# Non Linear Thermal Decaying Functions

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*Abstract– The present manuscript deals with a deep mathematical analysis of the functions that should be used in the Clausius Clapeyron thermodynamic modelling, which is usually modelled linearly, this research emphasizes that the thermal models are nonlinear even taking into account the heat capacities as a constant. Specifically, the mathematical analysis of the thermal decaying models proposes what equations should be used depending on the type of enthalpy function. Consequently, the enthalpy functions depend on the model of the heat capacity proposed by Albert Einstein. The magnitude of the errors that would be committing by using linear regressions on experimental data were also estimated; as is the case for the vast majority of publications in this area. The study also shows how the models behave in wide temperature range; and how they are becoming apparent linear as the temperature range decreases.*

*Keywords— Clausius Clapeyron, heat capacities.*

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## I. INTRODUCTION

Thermodynamic properties are important to take them into account in the development of technologies for chemical assays and energy process efficiency studies [1-4], as well as in the transport and handling of bulk quantities. The analysis methods based on thermogravimetry, Langmuir and Clausius-Clapeyron expression have demonstrated to be accurate for many materials over a narrow temperature range; and they have been used extensively in the determination of many thermodynamic properties of materials with ideal behavior, in the pharmaceutical [5-9]; the applications also include the examination of antioxidants [10], dyes [11] and explosives [12] among others. Ideal thermal materials are those that do not decompose or melt over a wide temperature range.

Several researchers have used linear and non-linear physical chemistry models to determine transition enthalpies values. In 2001, Chatterjee et al used the linear equation of Clausius-Clapeyron to determine the sublimation enthalpy of hydroxyl benzoic acid [13]; while in 2005, Emel'yanenko and Verevkin used a non-linear equation to determine vaporizations enthalpies of amino-toluenes [14]. In this field of study is also typical to calculate the vapor pressure from rate constant values using the Langmuir equation and then to fit the obtained values according to Clausius-Clapeyron equation to find the standard enthalpy values. For example, in 2008, Gupta et al and in 2011, Felix et al calculated vapor pressure from constants rate and determined sublimation enthalpy of Fentanyl and TATP respectively using the Clausius-Clapeyron linear equation [15-16]. On the other hand, others authors have combined spectroscopic and thermal techniques in order to study physical chemistry properties of different materials [17-19]. In this work, we are proposing a mathematical analysis of the several thermal model of the pressure and constant evaporation depending on the $\Delta H$ function. It was modelled the experimental thermal decaying of acetyl salicylic (ASA) and nitro benzoic acid using thermogravimetry analysis in order to corroborate the veracity of the models.

## II. MATHEMATICAL DEDUCTION OF THE THERMAL DECAYING MODEL

This apart describes the mathematical deduction of the equations that should be used in the fitting of the experimental thermal data (Thermal decaying of vapor pressure or mass lost constant). First step explains the conversion of the Langmuir expression (eq.1) in an equation similar to the Clausius-Clapeyron equation in its differential form. In detail, it was resolved for the pressure, applied natural logarithm to both sides, and finally differenced the resultant expression with respect to the reciprocal temperature by obtaining the equation 3. On the other hand, it was replaced, the enthalpy functions in the equations 4-5 and finally, resolving these differential equations were obtained the proposed models to be used in the different fitting of the experimental thermal data. The enthalpy functions were derived from A. Einstein distribution approaching explained below, by integrating the approximated $\Delta Cp$ Einstein function. All of these equations are summarized in the table 1.

$$k = \frac{dm}{dt} = p\alpha \sqrt{\frac{M}{2\pi RT}} \qquad (1)$$

$$\ln p_{(T)} = \ln k_{(T)} - \frac{1}{2}\ln\left(\frac{1}{T}\right) + \frac{1}{2}\ln\left(\frac{2\pi R}{M\alpha^2}\right) \qquad (2)$$

$$R\frac{\partial \ln p_{(T)}}{\partial(1/T)} = R\frac{\partial \ln k_{(T)}}{\partial(1/T)} - \left(\frac{R}{2}\right)\left(\frac{1}{T}\right)^{-1} \qquad (3)$$

$$\frac{\partial \ln p_{(T)}}{\partial(1/T)} = \frac{-\Delta H_T}{R} \qquad (4)$$

$$\frac{\partial \ln k(T)}{\partial(1/T)} = \frac{-\Delta H_T}{R} + \frac{1}{2}\left(\frac{1}{T}\right)^{-1} \qquad (5)$$

As stated above, the proposed models were obtained using different approaches of the A. Einstein distribution [20], which were considered as follows: at low (below 50°K) and high (above 300°K) temperatures, the heat capacity change at constant pressure (Cp) behaves as a constant, from 30°K to 70°K behaves as a straight line, and at temperatures between 0°K and 70°K behaves as a quadratic function; In addition to these approaching, It was also proposed a model using Full Einstein's equation (see Figure 1), by finding the different thermodynamic models of which several of them have been previously used in related studies. An important result, is that the thermodynamical model considering the $\Delta Cp$ as a constant and the model considering the full Einstein function are significantly similar, which after considering the combined log-exponential term negligible (eq.8), both expressions are identical. The reason why the combined log-exponential term is dismissed, is that at temperatures under Einstein temperature, the term inside the logarithm tends to less than zero numbers, for which the logarithm function is not defined.



