The effects of gravitational potential on chemical reaction rates

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Abstract. This study aims to answer through a mathematical model and its numerical simulation the question whether the kinetic rate constants of chemical reactions are influenced by the strength of gravitational field. In order to calculate the effects of gravity on the kinetic rate constants, the model of kinetic rate constants derived from collision theory is amended by introducing the mass and length corrections provided by general relativity. Numerical simulations of the model show that the rate constant is higher where the gravitational field is more intense.

1. Introduction
The rate constant is the proportionality constant between the rate of change over time of the concentration of the products and the concentration of the reactants, and for this reason it is often called specific reaction speed. Currently, in view of new space programmes that have rekindled interest in human space missions, and astrobiology more generally, understanding gravitational effects on chemical kinetics is becoming imperative [1]. The gravitational effects on molecule–molecule interactions are largely unknown, and could be both relativistic and non-relativist effects. Indeed, the gravitational field is expected to influence the speed of a chemical reaction, not only because of the spatial reorganisation of the particle distribution due to gravitational force [2, 3, 4, 5, 6, 7] or the trigger of mechanisms of adaptation of the living system to gravity [1, 8], but also for the effect of time slowing down as the intensity of the gravitational field increases [9]. However, the state of the art in this field is rather poor as far as theoretical modelling is concerned and with mixed results as far as experimental tests are concerned.

Studies of Giachetti et al. [10] and Ranaldi et al. [11] claim that enzyme kinetics are not altered by gravity. Ranaldi’s team, supported by the European Space Agency and the Agenzia Spaziale Italiana, developed the Effect of Microgravity on Enzyme Catalysis project to test whether that the microgravity effect observed at cellular level could be mediated by enzyme reactions. An experiment to study the cleavage reaction catalyzed by the enzyme isocitrate lyase was flown on the sounding rocket MASER 7, both in microgravity and in standard gravity conditions. The experiment consisted of performing, in a microgravity environment, a number of velocity measurements of the enzyme catalyzed reaction at different substrate concentrations, to calculate the kinetic parameters (Km and Vmax), which were compared with those obtained at standard gravity, with identical experimental equipment. Giachetti et al. [10] and Ranaldi et al.
the enzyme reaction obeyed the same kinetic mechanism and none of the kinetic parameters, nor the equilibrium constant of the overall reaction were altered. The results presented by Ranaldi’s team contrast with those of a similar experiment of Maccarrone et al. [2, 12] and showed that microgravity increased the affinity of lipoxygenase-1 for linoleic acid and that the Michaelis constant of soybean lipoxygenase-1 for linoleic acid is decreased to one fourth of that of the ground control. A possible explanation of the reason for this contrast in results has not yet been found. This indicates the need for further study.

The problem of quantify the gravitational effect on chemical kinetics is much older than the studies we cited above, as publications on the subject dating from the late 1980s testify [13]. In those years the problem was addressed by giving a relativistic formulation of the law of mass action, one of the simplest mathematical models to describe and explain the behaviours of solutions in dynamic equilibrium. In this study, a relativistic correction to the kinetic rate constant model derived from collision theory is proposed, rather than a relativistic reformulation of the rate equation. The rate equation is in fact an extremely ductile mathematical model, and therefore less general than the microscopic kinetic model derived from collision theory, as it describes the macroscopic, almost always context-specific, dynamics of reactant concentrations.

The study focuses on the relativistic effects of the variation of the gravitational field on chemical kinetics, i.e. those effects caused by the slowing down of time and the variation of mass at rest. Referring to Heighway’s and Likui et al. works [14, 15], this study introduces in the expression of the kinetic rate constant a term for the reduction of the rest mass, which is the main cause of the slowing down of the clocks and the variation of the relative velocity between particles, and a relativistic correction to the measurement of the distances between particles.

2. Collision theory

For a chemical reaction to take place, molecules must collide with sufficient energy to create a transition of state. Ludwig Boltzmann developed a very general idea about how energy was distributed among systems consisting of many particles. He said that the number of particles with energy \( E \) would be proportional to the value \( \exp[-E/k_B T] \). The Boltzmann distribution predicts the distribution function for the fractional number of particles \( N_i/N \) occupying a set of states \( i \) which each have energy \( E_i \):

\[
\frac{N_i}{N} = \frac{g_i e^{-E_i/k_B T}}{Z(T)}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is temperature (assumed to be a sharply well-defined quantity), \( g_i \) is the degeneracy, or number of states having energy \( E_i \), \( N \) is the total number of particles: \( N = \sum_i N_i \) and \( Z(T) = \sum_i g_i e^{-E_i/k_B T} \).

