

JOUNI TUMMAVUORI, HANNU VENÄLÄINEN AND TIMO NYRÖNEN

THE USABILITY OF THERMOGRAVIMETRY IN FUEL RESEARCH. PART VIII

THE EFFECT OF MASS AND TEMPERATURE RATE ON THE VALUES OF KINETIC QUANTITIES IN THE THERMOGRAVIMETRY

TERMOGRAVIMETRIEN KÄYTTÖ KIIINTEIDEN POLTTO- AINEIDEN TUTKIMUKSISSA. OSA VIII. MASSAN JA LÄMPÖTILAN NOSTONOPEUDEN VAIKUTUS KINEETTISTEN SUUREIDEN ARVOIHIN

TummaVuori, J., Venäläinen, H. & Nyronen, T. 1983: The usability of thermogravimetry in fuel research. Part VIII. The effect of mass and temperature rate on the values of kinetic quantities in the thermogravimetry. (Termogravimetrian käyttö kiinteiden polttoaineiden tutkimuksissa. Osa VIII. Massan ja lämpötilan nostonopeuden vaikutus kineettisten suureiden arvoihin.) — Suo 34: 41—48 Helsinki.

We have investigated the influence of the sample mass and the temperature rate on the values of thermogravimetric quantities.

The substances used were powdered willow dust and calcium oxalate, since willow dust represents a relatively homogenous natural material whereas calcium oxalate is a very common reference material in thermogravimetric studies.

The temperature rate was varied from $0.5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ up to $100\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and the masses were ranging from 10 mg to 420 mg.

It is a widely adapted impression that a relatively large masses (several hundred milligrams) and a slow temperature rate (optimum $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ give the best experimental repetition and correct results.

We conclude, however, that the variation in sample masses and in temperature rate in this experiment had no significant influence on the kinetic quantities computed.

The deviations originate from the differences in the instrumental technique and this assesses a requirement for the improved instrumentation before the mathematical relationships between various quantities can be established.

Furthermore, the negligible small effect of the reaction order on the kinetic quantities was observed. This was rather surprising, because it was only partly expected due to the formulation of the basic expressions.

J. TummaVuori and H. Venäläinen, Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1—3, SF-40100 Jyväskylä 10

T. Nyronen, The State Fuel Centre (Vapo), Yrjönkatu 42, SF-40100 Jyväskylä 10

The aim of this study was to clarify the effect of mass and temperature rate on the values of kinetic quantities calculated from the thermogravimetric data.

The masses used in the thermogravimetric investigations range from few milligrams up to gram. Previously, samples between 50—100 mg were common, but presently 10

mg seems to be the most adopted sample size.¹ (Oswald and Wildemann 1977).

The temperature rate varies between 0.5 °C/min and to as high as 100 °C/min. For our purpose, 10 °C/min seems to be the most convenient temperature rate. (Keattch and Dollimore 1975).

It is a common impression that the slow temperature rate gives the best repeatable results although the optimum rate has been claimed to be 3 °C/min, but as a whole, the effect of the temperature rate and the mass on the kinetic quantities is still obscure.

Recent research, notably that of Nair and Ninan (1976, 1978, 1979) has aimed at investigating the effect of the temperature rate and the mass on the kinetic quantities. Calcium oxalate monohydrate and sodium tetraphenylborate were used in their experiment and kinetic quantities were calculated using methods of Coats and Redfern (1964), McCallum and Tanner (1970) and Horowitz and Metzger (1963).

Similarly we also chose calcium oxalate monohydrate as sample substance, since it has a variety of reference data. Willow was selected as the other sample material for research, it represents the homogenous mixture of several organic compounds we desired. The thermogravimetric decomposition of willow obeys the first order kinetics (Tummavuori et al.) and since this holds for calcium oxalate monohydrate, too, we were able to calculate at once the kinetic quantities according to the Equation of Horowitz and Metzger (1963).

$$\ln \ln (I/y) = \frac{E^*0}{RT_s^2} \quad (1)$$

where E^* is the activation energy and T_s the turning point temperature of the reaction. 0 is $T_s - T_t$, where T_t denotes the temperature at the point t , R is the common gas constant and

y is $\frac{w_i - w_f}{w_o - w_f}$, where w_i is the mass at the

temperature T_t , w_o is the sample mass in the beginning of the reaction and w_f is the sample mass at the end of the reaction (Horowitz and Metzger 1963).

