Thermochimica Acta, 23 (1978) 17–27

CHECKING OF MATHEMATICAL CALCULATION METHODS FOR THE DETERMINATION OF KINETIC PARAMETERS FROM NON-ISOTHERMAL MEASUREMENTS BY TEST FUNCTIONS

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(Received 21 March 1977)

ABSTRACT

The applied computing programs are checked by means of test values from theoretical models. First-order kinetics, the Avrami equation and the 2-dimensional diffusion equation have been calculated as theoretical values. The computer calculation was carried out both for the total reaction and for individual reaction intervals.

For the calculation of kinetic parameters and the distinction between the various models, in principle, the integral method should be used. The calculation does not give any answer to the question whether there exists another equation not involved in the models selected, which describes the processes better. If there is no indication of the reaction, it should first be checked by the differential method. The correlation coefficient does not allow the individual model equations to be distinguished with statistical significance.

INTRODUCTION

In recent years, several methods have been reported which enable the kinetic parameters to be calculated from the results of non-isothermal analyses. For the user of these methods, at present, it is not yet possible to select an appropriate evaluation method on the basis of decision criteria. The object of this investigation was to obtain test values from theoretical models, which allow the performance of the applied computing programme to be checked. This computing test was intended to be the first step in mathematical data evaluation. The mathematical calculations presuppose the validity of some kinetic model equations that describe the processes of diffusion, nucleation and phase-boundary reaction with adequate accuracy. In an earlier paper[1] it has already been suggested that no information about the "most probable" reaction mechanism can be obtained by comparing the experimental values with the model equations by means of the correlation coefficients. Furthermore, it has become

TABLE 1

THEORETICAL α-VALUES FOR FIRST ORDER-KINETICS

T	α	$\alpha' = d\alpha/dT$	T	α	$\alpha' = d\alpha/dT$
600	.91267E−03	.38272E−04	756	.22985E+00	.53147E−02
606	.11943E−02	.49089E−04	762	.26693E+00	.59205E−02
612	.15550E−02	.62651E−04	768	.30805E+00	.65242E−02
618	.20144E−02	.79575E−04	774	.35314E+00	.71035E−02
624	.25974E−02	.10060E−03	780	.40193E+00	.76313E−02
630	.33324E−02	.12657E−03	786	.45399E+00	.80767E−02
636	.42558E−02	.15855E−03	792	.50868E+00	.84064E−02
642	.54107E−02	.19771E−03	798	.56512E+00	.85877E−02
648	.68486E−02	.24547E−03	804	.62223E+00	.85916E−02
654	.86312E−02	.30345E−03	810	.67875E+00	.83967E−02
660	.10832E−01	.37349E−03	816	.73334E+00	.79942E−02
666	.13536E−01	.45774E−03	822	.78460E+00	.73912E−02
672	.16845E−01	.55858E−03	828	.83129E+00	.66134E−02
678	.20877E−01	.67869E−03	834	.87237E+00	.57047E−02
684	.25770E−01	.82101E−03	840	.90715E+00	.47235E−02
690	.31678E−01	.98876E−03	846	.93534E+00	.37364E−02
696	.38783E−01	.11853E−02	852	.95713E+00	.28089E−02
702	.47285E−01	.14142E−02	858	.97310E+00	.19951E−02
708	.57410E−01	.16790E−02	864	.98413E+00	.13304E−02
714	.69409E−01	.19831E−02	870	.99125E+00	.82704E−03
720	.83551E−01	.23294E−02	876	.99553E+00	.47557E−03
726	.10012E+00	.27201E−02	882	.99790E+00	.25084E−03
732	.11943E+00	.31566E−02	888	.99911E+00	.12023E−03
738	.14178E+00	.36383E−02	894	.99966E+00	.51843E−04
744	.16746E+00	.41628E−02	900	.99988E+00	.19994E−04
750	.19673E+00	.47245E−02	906	.99996E+00	.66954E−05
			912	.10000E+01	.19556E−05

evident that several reaction equations very well describe the reaction range by the criteria so far used.

For the integral method, it could be shown[2] that on the basis of the residual dispersion a statistically significant distinction between several kinetic models can be made.