**Figure 1.** $C_p$ and $C_v$ Einstein model function of heat capacity, considering $C_p$ and $C_v$ relate by R constant. The portion 1 is approaching to a constant function. The portion 2 is approaching to a linear function and the portion 3 is approaching to a quadratic function.

$$\Delta H = \int \left[ R + 3R \left(\frac{a}{T}\right)^2 \frac{e^{\frac{a}{T}}}{(e^{\frac{a}{T}} - 1)^2} \right] dT \qquad (6)$$

$$\Delta H == \frac{3aR}{e^{a/T} - 1} + b \left(\frac{1}{T}\right) + c \qquad (7)$$

$$\ln(p) = \int \left[ \frac{3a}{e^{\frac{a}{T}} - 1} + b \left(\frac{1}{T}\right) + \frac{c}{R} \right] d\left(\frac{1}{T}\right) \qquad (8)$$

$$\ln(p) = a' \left(\frac{1}{T}\right)^{-1} - b' \ln\left(\frac{1}{T}\right) + c' + d\ln(1 - e^{\frac{a}{T}}) \qquad (9)$$

$$\ln(p) = a' \left(\frac{1}{T}\right)^{-1} - b' \ln\left(\frac{1}{T}\right) + c' \qquad (10)$$

**TABLE 1.** Condensed thermal function deduced from different consideration of Einstein distribution [20].

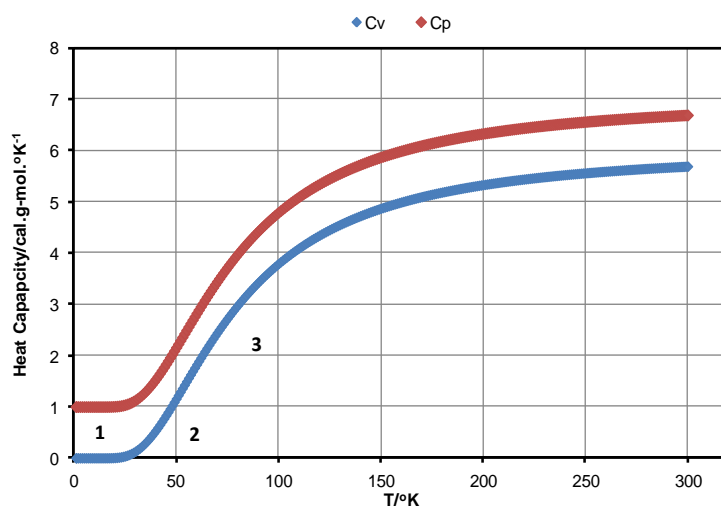| Ln (k) function [10] |
|---|
| $\ln(k) = -\frac{a-2}{R} \ln\left(\frac{1}{T}\right) - \frac{b}{R}\left(\frac{1}{T}\right) + c$ |
| $\ln(k) = \frac{a}{2R}\left(\frac{1}{T}\right)^{-1} - \frac{b-2}{R} \ln\left(\frac{1}{T}\right) - \frac{c}{R}\left(\frac{1}{T}\right)$ |
| $\ln(k) = \frac{a}{6R}\left(\frac{1}{T}\right)^{-2} - \frac{b-2}{R} \ln\left(\frac{1}{T}\right) + \frac{c}{R}\left(\frac{1}{T}\right)$ |
| $\ln(k) = a'\left(\frac{1}{T}\right)^{-1} - (b' - 1/2R)\ln\left(\frac{1}{T}\right) + c'$ |

## III. COMPARISON OF THE THERMAL MODELS WITH THE EXPERIMENTAL DECAYING

In this field of study, it is typical to calculate the vapour pressure from rate constant values using the Langmuir equation and then to fit the obtained values according to Clausius-Clapeyron equation to determine standard enthalpy values, assuming that the enthalpy change ($\Delta H$) is a thermodynamic property independent of the temperature; sometimes this approach works well for some ideal compounds and a narrow ranges of temperature; but others cases not.

