

**488. The Thermal Decomposition of Oxalates. Part II.<sup>1</sup>**  
*Thermogravimetric Analysis of Various Oxalates in Air and in Nitrogen.*

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The thermogravimetric analysis of several oxalates in air and in nitrogen is reported. It is shown that in some cases the decomposition proceeds directly to the oxide, but that in others the metal is first formed and is subsequently oxidised in air to the oxide. In general, the decomposition in nitrogen is simpler than in air, producing either the metal or a lower oxide.

THERMOGRAVIMETRIC analysis has been used by several investigators, notably by Duval,<sup>2</sup> for a wide range of materials, mainly in air but in a few cases in an inert atmosphere or in a vacuum. Duval reports the decomposition, with a somewhat restricted air-supply, at a heating rate of 8–10°/min., of oxalates of sixteen metals; his results differed from those of other investigators, including ourselves, probably because of the conditions used. Robin<sup>3</sup> reported that thermal decomposition, in air, of oxalates of certain bivalent transition metals gave in certain circumstances, first the metal, and that this was oxidised almost immediately to the oxide. From free-energy data for restricted temperatures Robin claimed that the metal would be expected as the immediate decomposition product of such oxalates. Ugai,<sup>4</sup> using a technique called thermographic analysis, found metals to be produced in a number of cases, and Kornienko,<sup>5</sup> who heated the oxalates isothermally in sealed evacuated containers, usually found mixtures of the metal and its oxides as the end products. In our previous paper<sup>1</sup> the changes which occurred in the surface properties of the residues resulting from the decomposition of various oxalates in air were reported; the present paper concerns the thermogravimetric analysis of these oxalates in air and in nitrogen, and suggestions are made as to the manner of their decomposition.

#### EXPERIMENTAL AND RESULTS

*Materials.*—Aluminium oxalate,  $\text{Al}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{--}6\text{H}_2\text{O}$ , and oxalates  $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  where  $\text{M} = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$ , chromium oxalate,  $\text{Cr}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ , ferric oxalate,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ , and copper oxalate,  $\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , were the materials described in our previous paper.<sup>1</sup> Other oxalates were commercial materials and gave analyses correct within 1%, namely, anhydrous cadmium, stannous, plumbous, and thorium(IV) oxalate. Commercial antimony and bismuth oxalate were also decomposed and analyses showed that the only metal ion present was antimony and bismuth, respectively.

*Apparatus.*—For decomposition in air a manually operated thermobalance was used. In this, the furnace was placed below the balance and the temperature measured by means of a chrome–alumel thermocouple. The tip of the thermocouple was as close as possible to the side of the crucible. Samples were decomposed in a nickel crucible of 1" diameter and were dried at 200° before each run. In calibration runs the crucible was suspended in the furnace without a sample and raised through the temperature range 0–600°; no gain or loss in mass exceeded 0.001 g., which is less than 0.1% of the sample weight.

The technique was to suspend 1.5 g. of material in the crucible from the balance, hold it at a constant temperature in the region 100–120°, raise the temperature at a steady rate of 2°/min. with a supply of freshly circulating air, and to measure the changes in weight and temperature at regular intervals of time. In duplicate experiments reproducibility was good.

An automatic balance devised by Pope<sup>6</sup> was used to ascertain the weight changes in an

<sup>1</sup> Part I, Dollimore and Nicholson, *J.*, 1962, 960.

<sup>2</sup> Duval, "Inorganic Thermogravimetric Analysis," Elsevier, Amsterdam, 1953, p. 531.

<sup>3</sup> Robin, *Bull. Soc. chim. France*, 1953, 1078.

<sup>4</sup> Ugai, *Zhur. obschei Khim.*, 1954, **24**, 1315.

<sup>5</sup> Kornienko, *Ukrain. khim. Zhur.*, 1957, **23**, 159.

<sup>6</sup> Pope, *J. Sci. Instr.*, 1957, **34**, 229.

atmosphere of nitrogen, the arrangement of the furnace equipment being as for the experiments in air.

