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COMPUTATION OF KINETIC PARAMETERS OF PYRIDINO COBALT (II), NICKEL (II), COPPER (II) COMPLEXES A COMPARATIVE STUDY

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ABSTRACT

There are various methods proposed for the computation of kinetic parameters based on thermoanalytical techniques available in the scientific literatures. Among those methods the most widely used kinetic methods are Freeman and Carroll Method, Coats and Redfern Method and Horowitz and Metzger Method. The former is a differential method while the second is an integral method and the third an approximation method for the computation of kinetic parameters. In this present research the thermal kinetic investigation of pyridino metal(II) complexes [Co(II), Ni(II) and Cu(II)] were computed based on these three (differential, integral and approximation) methods and compared. The linear regression analyses using computational methods and software were also carried out.

***Keywords** – Kinetic parameters, Pyridino complexes, Freeman and Carrol Method, Coats and Redfern method, Horowitz and Metzger method, Regression analysis .*

1. INTRODUCTION

The dynamic thermogravimetry based kinetic investigations of bivalent metal complexes have been reported in the research field with considerable but acceptable differences. Even though there exist many criticisms and discrepancies among the scientific community all the researchers and scientists accept the fact that the thermal decomposition reaction kinetics can only be better explained by the mass loss curves where the large amount of information is mined without sample-to-sample error, since the same sample is used throughout the determination. It should be pointed out, however, that the data observed from thermogravimetry are only narrowly definitive, consequently, merely going through the motions of kinetic analysis can lead only to trivial kinetic parameters for mass-loss under a particular set of experimental conditions. These kinetic parameters computed from the mass loss data are always remain empirical only and that can be admitted on a higher level of sophistication but only in the light of a large amount of additional complementary evidences[1]. These dynamic kinetic studies based on nonisothermal methods have certain advantages over conventional methods as these require fewer data that can be easily collected from the recorded thermogram obtained using a very small quantity of sample that can be calculated over an entire temperature range in a continuous manner when and where it undergoes considerable dynamic thermal reaction at a suitably raised temperature. The main disadvantage of nonisothermal compared with isothermal methods is that the reaction mechanisms cannot usually be determined and hence the meanings of the activation energy, order of reaction, and frequency factor always remain uncertain and empirical. The well accepted formal kinetic equation $-\frac{dX}{dt} = kX^n$ where X is the amount of reactant undergoes reaction, n is

the order of the reaction with respect to the reactant understudy and k is the specific rate constant, can also be applicable to the thermal reactions. The rate constant k is expressed by the Arrhenius equation $k = Ae^{-E/RT}$ where A is the preexponential factor, E is the activation energy and R is the gas constant. The mathematical treatment of the kinetic equations makes use of one of the following three methods of evaluation viz. (a) differential, (b) integral or (c) approximate. The relationship of X to mass loss, w, is given by the equation -dX $= \frac{m_0}{w_\infty}$ dw where m_0 is the initial mass of the sample and w_∞ is the maximum mass loss. Integrating by setting the limits m_0 to X for LHS and 0 to w to the RHS we get X $= \frac{m_0}{w_\infty}$ (w_∞ - w). By substituting this equation and Arrhenius equation in to the formal kinetic equation and by differentiating the logarithmic form and an expression is obtained which is one of the differential methods known as Freeman and Carroll method as follows, $-\frac{\left(\frac{E}{2.303R}\right)\Delta\left(\frac{1}{T}\right)}{\Delta \log w_r} = -n + \frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log w_r}$, where $w_r = w_c$ - w, in which w_c is the maximum mass loss and w is the total loss in mass up to time t. While the integral methods use the integrated form of formal kinetic equation after the transposition of the mass loss, w, in the equations -dX $= \frac{m_0}{w_\infty}$ dw and $= \frac{m_0}{w_\infty}$ (w_∞ - w) to derive an integral equation $\left(\frac{m_0}{w_\infty}\right)^{1-n} \int_0^w (w_\infty - w)^{-n} dw = \frac{A}{\Phi}\int_{T_1}^{T_2} e^{-E/Ru} dt$. The RHS of this equation can be solved by various methods, and the final solution to the equation is an infinite series of which the first two terms are of interest generally. This integral method is used by Coats and Redfern to compute the kinetic parameters. Similarly in the approximation methods, the RHS of the equation $\left(\frac{m_0}{w_\infty}\right)^{1-n} \int_0^w (w_\infty - w)^{-n} dw = \frac{A}{\Phi}\int_{T_1}^{T_2} e^{-E/Ru} dt$ is solved by an approximation using the temperature, T_i, corresponding to the maximum rate of decomposition. This method was used by Horowitz and Metzger to compute the kinetic parameters from the thermal data.

