A speculative study of non-linear Arrhenius plot by using fractional calculus

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Abstract

In this study, the Van’t Hoff differential equation is taken under consideration by making use of fractional derivative tools. In this context, the nonlinear Arrhenius behaviour can be obtained and some experimental values of reaction rate as function of temperature were fitted, with the proposed model. The new model showed better performance to fit rate constant data for different kinetics process, when compared with Arrhenius law. In these case, the Van’t Hoff differential equation with noniteger order found relative percentage error less that 3% within experimental error. The fractional order plays an important role in modeling temperature dependence of these kinetic processes. Thus it provides a new perspective in the handling of many problems (e.g., as solubility as function of temperature; temperature dependency of the viscosity and conductivity, etc).

Keywords non-linear Arrhenius plot; Van’t Hoff equation; fractional derivative
1 Introduction

Experimental data show that reaction rates have a sensitive dependence on temperature; this point lies at the beginning of chemical kinetics research. In 1889 Svante Arrhenius [1], by a thermodynamic argument due to Van’t Hoff [2], proposed the simple equation to model effect of temperature on reaction rates. The empirical Arrhenius equation was applied with great success in the modeling this influence by temperature on the rate of chemical reactions (e.g., one of these reactions is the inversion of cane sugar by acids which was discussed by Arrhenius in 1889). The Arrhenius equation describes that the rate of chemical reaction as decaying exponentially with $1/T$ temperature; this relationship is known today as Arrhenius law.

Currently, with development of new experimental techniques for studying the influence of temperature over a wide range and accurate experimental data, deviations from Arrhenius law has been observed [3, 4, 5]. Therefore, for some reactions the temperature dependence of the rate constant is not exponential with $1/T$, showing appreciable curvature of the Arrhenius semi-log plot of $(\ln k \times 1/T)$; these are called non-linear Arrhenius behaviours. This fault of the Arrhenius law can not be explained by experimental errors, wherefore new empirical equations has been used to model non-linear Arrhenius behaviour, such as d-Arrhenius model which is inspired in Euler’s approach to the exponential function [6].

The reference [7] presents a review of the development of the Arrhenius equation, showing some of the extensions of Arrhenius law to cases of deviation of Arrhenius plot from linearity. Thus today it is widely accepted that, over a limited range of temperature, the Arrhenius law for $\ln k$ as function as $1/T$ is acceptably linear but is not in general obeyed, for wide range of temperature. There are a large number of theoretical models that have been proposed to interpret this kind of process and several factors considered for deviations from linearity (e.g., quantum and collective effects [8, 9]). As discussed in reference [9] the diffusion process plays an important role in effect of temperature on reaction rate: this motivated us to study the fractional calculus in this context. Fractional calculus represents a natural instrument to model anomalous diffusion process, when memory effect have an important role therein [12]. One way to include this memory effect is to use fractional order derivatives in the original model, in this case Van’t Hoff equation.

Thus, we propose to analyze the non-linear Arrhenius plot in different way; by using Van’t Hoff differential generalized to non-integer order. Recent studies have shown that fractional calculus is a good alternative tool in many diverse fields of science, such as the study of the non-exponential growth of bacteria in culture media [10]. In reference [11], the fractional differential equation was used to model an anomalous luminescence decay process for longer observation time, in which deviation from exponential decay linear in the time variable is
expected. In the present study, for the first time, we employ Van’t Hoff equation modified with the fractional derivative to obtain the generalized model of Van’t Hoff equation, from which non-linear Arrhenius behavior can be explained. It will be shown that the curvature of non-linear Arrhenius behaviour can be described by adjusting the fractional derivative order.

In the next section 2, we will begin by introducing the necessary foundations of fractional calculus and then our generalized model, the FVHE [Fractional Van’t Hoff Equation]; it’s exact analytical solution via operational methods is presented in section 3. In section 4, numerical methods which are also used to solve the FVHE are discussed. Then in section 5, experimental data in a variety of contexts will be compared with our proposed model (these include deformed Arrhenius law, curved Arrhenius plot and Arrhenius law), showing that the FVHE is a good alternative model to describe these experimental data.

2 Fractional calculus background

Theoretical description of fractional calculus begins by generalizing the integral with noninteger order, so if we integrate \((Jf)(t) = \int_0^t f(s)ds\) with respect to \(s\) by \(m\) times we find the following result [12],

\[
(JJJJ...JJf)(t) = (J^m f)(t) = \frac{1}{(m-1)!} \int_0^t (t-s)^{m-1} f(s)ds
\]

Above equation is well defined for all positive integers \(m\).