1. CALCULATION OF THEORETICAL TG-CURVES

In this investigation the theoretical α-values have been calculated for the following reaction models (cf. Tables 1–3):

1. kinetics of first order

$$\frac{d\alpha}{dt} = k'(1 - \alpha) \tag{1}$$

2. Avrami equation with

$$\frac{d\alpha}{dt} = k''(-\ln(1 - \alpha))^{\frac{1}{2}}(1 - \alpha) \tag{2}$$

TABLE 2

THEORETICAL α-VALUES FOR TWO-DIMENSIONAL DIFFUSION

T	α	$\alpha' = d\alpha/dT$	T	α	$\alpha' = d\alpha/dT$
500	.29047E−02	.85762E−04	650	.11939E+00	.20886E−02
506	.35103E−02	.10150E−03	656	.13365E+00	.22891E−02
512	.42055E−02	.12015E−03	662	.14928E+00	.25027E−02
518	.50447E−02	.14090E−03	668	.16635E+00	.27296E−02
524	.60194E−02	.16481E−03	674	.18496E+00	.29696E−02
530	.71624E−02	.19183E−03	680	.20520E+00	.32227E−02
536	.84899E−02	.22248E−03	686	.22714E+00	.34882E−02
542	.10029E−01	.25709E−03	692	.25088E+00	.37658E−02
548	.11807E−01	.29602E−03	698	.27649E+00	.40546E−02
554	.13852E−01	.33969E−03	704	.30406E+00	.43532E−02
560	.16191E−01	.38873E−03	710	.33362E+00	.46603E−02
566	.18875E−01	.44321E 03	716	.36525E+00	.49736E−02
572	.21926E−01	.50396E−03	722	.39897E+00	.52911E−02
578	.25395E−01	.57132E−03	728	.43482E+00	.56091E−02
584	.29322E−01	.64587E−03	734	.47277E+00	.59240E−02
590	.33760E−01	.72805E−03	740	.51280E+00	.62310E−02
596	.38760E−01	.81841E−03	746	.55484E+00	.65238E−02
602	.44376E−01	.91753E−03	752	.59877E+00	.67950E−02
608	.50667E−01	.10260E−02	758	.64443E+00	.70349E−02
614	.57700E−01	.11442E−02	764	.69157E+00	.72318E−02
620	.65538E−01	.12728E−02	770	.73986E+00	.73693E−02
626	.74250E−01	.14123E−02	776	.78884E+00	.74256E−02
632	.83915E−01	.15632E−02	782	.83787E+00	.73694E−02
638	.94606E−01	.17259E−02	788	.88607E+00	.71501E−02
644	.10640E+00	.19010E−02	794	.93208E+00	.66751E−02
			800	.97354E+00	.57006E−02

3. two-dimensional diffusion equation

$$\frac{d\alpha}{dt} = k''(-\ln(1-\alpha))^{-1} \qquad (3)$$

The calculation was carried out with the following kinetics or reaction parameters given: $E = 30$ kcal mol^{-1}; $Z = 5.5 \times 10^4$ sec^{-1}; range of temperatures from 500 K to 1000 K; heating rate: 1 K min^{-1}.

For the integral and differential method the theoretical α-values were put into a computing programme by use of 11 model equations and the results were compared with each other.

The calculation was carried out both for the total reaction range and for individual reaction intervals. An example is given in Tables 4–7. With the differential method also the order of reaction is calculated, whereas with the integral method the comparison is performed with several reaction orders given.

As is shown in Table 4, despite of very low differences between the kinetic parameters, the real reaction mechanism can be exactly determined on the basis of the residual dispersion by the integral method.

TABLE 3

THEORETICAL α-VALUES FOR AVRAMI-EQUATION ($n = 2/3$)

