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KINETICS OF THERMAL DECOMPOSITION OF SOME NITROPHOSPHATE FERTILIZERS WITH MICRONUTRIENTS IN ISOTHERMAL CONDITIONS

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The thermal behavior under isothermal conditions of some ammonia nitrate, ammonia phosphates and calcium phosphates mixtures with added micronutrients was studied. In order to establish the variation of activation energy (E) *vs*. conversion (α), the TG data were interpolated with spline functions, followed by numeric derivation. Using the so determined reaction rate the Friedman differential-isoconversional method was applied. A dependence of the activation energy *vs*. conversion was observed, meaning a many-step reaction. Therefore a procedure based on the compensation effect (and suggested by Budrugeac and Segal) was applied.

Keywords: *Budrugeac–Segal method based on compensation effect, fertilizers, isoconversional methods, micronutrients non-isothermal kinetics*

Introduction

Nitrophosphate complex mineral fertilizers are mainly composed of NH_4NO_3, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ and $CaHPO_4 \cdot 2H_2O$ [1, 2]. They give the plants nitrogen and phosphorus, which are two important macronutrients. Micronutrients such as Zn, Fe, Co, Cu, Mn, B, Mo have a very important role in plants growing and development.

As reported before [1, 2] during heating with a constant heating rate up to 350°C, four transformations accompanied by mass loss take place in the nitrophosphates. The first three are each of about 2%. The fourth mass loss (of ~58%) is due mainly to the decomposition of the major component, NH_4NO_3. Transformations of other components: $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ and $CaHPO_4 \cdot 2H_2O$ can overlap. For the NP, NP–B, NP–Co, NP–Cu and NP–Mo samples the TG and DTG curves are similar and the processes take place in the same range of temperature.

The technology of such fertilizers requires a drying step with a long contact time, best simulated by heating under isothermal conditions, so that the necessity of consistent data about the thermal behavior of technical mixtures in such conditions is obvious. The aim of the present paper is to analyze the opportunity of using isothermal kinetics data for judgment upon the technological behavior of various complex fertilizers.

Experimental

The complex fertilizers of nitrophosphate type (NP) were obtained from an industrial NP solution which contains mainly HNO_3, H_3PO_4 and $Ca(NO_3)_2$. The NP solution without and with added micronutrient (as $Na_2B_4O_7$, $CoCl_2$, $CuSO_4$, $(NH_4)_2MoO_4$) was neutralized with 25% NH_3 solution until the pH was ~6.5. The reaction mass was dried 24 h at 80°C, grinded and sieved, and the –250+90 μm fraction was used. The samples will be identified in the paper with the symbol of the added micronutrient: NP (without micronutrient), NP–B, NP–Co, NP–Cu, NP–Mo.

The thermal measurements were carried out on a Perkin-Elmer TGA 7 Series thermobalance, in controlled dynamic atmosphere (synthetic air, 10 mL min^{-1} flow rate), with samples of 60 mg at three various temperatures corresponding to the main mass loss of the samples. The samples were heated with 5°C min^{-1} up to the desired temperature.

Results and discussion

The kinetics of the thermal decomposition can be described by the rate Eq. (1):

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \qquad (1)$$

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where α is the extent of reaction (conversion degree), t the time, T the temperature and $f(\alpha)$ the reaction model.

The experimental data are available as α *vs*. t diagrams at various temperatures, (Fig. 1, for example).

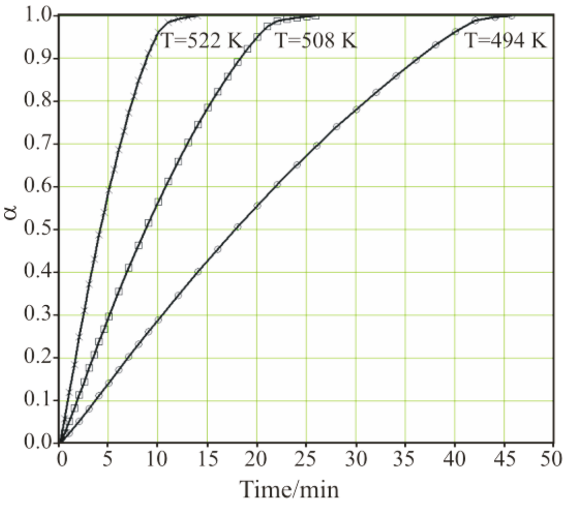

Fig. 1 Degree of conversion *vs*. time (min) plots at 494, 508 and 522 K, for NP–Cu sample

