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Note

Comparison of experimental kinetic decomposition data with master data using a linear plot method

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THE REDUCED TIME METHOD OF PRESENTING KINETIC DATA

A useful approach to the rapid selection of appropriate rate equations to describe the kinetics of isothermal solid state reactions has been made by Sharp et al.[1]. Many such reactions can be described by equations of the general form $f(\alpha) = kt$, where α is the fractional reaction at time t. Sharp et al. recast these equations in the form $f(\alpha) = A(t/t_{0.5})$, where $t_{0.5}$ is the time for the reaction to reach $\alpha = 0.5$. Taking the well-known *contracting area* expression as an example, $R_2(\alpha) = 1-(1-\alpha)^{1/2} = kt$. When $\alpha = 0.5$ this reduces to $R_2(0.5) = 0.293 = kt_{0.5}$ and therefore $R_2(\alpha) = 0.293\,t/t_{0.5}$.

Using these equations in the general form $f(\alpha) = A(t/t_{0.5})$ the theoretical or master curves showing the variation of α with $t/t_{0.5}$ for nine theoretical expressions was calculated by Sharp et al. Since both axes are dimensionless the plot is independent of the time scale involved. To compare experimental data with the master data, the experimental data (weight-loss against time) are converted to fractional reaction data (α against time) in the usual way. The time, $t_{0.5}$, corresponding to $\alpha = 0.5$ is then determined and the data converted to curves of α against $t/t_{0.5}$. Superposition of the experimental curve on any master curve immediately indicates the appropriate expression to be used. Rate constants are then evaluated from the appropriate linear plot of $f(\alpha)$ against t, calculated from the original experimental data.

This *reduced time* method allows a useful and rapid assessment of the various theoretical reaction rate equations to be made. However, as Hancock and Sharp[2] point out, it is generally preferable to use methods of analysis which produce a *linear* function rather than methods which involve comparison with theoretical curves. Hancock and Sharp have proposed an alternative method, based on a "log log"

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analysis which can be used to give reasonably linear plots of ln ln $(1-\alpha)$ against ln t for the range $\alpha = 0.15$–0.50. The method again provides a useful alternative approach but suffers the disadvantages that: (i) the use of a "log log" scale desensitises the analysis; (ii) the plots are only approximately linear (although the approximation may be a good one[2]); and (iii) the range of α is limited.

BASIS OF THE NEW METHOD OF PRESENTATION

We have sought to overcome these difficulties by reverting to the original reduced-time method of Sharp et al.[1]. In essence the method involves plotting the experimental data against the master data in such a way as to produce a linear plot. The agreement of the experimental data with the master data can then be readily assessed by deviations from a straight line.

The experimental data are first expressed in the form α_e as a function of $(t/t_{0.5})_e$, where e refers to the experimental data. Three broadly equivalent plotting procedures are then possible:

(i) The experimental value α_e at which $(t/t_{0.5})_e$ has the *same* value as that in the master data $(t/t_{0.5})_m$, is plotted against the master value of α (designated α_m). In the case where the experimental data are exactly described by the kinetic expression under consideration, $\alpha_e = \alpha_m$ and the resulting plot will be a straight line through the origin with slope α_e/α_m equal to unity.

(ii) Conversely, the experimental value $(t/t_{0.5})_e$ may be plotted against $(t/t_{0.5})_m$ for common values of α_e and α_m. The resulting plot should again be a straight line through the origin with slope $(t/t_{0.5})_e/(t/t_{0.5})_m$ equal to unity for absolute correlation.

(iii) The experimental time t_e may be plotted against $(t/t_{0.5})_m$ for common values of α_e and α_m. For complete correlation the plot should be a straight line through the origin with slope equal to $(t_{0.5})_e$.

An example based on method (i) is given in Fig. 1. using data for the isothermal decomposition of ammonium vanadyl oxalate in oxygen[3]. Figure 1a shows the usual comparison of the experimental data with the master curve of Sharp et al.[1], using the *Avrami–Erofe'ev* expression with $n = 2$. Figure 1b shows a similar comparison of the same data using the α_m-*Method*. The experimental data form a sigmoid curve and deviations from the theoretical line can be seen below $\alpha_e = 0.2$ and above $\alpha_e = 0.7$. For exact correlation with the master data the rate constant k can be directly evaluated from the expression $A_2(\alpha) = kt = 0.8850(t/t_{0.5})_e$, or $k = 0.8850(t_{0.5})_e$.