T	α	$\alpha' = d\alpha/dT$	T	α	$\alpha' = d\alpha/dT$
750	.38957E-03	.31369E-04	816	.81967E-01	.53421E-02
752	.46468E-03	.37221E-04	818	.94625E-01	.60939E-02
754	.55361E-03	.44112E-04	820	.10905E+00	.69316E-02
756	.65946E-03	.52265E-04	822	.12543E+00	.78592E-02
758	.78464E-03	.61856E-04	824	.14398E+00	.88796E-02
760	.93317E-03	.73161E-04	826	.16490E+00	.99927E-02
762	.11084E-02	.86441E-04	828	.18838E+00	.11195E-01
764	.13153E-02	.10203E-03	830	.21465E+00	.12480E-01
766	.15595E-02	.12033E-03	832	.24385E+00	.13833E-01
768	.18475E-02	.14179E-03	834	.27611E+00	.15235E-01
770	.21873E-02	.16696E-03	836	.31153E+00	.16660E-01
772	.25871E-02	.19641E-03	838	.35012E+00	.18070E-01
774	.30567E-02	.23083E-03	840	.39179E+00	.19419E-01
776	.36090E-02	.27104E-03	842	.43634E+00	.20651E-01
778	.42572E-02	.31792E-03	844	.48346E+00	.21703E-01
780	.50178E-02	.37273E-03	846	.53267E+00	.22505E-01
782	.59088E-02	.43648E-03	848	.58333E+00	.22982E-01
784	.69521E-02	.51066E-03	850	.63463E+00	.23069E-01
786	.81723E-02	.59687E-03	852	.68566E+00	.22705E-01
788	.95980E-02	.69695E-03	854	.73535E+00	.21855E-01
790	.11263E-01	.81301E-03	856	.78260E+00	.20513E-01
792	.13204E-01	.94738E-03	858	.82636E+00	.18710E-01
794	.15466E-01	.11028E-02	860	.86566E+00	.16520E-01
796	.18096E-01	.12822E-02	862	.89975E+00	.14060E-01
798	.21155E-01	.14891E-02	864	.92822E+00	.11476E-01
800	.24736E-01	.17272E-02	866	.95095E+00	.89348E-02
802	.28822E-01	.20007E-02	868	.96820E+00	.65938E-02
804	.33587E-01	.23141E-02	870	.98059E+00	.45796E-02
806	.39096E-01	.26727E-02	872	.98893E+00	.29697E-02
808	.45456E-01	.30817E-02	874	.99416E+00	.17819E-02
810	.52784E-01	.35470E-02	876	.99717E+00	.97935E-03
812	.61212E-01	.40747E-02	878	.99876E+00	.48743E-03
814	.70887E-01	.46710E-02	880	.99951E+00	.21689E-03

2. DISCUSSION

From the extensive test computations, the following generalizations as to the use of the integral and differential methods can be made:

(1) The integral method using theoretical α-values results in the given kinetic parameters both for the total reaction range and for individual intervals. With the differential method, for kinetics of first order (eqn (1)), we also obtain the theoretical values for the total reaction range and individual intervals. When initial and final values of α ($\alpha < 0.8$; $\alpha > 98$) are used in the calculation according to eqns (2) and (3), the kinetic parameters are distorted (cf. Table 8).

(2) By using the integral method with given theoretical α-values, the kinetic models can exactly be distinguished on the basis of the residual dispersion for the total range

TABLE 4

KINETIC PARAMETERS OBTAINED BY USING THEORETICAL α-VALUES FOR FIRST ORDER-KINETICS

α-range: 0.2–1.7%. T-range: 618–672 K

Name	*Integral method*						*Differential method*						
	n	E	ΔE	k_0	r[b]	$\sigma^2 \cdot 10^3$	n'[a]	Δn	E	ΔE	k_0	r	σ^2
phase	$^1/_3$	29.9	0.02	$4.9 \cdot 10^4$	100	$2.2 \cdot 10^{-4}$							
boundary	$^1/_2$	29.9	0.02	$4.9 \cdot 10^4$	100	$1.1 \cdot 10^{-4}$							
reaction	$^2/_3$	29.9	0.01	$5.45 \cdot 10^4$	100	$5.6 \cdot 10^{-5}$							
	1	30.0	0.002	$5.45 \cdot 10^4$	100	$1.9 \cdot 10^{-6}$	1.1	0.3	30.1	0.01	$6 \cdot 10^4$	100	$1.0 \cdot 10^{-4}$
	$^3/_2$	30.1	0.2	$5.45 \cdot 10^4$	100	$1.2 \cdot 10^{-4}$							
	2	30.1	0.04	$6 \cdot 10^4$	100	$5.9 \cdot 10^{-4}$							
Jander-eqn		62.1	10.1	$8.8 \cdot 10^{12}$	98.96	44.3							
Ginst.-Brounst.-eqn		58.9	13.1	$7.2 \cdot 10^{11}$	98.08	74.8							
one-dim. diffusion							1.1	0.3	62.1	0.01	—	100	$1.2 \cdot 10^{-1}$
two-dim. diffusion		63.0	14.4	$5.3 \cdot 10^{13}$	99.99	0.5	0.4	0.2	62.5	0.005	—	100	$2.6 \cdot 10^{-2}$
Avrami-eqn	$^1/_2$	13.7	0.02	2.03	100	$1.2 \cdot 10^{-4}$	1.3	0.3	13.9	0.01	2.5	100	$1.2 \cdot 10^{-1}$
	$^2/_3$	8.3	0.02	0.06	100	$2.2 \cdot 10^{-4}$	1.4	0.3	8.5	0.01	0.07	100	$1.2 \cdot 10^{-1}$