At the second stage, we also adopted the method presented by Broido (196)

$$\ln \ln (I/y) = -\frac{E^*}{RT} + \text{constant} \quad (2)$$

The frequency factor A has been evaluated according to the Equation

$$A = \frac{qE^*}{RT_s^2 e^{E^*/RT}} \quad (3)$$

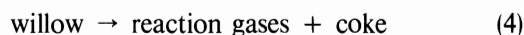
where q is the temperature rate °C min⁻¹ (Horowitz and Metzger 1963).

Calcium oxalate monohydrate powder was a product of B.D.H grade analar R. The Willow was pulverized, air-dry material without bark.

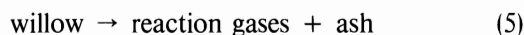
The thermobalance was a Fister TGA SYSTEM SERIES 100 type equipment. The investigations were performed both in nitrogen and in mixed gas (20 % O₂ and 80 % N₂) atmospheres. The flow rate of the gases was 0.13 dm³ min⁻¹. The calculations of kinetic quantities were performed with ABC-80 minicomputer using BASIC-coded programs. The reaction orders have been computed with Univac 1110-computer.

RESULTS AND DISCUSSION

Willow sample pyrolyses in nitrogen atmosphere obeying the first order kinetics. (Tummavuori et al). The brutto formula to this reaction is



In mixed gas the following reaction takes place



Tables 1 and 2 show the results of the measurements in either atmospheres and in Table 3 are the mean values of E^* and $\log A$ obtained as average results from different calculation methods.

The error limits are given as standard deviation from the mean. The results show, that in nitrogen atmosphere the changes in the temperature rate and mass have no significant effect on the T_s -temperature, whereas in mixed gas the T_s -temperature slightly increases while the temperature rate increases.

Both the values of E^* and $\log A$ in nitrogen atmosphere are constant but in mixed gas they obey linear equations as a function of the mass, however the regression coefficients are not quite satisfactory.

Table 1. The values of kinetic quantities of willow with different sample masses and with a temperature rate of 10 °C min⁻¹.

a) Eq (2) This notation holds also for next-coming values, so that the upper value is
 b) Eq (1) calculated according to the Eq (2) and the lower value according to the Eq (1).

Taulukko 1. *Salix*:n kineettisten suureiden arvot eri näytemassan arvoilla lämpötilan nostonopeudella 10 °C min⁻¹.

Sample	in nitrogen					in mixed gas				
	mass (mg)	T _c (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.	mass (mg)	T _c (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.
Salix	1.92	339	a) 95.1	5.82	0.963	1.91	307	112.4	7.94	0.972
			b) 97.8	6.06	0.973			114.9	8.17	0.979
	3.78	339	101.1	6.36	0.947	3.84	312	121.8	8.72	0.947
			104.6	6.67	0.959			125.7	9.08	0.954
	9.48	332	91.8	5.62	0.972	9.40	310	155.8	11.91	0.926
			94.9	5.90	0.971			160.0	12.29	0.936
	19.38	340	93.6	5.67	0.966	19.10	304	161.0	12.55	0.931
			96.4	5.92	0.975			165.4	12.96	0.939
	30.01	348	96.6	5.82	0.970	30.70	294	185.9	15.17	0.934
			99.1	6.04	0.978			190.0	15.56	0.941
	38.27	347	97.6	5.92	0.976	39.00	297	191.2	15.58	0.974
			99.8	6.12	0.983			193.2	15.70	0.977

Table 2. The values of kinetic quantities of willow (*Salix*) with different temperature rates and with a sample mass of approx. 10 mg. a) Eq (2) b) Eq (1)Taulukko 2. *Salix*:n kineettisten suureiden arvot lämpötilan eri nostonopeuksilla. Näytteen massa on ollut noin 10 mg.

