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# NON-ISOTHERMAL KINETIC STUDY OF THE SOLID–GAS THERMAL DECOMPOSITIONS OF SOME COORDINATION COMPOUNDS OF $Co^{II}$ AND $Ni^{II}$

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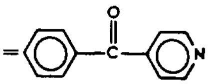
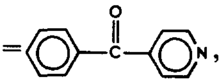
## ABSTRACT

Using a method developed by us, a non-isothermal kinetic study of the thermal decomposition of some coordination compounds (CC) with the general formula $Me^{II}L_pX_2$, where

$Me^{II} = Co^{II}$ or $Ni^{II}$, L = , $p = 2$ or 4, X = NCS or Cl, was performed.

## INTRODUCTION

Earlier papers were dedicated to the non-isothermal decomposition kinetics of coordination compounds (CC) with the general formula $Me^{II}L_pX_2$ (L = Py, $\alpha$-pic, $\beta$-pic, $\gamma$-pic) [1–3]. Following our research, in this paper, the results of a similar non-isothermal kinetic study concerning CC of $Co^{II}$ and $Ni^{II}$ with the same formula but with L = , are presented.

## THE METHOD OF WORKING THE EXPERIMENTAL DATA

In a recent paper [4] a new method for evaluating the non-isothermal kinetic parameters through integration over small temperature intervals and using several linear heating rates was presented. In this paper we will make use of a simplified variation of the mentioned method for two heating rates, $\beta_1$ and $\beta_2$, and assuming that $f(\alpha) = (1 - \alpha)^n$. The major change with respect to ref. 4 consists in the evaluation of the "reaction order" which is not done over small intervals. Actually, a value $\bar{n}$, corresponding to a higher interval which results from the addition of several small intervals, is calculated.

Starting from the fundamental kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\mathrm{f}(\alpha)\,\mathrm{e}^{-E/RT} \tag{1}$$

with

$$\mathrm{f}(\alpha) = (1-\alpha)^{n} \tag{2}$$

where the notations have the usual meanings, through variable separation and integration between $\alpha_i$ and $\alpha_k$, for two heating rates $\beta_1$ and $\beta_2$ ($\beta_2 > \beta_1$), one obtains

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{(1-\alpha)^{n}} = \frac{A}{\beta_{lik}} \int_{T_{li}}^{T_{lk}} \mathrm{e}^{-E/RT}\mathrm{d}T \;(l = 1, 2) \tag{3}$$

where $T_{li}$ and $T_{lk}$ are the temperatures corresponding to $\alpha_i$ and $\alpha_k$ for the two heating rates, and $\beta_{lik}$ is the local heating rate. The interval $\Delta\alpha = \alpha_k - \alpha_i$ has to be chosen in such a way that

$$\Delta T_l = T_{lk} - T_{li} \in (5, 20\ \mathrm{K}) \tag{4}$$

Taking into account eqn. (4) and using the average theorem [4–6], it follows that

$$\int_{T_{li}}^{T_{lk}} \mathrm{e}^{-E/RT}\mathrm{d}T \approx (T_{lk} - T_{li})\,\mathrm{e}^{-E/RT_{lik}} (l = 1, 2) \tag{5}$$

with

$$T_{lik} = \frac{T_{li} + T_{lk}}{2} \tag{6}$$

Taking into account these results, from the ratio of two relationships of the form (3) for $l = 1, 2$ one obtains

$$E = R\frac{T_{1ik}T_{2ik}}{T_{2ik} - T_{1ik}} \ln\frac{\beta_{2ik}\Delta T_1}{\beta_{1ik}\Delta T_2} \tag{7}$$

Because

$$\beta_{lik} = \frac{\Delta T_l}{\Delta t_l} (l = 1, 2) \tag{8}$$

where $\Delta t_l$ is the time interval corresponding to $\Delta\alpha = \alpha_k - \alpha_i$, relationship (7) becomes

$$E = R\frac{T_{1ik}T_{2ik}}{T_{2ik} - T_{1ik}} \ln\frac{\Delta t_1}{\Delta t_2} \tag{9}$$

Relationship (9) allows $E_1, E_2, \ldots E_m$ values to be obtained for $m$ intervals with

$\alpha \in [\alpha_i, \alpha_k]$.