[a] The connection between n and n' is described in ref. 3: in the case of phase-boundary reaction $n = n'$; in the case of diffusional equations $n' = 0$; in the case of Avrami equations $n' = 1$.

[b] Correlation coefficient (%).

TABLE 5

KINETIC PARAMETERS OBTAINED BY USING THEORETICAL α-VALUES FOR FIRST ORDER-KINETICS

α-range: 16.7–56.5%. T-range: 744–798 K.

Name	*Integral method*						*Differential method*						
	n	E	ΔE	k_0	r	$\sigma^2 \cdot 10^3$	n'	Δn	E	ΔE	k_0	r	σ^2
phase boundary reaction	$^1/_3$	25.6	0.9	$2.2 \cdot 10^3$	99.94	$2.1 \cdot 10^{-1}$							
	$^1/_2$	26.7	0.8	$4.9 \cdot 10^3$	99.97	$1.2 \cdot 10^{-1}$							
	$^2/_3$	27.8	0.5	$1.1 \cdot 10^4$	99.99	$5.7 \cdot 10^{-2}$							
	1	30.0	0.002	$5.45 \cdot 10^4$	100	$5.6 \cdot 10^{-7}$	1.0	0.02	30.1	0.003	$6 \cdot 10^4$	100	$6.6 \cdot 10^{-7}$
	$^3/_2$	33.6	0.9	$7.3 \cdot 10^5$	99.97	$1.7 \cdot 10^{-1}$							
	2	37.5	1.9	$1.1 \cdot 10^7$	99.90	$7.6 \cdot 10^{-1}$							
Jander-eqn		58.6	1.0	$8 \cdot 10^{11}$	99.99	$2.1 \cdot 10^{-1}$							
Ginst.-Brounst.-eqn		55.6	1.7	$9.3 \cdot 10^{10}$	99.96	$5.8 \cdot 10^{-1}$							
one-dim. diffusion							1.4	0.06	62.6	0.03	—	100	$4.4 \cdot 10^{-6}$
two-dim. diffusion		54.2	2.0	$1.1 \cdot 10^{11}$	99.95	$8.3 \cdot 10^{-1}$	1.0	0.03	63.0	0.005	—	100	$2.9 \cdot 10^{-6}$
Avrami-eqn	$^1/_2$	13.5	0.02	1.7	100	$5.9 \cdot 10^{-5}$	1.0	0.02	13.7	0.002	2.0	100	$4.2 \cdot 10^{-7}$
	$^2/_3$	8.0	0.02	0.045	100	$1.1 \cdot 10^{-4}$	1.0	0.02	8.2	0.003	0.061	100	$4.8 \cdot 10^{-7}$

TABLE 6

KINETIC PARAMETERS OBTAINED BY USING THEORETICAL α-VALUES FOR FIRST ORDER-KINETICS

α-range: 73.3–99.1%. T-range: 816–870 K.

