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Note

Thermal decomposition studies

VIII. A dynamic-thermogravimetric study of the mechanism of deamination of some transition metal complexes*

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In recent years dynamic thermogravimetry (TG) and differential thermal analysis (DTA) are being increasingly employed for the study of solid-state reactions[1–8]. As Šestak et al.[9] have pointed out, two different mathematical methods are employed for determining the kinetics of decomposition from dynamic TG, viz., (1) a study based on mechanisms, where a series of acceptable decomposition mechanisms are considered and from these, the one which fits best with experimental data is chosen; (2) a mechanism-non-invoking general kinetic study, which in its simplest form, assumes the equation $d\alpha/dt = kf(\alpha) = k(1-\alpha)^n$. Of these two approaches, the second has been more widely used; thus it is the basis of the well-known kinetic equations such as those of Freeman and Carroll[10], Horowitz and Metzger[11] and Coats and Redfern[12]. These methods, while giving satisfactory results, are open to the criticism[13] that they implicitly assume $f(\alpha) = (1-\alpha)^n$. This assumption really amounts to making an extrapolation of the considerations prevailing in homogeneous kinetics to solid state (mostly heterogeneous) kinetics.

The first approach, that is, the mechanism-based study, has been generally applied to *static* isothermal weight-change studies only. Recently a few attempts have been made to extend this approach to *dynamic* TG; but these studies were centred mainly on some isolated single compounds (e.g., the dehydration stage in calcium sulphate hemihydrate[14]). A survey of literature showed that very few attempts have been made to undertake a mechanism-based kinetic study for any one particular type of process occurring in a series of related compounds.

We are reporting here our studies on the escape of amine ,i.e., the deamination process, occurring in the following six complexes (py = pyridine, DMG = dimethylglyoxime): (1) $Mn(py)_4(SCN)_2$; (2) $Ni(py)_4(SCN)_2$; (3) $Cu(py)_2(SCN)_2$; (4) $Zn(py)_2(SCN)_2$; (5) $Co[(DMG)_2(p\text{-ethylaniline})_2](SCN)_2$; (6) $Co[(DMG)_2(\gamma\text{-picoline})_2](SCN)_2$.

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*Parts IV to VII, see refs. 5–8.

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Symbols used

k = specific reaction rate
α = fractional decompositions
ϕ = heating rate in K $\sec^{-1}$
E = energy of activation
A = pre-exponential term
ΔS = entropy of activation
R = gas constant
$g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$

Source of data

α-T data for the first four complexes were taken from work done in our laboratories[5]. Data on the remaining two complexes (chosen because of their partial similarity to the first four) were taken from the published work of Zsako[15]. These are tabulated in Table 1.

Treatment of data

The forms of the functions $f(\alpha)$ and $g(\alpha)$ for the selected rate-controlling processes are given in Table 2. The values of $g(\alpha)$ for all the nine mechanisms were calculated for each of the deamination stages. Complexes 1 and 2 have two deamination stages each; these correspond to the loss of 2 molecules of pyridine first, and then the loss of the remaining two pyridine molecules. The remaining four complexes have only one deamination stage each, where both the amine molecules are lost. Thus the total number of deamination stages considered is 8. A total of $8 \times 9 = 72$ plots of $\log g(\alpha)$ versus $1/T$ were drawn. These are given in Figs. 1 to 8, each figure showing 9 plots (numbered 1 to 9) corresponding to the 9 mechanisms chosen for study.

In order to evaluate the parameters E and A, any of the kinetic equations may be suitably modified by imposing the new $g(\alpha)$ values in the left-hand-side expressions, but retaining the right-hand-side expressions as such. We chose the MacCallum–Tanner equation[16]:

$$\log g(\alpha) = \log \frac{AE}{R\phi} - 0.48E^{0.44} - \left(\frac{0.449+0.217E}{T} \times 10^{-3}\right)$$

If the correct form of $g(\alpha)$ is chosen, a plot of $\log g(\alpha)$ versus $1/T$ would be a straight line, from the slope and intercept of which, E and A, respectively, may be evaluated.