The data for construction of Fig. 1b were obtained by interpolation of the experimental curve in Fig. 1a at intervals of $\alpha_e = 0.1$. In order to improve the accuracy of the method, values of $(t/t_{0.5})_m$ for suitably small increments of α_m are given in the table for nine common kinetic expressions. The results were calculated from Table 1 of the publication by Sharp et al.[1] and the designation of reaction expressions follows that given by these authors.

It should be noted that each of the three linearising methods is well-suited to

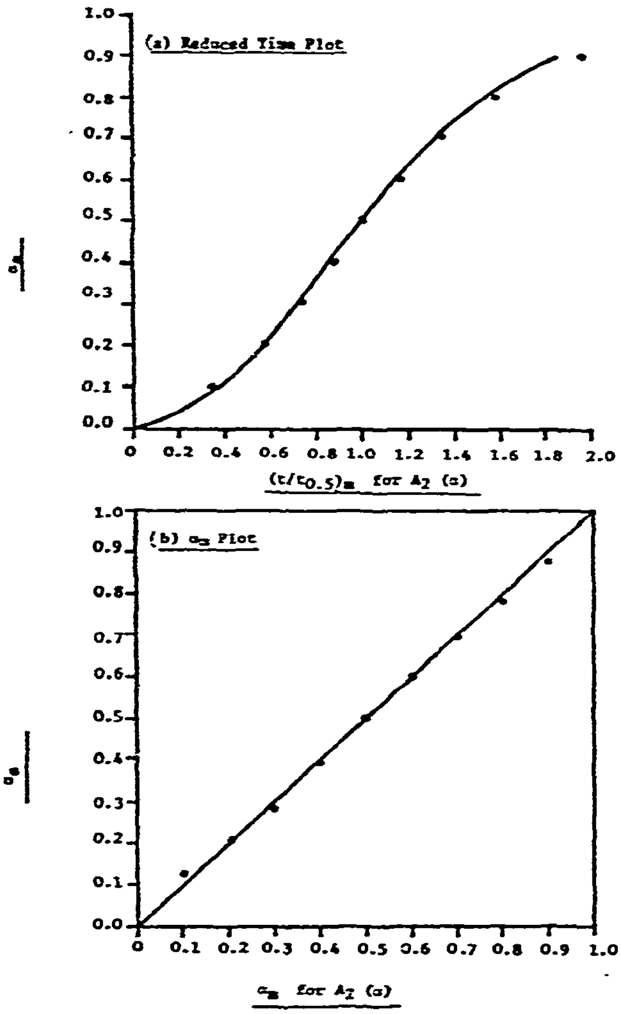

Fig. 1. Reduced plots for the isothermal decomposition of ammonium vanadyl oxalate using $A_2(\alpha)$ master data. Circles = experimental data; lines = theoretical for absolute correlation.

computer analysis and programmes for this purpose are currently under development. Using method (ii) for example, the various master values $(t/t_{0.5})_m$ corresponding to fixed values of α_m may be stored in the programme. The experimental values, α_e, corresponding to the same fixed values of α_m may then be examined by evaluation of the ratio $(t/t_{0.5})_e/(t/t_{0.5})_m$. The predetermined value of acceptable slope, say 1.00 ± 0.02, may then be used to assess the range of α_e over which the reaction expression under test applies. Similar remarks apply to method (i) although method (iii) requires a different criterion since the slope will depend on the experimental time scale. The criterion in this case may be the deviation from the value of $(t_{0.5})_e$ given by the ratio $t_e/(t/t_{0.5})_m$. Any of the three linearising methods will indicate the value of A in the general expression^2, $k = A/(t_{0.5})_e$, thus allowing k to be evaluated directly.