Name	Integral method						Differential method						
	n	E	ΔE	k_0	r	$\sigma^2 \cdot 10^3$	n'	Δn	E	ΔE	k_0	r	σ^2
phase	$^1/_3$	9.5	2.6	0.04	97.00	1.1							
boundary	$^1/_2$	13.1	2.5	0.55	98.59	0.93							
reaction	$^2/_3$	17.7	2.1	13.5	99.47	0.63							
	1	30.0	0.003	$5.45 \cdot 10^4$	100	$1.1 \cdot 10^{-6}$	1.0	0.02	29.9	0.01	$4.9 \cdot 10^4$	100	$1.9 \cdot 10^{-7}$
	$^3/_2$	57.0	6.3	$2.4 \cdot 10^{12}$	99.52	5.9							
	2	92.2	15.1	$1.3 \cdot 10^{22}$	98.94	34.1							
Jander-eqn		38.7	4.1	$2.2 \cdot 10^5$	99.56	2.5							
Ginst.-Brounst.-eqn		26.0	5.3	$5 \cdot 10^2$	98.35	4.3							
one-dim. diffusion							1.1	0.1	50.4	0.6	—	99.81	$2.8 \cdot 10^{-4}$
two-dim. diffusion		20.5	5.6	33.3	97.13	4.7	1.0	0.02	63.1	0.02	—	100	$3.2 \cdot 10^{-7}$
Avrami-eqn	$^1/_2$	13.3	0.02	1.5	100	$4.4 \cdot 10^{-5}$	1.0	0.02	13.4	0.02	1.7	100	$1.9 \cdot 10^{-7}$
	$^2/_3$	7.8	0.02	0.04	100	$7.8 \cdot 10^{-5}$	1.0	0.02	7.9	0.01	0.045	100	$2 \cdot 10^{-7}$

TABLE 7

KINETIC PARAMETERS OBTAINED BY USING THEORETICAL α-VALUES FOR FIRST ORDER-KINETICS

α-range: 0.2–95.7%. T-range: 618–852 K.

Name	*Integral method*						*Differential method*						
	n	E	ΔE	k_0	r	$\sigma^2 \cdot 10^3$	n'	Δn	E	ΔE	k_0	r	σ^2
phase	$^1/_3$	27.2	2.2	$6 \cdot 10^3$	99.68	21.5							
boundary	$^1/_2$	27.8	1.8	10^4	99.81	13.3							
reaction	$^2/_3$	28.5	1.2	$1.6 \cdot 10^4$	99.91	6.5							
	1	30.0	$5.7 \cdot 10^{-4}$	$5.45 \cdot 10^4$	100	$1.3 \cdot 10^{-6}$	1.0	0.07	30.1	0.004	$6 \cdot 10^4$	100	$2.4 \cdot 10^{-8}$
	$^3/_2$	32.6	2.3	$4 \cdot 10^5$	99.77	22.5							
	2	35.6	5.0	$4.4 \cdot 10^6$	99.06	110.4							
Jander-eqn		59.6	2.6	$1.3 \cdot 10^{10}$	99.91	30.4							
Ginst.-Brounst.-eqn		57.7	4.1	$3.2 \cdot 10^{11}$	99.76	73.5							
one-dim. diffusion							1.3	0.08	62.6	0.005	—	100	$3.2 \cdot 10^{-8}$
two-dim. diffusion		57.1	4.5	$5.9 \cdot 10^{11}$	99.70	89.1	0.9	0.07	62.6	0.004	—	100	$3.1 \cdot 10^{-8}$
Avrami-eqn	$^1/_2$	13.6	0.06	1.7	100	0.02	1.1	0.08	13.9	0.005	2.5	100	$3.2 \cdot 10^{-8}$
	$^2/_3$	8.1	0.08	0.05	100	0.03	1.1	0.08	8.4	0.005	0.066	100	$3.7 \cdot 10^{-8}$

TABLE 8

KINETIC PARAMETERS OBTAINED BY USING THEORETICAL α-VALUES FOR TWO-DIMENSIONAL DIFFUSION

α-range: 0.3–1.4%. T-range: 500–554 K.