2. MATERIALS AND METHODS

The reagents and chemicals used for preparing the metal complexes were of either of Merck or BDH. Most of them were used as such or purified wherever and whenever required. The thermogravimetric analyses and the following three methods (Differential, Integral and Approximation) were used for computing the kinetic parameters.

Freeman and Carrol Method: It is a differential method for computing the kinetic parameters. Freeman and Carroll method as follows, $-\frac{\left(\frac{E}{2.303R}\right)\Delta\left(\frac{1}{T}\right)}{\Delta \log w_r} = -n + \frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log w_r}$, where $w_r = w_c$ - w, in which w_c is the maximum mass loss and w is the total loss in mass up to time t. The plot $Y = \frac{\Delta \log\left(\frac{dw}{dt}\right)}{\Delta \log w_r}$ versus $X = \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log w_r}$ is a linear one with intercept C=-n and slope $M = \left(\frac{-E}{2.303R}\right)$. Thus, from the plotted graph the order of the reaction (n) and activation energy (E) of the thermal reaction can be computed. For two different temperatures T_1 and T_2 the term $\Delta\left(\frac{1}{T}\right)$ becomes $\left(\frac{T_1-T_2}{T_1 T_2}\right)$. Another expression for the equation is $\log\{\frac{\left(\frac{dw}{dt}\right)}{w_r}\} = \left(\frac{-E}{2.303R}\right)\left(\frac{1}{T}\right) + \log(Z)$ where E is the activation energy and Z is the apparent frequency. Hence a plot $\log\{\frac{\left(\frac{dw}{dt}\right)}{w_r}\}$ against $\left(\frac{1}{T}\right)$ will also result a straight line with slope $M = \left(\frac{-E}{2.303R}\right)$ and intercept log (Z) where Z is the apparent frequency factor. [2]

Coats and Redfern Method: It is an integral method for computing the kinetic parameters by solving $\left(\frac{m_0}{w_\infty}\right)^{1-n} \int_0^w (w_\infty - w)^{-n} dw = \frac{A}{\Phi}\int_{T_1}^{T_2} e^{-E/Ru} dt$ for a reaction whose order is unknown. Coats and Redfern proposed a solution by applying the concept of Asymptotic series a kind of special function as follows.

$\log\left\{\frac{(1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{\alpha E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.3RT}$ for all values of n except n=1 and $\log\left[-log\frac{(1-\alpha)}{T^2}\right] = \log\frac{AR}{\alpha E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.3RT}$ for n=1.

Thus, by plotting either $Y = \log\left\{\frac{(1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\}$ or $Y = \log\left[-log\frac{(1-\alpha)}{T^2}\right]$ against $X = \frac{1}{T}$ shall result a straight line with a slope $M = \frac{-E}{2.303R}$ provided the order of the reaction "n" is correct. [3]

Horowitz and Metzger Method: It is an approximate method for computing kinetic parameters from thermal data. The approximation is based on the fact that the rate constant involves the concentration expressible as mole fractions and the total number of moles is a constant the following solution can be used. $\ln\left\{\ln\left[\frac{W0-Wt}{W-Wt}\right]\right\} = \frac{E\theta}{RT^2}$ where W is the mass remaining at a given temperature W0 and Wt and initial and final masses, respectively, and θ is a reference temperature. By plotting $\ln\left\{\ln\left[\frac{W0-Wt}{W-Wt}\right]\right\}$ against $\frac{\theta}{T^2}$ we get a straight line and from the slope $\frac{E}{R}$ the activation energy can be calculated. [4]