DISCUSSION

It may be noted that all the integral kinetic equations make use of approximations in evaluating the temperature integral and lead to the requirement that a plot of $\log g(\alpha)$ versus $1/T$ should be linear. A study of the plots in Figs. 1 to 8 shows that the best fit with linearity is obtained for mechanisms 5, 6 and 7 (see Table 2). Thus the

TABLE 1

α–T VALUES

Compound	*Stage*	α	T (K)	*Compound*	*Stage*	α	T (K)
$Mn(py)_4(SCN)_2$	1	0.0122	393	$Cu(py)_2(SCN)_2$	1	0.0171	433
		0.0549	403			0.0513	443
		0.1341	413			0.1196	453
		0.2927	423			0.4530	463
		0.5977	433			0.8718	473
		0.8293	443			0.9573	483
		0.9268	453			0.9915	493
		0.9756	463				
	2	0.0878	483	$Zn(py)_2(SCN)_2$	1	0.2241	483
		0.2297	493			0.3879	503
		0.4324	503			0.6121	523
		0.7027	513			0.7500	543
		0.9054	523			0.8621	563
						0.9397	583
$Ni(py)_4(SCN)_2$	1	0.0143	403	$Co[(DMG)_2$ (p-ethylaniline)$_2$] $(SCN)_2$	1	0.0340	433
		0.0314	413			0.1020	443
		0.0900	423			0.1190	453
		0.2029	433			0.3689	463
		0.3857	443			0.5887	473
		0.6571	453			0.8690	483
		0.9429	463			0.9175	493
	2	0.2581	503	$Co[(DMG)_2$ (γ-picoline)$_2$] $(SCN)_2$	1	0.0223	423
		0.4677	513			0.0393	433
		0.8387	523			0.0787	443
		0.9193	533			0.1910	453
		0.9839	543			0.3315	463
		0.9935	553			0.5842	473
						0.8764	483
						0.9718	493

Mampel[17] mechanism (5) and the two Avrami[18] mechanisms (6 and 7) appear to be satisfied. Of the three mechanisms which give straight-line fits, only one can be acceptable. A calculation of the E and A values would enable us in deciding the acceptable mechanism.

An examination of the kinetic parameters presented in Table 3 shows that only the Mampel equation gives reasonable values for E and A. For one thing, the E and A values obtained from the Mampel equation lie closest to these parameters obtained from mechanism-non-invoking kinetic equations. Secondly, considerations of the plausibility of the values also favour the Mampel equation. Thus, the theoretically expected normal value of the frequency for solid state reactions should be approximately 10^{13}. The experimental values should therefore lie within 2 to 3 orders of

TABLE 2

MECHANISTIC EQUATIONS

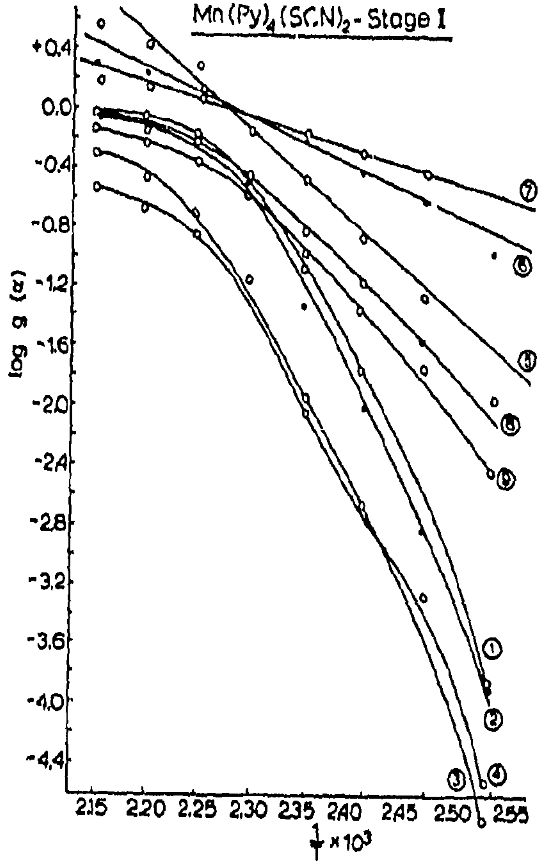
Type of equation	*Symbol*	*Form of $f(\alpha)$*	*Form of $g(\alpha)$*	*Rate-controlling process*
Parabolic law	1	$\frac{1}{2}\alpha$	α^2	One-dimensional diffusion with constant diffusion coefficient.
	2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion—cylindrical symmetry.
Jander	3	$\frac{3}{2}(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion—assumes spherical symmetry.
Ginstling-Brounshtein	4	$\frac{3}{2}(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion—assumes spherical symmetry—reaction starting at the exterior.
Mampel	5	$1-\alpha$	$-\ln(1-\alpha)$	Assumes random nucleation—one nucleus on one particle.
Avrami	6	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	Assumes random nucleation.
Avrami	7	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	Assumes random nucleation.
	8	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	Phase boundary reaction—cylindrical symmetry—movement of an interface.
	9	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	Phase boundary reaction—assumes spherical symmetry.