Isothermal model-fitting methods

Substitution of $(1-\alpha)^n$ for $f(\alpha)$ in Eq. (1) followed by linearization yields:

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln k(T)+n\ln(1-\alpha) \qquad (2)$$

Plotting the left hand side of Eq. (2) *vs*. $\ln(1-\alpha)$, one finds the values of $\ln k(T)$ and n for each temperature (Fig. 2). Then, the values of E and $\ln A$ are estimated by plotting $\ln k(T)$ *vs*. $1/T$. Table 1 provides the values of $k(T)$ and n computed from Eq. (2).

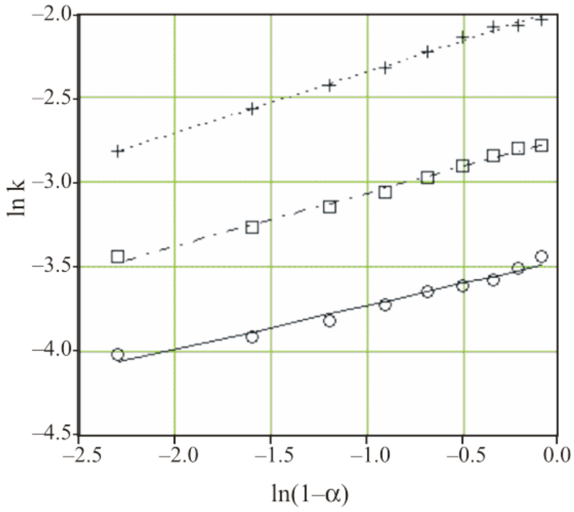

Fig. 2 Plots of ln of reaction rates *vs*. ln(1–α), for NP–Cu sample

Table 1 Rate constant and rate order evaluated from isothermal data Eq. (2)

Sample	T/K	$k(T)$/min^{-1}	n
NP	494	0.0244±0.0012	0.1782±0.0168
	507	0.0537±0.0033	0.3187±0.0209
	517	0.0974±0.0066	0.4117±0.0226
NP–B	494	0.0291±0.0013	0.2378±0.0147
	509	0.0673±0.0038	0.3217±0.0196
	522	0.1588±0.0140	0.3960±0.0292
NP–Co	500	0.0377±0.0018	0.2516±0.0168
	509	0.0641±0.0042	0.3165±0.0223
	519	0.1093±0.0029	0.3748±0.0091
NP–Cu	494	0.0312±0.0016	0.2607±0.0171
	508	0.0641±0.0018	0.3141±0.0098
	522	0.1382±0.0035	0.3633±0.0087
NP–Mo	499	0.0367±0.0012	0.2341±0.0011
	509	0.0674±0.0023	0.3359±0.0012
	519	0.1206±0.0017	0.3653±0.0048

The variation of the reaction order with the temperature indicates that the decomposition process we studied is complex. The variation in the reaction order for complex kinetics has been reported by Vyazovkin and Sbirrazzuoli [3] who observed it when fitting isothermal experimental data to $(1-\alpha)^n$ and $\alpha^m(1-\alpha)^n$ reaction models.

The corresponding Arrhenius plots (Fig. 3) are almost flawlessly linear and give the E and A values presented in Table 2.

Alternatively, we used another method for estimating the kinetic parameters, i.e. the Friedman`s isotherm-isoconversional method Eq. (3) for a given conversion degree:

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln[A(1-\alpha)^n]-\frac{E}{RT} \qquad (3)$$

It is important to note that Eq. (2) implies that the reaction obeys the same reaction model throughout the whole region of both temperature and conversion.