Sample	in nitrogen				in mixed gas					
	heating rate (°C/min)	T _c (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.	heating rate (°C/min)	T _c (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.
Salix	0.5	291	a) 91.0	4.88	0.954	0.5	253	126.9	9.25	0.976
			b) 93.6	5.13	0.966			129.1	9.48	0.981
	1.0	311	93.3	5.08	0.962	1.0	270	137.1	10.15	0.945
			96.3	5.35	0.971			140.5	10.49	0.952
	2.0	316	92.5	5.23	0.960	2.0	276	120.4	8.65	0.955
			95.5	5.50	0.970			123.6	8.97	0.963
	2.5	314	93.5	5.44	0.946	2.5	285	128.3	9.31	0.945
			96.8	5.75	0.960			131.8	9.66	0.954
	5.0	318	91.7	5.52	0.970	5.0	297	141.5	11.35	0.932
			93.8	5.71	0.979			153.0	11.68	0.940
	10.0	332	91.8	5.62	0.962	10.0	310	155.8	11.91	0.926
			94.9	5.90	0.971			160.0	12.29	0.936
	20.0	347	92.8	5.79	0.960	20.0	314	147.5	11.34	0.944
			95.8	6.06	0.971			150.7	11.65	0.949
	25.0	365	95.9	5.92	0.970	25.0	313	154.5	12.12	0.948
			98.5	6.14	0.978			158.2	12.45	0.955

Table 3. The values of E* and log A for willow.

Taulukko 3. *Salix*-näytteen E*:n ja log A:n arvot.

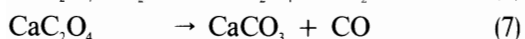
Quantity	in nitrogen		in mixed gas		Reaction
	log A or E* vs. mass	log A or E* vs. heating rate	log A or E* vs. mass	log A or E* vs. heating rate	
log A	11.2 ± 1.1	10.9 ± 1.9	10.7 ± 1.1	9.7 ± 0.6	(6)
	20.6 ± 0.8	20.8 ± 1.3	24.7 ± 1.5	25.9 ± 1.6	(7)
E*	109.9 ± 5.7	106.7 ± 15.2	106.3 ± 6.3	96.1 ± 4.0	(6)
	333.1 ± 12.2	335.5 ± 17.5	385.7 ± 23.9	400.7 ± 22.8	(7)

Table 4. The values of kinetic quantities of calcium oxalate monohydrate with different sample masses and with a temperature rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

Taulukko 4. Kalsiumoksaatti-monohydraatin kineettisten suureiden arvot eri näytemäärillä lämpötilan nousunopeudella $10\text{ }^{\circ}\text{C min}^{-1}$.

	in nitrogen				in mixed gas					
	mass (mg)	T_s ($^{\circ}\text{C}$)	E^* ($\text{kJ} \cdot \text{mol}^{-1}$)	log A	regression coeff.	mass (mg)	T_s ($^{\circ}\text{C}$)	E^* ($\text{kJ} \cdot \text{mol}^{-1}$)	log A	regression coeff.
reaction (6)	1.79	143	a) 117.4	12.86	0.993	1.85	139	114.5	12.63	0.990
			b) 117.8	12.92	0.994			115.6	12.78	0.992
	3.95	146	107.5	11.48	0.987	3.75	148	105.1	11.11	0.986
			108.5	11.61	0.990			106.1	11.24	0.990
	9.70	172	105.2	10.37	0.995	9.75	155	98.3	10.01	0.994
			105.7	10.42	0.998			99.0	10.10	0.997
	19.60	177	116.9	11.62	0.992	19.78	179	102.8	9.87	0.998
			116.4	11.56	0.991			103.2	9.92	0.998
	30.05	174	104.6	10.23	0.996	30.50	183	112.6	10.92	0.996
			104.7	10.25	0.997			112.4	10.90	0.997
39.40	183	107.3	10.29	0.996	39.50	187	103.0	9.68	0.990	
		106.6	10.21	0.996			103.2	9.69	0.992	
reaction (7)	1.79	490	329.6	20.60	0.990	1.85	483	374.8	23.99	0.998
			329.7	20.61	0.994			375.5	24.04	0.998
	3.95	493	325.7	20.24	0.995	3.75	483	368.1	23.53	0.994
			325.9	20.25	0.998			368.4	23.55	0.993
	9.70	498	342.9	21.28	0.996	9.75	473	368.0	23.87	0.994
			344.0	21.35	0.993			367.4	23.83	0.999
	19.60	499	352.7	21.91	0.995	19.78	493	426.5	27.22	0.988
			352.8	21.93	0.996			425.9	27.18	0.993
	30.05	497	322.9	19.92	0.994	30.50	487	402.6	25.79	0.967
			323.3	19.95	0.997			405.0	25.96	0.976
39.40	503	324.6	19.87	1.000	39.50	492	371.3	23.44	0.937	
		323.4	19.79	0.998			375.4	23.72	0.939	