*Results.*—The thermogravimetric results were plotted as percentage mass lost ( $W$ ) against temperature ( $T^\circ$ ), and the rate at which material is lost ( $dW/dT$ ) was plotted against temperature, to give the decomposition temperatures ( $T_p$ ) for each stage of the reaction from the positions of the maxima on this curve. All the oxalates thermally decomposed in both air and nitrogen could be classified into five groups, as recorded in Table 1 and Fig. 1.

Most of the oxalates of metals in Groups IB, IIB, IIIB, IVB, and VB of the Periodic Table, which were studied, showed a dehydration plateau, defining a temperature range over which the anhydrous oxalate was stable. This was followed, for work in air, by decomposition to

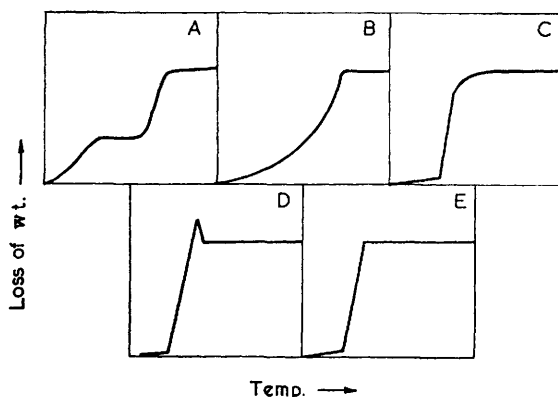


FIG. 1. Types of curve obtained on thermogravimetric analysis of oxalates.

TABLE 1.

Classification of thermogravimetric results into the types illustrated in Fig. 1.

Oxalate	Decomn. in		Oxalate	Decomn. in		Oxalate	Decomn. in	
	Air	N <sub>2</sub>		Air	N <sub>2</sub>		Air	N <sub>2</sub>
Copper .....	D	E	Lead .....	D	E	Manganese ...	A	A
Zinc .....	A	A	Thorium .....	A	A	Ferrous .....	C	C
Cadmium ...	E	E	Antimony .....	D	E	Ferric .....	C	—
Aluminium ...	B	B	Bismuth .....	D	E	Cobalt .....	A *	A
Tin .....	E	E	Chromium ...	B	B	Nickel .....	A *	A

\* Rapid heating in a limited supply of air can result in a curve of type D.

TABLE 2.

Thermogravimetric analysis of some oxalates.

Oxalate	Decomp. in	Loss (%) on dehydrn.		Loss (%) on decomp.		Loss (%) on decomp. calc. on anhyd. cpd.		End product *
		Found	Calc.	Found	Calc.	Found	Calc.	
CuC <sub>2</sub> O <sub>4</sub> ·½H <sub>2</sub> O	Air	3.5	5.6	49.7	50.0	47.9	47.5	CuO
	N <sub>2</sub>	3.5	5.6	58.6	60.4	57.1	58.0	Cu
ZnC <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O	Air	18.5	19.0	55.3	57.0	45.2	46.9	ZnO
	N <sub>2</sub>	18.3	19.0	55.3	57.0	45.3	46.9	ZnO
CdC <sub>2</sub> O <sub>4</sub>	Air	6.0	0 †	40.5	35.9	36.7	35.9	CdO
	N <sub>2</sub>	6.0	0	48.4	44.0	45.1	44.0	Cd
Al <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·3—6H <sub>2</sub> O	Air		NF	70% at 1000°		—	—	Al <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O
	N <sub>2</sub>		NF	70% at 1000°		—	—	Al <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O
SnC <sub>2</sub> O <sub>4</sub>	Air	0	0	27.1	27.1	27.1	27.1	SnO <sub>2</sub>
	N <sub>2</sub>	0	0	34.2	34.8	34.2	34.8	SnO
PbC <sub>2</sub> O <sub>4</sub>	Air	0	0	25.0	24.5	25.0	24.5	PbO
	N <sub>2</sub>	0	0	29.2	29.8	29.2	29.8	Pb
(SbO) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Air	0	0	19.8	19.8	19.8	19.8	Sb <sub>2</sub> O <sub>3</sub>
	N <sub>2</sub>	0	0	27.0	28.6	27.0	28.6	Sb <sub>2</sub> O ‡
Bi(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	Air	6.0	6.0	37.0	35.7	33.0	31.7	Bi <sub>2</sub> O <sub>3</sub>
	N <sub>2</sub>	6.0	6.0	39.7	40.3	35.8	36.4	Bi <sub>2</sub> O §