James Clerk Maxwell used Boltzmann’s ideas and applied them to the particles of an ideal gas to produce the distribution bearing both men’s names (the Maxwell-Boltzmann distribution). Maxwell also used for the energy \( E \) the formula for kinetic energy \( E = (1/2)mv^2 \), where \( v \) is the velocity of the particle. The distribution is best shown as a graph which shows how many particles have a particular speed in the gas [16].

Consider a bi-molecular reaction of the form

\[
S_1 + S_2 \rightarrow P
\]

which means that a molecule the chemical species \( S_1 \) is able to react with a molecule of the chemical species \( S_2 \) if the pair happens to collide with one another with sufficient energy, while moving around randomly, driven by Brownian motion. \( P \) is the final product of an effective collision between the reagent molecules. We introduce the concept of reaction propensity, expressing the collision probability per unit time. Consider a single pair of such molecules
in a closed volume $V$. Under the assumptions that the volume is not too large or well stirred, and in thermal equilibrium, it can be rigorously demonstrated that the reaction propensity is constant, provided that the volume is fixed and the temperature is constant. If the molecules are uniformly distributed throughout the volume and this distribution does not depend on time, then the probability that the molecules are within reaction distance is also independent of time. Consider now that the system composed of a mixture of the two molecular species, $S_1$ and $S_2$ in gas-phase and in thermal, but not necessarily chemical equilibrium inside the volume $V$. Let assume that the $S_1$ and $S_2$ molecules are hard spheres of radii $r_1$ and $r_2$, respectively. A collision will occur whenever the center-to-center distance between an $S_1$ molecule and an $S_2$ molecule is less than $r_{12} = r_1 + r_2$. To calculate the molecular collision rate, let pick an arbitrary 1-2 molecular pair, and denote by $v_{12}$ the speed of the molecule 1 relative to molecule 2. Then, in the next small time interval $\delta t$, molecule 1 will sweep out relative to molecule 2 a collision volume

$$\delta V_{\text{coll}} = \pi r_{12}^2 v_{12} \delta t$$

i.e. if the center of molecule 2 happens to lie inside $\delta V_{\text{coll}}$ at time $t$, then the two molecules will collide in the time interval $(t, t + \delta t)$. The classical frequentist approach to calculate the collision rate would (i) estimate the number of $S_2$ molecules whose centers lie inside $\delta V_{\text{coll}}$, (ii) divide this number by $\delta t$, and then (iii) take the limit $\delta t \to 0$. However, this procedure suffers from the following difficulty: as $\delta V_{\text{coll}} \to 0$, the number of $S_2$ molecules whose centers lie inside $\delta V_{\text{coll}}$ will be either 1 or 0, with the latter possibility become more and more likely as the limiting process proceeds. Then, in the limit of vanishingly small $\delta t$, it is physically meaningless to talk about "the number of molecules whose centers lie inside $\delta V_{\text{coll}}"$ [17]. This issue can be overridden in the condition of thermal equilibrium, in which the molecules will at all times be distributed randomly and uniformly throughout the containing volume $V$. As a consequence of the thermal equilibrium, the probability that the center of an arbitrary $S_2$ molecule will be found inside $\delta V_{\text{coll}}$ at time $t$ will be given by the ratio $\delta V_{\text{coll}}/V$; note that this is true even in the limit of vanishingly small $\delta V_{\text{coll}}$. By averaging this ratio over the velocity distributions of $S_1$ and $S_2$ molecules, we may conclude that the average probability that a particular 1-2 molecular pair will collide in the next vanishingly small time interval $\delta t$ is

$$\frac{\delta V_{\text{coll}}}{V} = \frac{\pi r_{12}^2 v_{12} \delta t}{V}$$

(2)

For Maxwellian velocity distributions [16] the average relative speed is

$$v_{12} = \sqrt{\frac{8 k_B T}{\pi m_{12}}}$$

where $k_B$ is the Boltzmann’s constant, $T$ the absolute temperature, and $m_{12}$ the reduced mass $m_1 m_2/(m_1 + m_2)$.