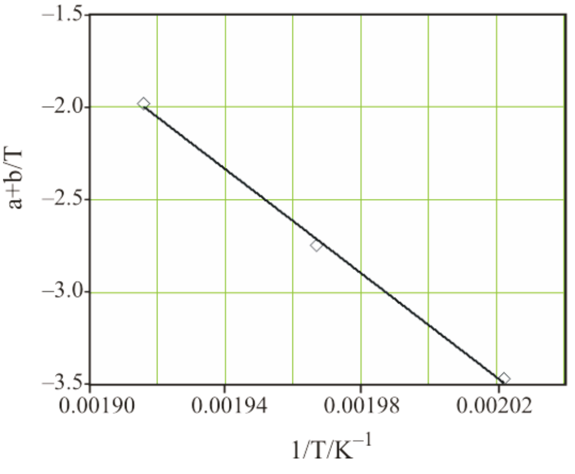

Fig. 3 Arrhenius plot for NP–Cu sample

Table 2 Activation energy and pre-exponential factor values resulted from Arrhenius plot (Fig. 3)

Sample	E/kJ mol^{-1}	A/min^{-1}	ln$A$	Correlation coefficient
NP	127.76± 5.05	$7.86\cdot10^{11}$	27.39±0.19	0.99998
NP–B	129.51±52.16	$1.40\cdot10^{12}$	27.97±1.96	0.998
NP–Co	120.78±14.01	$1.58\cdot10^{11}$	25.78±0.52	0.9998
NP–Cu	116.36±31.82	$5.97\cdot10^{10}$	24.81±1.19	0.9991
NP–Mo	129.00± 8.80	$1.15\cdot10^{12}$	27.77±0.32	0.99994

Table 3 Activation energy values (kJ mol^{-1}) obtained using the isotherm-isoconversional method (Friedman) Eq. (3)

Sample	α								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
NP	123.28	125.16	120.79	120.00	114.57	104.01	101.22	87.23	82.35
NP–B	122.33	126.62	125.86	127.51	128.01	122.49	104.96	108.39	103.60
NP–Co	113.05	115.04	117.03	118.73	113.15	110.86	104.90	97.43	86.18
NP–Cu	109.67	112.34	117.10	114.76	111.41	110.09	108.49	105.48	94.21
NP–Mo	124.74	124.09	122.18	125.60	119.02	117.77	114.93	106.80	83.18

Table 3 presents the values for the activation energy resulted using the isotherm-isoconversional method described by Eq. (3). Figure 4 illustrates the variation of the activation energy with the extent of conversion for NP–Cu sample.

From Table 4 and Fig. 4 one may notice that the activation energy depends on the extent of conversion, which leads to the conclusion that the process is complex. However, this effect would not be observed if one determines the parameters only at a single extent of conversion, which appears to be a rather usual situation.

So, using two different data processing, we obtained the same conclusions, i.e. the studied processes are multi-step.

Estimation of the kinetic parameters and the compensation effect parameters of reaction for which the activation energy depends on the degree of conversion (Budrugeac–Segal).

The procedure is based on the following assumptions [4–7]:

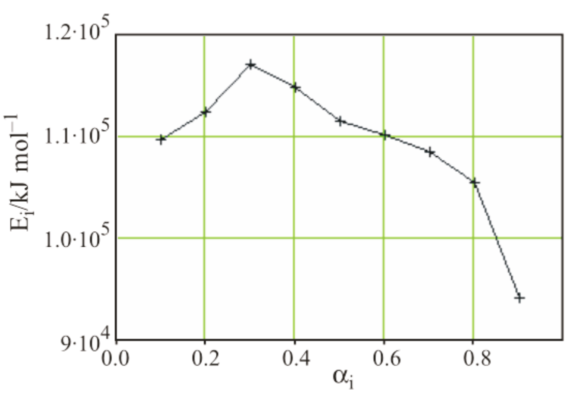

Fig. 4 Activation energy *vs*. degree of conversion, for NP–Cu sample

- E and A depend on the degree of conversion and do not depend on the heating rate;
- E and A are correlated through the compensation effect (CE):

$$\ln A=aE+b \tag{4}$$

- The dependence of E on the degree of conversion is given by:

$$E=E_0+E_1\ln(1-\alpha) \tag{5}$$

where E_0 and E_1 are constants (illustrated in Fig. 5 for NP–Cu sample, where $Q=\ln(1-\alpha)$).

