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Abstract

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ON THE COMPENSATION DEPENDENCE BETWEEN n AND K IN TOPOKINETIC REACTIONS

In the topokinetic equation ([1])

$$\alpha = 1 - e^{-Kt^n} \tag{1}$$

the constant K is given by the expression ([2])

$$K = \frac{2\omega v_0}{(i+\sigma)!}\varkappa_1 \cdots \varkappa_i u^\sigma, \tag{2}$$

where i is the number of elementary stages in the process of formation of initial reaction centers; $\varkappa_1, \ldots, \varkappa_i$ are the rate constants of these reactions; u is the linear growth rate of the nuclei of the solid product; σ is the dimensionality exponent of the latter (for spheroidal nuclei $\sigma = 3$, for cylindrical nuclei $\sigma = 2$, for planar nuclei $\sigma = 1$).

Introducing, in place of u, the designations $\varkappa_{i+1}, \ldots, \varkappa_{i+\sigma}$, we write expression (2) in the form

$$K = \frac{2\omega v_0}{(i+\sigma)!}\varkappa_1 \cdots \varkappa_n, \tag{3}$$

where $n = i + \sigma$. According to transition-state theory, the constants $\varkappa_j$ are represented by the expression ([3])

$$\varkappa_j = \frac{kT}{h} e^{S_j^{\neq}/R} e^{-\varepsilon_j^{\neq}/RT}, \tag{4}$$

where $S_j^{\neq}$ and $\varepsilon_j^{\neq}$ are the entropy and heat content of the transition state.

Combining (3) and (4), we obtain:

$$K = \frac{2\omega v_0}{n!}\left(\frac{kT}{h}\right)^n \prod_{j=1}^{n} e^{S_j^{\neq}/R} e^{-\varepsilon_j^{\neq}/RT}. \tag{5}$$

From a specific example, for instance the decomposition of the permanganate ion

$MnO_4^- \rightarrow [MnO_4^-] \rightarrow MnO_2 + O_2 + e$ (with subsequent $MnO_4^- + e \rightarrow MnO_4^{\cdot}$), it can be seen that the transition-state energy of the permanganate ion will be identical or, at least, sufficiently close at all stages of the formation of initial centers and the growth of nuclei of the solid product. This follows from the closeness of the electronic spectra of the permanganate ion in solid solutions, irrespective of the nature of the solid solvent ([4]). Thus, if the transition state of the MnO_4^- ion is one of its higher electronic states, then ε_j may be taken to be the same for all elementary stages. Then (5) may be represented in the form

$$\log K = \log \frac{2\omega v_0}{n!} + \frac{1}{R}\sum_{j=1}^{n} \Delta S_j - n\left(\frac{\varepsilon}{RT} - \frac{S_0^*}{R} - \log \frac{kT}{h}\right), \tag{6}$$

where $\Delta S_j^* = S_j^* - S_0^*$, and S_0^* is the entropy value in the slowest stage.

Denoting

$$a = \left(\log \frac{k\omega v_0}{n!} + \frac{1}{R}\sum_{j=1}^{n} \Delta S_j^*\right), \quad b = \left(\frac{\varepsilon}{RT} - \frac{S_0^*}{R} - \log \frac{kT}{h}\right)$$

we obtain

$$\log K = a - bn. \tag{7}$$

Expression (7) shows that K increases when n decreases and, conversely, decreases when n increases.

Experience shows that the values of a are small; this explains why a may be regarded as a constant, despite the presence of $n!$ in the denominator of the expression under the logarithm of the first of the terms entering into a.

The quantities n and K may change as a result of dispersion of the solid substance, i.e., owing to a change in the specific surface of the substance, owing to the introduction of foreign ions into the crystal lattice, owing to a change in the number of potential reaction centers under the action of radiation, etc. This makes it possible to carry out an experimental verification of expression (7).

For this purpose let us turn to experimental data obtained by us for the thermal decomposition of potassium permanganate. In the present article we shall

consider the data obtained by us exclusively from the standpoint of equation (7).

The experiments described by us were carried out on several dozen preparations of $KMnO_4$. Among these preparations there are those differing in time of preparation and, correspondingly, in the storage time elapsed before the decomposition experiment. Individual preparations differ from one another in surface area, which was achieved by grinding the initial preparations in a porcelain mill or in an agate mortar and by subsequent sieving into fractions on sieves. Additions of barium permanganate were introduced into some preparations.

Table 1 gives the distinguishing features of the preparations studied.

Table 1

Potassium permanganate preparations studied

Groups of experiments	Groups of preparations	Nos. of preparations	Addition	Time from preparation to experiment, days	Specific surface, m^2/g	Nos. of experiments
I	A	1–4	No addition	5–17	0.023–0.597	9–16
I		5–8	» »	40–43	0.003–0.406	26–29
I	[1]	9–10	» »	122–126	–	30–32
I	[2]	5′–8′	» »	273–372	0.012–0.406	46–55
I		$11–14_3$	» »	Not recrystallized	0.012–0.238	34–37, 42–45
I		15–18	» »	Washed	–	38–41
I		19–25	» »	2–18	0.023–0.406	62–68
I		26–31	» »	20–38	0.014–0.830	69–74
I		32–38	» »	2–22	0.007–0.229	91–100
II		39–45	No addition	1–25	0.006–0.400	119–125, 129

Groups of experiments	Groups of preparations	Nos. of preparations	Addition	Time from preparation to experiment, days	Specific surface, m^2/g	Nos. of experiments
II		46–53	With addition of 0.2 mol. % $Ba(MnO_4)_2$	118–200	0.022–0.768	204–223, 234, 236
II		54–63	0.5 mol. % $Ba(MnO_4)_2$	140–208	0.020–1.096	224–233, 235, 237–240
II		64–70	0.7 mol. % $Ba(MnO_4)_2$	22–33	0.007–0.416	126–128, 130–134

The thermal decomposition of all the preparations studied was carried out at 218° in a vacuum apparatus analogous to that described earlier ([5]). The decomposition curves have the typical autocatalytic character, repeatedly described for potassium permanganate ([6]), and therefore we do not present these curves here.