If at time $t$ there are $X_1$ molecules of the species $S_1$ and $X_2$ molecules of the species $S_2$, making a total of $X_1 X_2$ distinct 1-2 molecular pairs, then it follows from (2) that the probability that a 1-2 collision will occur somewhere inside $V$ in the next infinitesimal time interval $(t, t + dt)$ is

$$\frac{X_1 X_2 \pi r_{12}^2 v_{12} dt}{V}$$

where

$$k \equiv \frac{\pi r_{12}^2 v_{12}}{V} = \frac{r_{12}^2}{V} \sqrt{\frac{8 \pi k_B T}{m_{12}}}$$

(3)

is the rate constant (also known as specific velocity) of the chemical reaction (1).
3. Gravitational reformulation of the chemical rate constant
The reformulation of of the formula (3) in the context of general relativity makes it possible to understand whether and how the value of the rate constant $k$ depends on the position in the gravitational field in which the chemical reaction takes place.

In order to rewrite the formula (3) in the general relativity framework, we have to express the length $r_{12}$ and the mass $m_{12}$ according to the general relativity theory that predicts gravitational slowing of clocks, rest mass reduction, and elongation of roads [18, 19]. The well-established fact that the rate of a clock is reduced by the presence of nearby massive objects was predicted by Einstein in a 1916 paper [20]. In [21] Einstein also speculated regarding possible changes in the length of measuring rods, and, regarding the possible effect of gravity on the masses of objects. He concluded that the inertial mass of a test object would be increased when massive objects approach. As also reported by Heighway in [14], when a mass is raised against gravity, the increase in potential energy, $\Delta V$, is stored in the body itself as an increase in rest mass $\Delta m = \Delta V/c^2$. Heighway in [14] and even earlier in [22] went into great depth in understanding and explaining this fact, starting with the explanation of the cause of the slowing down of the clocks. He introduced the concept of telemetric measurement system, the key concept of whose implementation is the constancy of the speed of light. The telemetric measurement system is a system of space-time measurement that is unaffected by the gravitational field. In this system the observer measures time using the signals from a single remote clock and measures distances using electromagnetic echo ranging (radar) techniques, calculated using the time as measured by the same remote clock.

Heighway points out that the frequency of an atomic transition depends upon the four fundamental constants of quantum electrodynamics: the electronic charge, the speed of light, the Planck’s constant, and finally, the mass of the electron and in the same manner the mass of all fundamental particles. In looking for the cause of the gravitational slowing of clocks, it is assumed that one or more of these parameters, which are indeed constants, in the telemetric system must be dependent upon position in a gravitational field. In addition to accounting for the slowing of clocks, two other factors explain the variability of these parameters, i.e. the conservation of electric charge and the constancy of speed of light as measured by all local observers. In addition to the slowing of clocks, the variability of these parameters is constrained by two facts: first, the conservation of electric charge; second, that all local observers measure the apparent speed of light to be constant. The simplest way to satisfy these constraints - says Heighway - is requiring that the rest mass of the electron (and that of all particles), is reduced.
in a gravitational field [14, 22]. For a Schwarzschild weak gravitational field the reduction factor is

\[ \xi = \sqrt{1 - \frac{2GM}{c^2r}}, \quad \frac{2GM}{c^2r} < 1 \] (weak potential condition) \tag{4}

where \( M \) is the mass of the source of the gravitational field, \( G \) is the Newtonian constant of gravitation, \( r \) is a radial coordinate, and \( c \) is the speed of light (see Appendix for some brief notes on Schwarzschild metric).

The mass in the telemetric systems \( m_t \) is \( m_t = \xi m \), where \( m \) is the proper rest mass of a body as measured by a local observer. This result has been also reported by MacKenzie [23] and Schlegel [18], and a description of its foundations by Kogut in [24]. Fundamental quantum lengths, e.g. the Bohr radius, depend inversely upon the masses of elementary particles. Since rest masses are reduced by the factor \( \xi \), in a gravitational field, the Bohr radius, and hence the length of all objects, must increase by the factor \( \frac{1}{\xi} \) [15, 22]. As consequence we obtain that in the telemetric system the reduced mass \( m_{12} \) is \( m_{12}^{(t)} = \xi m_{12} \), and hence the rate constant of the reaction between the molecules of species \( S_1 \) and \( S_2 \) becomes

\[ k_t = \frac{1}{\sqrt{\xi}} \frac{r_{12}^2}{V} \sqrt{\frac{8\pi k_B T}{m_{12}}} = \frac{k}{\sqrt{\xi}} \equiv \nu_1 k. \] \tag{5}

4. Simulation results

Numerical simulations of formula (5) at fixed volume and temperature show that on the Earth \[ \nu_1(r) \in [1.000000000046996850855, 1.000000000347964768110]. \]

The amplitude of this range is \( 3.01 \times 10^{-10} \). The lower value of \( \nu_2 \) is obtained for \( r = 408 \times 10^5 \) meters above the Earth’s surface (100 times the distance of the International Space Station from the Earth surface), and the higher value is obtained on the Earth’s surface.