In order to evaluate the reaction order, an average value of the activation energy, $\bar{E}$, will be considered

$$\bar{E} = \frac{E_1 + E_2 \ldots + E_m}{m} \tag{10}$$

This value is associated with an average value of the pre-exponential factor, $\bar{A}$. For three values of $\alpha$ ($\alpha_a < \alpha_b < \alpha_c$) located, as far as possible, in the whole interval of the conversion values used to calculate $E$ (for instance $\alpha_a$ could be $\alpha_i$ from the first interval, $\alpha_c$ could be $\alpha_k$ from the last interval, and for $\alpha_b$ an intermediate value could be considered), the following relationship can be written

$$\frac{\displaystyle\int_{\alpha_a}^{\alpha_b} \frac{\mathrm{d}\alpha}{(1-\alpha)^{\bar{n}}}}{\displaystyle\int_{\alpha_b}^{\alpha_c} \frac{\mathrm{d}\alpha}{(1-\alpha)^{\bar{n}}}} = \frac{\displaystyle\frac{\bar{A}}{\beta_{lab}} \int_{T_{la}}^{T_{lb}} \mathrm{e}^{-\bar{E}/RT} \mathrm{d}T}{\displaystyle\frac{\bar{A}}{\beta_{lbc}} \int_{T_{lb}}^{T_{lc}} \mathrm{e}^{-\bar{E}/RT} \mathrm{d}T} \quad (l = 1, 2) \tag{11}$$

Introducing the notation

$$\frac{\displaystyle\frac{\bar{A}}{\beta_{lab}} \int_{T_{la}}^{T_{lb}} \mathrm{e}^{-\bar{E}/RT} \mathrm{d}T}{\displaystyle\frac{A}{\beta_{lbc}} \int_{T_{lb}}^{T_{lc}} \mathrm{e}^{-\bar{E}/RT} \mathrm{d}T} = R_l \qquad (l = 1, 2) \tag{12}$$

and

$$R = \frac{R_1 + R_2}{2} \tag{13}$$

by performing integration from the left-hand side of eqn. (11) one obtains

$$\frac{(1-\alpha_a)^{1-\bar{n}} - (1-\alpha_b)^{1-\bar{n}}}{(1-\alpha_b)^{1-\bar{n}} - (1-\alpha_c)^{1-\bar{n}}} = R \tag{14}$$

which allows $\bar{n}$ to be calculated. In order to calculate $R_1$ and $R_2$, the decomposition of the integrals in sums of integrals over small temperature intervals, which can be approximated as shown by eqn. (5) or integrated using numerical methods, is recommended. Once the $\bar{n}$ value is known, from relationships (3) and (5) one obtains

$$A = \beta_{lik} \frac{\mathrm{e}^{-E/RT_{lik}}}{\Delta T_l} \frac{(1-\alpha_i)^{1-\bar{n}} - (1-\alpha_k)^{1-\bar{n}}}{1-n} \quad (l = 1, 2) \tag{15}$$

or taking into account eqn. (8)

$$A = \frac{\mathrm{e}^{-E/RT_{lik}}}{\Delta t_l} \frac{(1-\alpha_i)^{1-\bar{n}} - (1-\alpha_k)^{1-\bar{n}}}{1-n} \quad (l = 1, 2) \tag{16}$$

In such a way, for every value of $E$ the associated value of $A$ can be obtained

$A_1 \rightarrow E_1, A_2 \rightarrow E_2, \ldots, A_m \rightarrow E_m$

The value of $\bar{A}$ associated with $\bar{E}$ is given by

$$\log \bar{A} = \frac{\log A_1 + \log A_2 + \ldots + \log A_m}{m} \tag{17}$$

or

$$\bar{A} = (A_1 A_2 \ldots A_m)^{1/m} \tag{18}$$

The values of $\bar{A}$, $\bar{E}$ and $\bar{n}$ are probably close to the classical ones as, for instance, obtained by using methods which consider that $A$, $E$ and $n$ are constant over all the decomposition temperatures.

## EXPERIMENTAL

The following powdered substances were used: $S_1$, $NiL_4(NCS)_2$; $S_2$, $CoL_2Cl_2$; $S_3$, $CoL_4(NCS)_2$; $S_4$, $NiL_4Cl_2$, which were synthesised and analysed according to methods described elsewhere [7]. The average crystallite sizes, $l$, were determined by help of a Philips (PW 1450) X-ray diffractometer with chromium $K_\alpha$ radiation using Scherrer's formula [8].

The heating curves were recorded on a Paulik–Paulik–Erdey derivatograph with various heating rates between 2.5 and 10 K $min^{-1}$.

