and directly proportional to the square of the frequency for crossing the barrier (ν*) at a maximum in the potential energy surface:

\[
d = -\frac{1}{3} \left( \frac{hv^*}{2\varepsilon} \right)^2,
\]

agreeing with Wigner’s tunnel formula.

This definition can be incorporated in transition-state theory to cover cases where reaction rates as a function of temperature deviate from Arrhenius law. When deviation can be ascribed to quantum mechanical tunneling, an explicit derivation is given and inserted in a proposed variant of transition-state-theory – deformed transition-state-theory (d-TST) – which permits comparison with experiments and tests against alternative formulations. The application of d-TST to several hydrogen transfer reactions has been showing promising results. Temperature ranges for the validity of the approach are assessed with respect to features of the potential energy barrier to reaction [37]. Elementary reactions, widely investigated both experimentally and theoretically, which have been described successfully, are F + H2 [2, 35], CH₄ + OH [38], CH₃Cl + OH [38], H₂ + CN [38], OH + HCl [39], abstraction and dissociation in the nitrogen trifluoride channels [40], and proton rearrangement in curcumin [41] and methylhydroxycarbene [42] and recently d-TST is shown to be suitable for describing the overall rate constant for the CH₃OH + H reaction [43].

As discussed in Refs. [44, 45], the degree of concavity in the Arrhenius plot can characterize the degree of tunneling in chemical reactions. The crossover temperature, \( T_c = \frac{h\nu^*}{k_B} \), is the parameter that delimits the degree of tunnelling regimes. The ranges of tunnelling regimes are important to quantify how the tunnelling affects the rate constant in particular cases. From a mathematical viewpoint, the d-TST formulation has clear limitations in the description of the deep tunnelling
regime (Wigner limit) [46, 47], since the Euler limit deformation of the exponential function fails to quantify the distributions of reactive particles with energy less than the height of the barrier. However, the flexibility of the distribution formula permits to cover the sub-Arrhenius behaviour, specifically typical of quantum tunnelling, smoothly extending into the Boltzmann distribution [48] of the classical regime.

Formula (2) is found adequate for moderate tunneling, $T > T_c$. Rarer cases of deep tunneling can be dealt by introducing a modified form [49]:

$$k_d^{ASC}(T) = A \left(1 - \frac{d \epsilon}{k_B T + h \nu^*} \right)^\frac{1}{a}.$$  \hspace{1cm} (5)

Its derivation and performances will be further discussed elsewhere.

2.3. Anti-Arrhenius cases

The rates of some processes increase as temperature decreases accordingly to an apparently negative activation energy. These processes can be classified as anti-Arrhenius. In gas-phase reaction the anti-Arrhenius behavior is frequently found in molecule-radical reactions [50-55]. Using a first-principles Born-Oppenheimer molecular dynamics approach, we were able to provide an interpretation of the negative dependence of the rate constant on temperature for the OH + HBr and OH + HI reactions [56-59], confirming the suggestion obtained experimentally that this phenomenon has stereodynamical origin, which until now has been neglected by theoretical studies. The analysis of simulations showed that for low temperature, the reactants reorient to find the propitious alignment leading to reaction; however, this adjustment is progressively less effective for higher temperatures, where the wandering paths evidence the «roaming» effect. Additionally, the smaller number of reactive trajectories and the time required for the mutual reactant orientations for the hydrogen exchange for the OH + HI suggest a greater role of stereodynamics here, which may be related to the higher observed rate constant for the same temperature compared to the OH + HBr reaction.

Currently, there is ample activity investigating whether advances in molecular dynamics simulations can provide quantitatively rate constants [60-62]. However, the methods have difficulty in estimating the rate constants, generally leading to overestimates and the discrepancy with experimental data is larger for high temperatures. With our methodology, we also find overestimating rate constant for OH + HBr and HI reactions [56, 57]. These uncertainties are often associated to inherent difficulties of possible direct evaluations from molecular dynamics simulation, and are ascribed to the statistical validity of samplings of the system phase space and the accurate characterization of transition state features [63-65]. These crucial issues in the applications of TST-type approaches to calculations of rates constitute hard problems in the extraction of rate constants from first-principles molecular dynamics
experiments, preventing them to represent an at least semiquantitative alternative to direct exact or approximate quantum mechanical methods, often prohibitive to be implemented.

As a final example on how the study of the anti-Arrhenius behavior offers opportunities for fundamental research and can guide scientific progress in different areas, we note a recent paper where the stereodirectionality effect contributed to understand the negative activation energy in addition reactions of arylchlorocarbenes to alkenes [66].

3. AN EXACT TRIATOMIC TREATMENT: THE $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ REACTION AND ITS ISOTOPIC VARIANTS

The rate constants for the $\text{F} + \text{H}_2$ reaction and its isotopic variants arises great attention from experimental and theoretical chemical kinetics studies [67-69]. This reaction is a prototypical exothermic elementary reaction driven by the tunneling effect. Furthermore, because of the population inversion of the vibrational levels in the HF product, this reaction was studied in much detail for leading to vibrational population inversion of interest of chemical lasers [70].