In the case of the thermal decomposition of calcium oxalate monohydrate we investigated the following reaction stages



In the reaction (6) the theoretical loss of mass is 12.33 %, we obtained in an average 12.13 %. In the reaction (7) the figures were 19.77 % and 19.52 %, respectively.

Tables 4 and 5 show the results of the measurements and in the Table 6 are the mean values of E^* and log A obtained as average results from different methods of calculations.

In those reactions the T_s -temperatures increase both in nitrogen and mixed gas atmospheres while the temperature rate and the mass are increased. When the temperature rate increases, a slight decrease in the values of E^* and log A can be observed and when the mass is increased, the values remain constant in either atmospheres.

Table 7 presents the values of activation energies as determined by several authors corresponding to the reactions (6) and (7).

The measuring accuracy of our equipment with respect to temperature is approximately

$\pm 2\text{K}$ and with respect to mass an average of $\pm 0.2\%$. Combined these cause an error of $\pm 5\%$ to the value of the activation energy. Keeping this in mind the results obtained for the activation energy of the willow in nitrogen atmosphere are well within the error limits established. Further, this is also evident for the mixed gas atmosphere as a function of the temperature ratio, when the ratio is $5\text{K} \cdot \text{min}^{-1}$ or more. In this case only the values of log A and E^* for the reactions of willow in mixed gas atmosphere obeyed the mathematical equation as a function of mass.

The deviations of the values of E^* for calcium oxalate are close to the instrumental deviations, the average deviation is about $\pm 6\%$. The activation energies thus remain constant with respect of temperature rate and mass in the range investigated. If we calculate the mean for the value of E^* using the results reported by several authors for reaction (6) in the case of calcium oxalate, we obtain $99\text{ kJ} \cdot \text{mol}^{-1}$, a value very similar to our figures.

Although the reaction orders vary between 0.65 and 1.2 and the atmosphere is altered, the temperature rate is in the range from 3.45 to $10\text{ K} \cdot \text{min}^{-1}$ and the masses from 10 to

Table 5. The values of kinetic quantities of calcium oxalate monohydrate with different temperature rates and with a sample mass of approx. 10 mg.

Taulukko 5. Kalsiumoksaalaatti-monohydraatin kineettisten suureiden arvot lämpötilan eri nostonopeuksilla. Näytteen massa on ollut noin 10 mg.