Linear Regression: The linear regression analyses and curve fittings were achieved using computational methods and software [5]. For a complete kinetic description of the decomposition of a solid it is highly necessary to understand the rate of formation along with the spatial distribution of the nuclei; the rate of growth of the nuclei that vary with crystallographic direction; and the size and shape of the parent particle(s). Hence the full mathematical formulation of the rate process must, in general, be expressed in terms of both spatial and time coordinates and all these are beyond the scope of the present work [6]. Hence eventhough there reported many methodologies the representative methods that are well liked were selected[7]. There are still areas that need much scientific attention to explain the size, shape and position of the resulting peaks observed in thermograms [7,8].
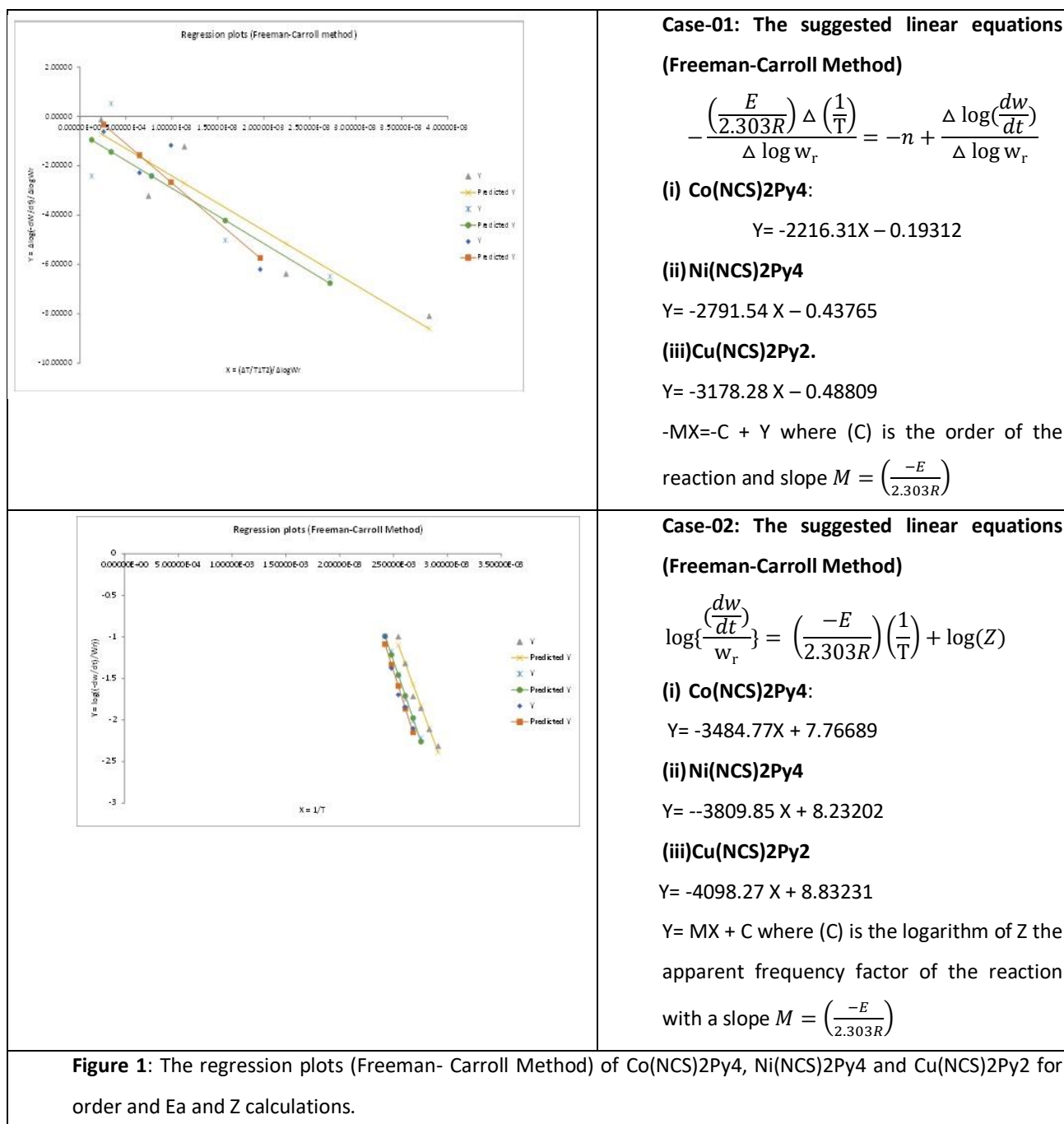
2.1 Experimental