For this reaction, the results of rigorous quantum scattering calculations, see ref. [71] for details, show a linear behavior of the rate constant at high temperature, when the thermal contributions are more pronounced; however, a strong curvature was observed at low temperature. We compare the abilities that two different approaches, namely the Bell’s 1935 [72] and the Aquilanti-Mundim $d$-Arrhenius [2, 48, 73] formulas, have to account for the deviation of the rate constant from the Arrhenius law in a temperature interval at the borderline between moderate and deep tunneling regimes, see Figure 2.

The rate constant obtained from close coupling calculations employing FXZ PES [74] has been fitted to the Bell’s 1935 formula:

$$k(T) = A \left[ \frac{RT \exp (-\epsilon/RT) - \hbar v^* \exp (-\epsilon/\hbar v^*)}{RT - \hbar v^*} \right]$$

as presented in Ref. [71]. Here, the $d$-Arrhenius [2, 48, 73] formula in Eq. (2) and Eq. (5) has been used to described the rate constants.

From Figure 2 one can note that the two formulas fit satisfactory well the close coupling data in the range of temperatures studied with a mean percent error within or close to the numerical accuracy of the data. Nevertheless, it had been shown in ref. [71] that Bell’s formulas reproduce much better the data (a factor near to five) with respect to $d$-Arrhenius. As introduced in the section 2.2, $d$-Arrhenius formula has clear limitations in the description the rate constant below of the crossover temperature, $T_c = \hbar v^*/k$, which for the $\text{F} + \text{HD}$ reaction is equal to 178 K. In general, Bell’s venerable approach turns out as very useful for extending the study of reactivity at very low temperatures, describing a dependence of rate constants in agree-
ment with Wigner threshold law. However, the ASCC formula shown here is definitively better and recommended.

The current challenge is to describe the temperature dependence on the rate constants for temperatures below 1K, where an anti-Arrhenius behavior, due to the presence of a resonance state near to reaction threshold, has been predicted by recent results not published yet.

4. AN EXACT TREATMENT OF THE ION-MOLECULAR REACTION $H + \text{HeH}^+ \rightarrow \text{H}_2 + \text{He}^+$: ROLE IN THE PRIMORDIAL UNIVERSE

Because $H$ and $\text{He}$ are the dominant species in the early Universe scenario and can be ionized to $H^+$ and $\text{He}^+$ by cosmic rays, the first collisions of the $\text{He}$ chemistry are $\text{He} + \text{H}_2^+$ and $\text{He}^+ + \text{H}_2$. The former collision is an adiabatic process on the $\text{HeH}_2^+$ ground electronic surface and was extensively investigated in the past [75].
The chemical reaction $\text{H} + \text{HeH}^+$ reaction plays an important role in astrophysics, because it is the key step in one of the main mechanisms of hydrogen molecule formation in the primordial plasma, strongly affecting the hydrogen abundance in the red shift range 150-300 nm. The temperature dependence of the rate of this simple exothermic process is therefore crucial in order to establish the molecular abundances and the early universe evolution. Also, the existence of $\text{HeH}^+$ in many different astrophysical environments (planetary nebulae, dense molecular clouds, white dwarfs) has been discussed in several papers [76, 77]. Because of the many astrochemical applications, accurate reaction data are required in the full collision energy range, from the ultra-cold regime to the three-body breakup and beyond.

The dynamics of the $\text{H} + \text{HeH}^+$ reaction has been studied from 0.001 K to 2000 K by close coupling quantum reactive scattering calculations, exact when the potential energy surface is given [78]. The main tools that allow the covering of so large a range of temperature, varying by six orders of magnitude, have been the...
implementation of the Enhanced Renormalized Numerov method [79] to improve the convergence in the ultra-cold regime and a massive parallelization of the code [74] to treat the large number of partial waves required for this ionic system.

The large difference at higher temperatures (see Fig. 3), where the rates are about double in the new time independent calculations, may have important consequences in the early universe scenario. In fact, a higher reactivity of the HeH$^+$ cation makes the title reaction more competitive with radiative dissociation favoring the formation of the H$_2$ (at higher red shifts, where the HeH$^+$ mechanism is the main channel of formation of the hydrogen molecule. It is highly relevant to date the formation of the first stars and galaxies because the H$_2$ molecule is, in the present state of the astrophysical knowledge [80], the most important coolant species in the early universe scenario.

5. CONCLUSION

In summary, in our journey to the understanding of the microscopic ingredients which are the driving-force in physical and chemical processes under extreme conditions, and specially at low temperatures, we can highlight some interesting new entries: (i) the introduction of a deviation parameter $d$ covering uniformly a variety of rate processes, from quantum mechanical tunneling and stereodynamical effects to Pareto-Tsallis distributions process culminating in deformed version of the Arrhenius law, the Aquilanti-Mundim $d$-Arrhenius; (ii) a relationship among the deformation parameter $d$ with structural properties of the physical and chemical processes evaluated; (iii) explanation of the role of stereodynamical and roaming effects for elementary chemical reactions under anti-Arrhenius behavior; and (iv) presentation of exact rate constant at extreme low temperature for three-body reactions which emphasize the limitations of the phenomenological formulas available and the need of advance in formulations which describe processes in this regime.

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