If we also consider the effect on the center-to-center distance, i.e. \( r_{12}^{(t)} = r_{12}/\xi \), we get

\[ k_t = \frac{k}{\xi^2 \sqrt{\xi}} \equiv k\nu_2. \] \tag{6}

where \( \nu_2(r) \in [1.00000000234984254277, 1.000000001739823618507]. \) The amplitude of this interval is very small: \( 1.504 \times 10^{-9} \). Including in the formula also the reduction of lengths due to the effects of gravitational potential, the variation of the rate constant in dependence of altitude becomes not exactly negligible. Figure 2 shows the behaviour of the derivative \( \frac{d\nu_2(r)}{dr} \) in the same range: it is very close to zero and re-confirms an extremely slight variation of \( \nu_2(r) \) in this range of altitudes.

By repeating the simulations in a hypothetical unrealistic range from 2 times to \( 10^6 \) the Schwarzschild radius (see Appendix) of the Earth at steps of 10 Schwarzschild radii, we obtain an interval for \( \nu_2(r) \)

\[ \nu_2(r) \in [1.00, 2.378]. \]

5. Conclusions

Relativistic chemistry as well as relativistic molecular dynamics are certainly very complex timely domains [25], the study of which is still in its infancy, especially with regard to the medical and pharmacological implications that the relativistic reformulation of chemical kinetics may have. Considering that the association rates of may protein-protein complexes are in the \( 10^5 - 10^6 \) M\(^{-1}\) sec\(^{-1}\) range [26], the numerical estimates of the gravitational effects (in condition
Figure 2. Behaviour of the derivative of $\nu_2(r)$ with respect to $r$. It is very close to 0, and testifies a slow and minimal decrement of $\nu_2$ in the considered range for $r$.

of gravitational potential favourable to life) on $k$ presented here, show that the effect on many biochemical systems is very small but nevertheless it is not completely negligible and hence worth to be studied.

The study presented here concerns the relativistic effects of varying the gravitational field intensity on the value of the kinetic rate constant derived from the theory of chemical reactions as collisions. Time slowing down and rest mass reduction are the two intimately connected causes of the relativistic effects. However, gravitational effects on the kinetic rate constants could be also due to non-relativistic transformation, so that the study of the influence of gravity on chemical kinetics have to be approached by multi-physics modelling. The term multiphysics is used here in two meanings, the first referring to the inclusion of gravitational effects operating on different physical processes (such as diffusion, concentration gradient formation) and the second referring to different theoretical and/or empirical models for a given quantity. Indeed, it is worth to note that the equation (3) is not the only model for the kinetic rate constant. The reaction rate coefficient $k$ has a temperature dependency, which according to thermodynamic considerations is usually given by the empirical Arrhenius law:

$$k_{\text{Arrhenius}} = A \exp \left[ - \frac{E_a}{RT} \right]$$

where $E_a$ is the activation energy and $R$ is the gas constant. $A$ is the frequency factor that indicates how many collisions between reactants have the correct orientation to lead to the products. The values for $A$ and $E_a$ are dependent on the reaction. Relativistic and non-relativistic gravitational effects should be investigated on the activation energy in the Arrhenius model, and it should be verified that the results on the kinetic constant model obtained from the collisions are in agreement with those obtained from the thermodynamic model.

Of interest, particularly with regard to its relativistic generalization, could be the Rice-Ramsperger-Kassel-Marcus (RRKM) model of the kinetic constant for unimolecular reactions. In the RRKM model the rate is proportional to the number of ways of distributing the energy among the internal degrees of freedom of the reactant, in such a manner that the critical energy is localized in one particular degree of freedom [27]. The fundamental concept underlying the RRKM model is the possibility of distributing the energy possessed by a molecule over all the oscillatory modes. The reaction will take place when sufficient energy has accumulated at a certain point (such as a chemical bond), a condition that has probability

$$p = \left(1 - \frac{E_b}{E}\right)^s$$

where $E_b$ is the energy required to break the bond and $s$ is the number of ways in which the energy can be dissipated, that is a number increasing as the size of the molecular structure decreases.
increases. It is then possible to calculate the kinetic constant using this probability with the following formula [28].

