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DIFFERENTIAL TECHNIQUES FOR THE KINETIC ANALYSIS OF DSC DATA

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ABSTRACT

A simple technique for the kinetic analysis of rate vs. time data from an isothermal DSC experiment is presented. Selected ascending or descending sections of the rate curve are fitted to $dq/dt = k(q_0 \pm q)^n$. Values for n are determined and their consistency tested by the ratios of times to reach reduced rates of reaction.

INTRODUCTION

The differential scanning calorimeter (DSC) measures differential power supplied to a specimen undergoing transformation. If the enthalpy of this transformation does not chenge with extent of reaction, then the power difference is linearly proportional to the reaction rate. Thus robust values of the reaction rate are obtained as a function of time without differentiation.

The kinetics of condensed phase reactions are usually quite complex. Therefore it is an advantage to analyze the differential rate equation as it is simpler than the integrated expression and is more often expressible in a closed mathematical form. Also the use of the differential rate equation avoids the necessity of determining initial or final values of the degree of advancement (integration limits).

In this paper we develop methods to be applied only to isothermal data. Programmed heating rate experiments can add considerable auxilliary knowlege about the detail of the kinetics of reactions, but isothermal experiments are usually necessary to determine the form of the rate expression without ambiguity.

Only a few efforts to fit data for solid state reactions with complex mathematical expressions have been successful. Therefore a different approach has been taken in this paper. We attempt to resolve complications by fitting limited ascending or descending portions of the rate curve with simple functions. In some cases, it will be possible to combine several of these asymptotic solutions to synthesize a more general equation for the total process. In any event, rate constants for a selected portion of a reaction can be compared. For example, rate constants can be obtained from data for several temperatures, and an activation energy calculated for a region of interest.

KINETIC ALALYSIS OF DSC DATA

The simple rate expression

$$dq/dt = k(q_0 \pm q)^n \tag{1}$$

is used for curve fitting where dq/dt is the rate of enthalpy change, t is the time from an arbitrary initial zero time, n is the order, k is the nth order rate constant, kq_0^n is the initial rate at t=0, and q is a running variable which need not be known.

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Eq. (1) with its three arbitrary parameters has considerable flexibility. It fits a wide selection of ascending rate curves when $n>0$ for $(q_0+q)^n$ and when $n<0$ for $(q_0-q)^n$. Conversely, it fits descending rate curves when $n>0$ for $(q_0-q)^n$ and when $n<0$ for $(q_0+q)^n$.

Elimination of $(q_0 \pm q)$ between equation (1) and its integrated form yields [1]

$$\ln(dq/dt) = \pm kt + \ln kq_0 \qquad (n=1) \qquad (2)$$

and

$$(dq/dt)^{1-n/n} = \mp(n-1)k^{1/n}t + k^{1-n/n}q_0^{1-n} \qquad (n \neq 1). \qquad (3)$$

Since dq/dt and t are obtained directly from the ordinate and the abscissa, respectively, of the DSC curve, one may plot various powers of the rate vs. time to determine a value of n which gives a linear relationship. However, the order, n, may be determined in a more objective manner which also tests its constancy over the range of interest. This is achieved by use of tables of ratios of times to reach reduced rates for various values of n [2].

The reduced rate, $R_1 = (dq/dt)_1/(dq/dt)_0$, is defined as the rate at time t_1 divided by the rate at an arbitrary zero time. From eqs. (2) and (3) the ratio of times, t_2/t_1, to reach reduced rates, R_2 and R_1, respectively is:

$$t_2/t_1 = \ln R_2/R_1 \qquad (n = 1) \qquad (4)$$

$$t_2/t_1 = (R_2^{1-n/n} - 1)/(R_1^{1-n/n} - 1) \qquad (n \neq 1). \qquad (5)$$

The initial rate is obtained from the amplitude of the DSC curve at zero time. For the case where the rate is decreasing with time, times to reach 95%, 85%, ..., 5% of the initial rate are measured and the ratios, t_{85}/t_{95}, t_{75}/t_{85}, ..., determined. The values for these ratios may be compared with values in Table I where ratios are given for selected values of n. For example, if t_{85}/t_{95} is 3.000, then the reaction is one-half order. Comparison of ratios at differing reduced rates will indicate whether n is constant or changes as the reaction proceeds.

When the initial rate is increasing, times for the rate to increase to 3/2, 2, 4, 8, ..., 256 its initial value may be determined and compared with values in Table II where ratios of times to reach ascending values of the initial rate are given for selected values of n.

This approximate value of n may be used to calculate the n which gives the best linear fit to eqs. (2) and (3). The parameters k and q_0 may then be calculated. This technique has been applied to the investigation of the kinetics of the cure of printing inks and resins [3,4]. It is obvious, of course, that this technique is not limited to DSC data and can be applied to data from any measurement technique.

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Table I.