Sample	in nitrogen				in mixed gas					
	heating rate (°C/min)	T _s (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.	heating rate (°C/min)	T (°C)	E* (kJ · mol ⁻¹)	log A	regression coeff.
reaction (6)	0.5	110	171.0	20.36	0.996	0.5	113	195.3	23.52	0.979
			171.0	20.36	0.998			196.0	23.62	0.981
	1.0	121	142.5	16.14	0.980	1.0	127	147.1	16.46	0.967
			143.6	16.29	0.983			148.5	16.64	0.971
	2.0	135	129.1	14.00	0.991	2.0	131	130.8	14.40	1.000
			129.9	14.11	0.993			130.9	14.41	0.999
	2.5	131	114.9	12.39	0.992	2.5	123	104.8	11.33	0.998
			115.1	12.41	0.993			104.3	11.26	0.998
	5.0	152	127.9	13.55	0.992	5.0	146	99.4	10.13	0.981
			128.7	13.66	0.993			101.0	10.33	0.985
	10.0	172	105.2	10.37	0.995	10.0	155	98.3	10.01	0.994
			105.7	10.42	0.998			99.0	10.10	0.997
	20.0	173	92.5	9.10	0.995	20.0	176	93.7	9.16	1.000
			92.7	9.11	0.995			93.8	9.17	0.999
	25.0	181	103.9	10.34	0.996	25.0	169	91.8	9.22	0.997
103.2			10.26	0.996	91.8			9.21	0.999	
reaction (7)	0.5	428	319.9	20.63	0.993	0.5	432	416.0	27.72	1.000
			320.4	20.67	0.997			414.3	27.60	0.996
	1.0	445	308.7	19.52	0.995	1.0	450	427.2	28.05	0.997
			309.9	19.54	0.997			426.4	27.99	0.999
	2.0	459	301.3	18.84	0.995	2.0	454	410.0	26.93	0.995
			301.8	18.87	0.994			410.9	26.99	0.993
	2.5	462	298.0	18.60	0.975	2.5	446	373.6	24.68	0.998
			301.0	18.82	0.997			371.8	24.55	0.996
	5.0	486	339.5	21.12	0.991	5.0	472	414.2	26.89	0.996
			340.4	21.18	0.993			415.0	26.95	0.998
	10.0	498	342.9	21.28	0.996	10.0	473	368.0	23.87	0.994
			344.0	21.35	0.993			367.4	23.83	0.999
	20.0	507	348.3	21.67	0.996	20.0	490	417.4	27.01	0.997
			349.1	21.72	0.993			417.9	27.04	0.996
	25.0	518	309.7	18.83	0.995	25.0	493	416.3	26.91	0.981
309.7			18.83	0.996	417.7			27.02	0.988	

423 mg, they do not seem to have an influence on the values of activation energies. The results now obtained are supported by the fact that in practice the temperature rate and the mass have only a minor influence. Our previous studies with peat confirm this deduction (Tummavuori et al. 1978, Part I).

When we inspect reaction (7), the calculated mean from the results of several authors for E* is 299 kJ · mol⁻¹. The deviations in reaction orders, atmospheres, temperature rates and masses are the same

order of magnitude as were found in reaction (6), although the deviation in values of the activation energies is larger. The reason may be that the reactions in high temperatures, being more complicated than reaction (6), are in a larger extent affected by the sample treatment, the instrumental parameters and the methods of calculations. Our result for the activation energy exceeds the mean value. This result, however, is similar to results obtained previously for cellulose (Tummavuori et al. 1978, Part II and references cited therein). We

Table 6. The values of E* and log A for calcium oxalate monohydrate.

Taulukko 6. Kalsiumoksaalaatti-monohydraatin E:n ja log A:n arvot.*

Quantity	In nitrogen		In mixed gas	
	log A or E* vs. mass	log A or E* vs. heating rate	log A or E* vs. mass	log A or E* vs. heating rate
log A	6.0 ± 0.3	5.6 ± 0.4	log A = 0.20 m + 8.9 r = 0.889	log A = 26.2 ± 1.6
E*	97.4 ± 3.3	94.2 ± 1.5	E* = 2.0 m + 121 r = 0.944	E* = 404 ± 24

Table 7. Some values of kinetic quantities for calcium oxalate monohydrate as determined by several authors.

Taulukko 7. Eri tutkijoiden määrittämiä kineettisten suureiden arvoja kalsiumoksalaatti-monohydraatille.