TABLE 1

MASTER VALUES OF $t/t_{0.5}$ AS A FUNCTION OF α FOR SOME COMMON SOLID STATE REACTION EXPRESSIONS

α	$D_1(\alpha)$	$D_2(\alpha)$	$D_3(\alpha)$	$D_4(\alpha)$	$F_1(\alpha)$	$R_2(\alpha)$	$R_3(\alpha)$	$A_2(\alpha)$	$A_3(\alpha)$
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0076
0.0100	0.0004	0.0006	0.0000	0.0000	0.0146	0.0171	0.0160	0.1205	0.2438
0.0200	0.0016	0.0013	0.0000	0.0000	0.0291	0.0345	0.0325	0.1707	0.3078
0.0300	0.0036	0.0033	0.0023	0.0027	0.0440	0.0516	0.0490	0.2096	0.3529
0.0400	0.0064	0.0052	0.0047	0.0054	0.0589	0.0690	0.0654	0.2426	0.3890
0.0500	0.0100	0.0085	0.0070	0.0082	0.0740	0.0864	0.0824	0.2720	0.4199
0.0600	0.0144	0.0117	0.0094	0.0109	0.0893	0.1041	0.0989	0.2987	0.4469
0.0700	0.0196	0.0163	0.0141	0.0163	0.1047	0.1215	0.1159	0.3236	0.4713
0.0800	0.0256	0.0215	0.0188	0.0191	0.1203	0.1393	0.1328	0.3469	0.4937
0.0900	0.0324	0.0274	0.0235	0.0245	0.1361	0.1574	0.1498	0.3689	0.5143
0.1000	0.0400	0.0339	0.0282	0.0327	0.1521	0.1751	0.1672	0.3899	0.5337
0.1100	0.0484	0.0411	0.0352	0.0381	0.1681	0.1932	0.1847	0.4101	0.5518
0.1200	0.0576	0.0489	0.0399	0.0463	0.1844	0.2113	0.2021	0.4294	0.5691
0.1300	0.0676	0.0574	0.0493	0.0545	0.2010	0.2298	0.2201	0.4483	0.5856
0.1400	0.0784	0.0671	0.0563	0.0627	0.2176	0.2479	0.2375	0.4665	0.6014
0.1500	0.0900	0.0776	0.0657	0.0736	0.2345	0.2663	0.2555	0.4842	0.6166
0.1600	0.1024	0.0880	0.0751	0.0845	0.2516	0.2851	0.2739	0.5016	0.6313
0.1700	0.1156	0.0997	0.0845	0.0954	0.2688	0.3039	0.2918	0.5185	0.6454
0.1800	0.1296	0.1128	0.0962	0.1063	0.2864	0.3226	0.3102	0.5351	0.6591
0.1900	0.1444	0.1258	0.1080	0.1199	0.3040	0.3414	0.3286	0.5513	0.6724
0.2000	0.1600	0.1402	0.1197	0.1335	0.3219	0.3605	0.3476	0.5674	0.6853
0.2100	0.1764	0.1551	0.1338	0.1471	0.3401	0.3796	0.3665	0.5831	0.6979
0.2200	0.1936	0.1708	0.1479	0.1635	0.3585	0.3988	0.3854	0.5987	0.7104
0.2300	0.2116	0.1871	0.1643	0.1798	0.3771	0.4182	0.4043	0.6140	0.7225
0.2400	0.2304	0.2047	0.1784	0.1962	0.3959	0.4377	0.4237	0.6293	0.7343
0.2500	0.2500	0.2229	0.1972	0.2153	0.4151	0.4575	0.4430	0.6443	0.7458
0.2600	0.2704	0.2425	0.2136	0.2316	0.4344	0.4773	0.4629	0.6590	0.7574
0.2700	0.2916	0.2627	0.2324	0.2534	0.4540	0.4971	0.4828	0.6738	0.7686
0.2800	0.3136	0.2836	0.2535	0.2725	0.4740	0.5172	0.5027	0.6885	0.7796
0.2900	0.3364	0.3051	0.2723	0.2943	0.4942	0.5374	0.5230	0.7029	0.7906
0.3000	0.3600	0.3279	0.2958	0.3161	0.5146	0.5575	0.5434	0.7173	0.8013
0.3100	0.3844	0.3520	0.3169	0.3406	0.5354	0.5780	0.5637	0.7316	0.8119
0.3200	0.4096	0.3761	0.3427	0.3651	0.5565	0.5988	0.5846	0.7459	0.8225
0.3300	0.4356	0.4022	0.3662	0.3896	0.5778	0.6333	0.6059	0.7601	0.8328
0.3400	0.4624	0.4289	0.3920	0.4169	0.5995	0.6405	0.6268	0.7742	0.8431
0.3500	0.4900	0.4563	0.4202	0.4441	0.6216	0.6617	0.6486	0.7883	0.8533
0.3600	0.5184	0.4850	0.4484	0.4714	0.6439	0.6828	0.6699	0.8023	0.8635
0.3700	0.5476	0.5143	0.4789	0.5014	0.6666	0.7043	0.6917	0.8164	0.8735
0.3800	0.5776	0.5450	0.5094	0.5341	0.6897	0.7258	0.7140	0.8304	0.8835
0.3900	0.6084	0.5769	0.5422	0.5640	0.7312	0.7477	0.7363	0.8445	0.8934
0.4000	0.6400	0.6095	0.5751	0.5995	0.7370	0.7695	0.7591	0.8584	0.9032
0.4100	0.6720	0.6434	0.6103	0.6322	0.7612	0.7917	0.7819	0.8725	0.9131
0.4200	0.7056	0.6786	0.6479	0.6676	0.7859	0.8139	0.8047	0.8865	0.9228
0.4300	0.7396	0.7145	0.6854	0.7057	0.8110	0.8365	0.8284	0.9005	0.9325
0.4400	0.7744	0.7516	0.7253	0.7439	0.8365	0.8593	0.8517	0.9146	0.9422
0.4500	0.8100	0.7901	0.7653	0.7820	0.8625	0.8824	0.8759	0.9287	0.9518
0.4600	0.8464	0.8299	0.8099	0.8229	0.8891	0.9054	0.9001	0.9429	0.9615
0.4700	0.8836	0.8703	0.8545	0.8665	0.9161	0.9286	0.9244	0.9571	0.9711