## RESULTS AND DISCUSSION

By working the experimental data according to the method described in the second section of this paper, results for the following reactions were obtained and are presented in Tables 1–20.

$S_1R_1$ *($l = 198$ Å)

$$NiL_4(NCS)_2(s) \rightarrow NiL_2(NCS)_2(s) + 2L(s) \tag{I}$$

$S_1R_2$

$$NiL_2(NCS)_2(s) \rightarrow Ni(NCS)_2(s) + 2L(g) \tag{II}$$

$S_2R_1$ ($l = 251$ Å)

$$CoL_2Cl_2(s) \rightarrow CoL_{0.75}Cl_2(s) + 1.25L(g) \tag{III}$$

$S_2R_2$

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* $S_xR_y$ means compound $x$ with reaction $y$.

TABLE 1

Experimental data for reaction (I)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 10$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 6$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 489.0 | 480.0 |
| 2 | 0.4000 | 501.5 | 492.0 |
| 3 | 0.5500 | 509.0 | 499.0 |
| 4 | 0.6000 | 512.0 | 500.5 |
| 5 | 0.9000 | 524.0 | 510.5 |

TABLE 2

Calculated $E$ and $A$ values for reaction (I)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.4000 | 2.093 | 1.291 | 24.995 | $3.06 \times 10^8$ |
| 2 | 0.4000 | 0.6000 | 1.419 | 0.988 | 17.197 | $1.07 \times 10^5$ |
| 3 | 0.6000 | 0.9000 | 1.826 | 1.186 | 17.951 | $2.36 \times 10^5$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.5500$; $\alpha_c = 0.9000$; $R_1 = 0.809$; $R_2 = 0.756$; $R = 0.783$; $\bar{E} = 20.1$ kcal mol$^{-1}$; $\bar{A} = 1.97 \times 10^6$ s$^{-1}$; $\bar{n} = 0.27$.

TABLE 3

Experimental data for reaction (II)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 10$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 6$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 567.5 | 553.0 |
| 2 | 0.4000 | 579.5 | 564.7 |
| 3 | 0.5500 | 585.5 | 572.0 |
| 4 | 0.6000 | 588.0 | 573.0 |
| 5 | 0.9000 | 598.0 | 584.0 |

TABLE 4

Calculated $E$ and $A$ values for reaction (II)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.4000 | 2.163 | 1.186 | 26.116 | $2.81 \times 10^7$ |
| 2 | 0.4000 | 0.6000 | 1.628 | 0.843 | 29.141 | $3.98 \times 10^8$ |
| 3 | 0.6000 | 0.9000 | 1.884 | 0.954 | 32.008 | $5.13 \times 10^9$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.5500$; $\alpha_c = 0.9000$; $R_1 = 0.748$; $R_2 = 0.778$; $R = 0.763$; $\bar{E} = 29.1$ kcal mol$^{-1}$; $\bar{A} = 3.86 \times 10^8$ s$^{-1}$; $\bar{n} = 0.30$.

TABLE 5

Experimental data for reaction (III)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 6$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 2.5$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2500 | 524.0 | 514.0 |
| 2 | 0.4000 | 540.0 | 527.0 |
| 3 | 0.6000 | 553.0 | 537.5 |
| 4 | 0.9000 | 570.5 | 550.5 |

TABLE 6

Calculated $E$ and $A$ values for reaction (III)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2500 | 0.4000 | 5.047 | 2.791 | 28.343 | $4.45 \times 10^8$ |
| 2 | 0.4000 | 0.6000 | 3.999 | 2.465 | 19.633 | $1.19 \times 10^5$ |
| 3 | 0.6000 | 0.9000 | 4.791 | 3.070 | 15.226 | $2.13 \times 10^3$ |

$\alpha_a = 0.2500$; $\alpha_b = 0.6000$; $\alpha_c = 0.9000$; $R_1 = 0.980$; $R_2 = 0.790$; $R = 0.885$; $\bar{E} = 21.1$ kcal mol$^{-1}$; $\bar{A} = 4.83 \times 10^5$ s$^{-1}$; $\bar{n} = 0.31$.