TABLE 3

KINETIC PARAMETERS

Compound	*Stage*	*From mechanism-non-invoking equation*		*From mechanism-based equations*					
				Mampel equation (5)		*Avrami equation (6)*		*Avrami equation (7)*	
		E	*A*	*E*	*A*	*E*	*A*	*E*	*A*
$Mn(py)_4(SCN)_2$	1	113.3[a]	1.44×10^{11}	114.9	1.24×10^{11}	53.09	3.70×10^{3}	32.53	1.00×10^{1}
	2	160.8[a]	1.36×10^{14}	161.8	1.66×10^{14}	76.53	1.22×10^{5}	48.16	1.12×10^{2}
$Ni(py)_4(SCN)_2$	1	129.1[a]	4.47×10^{12}	124.2	1.12×10^{12}	57.78	8.65×10^{3}	35.65	1.17×10^{1}
	2	146.0[a]	1.78×10^{12}	125.8	1.63×10^{10}	58.53	2.1×10^{3}	36.15	1.11×10^{1}
$Cu(py)_2(SCN)_2$	1	186.8[a]	3.43×10^{18}	169.6	3.76×10^{16}	80.50	1.81×10^{6}	50.79	5.88×10^{2}
$Zn(py)_2(SCN)_2$	1	47.04[a]	5.58×10^{1}	47.57	9.14×10^{1}	19.47	—	10.12	—
$Co[(DMG)_2(p\text{-ethyl aniline})_2](SCN)_2$	1	120.9[b]	5.15×10^{11}	120.2	6.75×10^{10}	55.81	2.18×10^{3}	34.32	7.1×10^{0}
$Co[(DMG)_2(\gamma\text{-picoline})_2](SCN)_2$	1	118.4[b]	2.76×10^{11}	127.8	5.12×10^{11}	62.47	1.3×10^{4}	38.79	5.8×10^{1}

[a] Coats-Redfern. [b] Zsako.