Quantity	in nitrogen log A or E* vs. mass	log A or E* vs. heating rate	in mixed gas log A or E* vs. mass	log A or E* vs. heating rate	Reaction
log A	11.2 ± 1.1	10.9 ± 1.9	10.7 ± 1.1	9.7 ± 0.6	(6)
	20.6 ± 0.8	20.8 ± 1.3	24.7 ± 1.5	25.9 ± 1.6	(7)
E*	109.9 ± 5.7	106.7 ± 15.2	106.3 ± 6.3	96.1 ± 4.0	(6)
	333.1 ± 12.2	335.5 ± 17.5	385.7 ± 23.9	400.7 ± 22.8	(7)

	Activation energy (kJ · mol ⁻¹)	Reaction order	Atmosphere	Heating rate °C/min	Samples mass mg	References
Reaction (6)	92.0	1.0	air	10	423	Freeman 1958
	91.1—98.2	0.93—1.0	air	—	—	Segal 1976a
	84.4	—	—	—	—	Horowitz 1963
	89.5	0.71	air	3.45	100	Coats 1964
	115.8	1.0	—	8	160	Dharwadkar 1969a
	99.2—115.0	0.65	nitrogen	10	10	Nair 1978
	91.1	1.2	—	—	—	Segal 1976b
	96.1	1.1	—	—	—	Segal 1976b
	104.5	0.9	air	10	35	Subramanian 1969
	112.9	1	helium	10	20	Wendlandt 1961
	92.8	1	—	8	160	Dharwadkar 1969b
	94.1	1	—	8	160	Dharwadkar 1969b
	99.8	0.65	nitrogen	10	10	Ninan 1979
	99	1	air	10	10	This work
	105	1	N ₂	10	10	This work
Reaction (7)	309.3	0.7	air	10	423	Freeman 1958
	259.2	0.38	air	3.14	100	Coats 1964
	236.8—263.8	0.50	nitrogen	10	10	Nair 1978
	355.3	1	helium	10	20	Wendlandt 1961
	326.0	1	air	12—140	300	Ozawa 1965
	236.8	0.50	nitrogen	10	10	Ninan 1979
	368	1	air	10	10	This work
	344	1	nitrogen	10	10	This work

conclude, that this similarity has arisen from technical reasons. We have computed the reaction orders and the activation energies for the reactions (6) and (1) with the approximate methods as proposed by Broido and Coats and Redfern (Broido, 1969, Coats and Redfern 1964). We also used the integration method presented by Balarin in order to achieve an improved accuracy (Balarin 1976). We noticed, however, that this improvement produced a relatively small gain in the results for the kinetic quantities (Tummauori and Suontamo 1979).

For reaction (6) using a 10 mg sample size and the temperature rate of 10 K · min⁻¹, we obtained the following results: the reaction order = 1.00, the E* (mean) = 104 kJ · mol⁻¹ and 0.998, respectively.

It seems obvious in the light of these results and the results presented in Table 7 that the significance of the reaction order is surprising-

ly small and its content with the values other than unity is rather obscure.

The attempt to solve the dependence of the kinetic quantities on the temperature rate of the mass successfully produced instrumental parameters, as long as the measurements are made with normal, commercially available instruments where the temperature is registered with the thermoelement. Several authors have claimed that if the exact kinetics of the decomposition reaction is unknown, the calculated kinetic values have no merit (Garn 1976).

Our impression is, that if the investigations are performed with the same instrument using the same principles in the calculation, comparable results are obtainable.

This is supported by results reported in this series concerning solid fuels, since the results are supported in many occasions by practical experience we feel their presentation is logical. (Tummauori et al., Parts II—X, 1979).

