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ON THE MAXIMUM REACTION RATE AND INFLEXION POINTS ON THE DTG CURVE

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The authors present some theoretical considerations concerning the influence of the form of the conversion function $f(\alpha)$ on the values of the degree of conversion corresponding to the maximum value of the reaction rate (α_{max}) as well as on the inflexion points (α_{inf}) of the DTG curve. The obtained equations are characterized by a general validity no matter the form of $f(\alpha)$.

Keywords: kinetics

Introduction

As known from literature, the shapes of TG and DTG curves depend essentially on the reaction mechanism i.e. on the form of $f(\alpha)$ [1–12].

Among the various parameters introduced to characterize the shapes of TG and DTG curves one has to mention the degree of conversion corresponding to the maximum value of the reaction rate (α_{max}) and the inflexion points of the DTG curve (α_{inf}).

In this paper equations which allow to calculate α_{max} and α_{inf} for any form $f(\alpha)$, will be derived. These equations will be applied to the common form of the conversion function corresponding to the 'model of the reaction order'.

Theoretical aspects

As a starting point the well known differential kinetic equation:

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$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\, e^{-E/RT} \tag{1}$$

where the notations have their usual meanings, will be used. Through variable separation and integration one obtains:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} e^{-E/Ry_{dy}} \tag{2}$$

The temperature integral from the right side of Eq. (2) can be approximated as follows [13]:

$$\int_0^{T} e^{-E/Ry} \approx \frac{RT^2}{E} e^{-E/RT} Q(x) \tag{3}$$

where

$$x = E/RT \tag{4}$$

and $Q(x)$ is a function with smooth variation with x and close to unity.

Introducing the notation:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \tag{5}$$

Equation (2) taking into account the approximation (3), turns into:

$$g(\alpha) = \frac{A}{\beta} \frac{RT^2}{E} e^{-E/RT} Q(x) \tag{6}$$

The value α_{max} can be obtained from the condition

$$\left(\frac{d^2\alpha}{dT^2}\right)_{max} = 0 \tag{7}$$

taking into account relationships (1) and (6). After performing the detailed calculations one obtains [7, 11, 12]:

$$g(\alpha_{max}) f'(\alpha_{max}) = -Q(x) \tag{8}$$

In order to evaluate the α_{inf} of the DTG curve the condition

$$\left(\frac{d^3\alpha}{dT^3}\right)_{inf} = 0 \tag{9}$$

together with the relationships (1) and (6) will be used. The detailed calculations lead to

$$\frac{g^2(\alpha_{inf})f'^2(\alpha_{inf})}{Q^2(x)}\cdot\left(1+\frac{f(\alpha_{inf})f''(\alpha_{inf})}{f'^2(\alpha_{inf})}\right)+3\frac{g(\alpha_{inf})f'(\alpha_{inf})}{Q(x)}+\frac{x-2}{x}=0 \tag{10}$$

Equation (10) allows to obtain the value of α_{inf}, no matter the form of $f(\alpha)$ and is equivalent to equation (7) from paper [12]. This equation admits in the general case two solutions α^1_{inf} and α^2_{inf}, while in some particular cases only one solution α^1_{inf}.

Applications

Equations (8) and (10) will be used for $f(\alpha)=(1-\alpha)^n$, i.e. on the framework of the model of the reaction order.

The following second degree rational approximation from [13]

$$Q(x)=\frac{x^2+5.347x+1.376}{x^2+7.347x+10.069} \tag{11}$$

was used. This approximation ensures an error lower than $2\cdot10^{-4}\%$ for $x\geq10$.

The values of α_{max}, α^1_{inf} and α^2_{inf} have been calculated for $n\in[0, 3]$ and $x\in[10, \infty]$.

From Eq. (10) one can see that for $n<1/2$, α^2_{inf} does not exist while for $n\to 1/2$, $\alpha^2_{inf}\to 1$.

The results obtained are listed in Tables 1–3.

A comparison between the calculated values of α_{max}, α^1_{inf} and α^2_{inf} and the experimental ones for the reactions

$$[Ni(NH_3)_6]Br_2\,(s)\xrightarrow{\beta=5\ deg\cdot min^{-1}}[Ni(NH_3)_2]Br_2\,(s)+4NH_3\,(g) \tag{I}$$

$$Mg(OH)_2\,(s)\xrightarrow{\beta=5\ deg\cdot min^{-1}}MgO\,(s)+H_2O\,(g) \tag{II}$$