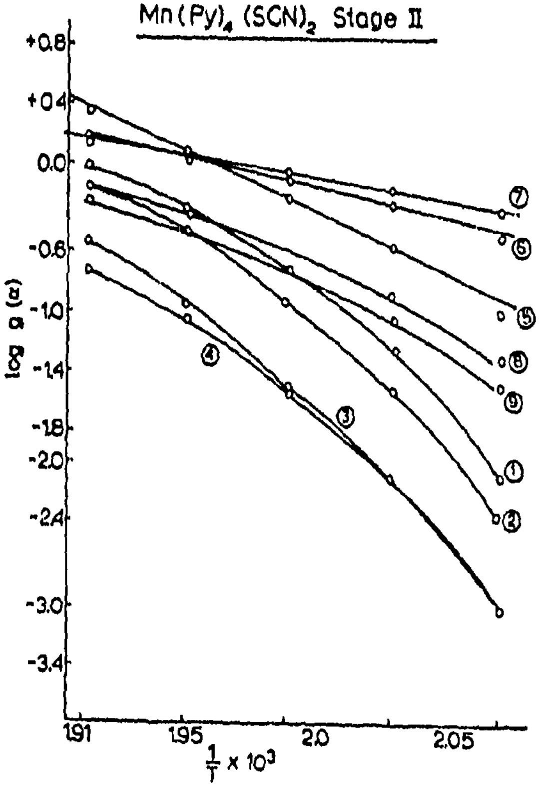
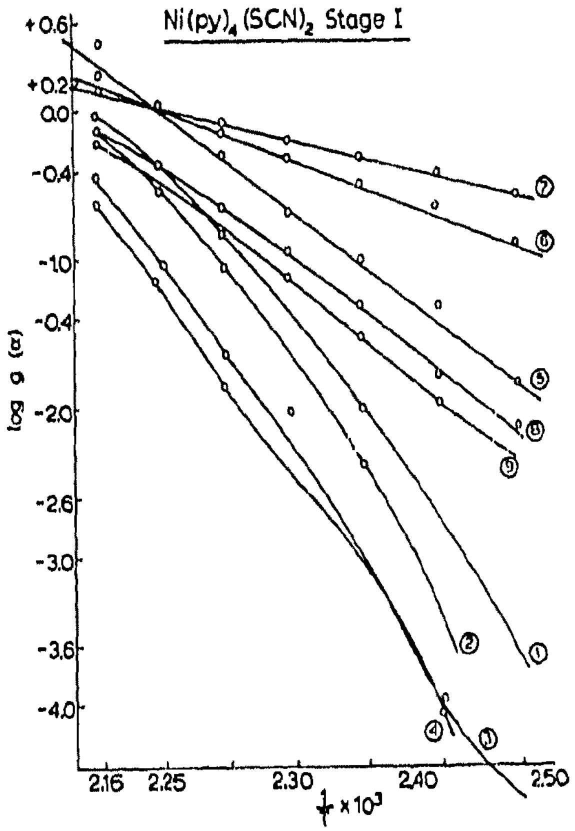


Fig. 1. Plot of log g(α) versus 1/*T*.

Fig. 2. Plot of log g(α) versus 1/*T*.



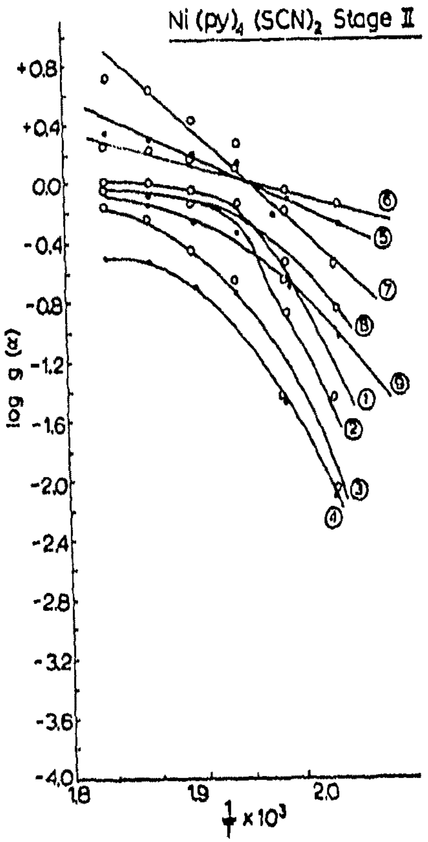
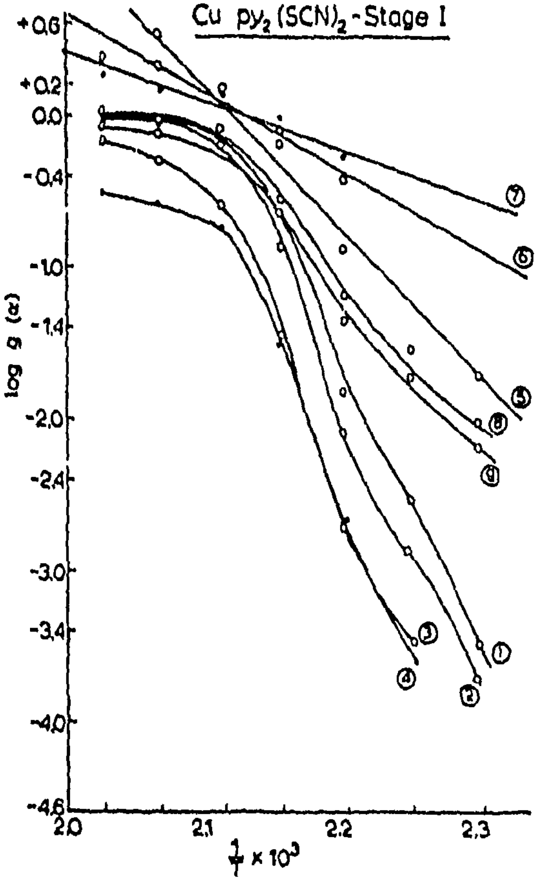