REFERENCES

- Balarin, M. 1977: — Improved Approximations of the Exponential Integral in Tempering Kinetics. — *J. Thermal. Anal.* 12: 169—177.
- Broido, A. 1969: — A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data. — *J. Polymer Sci. A2*, 7: 1761—1773.
- Coats, A. W. and Redfern, J. P. 1964: — Kinetic Parameters from Thermogravimetric Data. — *Nature* 201: 68—69.
- Dharwadkar, S. R. and Karkhanawala, M. D. 1969 a: — *Thermal Analysis*, vol. II Academic Press, New York; 1049.
- Dharwadkar, S. R. and Phadnis, A. B. 1969 b: — Kinetics of Thermal Dehydration of Calcium Oxalate Monohydrate from Dynamic TG Curves. — *Ind. J. Chem.*: 1032—1034.
- Freeman, E. S. and Carroll, B. 1958: — The Application of Thermoanalytical Techniques to Reaction Kinetics. Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate. — *J. Phys. Chem.* 62: 394—397.
- Garn, P. D. 1976: — The Kinetic Compensation Effect. — *J. Thermal Anal.* 10: 99—102.
- Horowitz, H. H. and Metzger, G. 1963: — A New Analysis of Thermogravimetric Traces. — *Anal. Chem.* 35: 1464—1468.
- Keatch, C. J. and Dollimore, D. 1975: — *An Introduction to Thermogravimetry*, Heyden and Son, London: 30.
- MacCallum, J. R. and Tanner, J. 1970: — The Kinetics of Thermogravimetry. — *Eur. Polym. J.* 6: 1033—1039.
- Nair, C. G. R. and Ninan, K. N. 1978: — Thermal Decomposition Studies. Part X. Thermal Decomposition Kinetics of Calcium Oxalate Monohydrate — Correlations with Heating Rate and Sample Mass. — *Thermochimica Acta* 23: 161—169.
- Ninan, K. N. and Nair, C. G. R. 1976: — Thermal Decomposition Kinetics. Part IX. A Study of Thermal Decomposition of Sodium Tetraperthyl Borate. — *Thermochimica Acta* 15: 345—353.
- Ninan, K. N. and Nair, C. G. R. 1979: — Thermal Decomposition Kinetics, Part XI. Mechanism of Thermal Decomposition of Calcium Oxalate Monohydrate from a Thermogravimetric Study — The Effects of Heating Rate and Sample Mass on Kinetic Parameters from Mechanistic Equations. — *Thermochimica Acta* 30: 25—35.
- Oswald, H. R. and Wiedemann, H. G. 1977: — Factors Influencing Thermoanalytical Curves. — *J. Therm. Anal.* 12: 147—168.
- Ozawa, T. 1965: — A New Method of Analyzing Thermogravimetric Data. — *Bull. Chem. Soc. Jap.* 38: 1881—1886.
- Segal, E. and Vlody, M. 1976 a: — Non-isothermal Kinetics with Non-linear Temperature Programme. — *Thermochimica Acta* 16: 115—120.
- Segal, E. and Fatu, D. 1976b: — Some Variants of the Freeman-Carroll Method. — *J. Thermal. Anal.* 9: 65—69.
- Subramanian, M. S., Singh, R. N. and Sharma, H. D. 1969: — Reaction Kinetics of Some Actinide Oxalates by Differential Thermal Analysis. — *J. Inorg. Nucl. Chem.* 31: 3789—3795.
- Tummavuori, J., Venäläinen, H. and Nyrönen, T. 1978: — The Usability of the Thermogravimetry in Fuel Research. Part I. On the Applications in Peat Research. — *Suo* 29: 33—38.
- Tummavuori, J., Venäläinen, H. and Nyrönen, T. 1978: — The Usability of Thermogravimetry in Fuel Research. Part II. On the Kinetics of Different Peat Types. — *Suo* 29: 59—67.
- Tummavuori, J., Venäläinen, H. and Nyrönen, T. 1978: — The Usability of the Thermogravimetry in Fuel Research. Part III. Comparison of the Kinetics of the Pyrolysis of Solid Fuels. — *Suo* 29: 99—104.
- Tummavuori, J., Venäläinen, H. and Nyrönen, T. 1979: — The Usability of the Thermogravimetry in Fuel Research. Part IV. The Effect of the Reduced Pressure on the Pyrolysis. — *Suo* 30: 1—5.
- Tummavuori, J., Venäläinen, H. and Nyrönen, T. 1979: — The Usability of the Thermogravimetry in Fuel Research. Part V. On the Kinetics of the Pyrolysis of Materials Suitable for Fuel. — *Suo* 30: 65—69.
- Tummavuori, J. and Suontamo, R. 1979: — The Thermal Decomposition of Copper(II) Acetate, Its Mono-, Di-, and Trichloro Derivatives, and Copper(I) and Copper(II) Chlorides. — *Finn. Chem. Lett.* 1979: 176—181.
- Wendlandt, W. W. 1961: — Reaction Kinetics by Differential Thermal Analysis. — *J. Chem. Ed.* 38: 571—573.