(Table continued on p. 244)

TABLE 1 (*continued*)

α	$D_1(\alpha)$	$D_2(\alpha)$	$D_3(\alpha)$	$D_4(\alpha)$	$F_1(\alpha)$	$R_2(\alpha)$	$R_3(\alpha)$	$A_2(\alpha)$	$A_3(\alpha)$
0.4800	0.9216	0.9126	0.9014	0.9101	0.9434	0.9522	0.9496	0.9713	0.9808
0.4900	0.9604	0.9557	0.9483	0.9537	0.9714	0.9761	0.9743	0.9856	0.9904
0.5000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.5100	1.0404	1.0463	1.0516	1.0490	1.0293	1.0242	1.0257	1.0144	1.0096
0.5200	1.0816	1.0932	1.1056	1.0981	1.0590	1.0488	1.0519	1.0290	1.0192
0.5300	1.1236	1.1415	1.1620	1.1499	1.0893	1.0734	1.0785	1.0436	1.0289
0.5400	1.1664	1.1917	1.2206	1.2016	1.1203	1.0987	1.1057	1.0584	1.0385
0.5500	1.2100	1.2432	1.2817	1.2561	1.1521	1.1239	1.1328	1.0733	1.0482
0.5600	1.2544	1.2960	1.3451	1.3134	1.1845	1.1495	1.1604	1.0883	1.0580
0.5700	1.2996	1.3501	1.4108	1.3706	1.2177	1.1755	1.1886	1.1035	1.0678
0.5800	1.3456	1.4055	1.4812	1.4305	1.2516	1.2014	1.2172	1.1187	1.0776
0.5900	1.3924	1.4628	1.5516	1.4932	1.2864	1.2281	1.2462	1.1341	1.0875
0.6000	1.4400	1.5222	1.6267	1.5559	1.3220	1.2547	1.2758	1.1497	1.0975
0.6100	1.4884	1.5828	1.7042	1.6213	1.3585	1.2820	1.3059	1.1655	1.1074
0.6200	1.5376	1.6447	1.7840	1.6894	1.3960	1.3096	1.3364	1.1815	1.1176
0.6300	1.5876	1.7086	1.8685	1.7602	1.4346	1.3373	1.3674	1.1976	1.1278
0.6400	1.6384	1.7744	1.9554	1.8338	1.4741	1.3656	1.3989	1.2141	1.1380
0.6500	1.6900	1.8422	2.0469	1.9074	1.5147	1.3943	1.4314	1.2306	1.1483
0.6600	1.7424	1.9113	2.1408	1.9864	1.5565	1.4233	1.4639	1.2476	1.1588
0.6700	1.7956	1.9824	2.2418	2.0654	1.5996	1.4527	1.4978	1.2646	1.1694
0.6800	1.8496	2.0561	2.3451	2.1471	1.6439	1.4827	1.5317	1.2821	1.1802
0.6900	1.9044	2.1310	2.4530	2.2343	1.6898	1.5131	1.5666	1.2998	1.1910
0.7000	1.9600	2.2086	2.5657	2.3215	1.7371	1.5442	1.6025	1.3180	1.2020
0.7100	2.0164	2.2881	2.6831	2.4114	1.7860	1.5756	1.6389	1.3363	1.2132
0.7200	2.0736	2.3703	2.8075	2.5068	1.8367	1.6074	1.6762	1.3552	1.2246
0.7300	2.1316	2.4544	2.9366	2.6049	1.8891	1.6401	1.7145	1.3744	1.2361
0.7400	2.1904	2.5411	3.0727	2.7057	1.9436	1.6733	1.7533	1.3940	1.2479
0.7500	2.2500	2.6297	3.2136	2.8093	2.0002	1.7071	1.7935	1.4142	1.2598
0.7600	2.3104	2.7216	3.3638	2.9183	2.0590	1.7415	1.8352	1.4348	1.2722