If we consider the fundamental theorem of calculus, in which \((DJf)(t) = f(t)\), then we can write that

\[
(D^m J^m f)(t) = f(t)
\]

by finite induction method, where \(m\) is an integer. In order to find a fractional derivatives definition, take \(m = n - \alpha\) and apply differential operator \(D^n\) on both sides of equation [2] getting \((D^n D^m J^m f)(t) = (D^n f)(t)\), thus it can be written as

\[
(D^n f)(t) = (D^n J^{n-\alpha} f)(t) = \frac{1}{\Gamma(n - \alpha - 1)} \frac{d^n}{dt^n} \int_0^t \frac{f(s)ds}{(t-s)^{n-\alpha+1}}
\]

using composition rule [12]. Since equation (3) is well defined when \(n - 1 \leq \alpha \leq n\) where \(n \in \mathbb{Z}^+\) a positive integer, for \(\alpha\) a noninteger number.

Thus one obtains a Riemann-Liouville fractional derivative, where \(\alpha\) is defined as the fractional derivative order. This is in contrast to a derivative of integer order (a local operator), as the fractional operator is clearly non-local, since the fractional derivative depends on the lower boundary of the Riemann-Liouville integral. To make the notation clear we will use \(D_0^n\) as symbol of Riemann-Liouville fractional derivative.
3 Fractional Van’t Hoff differential equation

Van’t Hoff found the dependence of the equilibrium constant $K$ from the absolute temperature $T$, such as $d(\ln(K(T)))/dT = \Delta H/RT^2$ \[2\], where $\Delta H$ is the heat of reaction and $R$ is the gas constant. From this equation and the relation of $K$ with the rate $k$, Arrhenius obtained the expression for the dependence of the rate $k$ with temperature absolute $T$ \[1\],

$$\frac{d(\ln(k(T)))}{dT} = \frac{E}{RT^2}$$

in which $E$ is an empirically determined quantify called the activation energy. Integrating above equation, assuming $E$ is independent of temperature we get

$$\ln(k(T)) = \ln A - \frac{E}{RT}$$

where $\ln A$ is an integration constant. Above equation is known as Arrhenius law in which a plot of $\ln k$ versus $1/T$ will be linear with a negative slope equal to $-E/R$ and an intercept equal to $\ln A$. As stated previously, this expression has had great success in describing the temperature dependence of reaction rates, but for some reactions the behaviour of the plot of $\ln k \times 1/T$ is not linear.

In an attempt to explain deviations from linearity encountered in experimental results, we propose a fractional-order generalization of the Van’t Hoff equation: our FVHE, as

$$D^\alpha_0(\ln(k(T))) = \frac{E}{RT^2}$$

in which $0 \leq \alpha \leq 1$ is order of fractional Riemann-Liouville derivative. If the limit of the fractional order Limit $\alpha \to 1$, then the usual description of this process equation \[1\] is recovered. The curvature deviations of the Arrhenius plot ($\ln k \times 1/T$), according to our proposed model, can be obtained by numerically solving above equation \[6\] with Adams-Bashforth-Moulton method \[12\], as discussed in section 4.

For equation \[6\], we also attempt an operational solution: Taking the Fourier transform of equation \[6\] with respect to temperature $T$ mapping to entropy $S$ yields

$$(-iS)^\alpha \hat{y}(S) = \frac{E}{R} \pi S \sgn(S)$$

$$\hat{y}(S) = \mathcal{F}_{T\rightarrow S}(\ln(k(T)))$$

$$\mathcal{F}_{T\rightarrow S}(\ln(k(T))) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \ln(k(T)) e^{-iST} dT$$

Although the particular value of the lower temperature limit in this work will be determined from experimental temperature data restrictions in the temperature domain for our subsequent
analysis, said considerations do not restrict the domain of validity of equation (7) being evaluated over the entire real line $\mathbb{R}$, which of course includes all real temperature domains. The Fourier transforms used were taken from [12, 13]. Recall that temperature $T$ and entropy $S$ are conjugate thermodynamic variables; consequently the exact analytical solution to equation (6) in entropy space may be expressed as

$$\tilde{y}(S) = \frac{E}{R} \pi S (-iS)^{-\alpha} \text{sgn}(S)$$  \hspace{1cm} (8)

where $\text{sgn}(.)$ is sign function. Hence via the inverse Fourier transform of (8) from entropy space back to the temperature domain we obtain

$$\ln(k(T)) = -\frac{E}{R} \mathcal{F}_{S \rightarrow T}^{-1} \{ -\pi i (-iS)^{1-\alpha} \text{sgn}(S) \}$$