YHTEENVETO:

TERMOGRAVIMETRIAN KÄYTTÖ KIINTEIDEN POLTTOAINEIDEN
TUTKIMUKSISSA. OSA VIII. MASSAN JA LÄMPÖTILAN NOSTONOPEUDEN
VAIKUTUS KINEETTISTEN SUUREIDEN ARVOIHIN

Olemme tutkineet massan määrän ja lämpötilan nostonopeuden vaikutuksia termogravimetrinen kineettisten suureiden arvoihin.

Puolimikrotyöskentelyssä ainemäärät vaihtelevat muutamasta milligrammasta grammaan. Viime aikoina 10 mg:n massa näyttää vakiintuneen yleisimmäksi määräksi.

Vastaavasti lämpötilan nostonopeuden vaihtelu välillä 0.5 °C/min:sta aina 100 °C/min:iin asti.

Yleisesti on uskottu, että suhteellisen suuri massan määrä (satoja milligrammoja) ja hidas lämpötilan nostonopeus (optimi 3 °C/min) antavat parhaiten toistettavat ja oikeat tulokset. Lisäksi ote on esitetty massan koon ja lämpötilan nostonopeuden matemaattisia riippuvuuksia termodynaamisista suureista.

Tutkimuksiimme käytimme hienoa puupölyä (paju) ja kalsiumoksalaattia. Pajupöly on suhteellisen homogeeninen luonnonnäyte ja kalsiumoksalaattia on käytetty usein termogravimetrian testausmenetelmässä. Mittaustulokset on esitetty taulukoissa 1 ja 2 sekä 4 ja 5.

Laitteiston mittaustarkkuus on ± 2 K ja massan mittaustarkkuus ± 0.2 %. Kun huomioimme mittaustarkkuuden, niin ainoastaan pajun kineettiset suureet E^* ja $\log A$ seoskaasussa noudattivat heikokosti lineaarista riippuvuutta massan suhteen mutta ei enää lämpötilan nostonopeuden suhteen (Taulukko 3). Muissa olosuhteissa massan ja lämpötilan nos-

tonopeuksien vaihteluilla ei ollut merkitystä.

Taulukossa 6 ovat saamamme tulokset kalsiumoksalaatille ja taulukossa 7 ovat useiden muidenkin tutkijoiden saamat tulokset reaktioille (6) ja (7). Reaktio (6):n suurin ja E^* :n arvot ovat ± 6 % sisällä, joka aiheutuu mittausten epätarkkuudesta. Tämä on hämmästyttävää, sillä lämpötilan nostonopeus on vaihdellut välillä 3.45—10 °C/min ja massa välillä 10—423 mg. Myöskin on todettavissa reaktion kertaluvuissa huomattavaa vaihtelua, joka ei ole vaikuttanut E^* :n arvoihin. Reaktio (7) tutkimuksissa massan ja lämpötilan vaihtelurajat ovat olleet suurinpiirtein samat kuin reaktiossa (6). E^* arvoissa on nyt enemmän hajontaa, joka selittyy lähinnä lämpötilan mittaustarkkuuden huonontumisesta korkeamassa lämpötiloissa, joissa lämmön jakautuminen on helposti myös epätasaista.

Yhteenvetona voidaan todeta, että massan määrän ja lämpötilan nostonopeudella ei juuri ole vaikutusta kineettisten suureiden arvoihin ja poikkeamat lukuarvoista johtuvat laiteeroista ja laitteiden tulee parantua huomattavasti, ennenkuin pystymme osoittamaan matemaattisia riippuvuuksia eri suureiden välillä. Yllätys oli myöskin reaktion kertaluvojen vähäinen merkitys kineettisiin suureihin, mikä vain osin on odotettavissa perusyhtälöiden muodon perusteella.