0.7700	2.3716	2.8162	3.5211	3.0327	2.1205	1.7767	1.8774	1.4561	1.2846
0.7800	2.4336	2.9133	3.6878	3.1499	2.1845	1.8098	1.9210	1.4780	1.2975
0.7900	2.4964	3.0137	3.8615	3.2698	2.2516	1.8494	1.9661	1.5005	1.3106
0.8000	2.5600	3.1167	4.0469	3.3978	2.3220	1.8873	2.0126	1.5237	1.3241
0.8100	2.6244	3.2236	4.2418	3.5286	2.3961	1.9259	2.0606	1.5479	1.3380
0.8200	2.6896	3.3331	4.4507	3.6649	2.4741	1.9655	2.1105	1.5728	1.3524
0.8300	2.7556	3.4472	4.6690	3.8093	2.5566	2.0065	2.1619	1.5988	1.3673
0.8400	2.8224	3.5645	4.9061	3.9591	2.6441	2.0485	2.2157	1.6259	1.3827
0.8500	2.8900	3.6858	5.1572	4.1144	2.7371	2.0918	2.2719	1.6544	1.3987
0.8600	2.9584	3.8116	5.4248	4.2779	2.8367	2.1365	2.3306	1.6842	1.4155
0.8700	3.0276	3.9426	5.7159	4.4523	2.9436	2.1830	2.3917	1.7157	1.4331
0.8800	3.0976	4.0782	6.0281	4.6322	3.0592	2.2315	2.4566	1.7489	1.4516
0.8900	3.1684	4.2190	6.3685	4.8256	3.1847	2.2816	2.5250	1.7845	1.4711
0.9000	3.2400	4.3657	6.7394	5.0300	3.3222	2.3346	2.5972	1.8225	1.4920
0.9100	3.3124	4.5196	7.1478	5.2452	3.4741	2.3899	2.6752	1.8639	1.5144
0.9200	3.3856	4.6799	7.6032	5.4768	3.6441	2.4486	2.7586	1.9089	1.5387
0.9300	3.4596	4.8494	8.1126	5.7275	3.8368	2.5107	2.8497	1.9586	1.5654
0.9400	3.5344	5.0274	9.6924	5.9973	4.0592	2.5780	2.9496	2.0146	1.5951
0.9500	3.6100	5.2164	9.3638	6.2916	4.3222	2.6507	3.0616	2.0789	1.6289
0.9600	3.6864	5.4185	10.1642	6.6213	4.6442	2.7313	3.1895	2.1549	1.6683
0.9700	3.7636	5.6375	11.1525	6.9973	5.0593	2.8228	3.3412	2.2492	1.7165
0.9800	3.8416	5.8787	12.4600	7.4387	5.6442	2.9313	3.5317	2.3757	1.7804
0.9900	3.9204	6.1532	14.4482	8.0000	6.6444	3.0727	3.8032	2.5776	1.8798

CONCLUSIONS

The main advantages of the proposed method may be summarised as follows: (i) the method applies to the complete range of decomposition $0<\alpha<1$; (ii) absolute correlation with any reaction expression is readily determined; (iii) deviations from the master data are assessed by deviations from a *theoretical straight line*; (iv) distinction between closely similar master data is facilitated, e.g., equations describing diffusion-controlled reactions; (v) the sensitivity of normal kinetic analysis is preserved.

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