- The differential conversion function, $f(\alpha)$ has the form:

$$f(\alpha)=(1-\alpha)^n \tag{6}$$

From the differential conversion function (6) it follows that:

$$\ln[Af(\alpha)]=\ln A+n\ln(1-\alpha) \tag{7}$$

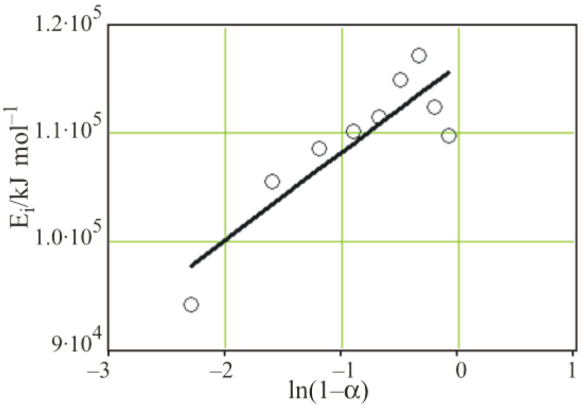

Fig. 5 Plot of activation energy *vs*. ln(1–α), for NP–Cu sample

Table 4 Kinetic parameters according to Eq. (8)

Sample	E_0/kJ mol^{-1} (Eq. (5))	E_1/kJ mol^{-1} (Eq. (5))	$a\cdot10^4$mol J–1 (Eq. (4))	b(Eq. (4))	n	Correlation coefficient
NP	127.76±4.34	21.61±2.04	2.425±0.008	–3.59±0.26	0.2	0.99997
NP–B	129.51±7.52	12.10±3.15	2.323±0.001	–2.10±0.50	0.4	0.9998
NP–Co	120.78±3.70	13.98±1.99	2.301±0.004	–2.00±0.12	0.4	0.99998
NP–Cu	116.36±4.17	8.04±1.75	2.373±0.011	–2.80±0.35	0.3	0.99993
NP–Mo	130.00±3.28	14.23±1.38	2.301±0.031	–1.92±0.91	0.4	0.99999

and from the values of [*Af*(α)] and α, the values of ln*A* corresponding to various values of *n* can be obtained. The plot of ln*A* *vs*. *E* should be linear as required by the existence of compensation effect (Eq. (4)). The correct value of *n* will be that which gives the correlation coefficient closest to 1.00 for the straight line ln*A* *vs*. *E*.

From Eqs (4)–(8) we obtain:

$$\ln\left(\frac{d\alpha}{dt}\right)=\left(b+aE_0-\frac{E_0}{RT}\right)+ \\ +\left(aE_1-\frac{E_1}{RT}+n\right)\ln(1-\alpha) \tag{8}$$

The data obtained using the Budrugeac–Segal method described in Eqs (4)–(8) are given in Table 4. The reaction order was tested for values between 0.1–2.0, with a step of 0.1.

The plots of reaction rates (experimental and calculated with Eq. (8) and parameters given in Table 4) *vs*. conversion degree are showed in Fig. 6, for NP–Cu sample. One may notice a good fitting between calculated and experimental data.

This mean that the obtained data by this method are doubtless in using for predictive aims.

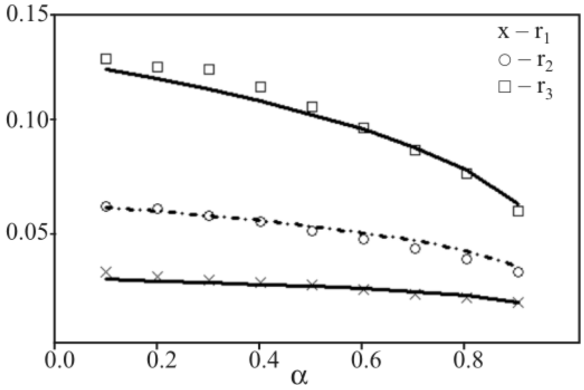

Fig. 6 Plots of reaction rates (experimental-points, calculated-lines) *vs*. α for NP–Cu sample at 494, 508 and 522 K

Conclusions

By processing experimental data on decomposition of solid samples, obtained under isothermal conditions, same care are imperative. An isothermal-isoconversional approach is rather compulsory, due to the fact of variation of activation energy *vs*. conversion degree.

The use of Budrugeac–Segal method, based on such dependence is more realistic, especially when the obtained parameters are used only for behavior predictions and not for mechanistic speculations.

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