Name	*Integral method*						*Differential method*						
	n	E	ΔE	k_0	r	$\sigma^2 \cdot 10^3$	n'	Δn	E	ΔE	k_0	r	σ^2
phase	$^1/_3$	13.9	0.05	1.5	100	$2.3 \cdot 10^{-3}$							
boundary	$^1/_2$	13.9	0.05	1.5	100	$2.6 \cdot 10^{-3}$							
reaction	$^2/_3$	13.9	0.05	1.5	100	$2.9 \cdot 10^{-3}$							
	1	13.9	0.06	1.5	100	$3.2 \cdot 10^{-3}$							
	$^3/_2$	13.9	0.06	1.5	99.99	$3.9 \cdot 10^{-3}$							
	2	13.9	0.07	1.5	99.99	$4.5 \cdot 10^{-3}$	−4.8	1.6	13.4	0.16	—	99.97	23.0
Jander-eqn		28.9	4.0	$6 \cdot 10^3$	99.25	15.6							
Ginst.-Brounst.-eqn		32.0	3.8	$1.3 \cdot 10^5$	99.45	14.0							
one-dim. diffusion							−7.3	1.6	29.1	0.02	—	99.95	2.5
two-dim. diffusion		30.0	0.1	$5.45 \cdot 10^4$	100	$1.2 \cdot 10^{-2}$	−7.6	1.6	29.1	0.16	—	99.95	25.0
Avrami-eqn	$^1/_2$	5.9	0.02	$0.83 \cdot 10^{-3}$	100	$2.5 \cdot 10^{-4}$	−3.3	1.5	5.6	0.15	—	98.86	23.0
	$^2/_3$	3.2	0.01	$1.2 \cdot 10^{-3}$	100	$1.2 \cdot 10^{-4}$	−2.8	1.5	3.0	0.15	—	96.30	23.0

and for small intervals (in this case with the exception of the diffusion equation). The correlation coefficient used in the differential method, even for the total reaction range, does not allow the individual model equations to be distinguished with statistical significance.

(3) In order to obtain a statistically significant distinction between the various models in any case, the reaction intervals must not be defined at random. The critical length of an interval which is sufficient for distinguishing the individual models depends on the position of the interval within the total reaction range.

(4) The calculation of the formal reaction order by the differential method serves to obtain an indication as to the validity of one or more of the kinetic model equations given.

The test results presented have shown that the applied computing programmes allow the determination of the kinetic parameters. At the same time the calculations indicate that the use of only one reaction equation, as has been done in many papers, is problematical. A statement as to the correctness of the selected model equation can be made only, if a comparison with other models has been carried out. With the test calculations carried out it could be demonstrated that by use of the integral method a statistically significant distinction between models becomes possible. The calculation, however, does not give any answer to the question whether there exists an equation not involved in the 11 models selected, which describes the process studied better.

By calculating the formal reaction order by use of the differential method, with the low and high α-values not taken into consideration, we can obtain an indication that none of the models applied describes the reaction. When we decide to use one evaluation method or the other, we also have to consider the expenses of programming and computing. For the differential method a computer of medium performance (memory capacity 32 K) was used. This memory capacity is relatively small for the calculation problem and, consequently, programming expenses were relatively high due to the use of external memories. Taking into account the formation of intervals[1], a computing time of about 30 min is required for a complete calculation with about 50 measuring points.

The calculations by the integral method are performed by use of a small computer (memory capacity 16 K). The programming expenses for one process of computation are considerably lower. Depending on the programming language (problem-oriented, interpretative) the computing time is about 2 to 3 times as long as that for the differential method with equal computation volume. For economic reasons, the calculation of k_0 by the differential method is expedient only for selected E and n. Within the programme for the integral method, all kinetic parameters can be calculated simultaneously.

In principle, the integral method causes a smoothing of the measured values, whereas the differential method cannot be used for α-values varying around a mean value, i.e., the latter is very susceptible to variations in reaction rate. It has to be checked whether the variation observed is due to an analytical error or to a real change in the reaction rate.

Comparison of both evaluation methods allows the following conclusions to be drawn:

For the calculation of kinetic parameters and the distinction between the various models, in principle, the integral method should be used.

If there are no indications as to the reaction course, it should first be checked by the differential method whether one of the model equations used by the integral method is valid.

In principle, the differential method is particularly susceptible to dispersion of the measured values because of the difference quotients applied. Its use is expedient only, if the limitations mentioned above are observed (especially when the initial and final values of α are not taken into account).

In conclusion it has to be pointed out that the physico-chemical aspects are not considered in this mathematical distinction of models In any case, the mathematical results obtained have experimentally to be checked with respect to their physico-chemical meaning.

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