The synthesis of Diisothiocyanatotetrapyridine and Diisothiocyanatodipyridine metal complexes were prepared as per the method suggested in the scientific literatures. The prepared metal complexes were purified and dried before analyses [9]. TGA were carried out and the kinetic parameters were computed according to the methods viz. Freeman and Carrol Method (Differential Method), Coats and Redfern Method (Integral Method) and Horowitz and Metzger Method (Approximation Method) as explained. The linearity of the curves was achieved by regression analysis using software. The computed kinetic parameters are tabulated and compared. The various linearity graphs are shown below (Figure 1 and Figure 2). The decomposition was observed with a rate of heating maintained at ten degrees centigrade per minute. The loss of weight (Wr) of the samples at different temperatures were tabulated (Table 1). The computed order and Energy of activation for the samples understudy using the differential, integral and approximate methods were tabulated and compared (Table 2). Different parameters were computed and tabulated for the samples understudy based on the differential and integral methods (**Table 3**) [10]. The lines with different b (0, 1, 2) values were plotted for solving the reaction kinetic equation using Coats and Redfern method and the curve fitting and systematic linear regression analyses were carried out.

3. RESULTS AND DISCUSSION

The synthesis of the samples for the present study were synthesized and purified as per the available literature's. The order of the thermal reactions understudy was computed from the differential method (Freeman and Carroll method) and found nearly zero (Freeman and Carroll Case-01). Similarly, the lines with different b values were plotted for solving the reaction equation using Coats and Redfern method. On regression analysis the most suitable linear graph was for b=0 suggested the zero-order reaction as supported by the order of the reactions computed from Freeman and Carroll method. The activation energies computed by the all the three methods (differential, integral and approximation) were found comparable. The activation energies computed using Freeman and Carroll methods from two differential equations (Case-01 and Case-02) were found differing largely and observed

that the activation energies computed as in Case-01 were deviating from the other methods. The activation energies computed using the differential method as Case-02 were found in acceptance to the results of the other integral and approximation methods. Various parameters viz. apparent reaction frequency (Z), activation energy (E), entropy of activation (ΔS), enthalpy of activation(ΔH), free energy of activation(ΔG) and the reaction rate constant (K) were computed based on the differential (Freeman-Carroll Case-02) and integral (Coats-Redfern) methods. The results were found comparable and are in the acceptance limits (Table 3). The actual science behind thermal decomposition of the metal complexes is not simple but complicated and many arguments are there to correlate their stabilities [11,12].

	Case-01: The suggested linear equations (Freeman-Carroll Method) $$-\frac{\left(\frac{E}{2.303R}\right)\Delta\left(\frac{1}{T}\right)}{\Delta\log w_r} = -n + \frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log w_r}$$ **(i) Co(NCS)2Py4:** $$Y= -2216.31X - 0.19312$$ **(ii) Ni(NCS)2Py4** $$Y= -2791.54\ X - 0.43765$$ **(iii)Cu(NCS)2Py2.** $$Y= -3178.28\ X - 0.48809$$ -MX=-C + Y where (C) is the order of the reaction and slope $M = \left(\frac{-E}{2.303R}\right)$
	Case-02: The suggested linear equations (Freeman-Carroll Method) $$\log\left\{\frac{\left(\frac{dw}{dt}\right)}{w_r}\right\} = \left(\frac{-E}{2.303R}\right)\left(\frac{1}{T}\right) + \log(Z)$$ **(i) Co(NCS)2Py4:** $$Y= -3484.77X + 7.76689$$ **(ii) Ni(NCS)2Py4** $$Y= --3809.85\ X + 8.23202$$ **(iii)Cu(NCS)2Py2** $$Y= -4098.27\ X + 8.83231$$ Y= MX + C where (C) is the logarithm of Z the apparent frequency factor of the reaction with a slope $M = \left(\frac{-E}{2.303R}\right)$

Figure 1: The regression plots (Freeman- Carroll Method) of Co(NCS)2Py4, Ni(NCS)2Py4 and Cu(NCS)2Py2 for order and Ea and Z calculations.

The suggested linear equations (Coats-Redfern Method)

$$\log\left\{\frac{(1-(1-\alpha)^{1-n})}{T^2(1-n)}\right\} = -\frac{E}{2.303RT} + \log\frac{AR}{\alpha E}\left[1 - \frac{2RT}{E}\right] \text{ where } n \neq 1$$

(i) Co(NCS)2Py4:

Y= -3573.58X + 3.76492

(ii) Ni(NCS)2Py4

Y= -4066.43 X + 4.59002

(iii) Cu(NCS)2Py2.