\* Used for calculation of theoretical weight loss on decomposition. † Samples contained moisture which could be removed by heating at 100°. ‡ Mixture of Sb and SbO. § Mixture of Bi and BiO. NF = Not formed.

the oxide. Under an atmosphere of nitrogen the anhydrous oxalate decomposed further, sometimes to the oxide and in other instances to the metal. Details of the weight losses incurred at each of these stages are recorded in Table 2. Similar results are presented in Table 3 for oxalates of some metals of Groups IVA, VIA, VIIA, and VIII. The dehydration and decomposition temperatures of all these oxalates in air are given in Table 4.

The availability of what is effectively an infinite amount of air in the experiments performed in air has meant that the end products of the decomposition described here are usually less complex than products obtained from experiments in a limited supply of air<sup>2</sup> or from those carried out in the presence of a predominating amount of escaping gases.<sup>5</sup>

TABLE 3.  
Thermogravimetric analysis of some oxalates.

Oxalate	Decomp. in	Loss (%) on dehydrn.		Loss (%) on decomp.		Loss (%) on decomp. calc. on anhyd. cpd.		End product *
		Found	Calc.	Found	Calc.	Found	Calc.	
Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> .....	Air	8.5	8.1	41.0	40.5	35.5	35.3	ThO <sub>2</sub>
	N <sub>2</sub>	8.3	8.1	41.1	40.5	35.7	35.3	ThO <sub>2</sub>
Cr <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .6H <sub>2</sub> O	Air		NF	69.5	68.1	—	—	Cr <sub>2</sub> O <sub>3</sub>
	N <sub>2</sub>		NF	70.0	68.1	—	—	Cr <sub>2</sub> O <sub>3</sub>
MnC <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O ...	Air	20.1	20.1	57.4	57.4	46.6	46.7	Mn <sub>2</sub> O <sub>4</sub>
	N <sub>2</sub>	20.2	20.1	60.3	60.3	50.3	50.3	MnO
FeC <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O ...	Air		NF	55.6	55.5	—	—	Fe <sub>2</sub> O <sub>3</sub>
	N <sub>2</sub>		NF	57.0	55.5	—	—	Fe <sub>2</sub> O <sub>3</sub>
Fe <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> .4H <sub>2</sub> O	Air		NF	63.0	—	—	—	Fe <sub>2</sub> O <sub>3</sub>
	N <sub>2</sub> †	—	—	—	—	—	—	—
CoC <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O ...	Air	21.0	19.7	55.0	56.1	43.0	45.3	Co <sub>2</sub> O <sub>4</sub>
	N <sub>2</sub>	19.7	19.7	67.7	67.8	59.8	59.9	Co
NiC <sub>2</sub> O <sub>4</sub> .2H <sub>2</sub> O ...	Air	22.0	19.7	61.5	59.1	50.6	49.1	NiO
	N <sub>2</sub>	19.7	19.7	67.8	67.8	59.9	59.9	Ni

\* See Table 2. † Not studied. NF = Not formed.

TABLE 4.  
Dehydration and decomposition temperatures of oxalates in air.

Metal	Dehydrn. temp.	Decomp. temp.	Metal	Dehydrn. temp.	Decomp. temp.	Metal	Dehydrn. temp.	Decomp. temp.
Copper.....	200°	310°	Lead .....	—	390°	Manganese	150°	275°
Zinc .....	170	390	Antimony...	—	270	Ferrous .....	—	235
Cadmium...	130	350	Bismuth ...	190°	240	Ferric .....	—	170
Aluminium	—	220—1000	Thorium ...	130	360	Cobalt .....	240	305
Tin .....	—	310	Chromium...	—	160—360	Nickel .....	260	352

### DISCUSSION

The experiments show two classes of oxalate decomposition; in the first are materials such as the oxalates of chromium, manganese, iron, and zinc which produce oxides as a result of decomposition in air or nitrogen, and in the second oxalates such as those of cobalt, nickel, and copper whose decomposition produces the oxide in air but the metal in nitrogen.