\[ k_E = \nu \left( 1 - \frac{E_b}{E} \right)^{s-1}, \quad E \geq E_b \]  

(9)

which expresses the variation of the rate constant as a function of energy \( E = n\hbar \nu \) [28], \( n \) begin the number of total vibrational quanta, and \( \nu \) the radiation frequency as in Planck’s energy formula. When the energy of the molecule is very high, the kinetic constant is practically independent of the energy itself and of the vibrational modes. Marcus generalised and revised the theory by taking into account the theory of transition states and the concepts of statistical mechanics. A basic introduction of RRKM theory can be found in [29] and its review and discussion as extension of Marcus theory can be found in [30, 31] for thermal unimolecular reactions usually described by first-order kinetics. Applications and recent developments of RRKM theory in biological contexts are expected to increases in the next future, and can be found in [8, 32, 33, 34, 35]. Applications are expected to grow, especially with regard to photobiological processes of potential interest for the planning the risks and sustainment of long-term human missions in space [36].

A rigorous study of gravitational transformations due to relativistic effects on the kinetic rate constant RRKM model is necessary, although it proves to be a very difficult challenge to integrate concepts of statistical mechanics, quantum mechanics proper to RRKM theory with concepts of general relativity. The final test suggested by the multi-physics approach will then consist in verifying that the results obtained from the various models are experimentally valid and in agreement with each other.

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Appendix
The invariant interval outside a mass \( M \) is described by the Schwarzschild metric [24, 23]

\[ ds^2 = \left( 1 - \frac{2GM}{c^2r} \right) c^2 dt^2 - \frac{dr^2}{1 - \frac{2GM}{c^2r}} - r^2(d\theta^2 + \sin^2 \theta d\phi^2). \]

\( ds \) denotes the invariant space-time interval, an absolute measure of the distance between two events in space and time, \( t \) is a ‘universal’ time coordinate, \( r \) is the circumferential radius, defined so that the circumference of a sphere at radius \( r \) is \( 2\pi r \), and \( d\phi \) is an interval of spherical solid angle.

According to the Schwarzschild metric, a the length of a rod placed in the radial direction from the origin is \( dl \approx \left( 1 - \frac{2GM}{c^2r} \right) dr \). The coordinate length \( dr \) of a meter stick of proper length \( dl = 1 \) meter, placed on a spoke from the origin, is less than 1 meter and its coordinate extent is \( \left( 1 - \frac{2GM}{c^2r} \right) \) meters. As consequence, more meter sticks are needed to reach \( r_b \) from \( r_a \) than in the flat space. If the meter stick is placed in the transverse direction, then its proper length is not affected by gravity, as it satisfies \( dl^2 = r^2 d\theta^2 \).

Outside the mass \( M \) where \( \frac{2GM}{c^2r} < 1 \), when the radius of a circle is increased by a proper length \( \Delta l \), the radial coordinate increases by \( \left( 1 - \frac{2GM}{c^2r} \right) \Delta l \) and the circumference increases by
\(2\pi \left(1 - \frac{2GM}{c^2 r}\right) \Delta l\), that is and indication of the positive curvature of the metric.

The Schwarzschild metric has a singularity for \(\frac{2GM}{c^2 r} = 1\) at which the proper time

\[d\tau = \sqrt{1 - \frac{2GM}{c^2 r}} \, dt\]

vanishes, and the proper distance

\[dl = \frac{dr}{\sqrt{1 - \frac{2GM}{c^2 r}}}\]

diverges. The critical distance

\[r^* = \frac{2GM}{c^2}\]

is known as Schwarzschild radius. For a typical celestial body \(r^*\) is much smaller than the body’s actual radius, and the expression of \(ds^2\) holds only outside the massive body, just like Newton’s gravitational potential \(V(r) = -\frac{GM}{r}\). The Schwarzschild metric is not appropriate for distances less than \(r^*\) because of the singularity of the second term \(\frac{dr^2}{1 - \frac{2GM}{c^2 r}}\). This is a limitation of the polar coordinates, not a real physical singularity [24, 37]. Switching to Eddington-Finkelstein coordinates allows the treatment of the full range of radial coordinates. However since strong gravitational fields are out of the scope of this study, we do not deal with this limitation.

6. References

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