Y= -4341.60 X + 5.11016

Y= MX + C where the slope $M = \left(\frac{-E}{2.303R}\right)$

The suggested linear equations (Horowitz-Metzger Method)

$$\ln\left\{\ln[\frac{W0 - Wt}{W - Wt}]\right\} = \frac{E\theta}{RT^2}$$

(i) Co(NCS)2Py4:

Y= 8193.90 X + 2.13907

(ii) Ni(NCS)2Py4

Y= 9575.76 X + 3.56839

(iii) Cu(NCS)2Py2.

Y= 10810.96 X + 1.86215

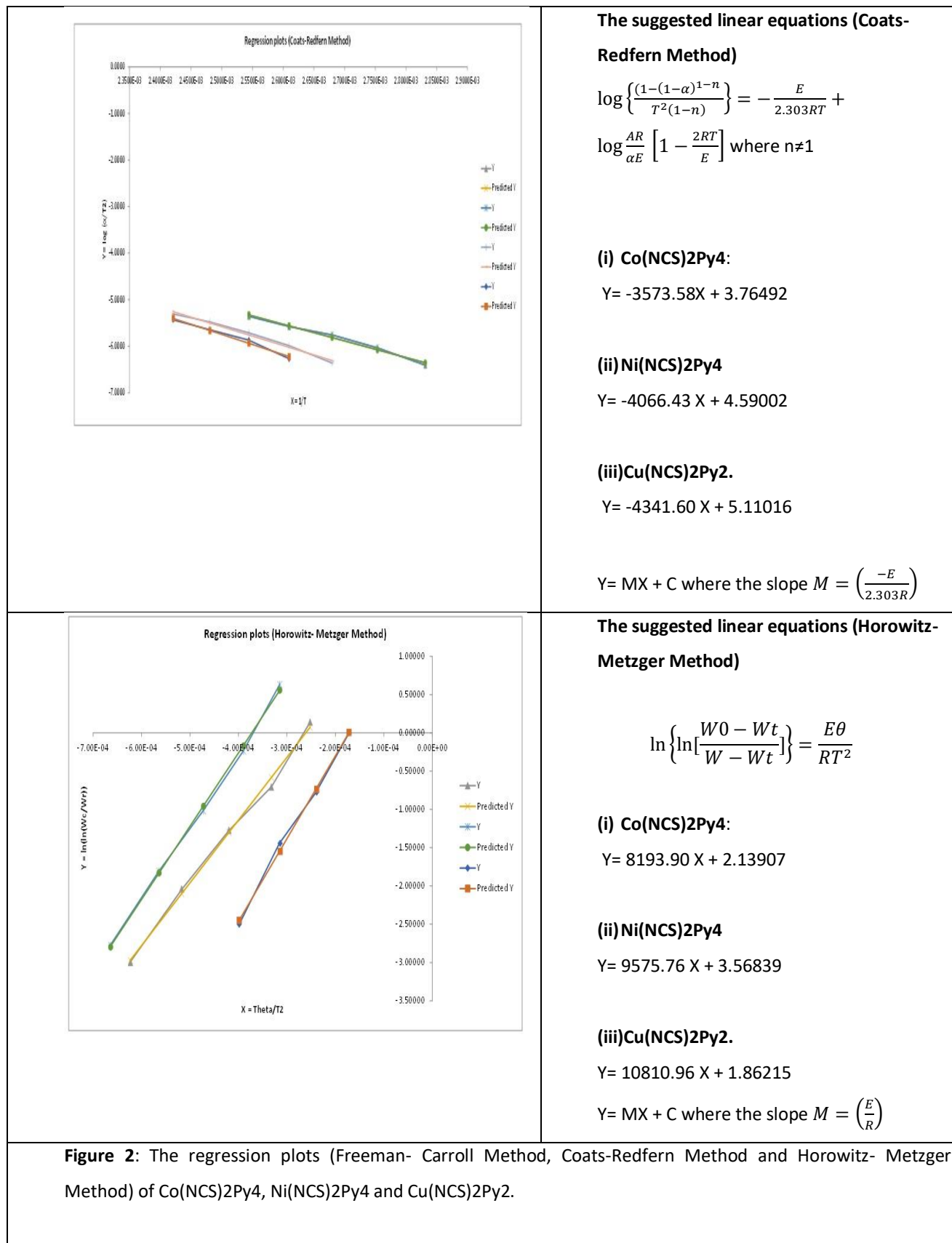Y= MX + C where the slope $M = \left(\frac{E}{R}\right)$

Figure 2: The regression plots (Freeman- Carroll Method, Coats-Redfern Method and Horowitz- Metzger Method) of Co(NCS)2Py4, Ni(NCS)2Py4 and Cu(NCS)2Py2.