When the decomposition is carried out in nitrogen, the oxide or the metal may be formed, and for oxalates of bivalent metal ions these reactions may be described by the equations:



and



If the discussion at this point is confined to equilibrium conditions, then for reaction (1) the equilibrium constant is given by

$$K_1 = [MO][CO][CO_2]/[MC_2O_4], \tag{3}$$

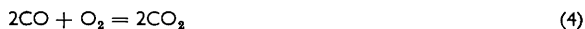
where square brackets denote activities; the equilibrium constant ( $K_2$ ) for reaction (2) is given by

$$K_2 = [M][CO_2]^2/[MC_2O_4].$$

Then

$$K_1/K_2 = [MO][CO]/[M][CO_2].$$

For the reactions



we have

$$(K_5/K_4)^{\frac{1}{2}} = [MO][CO]/[CO_2][M], \quad (6)$$

where  $K_4$  is the equilibrium constant for reaction (4) and  $K_5$  that for reaction (5). Then

$$K_1/K_2 = (K_5/K_4)^{\frac{1}{2}}. \quad (7)$$

If the standard free energy of formation ( $\Delta G^\circ = -RT \ln K$ ) for reaction (4) is denoted by  $\Delta G_a$ , and for reaction (5) by  $\Delta G_b$ , then for  $\Delta G_a > \Delta G_b$ , there must be the relation  $K_4 < K_5$ . Thence by equation (7) it also follows that  $K_1 > K_2$ .

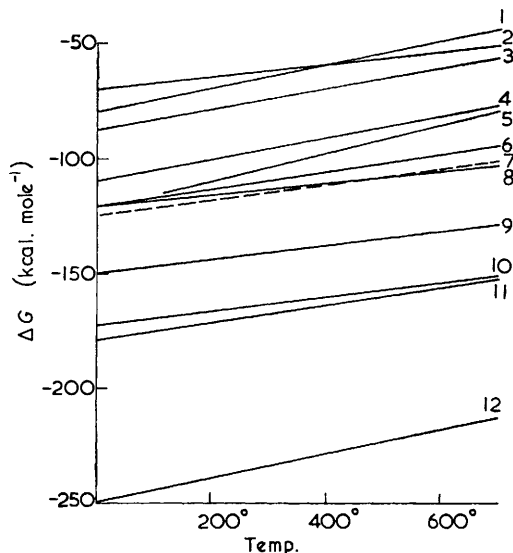


FIG. 2. Variation of free energy of formation with temperature for the following oxides: (1)  $\frac{4}{3}Sb + O_2 = \frac{2}{3}Sb_2O_3$ . (2)  $4Cu + O_2 = 2Cu_2O$ . (3)  $2Pb + O_2 = 2PbO$ . (4)  $\frac{2}{3}Co + O_2 = Co_3O_4$ ;  $2Ni + O_2 = 2NiO$ . (5)  $2Cd + O_2 = 2CdO$ . (6)  $\frac{4}{3}Fe + O_2 = \frac{2}{3}Fe_2O_3$ . (7)  $2CO + O_2 = 2CO_2$ . (8)  $2Fe + O_2 = 2FeO$ . (9)  $2Zn + O_2 = 2ZnO$ . (10)  $\frac{4}{3}Cr + O_2 = \frac{2}{3}Cr_2O_3$ . (11)  $2Mn + O_2 = 2MnO$ . (12)  $\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3$ .

Therefore, if reactions (1) and (2) are set up as equilibria, (1) is more to the product side than is (2); or, alternatively, reaction (1) will predominate over (2).

The variations of  $\Delta G_a$  and  $\Delta G_b$  with temperature have been provided in graphical form by Ellingham.<sup>7</sup> The appropriate lines are reproduced in Fig. 2. It can be seen that only for zinc, manganese, and tin among oxalates of bivalent metals does  $\Delta G_a$  exceed  $\Delta G_b$ , and then under equilibrium conditions, reaction (1) predominates over reaction (2).

<sup>7</sup> Ellingham, *J. Soc. Chem. Ind.*, 1944, **63**, 125.