The Figures 2-6 show the different thermal profiles depending on the enthalpy function used. In general, in all cases a non-linear trend prevails, when considering wide temperature ranges. As the temperature range decreases, the thermal behavior profiles approximates a straight line. Consequently, each temperature range value will have a different slope in the global curve, which leads to variability in the reported enthalpies. Another important finding, is that the apparently linear trends can also be modeled using mathematical models presented in Table 1 (see Figure 8). On the other hand, in all cases is notable that as the $\Delta Cp$ value decreases, the thermal profile is getting closer to linear behavior, traditionally used in this field of the thermodynamic chemistry. Although, significant values of $\Delta Cp$ with an order of magnitude less than the $\Delta H$ obtained by linear fitting could be fitted using the linear model.

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**Fig 4.** Thermal decay of ln(p) or ln(k) model using a cubic enthalpy function in a wide temperature range

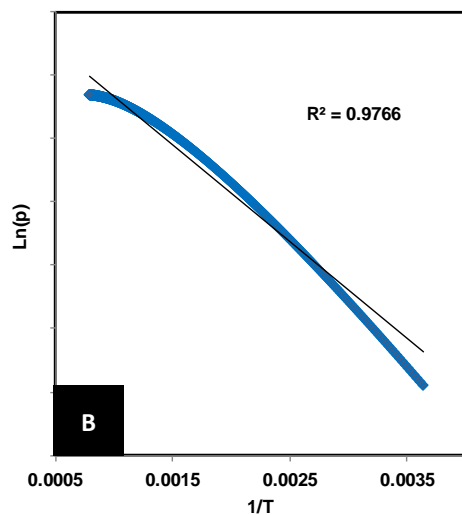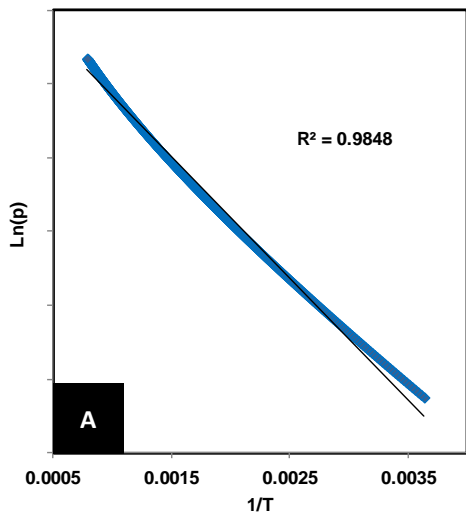**Fig 2.** Thermal decay of ln(p) or ln(k) model using a linear enthalpy function in a wide temperature range. **A.** when ΔCp is a positive value, **B**. When ΔCp is a negative value. It is notable the concavity dependence with the ΔCp sense.
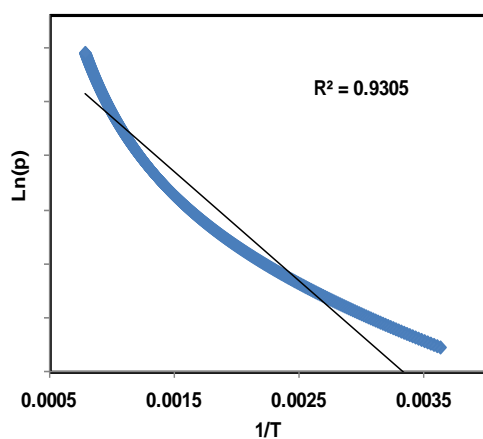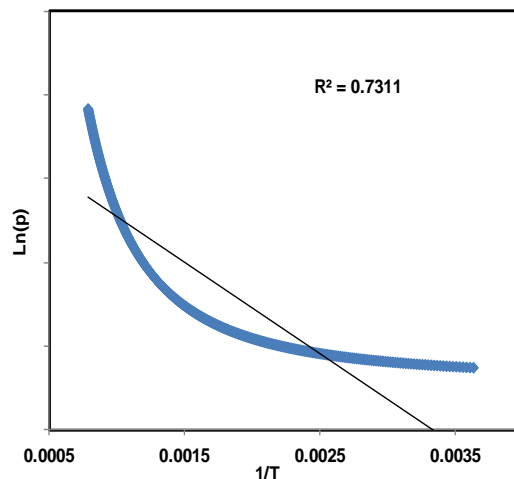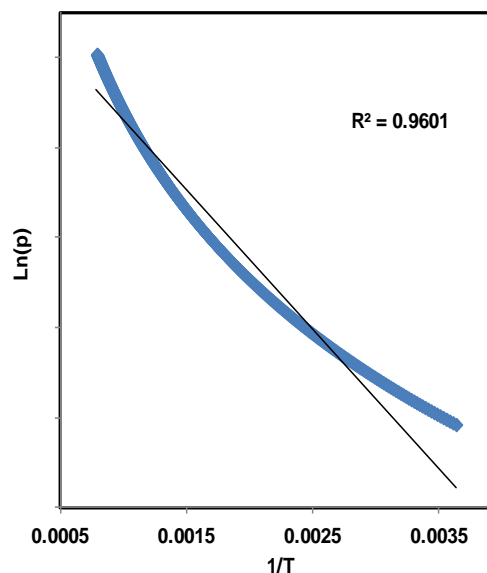