Fig. 3. Plot of log g(α) versus 1/T.

Fig. 4. Plot of log g(α) versus 1/T.



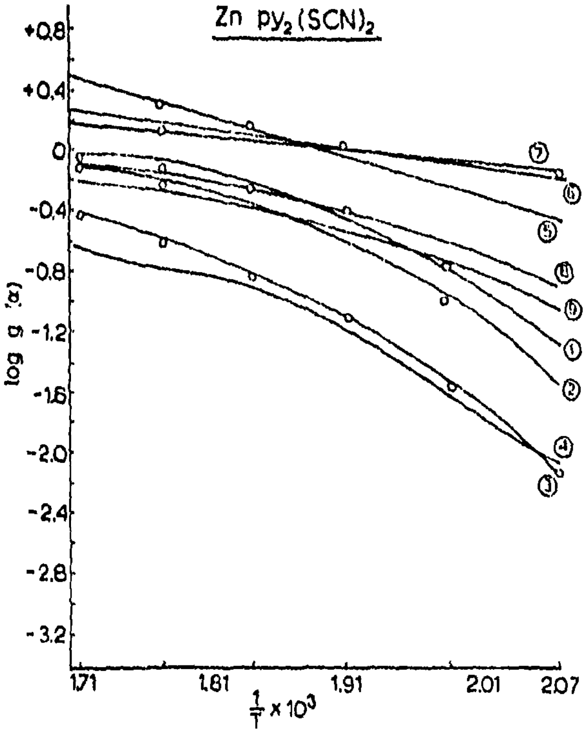
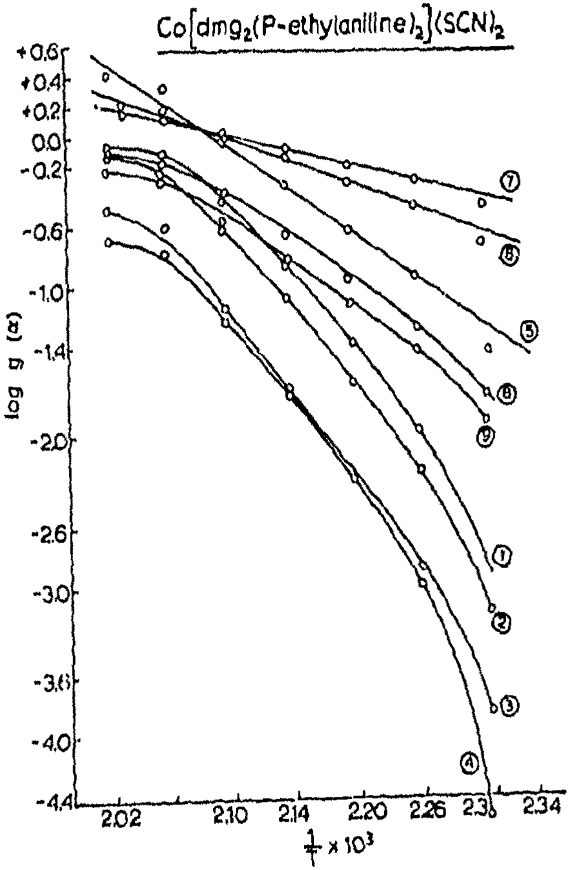


Fig. 5. Plot of log g(α) versus 1/*T*.