For copper, lead, nickel, cobalt, and cadmium,  $\Delta G_a$  exceeds  $\Delta G_b$  and the reverse is true. Ferrous iron is unique in that the  $T-\Delta G_b$  plot crosses the  $T-\Delta G_a$  plot at  $>700^\circ$  and lies only 4 kcal. mole<sup>-1</sup> above it at the decomposition temperature.

For oxalates of trivalent metals three reactions are possible, of which two are analogous to (1) and (2), namely:



and a third which would yield the oxide  $M_2O_3$ :

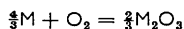


Again under equilibrium conditions, if reactions (8) and (9) are set up as equilibria, reaction (8) is more to the product side than is reaction (9) if  $\Delta G_a$  exceeds  $\Delta G_b$ .

Similarly, for reactions (8) and (10), the condition that  $\Delta G_a > \Delta G_c$  must be observed, if reaction (10) is to be set up more to the product side than reaction (8), where  $\Delta G_c$  is the free-energy change for the reaction



For reaction (10) to be set up under equilibrium conditions more to the product side than reaction (9), the condition is that  $\Delta G_a$  exceeds  $\Delta G_d$ , where  $\Delta G_d$  is the free-energy change of the reaction



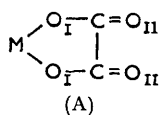
It should be emphasised that these arguments apply to equilibrium conditions. In the experiments described in this paper the rate at which the temperature was raised was slower than in previous work<sup>2</sup> and so achieved a closer approximation to equilibrium. The gaseous products were also removed as formed in the convection currents or in the stream of nitrogen passing through the furnace, and this would favour the tendency shown to produce only one final solid product, the metal or the metal oxide, and not a mixture. Nevertheless, where the thermodynamic treatment suggests that a metal should predominate in the solid residue from the reaction in a nitrogen atmosphere, our experiments lead only to the metal on thermal decomposition of the oxalates of copper, lead, nickel, cobalt, and cadmium.

For ferric oxalate, however, there are only a few kcal. mole<sup>-1</sup> difference between the values of  $\Delta G_a$ ,  $\Delta G_b$ ,  $\Delta G_c$ , and  $\Delta G_d$  at the decomposition temperatures, so that a departure from standard conditions could cause the formation of the oxide to predominate. Decomposition of antimony and bismuth oxalate should show, under equilibrium conditions, the reaction products from reaction (9) predominating; yet in our work on decomposition in nitrogen the oxide persists alongside the metal; this might be a reflection on the uncertain nature of the original material, which might have been basic in form and might have contained oxide originally. For chromium or aluminium the  $\Delta G_a-T$  plots lie well below the  $\Delta G_b-T$  plots and, at equilibrium, equilibrium (10) will set up predominantly on the product side; in nitrogen both these materials give oxides  $M_2O_3$ .

Attempts to relate decomposition temperatures with the fundamental properties of the metal ions have been made for the transition-metal oxalates by Kornienko<sup>5</sup> and Robin.<sup>3</sup> Robin plotted the temperature of departure from the dehydration plateau against atomic number for the oxalates of manganese, ferrous iron, cobalt, nickel, and zinc and obtained a curve similar to Fig. 3, which represents our results (see Table 4) and is based on a larger number of oxalates than were Robin's data.

The decomposition temperature of the copper oxalate does not fit into the general pattern. It is also difficult from such a plot to understand why materials such as the oxalates of chromium, manganese, iron, and zinc, which produce oxides as a result of

decomposition both in air and in nitrogen, should be expected to fit any scheme including cobalt, nickel, and copper oxalate which give the oxide on decomposition in air but the metal in nitrogen.



In oxalates (A) of bivalent metals, the extent to which the metal-O<sub>I</sub> bond is covalent depends on the electronegativity of the metal. Decomposition will occur when a temperature is reached at which rupture of the M-O link is possible, or at which rupture of the C-O<sub>I</sub> bond occurs: Fujita *et al.*<sup>8</sup> suggested from infrared studies that as the M-O<sub>I</sub> bond becomes stronger, so the C-O<sub>I</sub> bond is lengthened and the C-O<sub>II</sub> bond is shortened.