Moreover, it follows that the operational exact analytical solution for temperature dependence rate coefficient $k(T)$ of the FVHE may thus be expressed as

$$k(T) = A \exp \left\{ \frac{\Gamma(2-\alpha) \cos(\pi \alpha) E}{RT^{2-\alpha}} \right\}$$  \hspace{1cm} (10)

in which $A = \ln k(T = T_0)$ is scaling constant with fractional order $\alpha \in (0, 1)$ where $T > 0$ with initial temperature $T_0 > 0$ for temperature $T$ expressed in absolute Kelvin degrees. Notwithstanding, this restriction $T > 0$ ($T$ greater than absolute 0 degrees Kelvin) presents no difficulty for our physical work, as there are no physical processes (e.g., chemical or otherwise) that occur at $T \leq 0$ degrees Kelvin: at $T = 0$ (absolute 0 Kelvin degrees): free bodies are still, no interaction within or without a thermodynamic system) It follows that the result equation (10) is indeed valid for the entire physical work herein. We simply note that if for some reason a temperature scale other than Kelvin where chosen [e.g, Fahrenheit, Celsius or Rankine], then a different domain of the temperature variable $T \in \mathbb{R}$ would be necessary, since in such cases, equation (10) would then 'blow up' to infinity for 0 degrees Fahrenheit, Celsius or Rankine; of course this is immediately remedied by simply re-scaling the temperature to absolute Kelvin units. Therefore the above result is obtained for the particular choice of $T_0 > 0$. As stated previously in the present Section 3, if the limit of Limit $\alpha \rightarrow 1$, then in such case equation (10) is equivalent to equation (5).

In order to discuss interpretation of the noninteger order $\alpha$ in our FVHE, as a consequence of equation (9) we have

$$\ln(k(T)) = -\frac{E}{R} \mathcal{F}_{S \rightarrow T}^{-1} \{ ((-iS)^{1-\alpha} \ast \mathcal{F}_{T \rightarrow S}(1/T)) \}$$  \hspace{1cm} (11)
Now, considering that $\mathcal{F}_{T \to S}\{J^\beta[f(T)]\} = ((-iS)^{-\beta} * \mathcal{F}_{T \to S}\{f(T)\})$, as shown in reference [12], one obtains

$$\ln(k(T)) = -\frac{E}{R} J^{\alpha-1}[1/T]$$

(12)

in which $\beta = \alpha - 1$ so that $J^{\alpha-1}[f(T)]$ is given by equation (1) with $m = \beta = \alpha - 1, t$ replaced by $T$, and $s$ still being a 'dummy variable' as in equation (1), which with these replacements becomes

$$(J^{\alpha-1})(T) = \frac{1}{\Gamma(\alpha)} \int_0^T \frac{f(s)}{(T-s)^{\alpha-2}} ds$$

(13)

If $\alpha = 1$ thus $J^0[1/T] = \frac{1}{T}$ as expected. Above equation (12) is then a convolution integral $\phi_{\alpha-1} * f$ in the range $[0, T]$ having memory kernel $\phi_{\alpha-1} = (T - S)^{\alpha-2}$ and $f(T) \to f(s) = 1/s$ in the above fractional integral, thus allowing an identification with retarded temperature dependence of the system (i.e., a non-local temperature phenomenon). Notwithstanding the zero lower bound in the fractional integral above, the solution $k(T)$ of equation (10) for our physical work is only being considered for the temperature domain interval from initial non-zero temperature $T_0$ to infinity (i.e., $[T_0, \infty), \ni T_0 = 0$).

In the present report, this concludes our introductory sketch of the analytical solution to the FVHE. In the remainder of this work, we shall primarily utilise numerical solution techniques for the FVHE, to which we now turn.