Table 1 The values of α_{max} calculated by using Eq. (8) for various values of the reaction order n and x

n	x							
	10	20	30	40	50	75	100	∞
0.1	0.9084	0.9152	0.9176	0.9188	0.9195	0.9205	0.9210	0.9226
0.2	0.8419	0.8536	0.8577	0.8597	0.8610	0.8627	0.8636	0.8663
0.3	0.7887	0.8040	0.8095	0.8122	0.8139	0.8163	0.8174	0.8209
0.4	0.7441	0.7624	0.7690	0.7723	0.7744	0.7772	0.7786	0.7828
0.5	0.7058	0.7266	0.7341	0.7379	0.7403	0.7435	0.7451	0.7500
0.6	0.6723	0.6952	0.7035	0.7077	0.7103	0.7139	0.7157	0.7211
⅔	0.6521	0.6762	0.6849	0.6895	0.6922	0.6960	0.6979	0.7037
0.7	0.6426	0.6672	0.6762	0.6808	0.6837	0.6875	0.6895	0.6954
0.8	0.6159	0.6421	0.6517	0.6566	0.6597	0.6638	0.6659	0.6723
0.9	0.5918	0.6193	0.6294	0.6347	0.6379	0.6423	0.6445	0.6513
1.0	0.5699	0.5985	0.6091	0.6146	0.6180	0.6226	0.6249	0.6321
1.1	0.5498	0.5794	0.5904	0.5961	0.5996	0.6045	0.6069	0.6145
1.2	0.5312	0.5617	0.5731	0.5791	0.5827	0.5877	0.5903	0.5981
1.3	0.5141	0.5454	0.5571	0.5632	0.5670	0.5722	0.5748	0.5829
1.4	0.4982	0.5301	0.5421	0.5484	0.5523	0.5577	0.5604	0.5688
1.5	0.4834	0.5159	0.5281	0.5346	0.5386	0.5441	0.5469	0.5556
1.6	0.4695	0.5025	0.5150	0.5216	0.5257	0.5313	0.5342	0.5431
1.7	0.4565	0.4899	0.5027	0.5094	0.5136	0.5194	0.5223	0.5314
1.8	0.4442	0.4781	0.4910	0.4979	0.5022	0.5080	0.5110	0.5204
1.9	0.4327	0.4669	0.4800	0.4870	0.4914	0.4973	0.5004	0.5099
2.0	0.4218	0.4563	0.4696	0.4767	0.4811	0.4872	0.4903	0.5000
2.25	0.3971	0.4321	0.4458	0.4531	0.4576	0.4639	0.4672	0.4773
2.5	0.3753	0.4106	0.4246	0.4321	0.4368	0.4433	0.4466	0.4571
2.75	0.3559	0.3915	0.4057	0.4133	0.4181	0.4248	0.4282	0.4390
3.0	0.3385	0.3742	0.3886	0.3964	0.4012	0.4080	0.4115	0.4226

Table 2 The values of α_{inf}^{1} calculated by using Eq. (10) for various values of the reaction order n and x

n	x							
	10	20	30	40	50	75	100	∞
0.1	0.6162	0.6565	0.6695	0.6760	0.6799	0.6850	0.6876	0.6953
0.2	0.4990	0.5463	0.5620	0.5699	0.5746	0.5809	0.5841	0.5936
0.3	0.4256	0.4754	0.4922	0.5007	0.5058	0.5127	0.5161	0.5265
0.4	0.3733	0.4237	0.4411	0.4498	0.4551	0.4623	0.4659	0.4767
0.5	0.3336	0.3837	0.4011	0.4100	0.4154	0.4227	0.4264	0.4375
0.6	0.3021	0.3514	0.3688	0.3777	0.3831	0.3904	0.3941	0.4054
⅔	0.2844	0.3330	0.3503	0.3592	0.3646	0.3719	0.3756	0.3867
0.7	0.2763	0.3246	0.3418	0.3507	0.3561	0.3634	0.3671	0.3784
0.8	0.2548	0.3019	0.3189	0.3277	0.3330	0.3403	0.3440	0.3553
0.9	0.2366	0.2824	0.2991	0.3078	0.3131	0.3203	0.3240	0.3352
1.0	0.2209	0.2655	0.2819	0.2904	0.2956	0.3027	0.3064	0.3175
1.1	0.2072	0.2506	0.2666	0.2750	0.2802	0.2872	0.2908	0.3018
1.2	0.1951	0.2373	0.2531	0.2613	0.2664	0.2733	0.2768	0.2877
1.3	0.1845	0.2255	0.2409	0.2490	0.2539	0.2608	0.2642	0.2750
1.4	0.1749	0.2148	0.2299	0.2378	0.2427	0.2494	0.2528	0.2634
1.5	0.1663	0.2051	0.2199	0.2277	0.2325	0.2391	0.2424	0.2529
1.6	0.1585	0.1963	0.2108	0.2184	0.2231	0.2296	0.2329	0.2432
1.7	0.1515	0.1883	0.2024	0.2099	0.2145	0.2209	0.2242	0.2343
1.8	0.1450	0.1808	0.1947	0.2020	0.2066	0.2129	0.2161	0.2261
1.9	0.1391	0.1740	0.1876	0.1948	0.1993	0.2054	0.2086	0.2184
2.0	0.1337	0.1677	0.1810	0.1880	0.1924	0.1985	0.2016	0.2113
2.25	0.1218	0.1538	0.1664	0.1732	0.1774	0.1832	0.1862	0.1955
2.5	0.1118	0.1421	0.1541	0.1605	0.1645	0.1701	0.1730	0.1820
2.75	0.1034	0.1326	0.1435	0.1496	0.1535	0.1588	0.1616	0.1703
3.0	0.0962	0.1233	0.1342	0.1402	0.1439	0.1490	0.1517	0.1601