Ratios of Times to Reach Reduced Rates for Various Orders

(descending rates)

Reduced Rate Ratios (100/100)

n	85/95	75/85	65/75	55/65	45/55	35/45	25/35	15/25	05/15
0.1	2.0781	1.2037	1.0588	1.0164	1.0039	1.0007	1.0001	1.0000	1.0000
0.3	2.7979	1.5492	1.2967	1.1863	1.1232	1.0815	1.0514	1.0285	1.0112
0.5	3.0000	1.6667	1.4000	1.2857	1.2222	1.1818	1.1538	1.1333	1.1176
0.7	3.0944	1.7240	1.4533	1.3408	1.2822	1.2502	1.2363	1.2423	1.2993
0.9	3.1489	1.7579	1.4856	1.3751	1.3210	1.2968	1.2966	1.3313	1.4897
1.0	3.1684	1.7701	1.4974	1.3878	1.3357	1.3147	1.3205	1.3685	1.5791
1.2	3.1980	1.7888	1.5154	1.4075	1.3586	1.3433	1.3593	1.4308	1.7413
1.5	3.2281	1.8079	1.5343	1.4281	1.3829	1.3739	1.4020	1.5017	1.9436
2.0	3.2586	1.8275	1.5536	1.4496	1.4085	1.4067	1.4486	1.5820	2.1948
3.0	3.2896	1.8475	1.5736	1.4719	1.4355	1.4419	1.4996	1.6727	2.5049
4.0	3.3052	1.8577	1.5838	1.4835	1.4495	1.4603	1.5267	1.7222	2.6858
5.0	3.3147	1.8638	1.5903	1.4905	1.4581	1.4717	1.5436	1.7533	2.8036
±∞	3.3529	1.8889	1.6154	1.5495	1.4938	1.5195	1.6154	1.8889	3.3529
-5.0	3.3919	1.9147	1.6417	1.5499	1.5318	1.5710	1.6945	2.0437	4.0503
-4.0	3.4018	1.9212	1.6485	1.5577	1.5417	1.5845	1.7155	2.0856	4.2518
-3.0	3.4183	1.9322	1.6599	1.5710	1.5584	1.6076	1.7515	2.1585	4.6149
-2.0	3.4518	1.9546	1.6831	1.5983	1.5932	1.6558	1.8279	2.3162	5.4550
-1.5	3.4857	1.9776	1.7072	1.6267	1.6296	1.7071	1.9103	2.4906	6.4720
-1.2	3.5202	2.0010	1.7319	1.6562	1.6679	1.7614	1.9989	2.6837	7.7010
-1.0	3.5552	2.0250	1.7574	1.6869	1.7080	1.8189	2.0940	2.8963	9.1841
-0.9	3.5789	2.0413	1.7748	1.7080	1.7358	1.8591	2.1613	3.0489	10.339
-0.7	3.6478	2.0893	1.8266	1.7713	1.8200	1.9823	2.3711	3.5454	14.547
-0.5	3.7772	2.1810	1.9275	1.8970	1.9906	2.2382	2.8221	4.6872	27.088
-0.3	4.1072	2.4244	2.2057	2.2568	2.4982	3.0354	4.3328	9.1685	116.85
-0.1	6.5636	4.5575	4.9952	6.3280	9.1031	15.873	40.496	275.62	177150

Table II

Ratios of Times to Reach Reduced Rates for Various Orders
(ascending rates)

Reduced Rate Ratios

n	2/1.5	4/2	8/4	16/8	32/16	64/32	128/64	256/128
-1/10	1.0112	1.0005	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
-1/5	1.0791	1.0156	1.0002	1.0000	1.0000	1.0000	1.0000	1.0000
-1/4	1.1157	1.0313	1.0009	1.0000	1.0000	1.0000	1.0000	1.0000
-1/3	1.1683	1.0625	1.0037	1.0002	1.0000	1.0000	1.0000	1.0000
-1/2	1.2434	1.1250	1.0139	1.0017	1.0002	1.0000	1.0000	1.0000
-2/3	1.2921	1.1768	1.0266	1.0046	1.0008	1.0001	1.0000	1.0000
-1	1.3500	1.2500	1.0500	1.0119	1.0029	1.0007	1.0002	1.0000
-3/2	1.3945	1.3150	1.0755	1.0221	1.0068	1.0021	1.0007	1.0002
-2	1.4187	1.3536	1.0923	1.0299	1.0103	1.0036	1.0013	1.0004
-3	1.4443	1.3969	1.1127	1.0402	1.0153	1.0060	1.0024	1.0009
-4	1.4576	1.4204	1.1245	1.0465	1.0187	1.0077	1.0032	1.0013
-5	1.4658	1.4353	1.1320	1.0508	1.0210	1.0090	1.0039	1.0017
-10	1.4826	1.4665	1.1484	1.0603	1.0265	1.0121	1.0056	1.0026
±∞	1.5000	1.5000	1.1667	1.0714	1.0333	1.0161	1.0079	1.0039
10	1.5180	1.5359	1.1870	1.0844	1.0417	1.0215	1.0113	1.0060
5	1.5365	1.5743	1.2095	1.0995	1.0520	1.0284	1.0158	1.0090
4	1.5461	1.5946	1.2217	1.1079	1.0579	1.0326	1.0187	1.0109
3	1.5623	1.6300	1.2435	1.1233	1.0692	1.0408	1.0247	1.0152
2	1.5961	1.7071	1.2929	1.1602	1.0976	1.0629	1.0418	1.0284
3/2	1.6319	1.7937	1.3512	1.2063	1.1354	1.0949	1.0687	1.0511
1	1.7095	2.0000	1.5000	1.3333	1.2500	1.2000	1.1667	1.1429
2/3	1.8430	2.4142	1.8284	1.6408	1.5523	1.5032	1.4734	1.4544
1/2	2.0000	3.0000	2.3333	2.1429	2.0667	2.0323	2.0159	2.0079
1/3	2.4000	5.0000	4.2000	4.0476	4.0118	4.0029	4.0007	4.0002
1/4	2.9474	9.0000	8.1111	8.0137	8.0017	8.0002	8.0000	8.0000
1/5	3.6923	17.000	16.059	16.004	16.000	16.000	16.000	16.000
1/10	13.643	513.00	512.00	512.00	512.00	512.00	512.00	512.00