**Fig. 5.** Thermal decay of ln(p) or ln(k) model using an enthalpy function derived from Einstein model in a wide temperature range

Finally, to corroborate the truth of the principles outlined in this manuscript, we found that the equations shown up here perfectly modeled some experimental decays reported in the literature [8-9, 13, 21] and others tested in our laboratory, as is the case of the compounds nitro benzoic and acetyl salicylic acid, which showed high concordance with respect to model previously postulated reflected in the $R^2$ value of statistical modeling (see Figures 6-7). On the other hand, the models when ΔCp is considered a constant are often published in a linearized form as usual [8-9, 13]. Another important aspect, is

that the concavity of global decay depends on the sense of the ΔCp value; when ΔCp is positive, the decaying curve is convex and concave when ΔCp is negative (see Figures 2A and 2B). Also, it is notable that as increasing ΔCp value, the concavity of curve is more pronounced, and as ΔCp goes decaying to negligible values, the thermal decay gradually becomes completely linear.

On the other hand, ΔH functions helped estimate the magnitude of errors that could be committed in the ΔH values reported in the literature in a temperature range from 0 °C to 100°C, which is the temperature range, where most of the thermodynamic studies are performed. In general, the errors in the enthalpies reported would be approximately one order of magnitude.
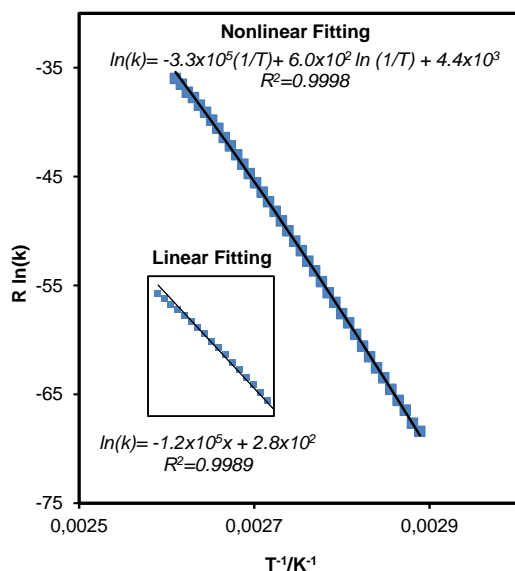


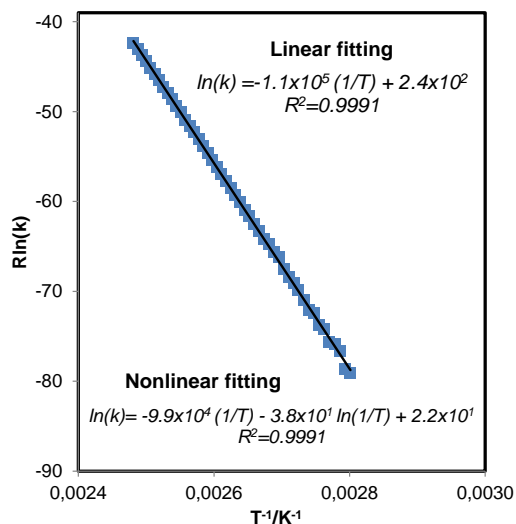**Fig. 6.** Experimental decaying of Acetyl salicylic acid. By considering a linear and nonlinear fitting.



**Fig. 7.** Experimental thermal fitting of Nitro benzoic acid using a linear and nonlinear model.

## IV CONCLUSION

In general, all models follow a nonlinear trend at high temperature ranges. The experimental thermal decaying of the compounds nitro benzoic and acetyl salicylic acid showed high concordance with respect to one of the models presented in the Table 1; this approaching is reflected in the $R^2$ value of the statistical modeling, which was closer to one. The theoretical models considering: a ΔH linear function and a ΔH function derived from Einstein model, presented higher similarity. The thermal experimental decaying of the compounds ASA y nitrobenzoic acid adjusted to the model sketched in the figures 2 and 5. According to reported ΔH functions, the errors committed in the reported values would be near to one order a magnitude.

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