54. *The Temperature Coefficient of the Thermal Decomposition of Silver Oxalate.*

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BENTON and CUNNINGHAM, studying the decomposition of silver oxalate (*J. Amer. Chem. Soc.*, 1935, **57**, 2227), claimed to have evidence that the energy of activation of the formation of nuclei was much greater than that of the rate of propagation of decomposition through the crystals. This would mean an increase in the temperature coefficient of the whole reaction at low temperatures, since its course would be governed by the relatively slow rate of formation of nuclei. At higher temperatures, the rate of spreading of decomposition from nuclei would become the " slow " reaction which would control the form of the reaction as a whole. The figure which they give, *viz.*, 64,000 cals., is equivalent to a temperature coefficient of 11·0 in the range 80—110°, and in support of this they quote experiments in which they were unable to detect any reaction during 13½ hours at 80°. On the other hand, the author (J., 1936, 839) showed that their calculation was erroneous, and found that the over-all temperature coefficient of the reaction was about 3·0, and that it was constant over the more limited range examined. Unfortunately, his experiments at the lowest temperature (85°) had to be curtailed for technical reasons, and were not considered sufficiently trustworthy to quote. In order to settle the point, two complete runs have now been made at 80°, and these are compared below with runs with the same specimen at 110° and 130°. It will be seen that all the characteristics of the reaction are maintained at the low temperature, and that a coefficient of about 3·0 was obtained, in agreement with the author's earlier results.

EXPERIMENTAL.

The specimen used (*R*) had been prepared about 1931 in complete darkness, and had never been exposed to light. The initial rate of decomposition was found to be rather high, in accordance with the assumption that slight decomposition had taken place at room temperature, and calculation showed that this was of the right order of magnitude for a temperature of 18°, a time of 5 years, and a coefficient of 3·0. The specimen had been prepared with an excess of sodium oxalate, and was therefore of the more unstable type. Its rate of decomposition was measured exactly as described by the author (J., 1936, 832), and the two runs at 80° were conducted simultaneously, the same thermostat and the same vacuum backing being used.

In the following table, cols. 2—5 give the times (in mins.) taken by the various samples to attain the degree of decomposition given in col. 1. These figures were obtained by integrating the rate–time graphs, as already described (*loc. cit.*). Cols. 6 and 7 give, respectively, the temperature coefficient between 80° and 110° (the mean of the two experiments at 80° being used) and that between 110° and 130°. The coefficients are worked out for each percentage decomposition, and their constancy shows that the shape of the graphs is independent of temperature.

Decomptn., %.	80°.	80°.	110°.	130°.	Coeff., 80—110°.	Coeff., 110—130°.
5	1850	1850	94·0	8·0	2·70	3·42
10	2500	2460	124·1	11·1	2·71	3·34
20	3360	3200	156·0	14·5	2·76	3·27
30	3660	3910	179·0	16·9	2·76	3·28
40	4070	4330	197·6	18·4	2·76	3·26
50	4430	4750	214·0	20·4	2·78	3·24
60	4850	5210	231·0	22·0	2·79	3·24
70	5350	5710	249·8	23·9	2·81	3·22
80	5910	6300	270·5	26·0	2·83	3·22
90	6660	7090	303·0	29·7	2·83	3·19
					Mean 2·77	3·27

The second table gives the values of a and p in the equation $dx/dt = ae^{pt}$ [*loc. cit.*, p. 843, equation (3)], and these may be compared with the values for other specimens given in that paper. In the present case, the figures are not very reliable, because the logarithmic graphs from which they are obtained show considerable curvature.

	80°.	110°.	130°.	Coeff.
$a \times 10^6$	0·358	11·0	90·8	3·03
$p \times 10^4$	0·0987	1·82	20·6	2·87

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