## 4 Numerical approach for fractional differential equation

In this section, we describe the numerical method based on trapezoidal rule to solve fractional integral equation (1). Suppose that interval $[0, t]$ is subdivided into $n$ between $s_k = kh$ and $s_{k+1} = (k+1)h$ in which $h = t/n$,

$$J^\alpha f(t) = \frac{1}{\Gamma(\alpha)} \sum_{k=0}^{n-1} \int_{kh}^{(k+1)h} (t-s)^{\alpha-1} f(s) ds$$

(14)

The function $f(s)$ between $s_k$ and $s_{k+1}$ is given by linear interpolation, such as, $f(s) \approx f(kh) + \frac{\Delta f}{h}(s - kh)$ in which $\Delta f = f((k+1)h) - f(kh)$. Therefore, equation (13) can be rewritten as the following equation

$$J^\alpha f(t) = \frac{1}{\Gamma(\alpha)} \sum_{k=0}^{n-1} [f(kh) w_{n-k}^\alpha + \frac{\Delta f}{h} g_{n-k}^\alpha]$$

(15)

in which

$$w_{n-k}^\alpha = \int_{kh}^{(k+1)h} (t-s)^{\alpha-1} ds = \frac{h^\alpha}{\alpha} [\zeta^\alpha - (i-1)^\alpha]$$

(16)
with \( i = n - k \), and
\[
g^\alpha_n = \int_{kh}^{(k+1)h} (s - kh)(t - s)^\alpha ds = \frac{h^{\alpha+1}}{\alpha(\alpha + 1)}[(\alpha+1) - (i + \alpha)(i - 1)^\alpha]
\]
(17)
The details of this method can be found in reference [14]. This way can be generalized to interval \([a, t']\) and result used to solve a fractional differential equation, as for our VFHE equation (6) where \( a \rightarrow T_0 \), \( t \rightarrow T \) for \( T > 0 \) and \( T_0 > 0 \).

The FVHE (6) can be generalized as \( D^\alpha_a y(t) = f(t) \) with initial conditions \( y(a) = y_a \) which is necessary when \( 0 < \alpha < 1 \). The initial value problem (16) is equivalent to following equation
\[
y(t) = y_a + J^\alpha_a f
\]
which is a generalization of Adams-Bashforth-Moulton method to fractional differential equation [12]. Therefore knowing \( J^\alpha_a f \) from equation (14) we can find \( y(t) \) for all time. The symbol \( J^\alpha_a f \) represents fractional integral equation on interval between \( a \) and \( t \).

The \( \alpha \) parameter is estimated by fitting the result of equation (14) to the experimental data using the graphical method that minimizes the sum of squares of the residual error,
\[
E = \frac{1}{2} \sum_i (\ln k_i^{cal} - \ln k_i^{exp})^2.
\]
The aim of this paper does not involve only a curve fitting problem, but the success of our FVHE shows that fractional calculus may provides a new insight to these phenomena.

5 Results and discussions

In this section we show that the usual assumption of Arrhenius plot is not valid in many cases. The first example reports study of thermal decomposition of Diacetylene between 973 e 1223 K [5]. The next example deals with experimental data of the respiration rate for \( O_2 \) consumption by leaves of Camellia Japonica [3]. Finally, some cases to bacterial growth will be studied [4].

When there are significant inconsistencies between experimentally measured and theoretically calculated rate constant, calculated values can be brought into agreement with experimental values by making use of the fractional differential order. As shows in figure 1, the \( \alpha \) parameter play an important role in temperature dependence of rate constant. When \( \alpha \) decreases the rate constant increases with temperature, but this increase is less than observed for the \( \alpha = 1 \). In the following, the proposed model will be compared with Arrhenius, d-Arrhenius, quadratic equations and experimental data cited.

The best parameter \( \alpha \) was found minimizing the sum of squared residuals by using graphical technique. The Figure 2 shows the relative percentage error as function as fractional order \( \alpha \),
obtained to thermal decomposition kinetics of \( C_4H_4 \) \[5\]. The minimum value in this curve was used as the best value of \( \alpha \), 0.734. The results from best fractional order when used in equation (6) to fit experimental data are shown in Table 1. Table 2 presents the parameters \( E/R \) to the best fractional order together with \( E/R \) obtained from adjust of Arrhenius equation. Table 2 too includes the experimental initial conditions \( y_a \).

The code developed by Garrappa \[15\] was used in this paper to solve an initial value problem for a nonlinear fractional differential equation (6). This implementation is based in predictor-corrector method of Adams-Bashforth-Moulton, as described in same reference.

As shown in Figure 3 experimental data retired from reference \[5\] presents a concave curve in Arrhenius plot, with curvature \( \kappa = -3.7 \times 10^7 \). The similar behavior is seen in all experimental data studied here \[5, 3, 4\]. The performance of the fractional Van’t Hoff equation to fit experimental data was assessed according to the relative percentage error criteria, as shown in Table 1. Results from equation (6) were compared with three different models: Arrhenius, d-Arrhenius and Quadratic polynomial.