The experimental data of all experiments were substituted into equation (1), expressed in logarithmic form:

$$\log[-\log(1-\alpha)] = \log K + n \log t. \tag{8}$$

The calculation of the values of $\log K$ and n was carried out by the method of least squares.

squares. In view of the large number of experiments, the latter were divided into two groups. Group I included experiments with potassium permanganate preparations without additives; group II included experiments with a potassium permanganate preparation with additions of 0.2, 0.5, and 0.7 mole % $Ba(MnO_4)_2$, as well as with potassium permanganate without additives, prepared simultaneously with the preparations containing barium. For lack of space, Table 2 gives the values of $\log K$ and n only for experiments of the second group. For both groups of experiments, the values of $\log K$ are plotted as a function of n in Fig. 1.

Fig. 1. Dependence of $\log K$ on n for the first (I) and second (II) groups of experiments

Table 2

Values of $\log K$ and n, calculated for individual experiments by the method of least squares
(group II of experiments)

Nos. of preparations and experiments	Storage time, days	Specific surface, m^2/g	$\log K$	n	Nos. of preparations and experiments	Storage time, days	Specific surface, m^2/g	$\log K$	n
39–119	1	0,006	$\overline{11},523$	4,27	55–230	186	–	$\overline{9},499$	3,79
39–125	9	0,006	$\overline{13},944$	5,03	56–224	163	0,046	$\overline{9},152$	3,87
40–123	7	0,020	$\overline{10},263$	4,19	56–235	200	0,046	$\overline{10},969$	3,88
41–122	6	0,034	$\overline{10},384$	4,14	57–231	187	–	$\overline{9},628$	3,70
42–124	8	0,051	$\overline{8},246$	3,37	57–237	203	–	$\overline{9},023$	3,90
43–121	5	0,135	$\overline{9},796$	3,54	58–238	204	–	$\overline{8},061$	3,52
44–129	25	0,125	$\overline{8},002$	3,52	58–232	188	–	$\overline{9},543$	3,70
45–120	2	0,400	$\overline{7},873$	2,85	59–225	164	0,737	$\overline{7},848$	2,71
46–204	118	0,022	$\overline{12},265$	4,92	62–226	166	0,930	$\overline{5},536$	2,10
47–220	151	0,033	$\overline{11},795$	4,35	60–229	185	–	$\overline{9},687$	3,66
48–240	120	0,056	$\overline{10},851$	3,76	60–240	208	–	$\overline{9},976$	3,51
48–234	199	0,056	$\overline{10},217$	4,17	61–228	181	0,826	$\overline{5},265$	2,23
49–211	122	0,090	$\overline{9},316$	3,57	64–131	28	0,007	$\overline{10},279$	4,14
49–236	201	0,090	$\overline{9},902$	3,55	65–130	27	0,019	$\overline{9},562$	3,73
50–221	152	0,103	$\overline{9},573$	3,64	66–132	29	0,031	$\overline{9},671$	3,61

Nos. of preparations and experiments	Storage time, days	Specific surface, m^2/g	$\log K$	n	Nos. of preparations and experiments	Storage time, days	Specific surface, m^2/g	$\log K$	n
51–219	146	0,392	$\overline{7},662$	2,84	67–128	24	0,123	$\overline{7},592$	2,84
52–212	123	0,661	$\overline{7},915$	2,71	68–133	30	0,163	$\overline{6},151$	2,57
53–227	167	0,096	$\overline{5},647$	2,09	69–127	23	0,267	$\overline{8},348$	3,36
53–223	160	0,768	$\overline{6},863$	2,32	69–134	33	0,267	$\overline{7},202$	2,99
54–233	191	–	$\overline{8},021$	3,54	70–126	22	0,416	$\overline{6},964$	2,37

As can be seen from Fig. 1, for both groups of experiments the experimental data fit well on straight lines with a negative slope, i.e., they are described by equation (7).

From the values of $\log K$ and n, the quantities a and b entering into equation (7) were calculated. The calculation of the quantities a and b was also carried out by the method of least squares.

For group I of the experiments, $a = -0.121$, $b = 2.288$; for group II, $a = +0.961$, $b = 2.573$. As can be seen, the differences between the two groups of experiments are reflected mainly in the values of a, and to a lesser extent in the values of b. The closeness of the values of b for the different groups of experiments indirectly confirms the assumption made above concerning the equality of the activation energies for the individual elementary stages of the reaction. Direct calculation of the activation energies from the values of b, however, is impossible, since the value of the coefficient b also includes part of the entropic factor.

It is appropriate to call the dependence (7) obtained by us the compensation dependence between K and n in topokinetic reactions.

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Note: Figure translations are in progress. See original paper for figures.