If the reaction proceeds by rupture of the C-O<sub>I</sub> bond, this would be followed by rupture of the second M-O bond because of the inability of the metal to accommodate two oxygen atoms. The total reaction would lead to the evolution of equimolecular proportions of

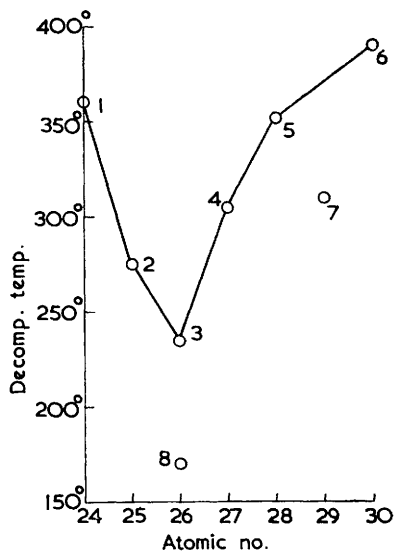


FIG. 3. Plot of decomposition temperature of oxalates in air against atomic number.

(1) Cr<sup>3+</sup>. (2) Mn<sup>2+</sup>. (3) Fe<sup>2+</sup>. (4) Co<sup>2+</sup>. (5) Ni<sup>2+</sup>. (6) Zn<sup>2+</sup>. (7) Cu<sup>2+</sup>. (8) Fe<sup>3+</sup>.

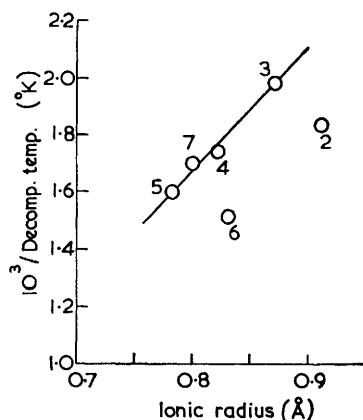


FIG. 4. Dependence of decomposition temperature on the ionic radius of the metal for oxalates of bivalent transition metals.

Key: as Fig. 3.

carbon monoxide and carbon dioxide. An alternative possibility, which has been shown to occur in the decomposition of silver oxalate,<sup>9</sup> is the direct rupture of the two M-O<sub>I</sub> bonds to produce the metal with the liberation of carbon dioxide.

For those oxalates which produce the metal in nitrogen the decomposition temperature represents the temperature at which the M-O link is ruptured and will depend critically on the size and charge of the metal ion, whereas in those decompositions where the oxide is produced in nitrogen the decomposition temperature represents the energy required to break the C-O<sub>I</sub> bond and this will depend less critically on the nature of the cation.

In those decompositions which proceed to the metal, the decomposition temperature should be related to the lattice energy, which is given by:

$$E_0 = e^2 X / r_1, \quad (13)$$

<sup>8</sup> Fujita, Nakamoto, and Kaboyashi, *J. Phys. Chem.*, 1957, **61**, 1014.

<sup>9</sup> McDonald and Hinshelwood, *J.*, 1925, **127**, 2764.

where  $E_0$  is the lattice energy,  $X$  is a constant,  $e$  is the charge on the ions, and  $r_i$  is their separation. When  $e = 2$ , then

$$T_D = \text{Constant}/(r_m + r_{ox}), \quad (14)$$

where  $T_D$ , the absolute decomposition temperature, is taken as being proportional to  $E_0$  (the log of maximum rate is assumed to be the same for each decomposition), and  $r_m$  and  $r_{ox}$  are the radii of the metal and the oxalate ion, respectively.

Thus for bivalent metals

$$1/T_D = r_m/\text{Constant} + r_{ox}/\text{Constant}. \quad (15)$$

This relation has been tested for the bivalent transition-metal ions. A straight line is obtained on plotting  $1/T_D$  against  $r_m$  for those oxalates which follow mechanism (2), in spite of the approximations introduced in equation (15) (cf. Fig. 4). The values for manganese and zinc lie off the line, and among the bivalent transition metals it is these two that give oxides as the end products of thermal decomposition of their oxalates both in nitrogen and in air.

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