The fractional Van’t Hoff equation to provide a good alternative to fit the experimental temperature dependence data, when compared with usual Van’t Hoff equation was obtained a relative percentage mean error of 1.9 % against 6.7 %. This success is due to the flexibility included by fractional order in Van’t Hoff differential equation. In some cases, equation (6) presents performance better than quadratic equation. When compared with d-Arrhenius equation, the equation (6) shows similar relative percentage errors, with relative percentage mean error of 1.9 % against 1.5%. Therefore, it is believed that our generalized model of the Van’t Hoff equation provides a new perspective on interpretation of temperature dependence of the rate constant at the microscopic level.

6 Conclusions

In this paper, was shown that the Arrhenius law fails in describing the temperature dependence of rate coefficients for some kinetics process, with relative percentage error greater than 10 %, which is greater than experimental error. In these cases, the generalized Van’t Hoff differential equation herein, can be used with good results to fit experimental kinetics data within experimental error with relative percentage error less that 3 %. The proposed model finds results consistent with the d-Arrhenius model by using of different tools [i.e., fractional derivatives]. The d-Arrhenius model uses Euler approach to exponential function in Arrhenius law, with additional parameter \( d \). While our FVHE model includes a fractional order \( \alpha \) instead of \( d \) in the
most fundamental equation from which Arrhenius law is derived, there has been no correlation observed between $\alpha$ and $d$ parameters; as well as any correlation between $\kappa$ and $\alpha$ parameters, for examples discussed in this paper. This approach can be applied to fit various other experimental data such as: solubility as function of temperature; temperature dependency of the viscosity and conductivity, etc.

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Figura 1: Simulated data using equation (6) with E/R=50 arbitrary unit.
Tabela 1: Comparison between Arrhenius model, this work, d-Arrhenius model and quadratic function.

| exp. data | $\kappa^{(f)}$ | $\alpha_{\text{best}}$ | $d_{\text{best}}$ | relative error, % | Arrhenius | This work | d-Arrhenius$^{(d)}$ | Quadratic$^{(e)}$ |
|-----------|----------------|------------------------|-------------------|-------------------|------------|-----------|-------------------|-------------------|
| [3]       | $-3.7 \times 10^7$ | 0.734                  | 0.389             |                   | 0.9739     | 0.2737    | 0.2530            | 0.3309            |
| [3]       | $-1.4 \times 10^7$ | 0.750                  | 0.228             |                   | 1.8636     | 1.0663    | 0.8938            | 0.6077            |
| [4]$^{(a)}$ | $-3.9 \times 10^7$ | 0.698                  | 0.142             |                   | 11.7670    | 4.0697    | 3.0871            | 2.1995            |
| [4]$^{(b)}$ | $-7.5 \times 10^7$ | 0.830                  | 0.200             |                   | 3.5652     | 2.6406    | 2.4432            | 2.0792            |
| [4]$^{(c)}$ | $-1.0 \times 10^8$ | 0.572                  | 0.236             |                   | 15.3584    | 1.4083    | 0.8900            | 4.4934            |

(a) Aerobacter aerogenes, (b) Bacillus circulans, (c) Lactobacillus delbruckii

(d) $\ln k = \ln A + \frac{1}{T} \ln \left(1 - d \frac{E}{RT}\right)$, (e) $\ln k = \ln A + B \frac{1}{T} + C \left(\frac{1}{T}\right)^2$, (f) $\kappa = 2C$
Tabella 2: Initial conditions of equation (6) and activation energy empirically determined.

| exp. data | eq. (6) | eq. (5) |
|-----------|---------|---------|
|           | $E/R$   | $y_0$   | $a,K$ | $E/R$   | $\ln A$ |
| [5]       | $5.87 \times 10^4$ | 16.15   | 973    | $6.01 \times 10^3$ | 13.36   |
| [6]       | $2.41 \times 10^4$ | -15.09  | 270    | $4.54 \times 10^3$ | 10.41   |
| [4] (a)   | $5.92 \times 10^4$ | 2.39    | 274    | $9.34 \times 10^3$ | 35.52   |
| [4] (b)   | $4.00 \times 10^4$ | 6.46    | 311    | $1.11 \times 10^4$ | 38.66   |
| [4] (c)   | $1.23 \times 10^5$ | 2.11    | 299    | $1.36 \times 10^4$ | 46.96   |
Figura 2: Relative percentage error as function of fractional differential order.
Figura 3: Comparison between Arrhenius model (dotted line), this work (square and continued line), d-Arrhenius model (triangle) and experimental data (circle).