Table 1: The observed loss of weight (W_r) of the samples under study at different temperatures.

Co(NCS)2Py4	(70^0C, 2.05mg), (80^0C, 1.95mg), (90^0C, 1.80mg), (100^0C, 1.55mg), (110^0C, 1.25mg), (120^0C, 0.65mg). Decomposition Temp. (160^0C)
Ni(NCS)2Py4	(90^0C, 1.65mg), (100^0C, 1.55mg), (110^0C, 1.40mg), (120^0C, 1.15mg), (130^0C, 0.75mg), (140^0C, 0.25mg) Decomposition Temp. (195^0C)
Cu(NCS)2Py2.	(100^0C, 1.90mg), (110^0C, 1.75mg), (120^0C, 1.50mg), (130^0C, 1.20mg), (140^0C, 0.70mg) Decomposition Temp. (170^0C)

Table 2: The computed order and Energy of activation for the samples understudy using the differential, integral and approximate methods

Method	Sample	Energy (Activation) kJmol^{-1}	Observed Order (n)	Corrected Order
Freeman-Carroll	Co(NCS)2Py4	42.44	0.19312	Zero
(Case-01)	Ni(NCS)2Py4	53.44	0.43765	Zero
	Cu(NCS)2Py2	60.85	0.48809	Zero
Freeman-Carroll	Co(NCS)2Py4	66.72	-	Zero
(Case-02)	Ni(NCS)2Py4	72.95	-	Zero
	Cu(NCS)2Py2	78.47	-	Zero
Coats-Redfern	Co(NCS)2Py4	68.43	b=0; n≠1	Zero
	Ni(NCS)2Py4	77.86	b=0; n≠1	Zero
	Cu(NCS)2Py2	83.13	b=0; n≠1	Zero
Horowitz-Metzger	Co(NCS)2Py4	68.12	0; n≠1	Zero
	Ni(NCS)2Py4	79.61	0; n≠1	Zero
	Cu(NCS)2Py2	89.88	0; n≠1	Zero

Table 3: Computed parameters for samples understudy based on the differential and integral methods

Sample	Ea (kJmol^{-1})	Z (s^{-1})	ΔS (kJ K^{-1} mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ)	K (mol L^{-1} s^{-1})
Freeman-Carroll Method (Differential method)						
Co(NCS)2Py4	66.72	5.85 x 10^7	-80.22	-35.34 x 10^2	31.21 x 10^3	5.74 x 10^7
Ni(NCS)2Py4	72.95	1.71 x 10^8	-71.96	-38.19 x 10^2	29.87 x 10^3	1.67 x 10^8
Cu(NCS)2Py2	78.47	6.80 x 10^8	-60.01	-36.06 x 10^2	22.99 x 10^3	6.65 x 10^8
Coats- Redfern Method (Integral Method)						
Co(NCS)2Py4	68.43	3.11 x 10^7	-84.94	-35.33 x 10^2	33.26 x 10^3	3.25 x 10^7
Ni(NCS)2Py4	77.86	2.52 x 10^8	-68.72	-38.14 x 10^2	28.36 x 10^3	2.47 x 10^8
Cu(NCS)2Py2	83.13	8.91 x 10^8	-57.76	-36.01 x 10^2	21.99 x 10^3	8.71 x 10^8

4. CONCLUSION

From the present study the Freeman- Carroll method can be used for computing the order of the reaction (Case-01) and for the kinetic parameters (Case-02). The Coats-Redfern method can be more precisely recommended for the computation of kinetic parameters. The Horowitz- Metzger method can be used for well comparing the activation energies. It is well known that the solid-state thermogravimetric studies are highly non predictable and may differ considerably in their results for the same samples of different weights. The subject of solid-state reaction kinetics is one of the everlasting controversies due to this type of ambiguities and unpredictable behaviours (kinetic compensation effects). Further the shape of the thermogravimetric (TG) curves are very much influenced by procedural variables as sample holder geometry and material, heating rate, atmosphere, sample mass, particle size, impurities, temperature measurement, construction of the apparatus and even prehistory of the sample.

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