TABLE 7

Experimental data for reaction (IV)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 6$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 2.5$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 591.5 | 571.5 |
| 2 | 0.5000 | 604.5 | 585.0 |
| 3 | 0.9000 | 614.0 | 597.5 |

TABLE 8

Calculated $E$ and $A$ values for reaction (IV)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.5000 | 5.442 | 2.419 | 28.212 | $4.39 \times 10^7$ |
| 2 | 0.5000 | 0.9000 | 4.698 | 1.860 | 36.831 | $6.50 \times 10^{10}$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.5000$; $\alpha_c = 0.9000$; $R_1 = 0.622$; $R_2 = 0.784$; $R = 0.703$; $\bar{E} = 32.5$ kcal mol$^{-1}$; $\bar{A} = 1.69 \times 10^9$ s$^{-1}$; $\bar{n} = 0.08$.

TABLE 9

Experimental data for reaction (V)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 10$ K min$^{-1}$) | $T$(K) ($\beta_1 = 6$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 490.5 | 476.0 |
| 2 | 0.4000 | 503.0 | 490.0 |
| 3 | 0.6000 | 516.5 | 500.5 |
| 4 | 0.9000 | 535.5 | 517.5 |

TABLE 10

Calculated $E$ and $A$ values for reaction (V)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.4000 | 2.512 | 1.302 | 22.772 | $3.28\times10^7$ |
| 2 | 0.4000 | 0.6000 | 1.674 | 1.244 | 10.274 | $1.01\times10^2$ |
| 3 | 0.6000 | 0.9000 | 2.698 | 1.744 | 13.647 | $3.10\times10^3$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.6000$; $\alpha_c = 0.9000$; $R_1 = 0.812$; $R_2 = 0.754$; $R = 0.783$; $\bar{E} = 15.6$ kcal mol$^{-1}$; $\bar{A} = 2.18\times10^4$ s$^{-1}$; $\bar{n} = 0.56$.

TABLE 11

Experimental data for reaction (VI)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 10$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 6$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.1000 | 546.5 | 528.0 |
| 2 | 0.3000 | 556.0 | 538.0 |
| 3 | 0.6000 | 571.5 | 552.0 |
| 4 | 0.8500 | 585.5 | 564.5 |

TABLE 12

Calculated $E$ and $A$ values for reaction (VI)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.1000 | 0.3000 | 1.628 | 0.907 | 18.712 | $1.16\times10^5$ |
| 2 | 0.3000 | 0.6000 | 2.349 | 1.378 | 17.366 | $3.24\times10^4$ |
| 3 | 0.6000 | 0.8500 | 2.279 | 1.395 | 15.547 | $6.72\times10^3$ |

$\alpha_a = 0.1000$; $\alpha_b = 0.3000$; $\alpha_c = 0.8500$; $R_1 = 0.186$; $R_2 = 0.201$; $R = 0.194$; $\bar{E} = 17.2$ kcal mol$^{-1}$; $\bar{A} = 2.93\times10^4$ s$^{-1}$; $\bar{n} = 0.81$.

TABLE 13

Experimental data for reaction (VII)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 10$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 6$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.1000 | 597.0 | 575.5 |
| 2 | 0.4500 | 605.0 | 583.5 |
| 3 | 0.8500 | 613.5 | 594.0 |

TABLE 14

Calculated $E$ and $A$ values for reaction (VII)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.1000 | 0.4500 | 1.465 | 0.721 | 22.826 | $1.88\times10^6$ |
| 2 | 0.4500 | 0.8500 | 1.826 | 0.837 | 27.104 | $7.04\times10^7$ |

$\alpha_a = 0.1000$; $\alpha_b = 0.4500$; $\alpha_c = 0.8500$; $R_1 = 0.649$; $R_2 = 0.571$; $R = 0.610$; $\bar{E} = 25$ kcal mol$^{-1}$; $\bar{A} = 1.15\times10^7$ s$^{-1}$; $\bar{n} = 0.45$.

TABLE 15

Experimental data for reaction (VIII)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 6$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 3$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 453.0 | 444.0 |
| 2 | 0.3500 | 468.5 | 457.5 |
| 3 | 0.6000 | 485.5 | 473.5 |
| 4 | 0.9000 | 501.5 | 488.0 |

TABLE 16

Calculated $E$ and $A$ values for reaction (VIII)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.3500 | 4.884 | 2.721 | 24.138 | $3.37\times10^8$ |
| 2 | 0.3500 | 0.6000 | 5.581 | 3.023 | 23.522 | $1.41\times10^8$ |
| 3 | 0.6000 | 0.9000 | 5.581 | 2.791 | 25.628 | $1.37\times10^9$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.6000$; $\alpha_c = 0.9000$; $R_1 = 0.592$; $R_2 = 0.624$; $R = 0.608$; $\bar{E} = 24.4$ kcal mol$^{-1}$; $\bar{A} = 4.02\times10^8$ s$^{-1}$; $\bar{n} = 0.81$.