Fig. 6. Plot of log g(α) versus 1/*T*.



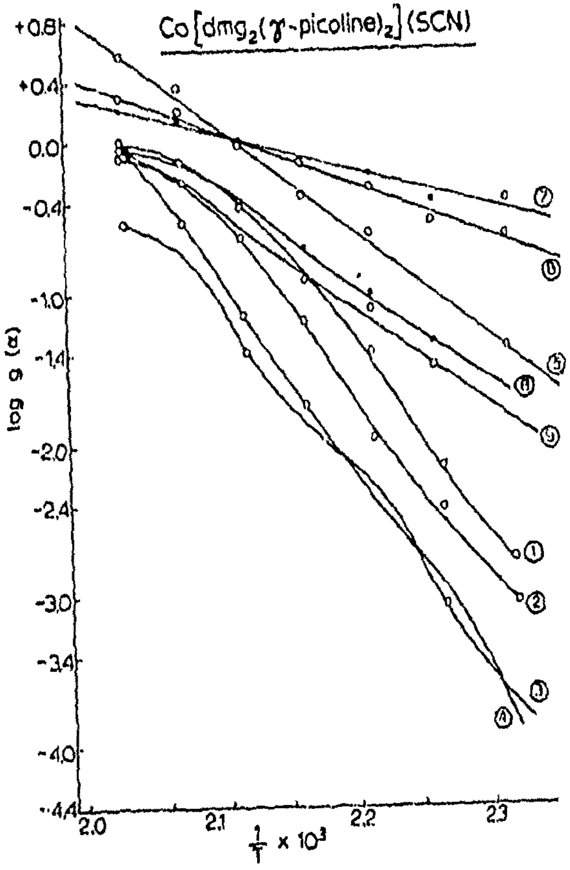


Fig. 7. Plot of log g(α) versus 1/T.

Fig. 8. Plot of log g(α) versus 1/T.

magnitude on either side of this value. This criterion is satisfied by the Mampel values in all cases, but not by the Avrami values, except in the case of zinc. The abnormally low A value for the zinc complex may be explained as a reflection of a highly negative entropy of activation ($\Delta S = -107.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$) which, in turn, implies a highly ordered configuration for the activated complex compared to the reactant.

Thus it may be concluded that the Mampel mechanism correctly represents all the deamination stages. This mechanism assumes a random nature for the nucleation process, with one nucleus formed on each particle. Neither phase boundary reactions nor diffusion-controlled processes appear to be operative.

REFERENCES

1 L. Reich and D. W. Levi, in A. Peterlin et al. (Eds.), *Macromolecular Reviews*, Vol. 1, Interscience Publishers, New York, 1967, p. 173.
2 A. Mackenzie (Ed.), *Differential Thermal Analysis*, Vols. 1 and 2, Academic Press, New York, 1972.
3 W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience, New York, 1964.
4 P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965.
5 C. G. R. Nair and P. Indrasenan, *Thermochim. Acta*, 11 (1975) 141.
6 C. G. R. Nair and P. M. Madhusudanan, *Thermochim. Acta*, 12 (1975) 97.
7 C. G. R. Nair and P. M. Madhusudanan, *Curr. Sci.*, 44 (1975) 212.
8 C. G. R. Nair and P. Indrasenan, *Ind. J. Chem.*, in press.
9 J. Šesták, A. Brown, V. Rihak and G. Berggren, in R. F. Schwenker, Jr., and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1039.
10 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
11 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
12 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
13 B. N. N. Achar, G. W. Brindley and J. H. Sharp, in L. Heller and A. Weiss (Eds.), *Proceedings of the International Clay Conference*, 1966.
14 V. Šatava and J. Šesták, *Anal. Chem.*, 45 (1973) 154.
15 J. Zsako, *J. Phys. Chem.*, 72 (1968) 2406.
16 J. R. MacCallum and J. Tanner, *Eur. Polym J.*, 6 (1970) 1033.
17 K. L. Mampel, *Z. Phys. Chem. A.*, 187 (1940) 235.
18 M. Avrami, *J. Chem. Phys.*, 7 (1939) 1103.