Table 3 The values of α^2_{inf} calculated by using Eq.(10) for various values of the reaction order n and x

n	x							
	10	20	30	40	50	75	100	∞
0.5	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.6	0.9882	0.9899	0.9905	0.9908	0.9909	0.9912	0.9913	0.9916
⅔	0.9748	0.9784	0.9797	0.9803	0.9806	0.9811	0.9814	0.9821
0.7	0.9675	0.9722	0.9737	0.9745	0.9750	0.9756	0.9759	0.9769
0.8	0.9445	0.9523	0.9550	0.9564	0.9572	0.9583	0.9588	0.9605
0.9	0.9210	0.9320	0.9358	0.9378	0.9389	0.9405	0.9413	0.9437
1.0	0.8979	0.9119	0.9168	0.9193	0.9208	0.9229	0.9239	0.9271
1.1	0.8753	0.8922	0.8982	0.9013	0.9032	0.9057	0.9069	0.9108
1.2	0.8536	0.8732	0.8802	0.8838	0.8860	0.8890	0.8905	0.8951
1.3	0.8328	0.8549	0.8628	0.8670	0.8695	0.8729	0.8746	0.8799
1.4	0.8128	0.8372	0.8461	0.8507	0.8535	0.8574	0.8593	0.8653
1.5	0.7937	0.8202	0.8300	0.8351	0.8382	0.8425	0.8446	0.8513
1.6	0.7755	0.8039	0.8145	0.8200	0.8234	0.8281	0.8305	0.8378
1.7	0.7580	0.7883	0.7996	0.8056	0.8093	0.8143	0.8168	0.8248
1.8	0.4713	0.7732	0.7853	0.7917	0.7956	0.8010	0.8037	0.8123
1.9	0.7253	0.7588	0.7715	0.7783	0.7824	0.7882	0.7911	0.8003
2.0	0.7100	0.7449	0.7583	0.7654	0.7698	0.7758	0.7790	0.7887
2.25	0.6745	0.7124	0.7272	0.7351	0.7401	0.7469	0.7504	0.7615
2.5	0.6424	0.6828	0.6988	0.7075	0.7129	0.7204	0.7243	0.7366
2.75	0.6133	0.6557	0.6728	0.6820	0.6879	0.6960	0.7003	0.7127
3.0	0.5868	0.6308	0.6488	0.6586	0.6648	0.6735	0.6781	0.6926

shows that for reaction (I) [14]

experimental: α_{max}=0.682; α^1_{inf}=0.346; α^2_{inf}=0.981

calculated: α_{max}=0.667; α^1_{inf}=0.325; α^2_{inf}=0.972

The calculated values were obtained by using the following kinetic parameters:

n=0.7 ; E=82.88 kJ·mol^{-1}; A=9.83·10^6 s^{-1}

For reactions (II) [15]

experimental: α_{max}=0.553; α^1_{inf}=0.229; α^2_{inf}=0.725

calculated: α_{max}=0.522; α^1_{inf}=0.218; α^2_{inf}=0.820

In this case

n=1.6; E=221.86 kJ·mol^{-1}; A=1.20·10^{15} s^{-1}

The agreement between the calculated values and the experimental ones is satisfactory.

Conclusions

1. Two equations corresponding to α_{max} and α_{inf} have been presented.

2. The two equations were used to calculated in the framework of the 'model of the reaction order' the values of α_{max}, α^1_{inf} and α^2_{inf}.

3. The calculated values agree satisfactorily with the experimental ones for the thermal decomposition of $[Ni(NH_3)_6]Br_2$ and $Mg(OH)_2$

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Zusammenfassung — Es werden einige theoretische Überlegungen bezüglich des Einflusses der Form der Konversionsfunktion $f(\alpha)$ auf die Werte der Konversionsrate bei maximalen Reaktionsgeschwindigkeiten (α_{max}) sowie auf Inflexionspunkte (α_{∞}) der DTG-Kurve angestellt. Die erhaltenen Gleichungen sind unabhängig von der Form von $f(\alpha)$ durch eine all-gemeine Gültigkeit charakterisiert.