TABLE 17

Experimental data for reaction (IX)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 6$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 3$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.1500 | 521.0 | 511.0 |
| 2 | 0.5000 | 528.0 | 517.0 |
| 3 | 0.8500 | 535.0 | 522.5 |

TABLE 18

Calculated $E$ and $A$ values for reaction (IX)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.1500 | 0.5000 | 2.372 | 1.395 | 27.071 | $8.65\times10^8$ |
| 2 | 0.5000 | 0.8500 | 2.093 | 1.093 | 30.349 | $2.05\times10^{10}$ |

$\alpha_a = 0.1500$; $\alpha_b = 0.5000$; $\alpha_c = 0.8500$; $R_1 = 0.830$; $R_2 = 0.888$; $R = 0.859$; $\bar{E} = 28.7$ kcal mol$^{-1}$; $\bar{A} = 4.21\times10^9$ s$^{-1}$; $\bar{n} = 0.2$.

TABLE 19

Experimental data for reaction (X)

| No. | $\alpha$ | $T$ (K) ($\beta_2 = 6$ K min$^{-1}$) | $T$ (K) ($\beta_1 = 3$ K min$^{-1}$) |
|---|---|---|---|
| 1 | 0.2000 | 546.0 | 536.5 |
| 2 | 0.5000 | 553.5 | 543.5 |
| 3 | 0.8000 | 561.0 | 549.5 |

TABLE 20

Calculated $E$ and $A$ values for reaction (X)

| No. | $\alpha_i$ | $\alpha_k$ | $\Delta t_1$ (min) | $\Delta t_2$ (min) | $E$ (kcal mol$^{-1}$) | $A$ (s$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0.2000 | 0.5000 | 2.395 | 1.419 | 31.693 | $1.64\times10^{10}$ |
| 2 | 0.5000 | 0.8000 | 2.140 | 1.140 | 35.461 | $5.22\times10^{11}$ |

$\alpha_a = 0.2000$; $\alpha_b = 0.5000$; $\alpha_c = 0.8000$; $R_1 = 0.772$; $R_2 = 0.823$; $R = 0.797$; $\bar{E} = 33.6$ kcal mol$^{-1}$; $\bar{A} = 9.25\times10^{10}$ s$^{-1}$; $\bar{n} = 0.35$.

$$CoL_{0.75}Cl_2(s) \rightarrow CoCl_2(s) + 0.75L(s) \qquad \text{(IV)}$$

$S_3R_1$ ($l = 165$ Å)

$$CoL_4(NCS)_s(s) \rightarrow CoL_{2.33}(NCS)_2(s) + 1.67L(g) \qquad \text{(V)}$$

$S_3R_2$

$$CoL_{2.33}(NCS)_2(s) \rightarrow CoL(NCS)_2(s) + 1.33L(g) \qquad \text{(VI)}$$

$S_3R_3$

$$CoL(NCS)_2(s) \rightarrow Co(NCS)_2(s) + L(g) \qquad \text{(VII)}$$

$S_4R_1$ ($l = 178$ Å)

$$NiL_4Cl_2(s) \rightarrow NiL_{1.5}Cl_2(s) + 2.5L(g) \qquad \text{(VIII)}$$

$S_4R_2$

$$NiL_{1.5}Cl_2(s) \rightarrow NiCl_2L_{0.75}(s) + 0.75L(g) \qquad \text{(IX)}$$

$S_4R_3$

$$NiL_{0.7Cl_2}(s) \rightarrow NiCl_2(s) + 0.75L(g) \qquad \text{(X)}$$

Analysis of the data presented shows that the trend for $S_1$ and $S_2$ is an increase of the reaction order values with increasing reaction temperature. The explanation of such a trend, due to the change of crystallite sizes through reaction, was given in our previous papers [1–3]. Such a trend has not been proven for $S_2$ and $S_4$, perhaps due to sintering phenomena.

## CONCLUSIONS

(1) A method for working the thermogravimetric data to obtain non-isothermal kinetic parameter values was developed.

(2) Using this method the non-isothermal kinetic analysis of ten decomposition reactions of some CC of Co$^{II}$ and Ni$^{II}$ was performed.

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