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SOLID-STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART VI. KINETICS OF ISOTHERMAL DECOMPOSITION OF $M_2Zr_2(O_2)_2F_6 \cdot 2\ H_2O$ ($M = Rb^+$, or Cs^+)

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ABSTRACT

The decomposition of solid fluoroperoxozirconates of alkali metals, $M_2Zr_2(O_2)_2F_6 \cdot 2\ H_2O$ ($M = Rb^+$, Cs^+), is carried out in vacuum under isothermal conditions. The stoichiometry of the reaction may be represented by the equation, $M_2Zr_2(O_2)_2F_6 \cdot 2\ H_2O(s)$ — $M_2Zr_2O_2F_6(s) + O_2(g) + 2\ H_2O(g)$ (condensed). The fractional decomposition α is determined by measuring the pressure of oxygen evolved during pyrolysis with a McLeod gauge. The α values range from 0.06 to 0.70 for the rubidium and from 0.06 to 0.79 for the caesium species in the temperature ranges 107—202°C and 101—219°C, respectively. The α—time data for both compounds show that the kinetics are deceleratory throughout the course of the decomposition reaction. In both compounds, the initial stages of decomposition are described by a unimolecular decay law, while the later stages obey a contracting volume equation at all temperatures. The activation energies from Arrhenius plots are 14.0 and 10.9 kcal $mole^{-1}$ for the rubidium and 12.9 and 11.2 kcal $mole^{-1}$ for the caesium compound.

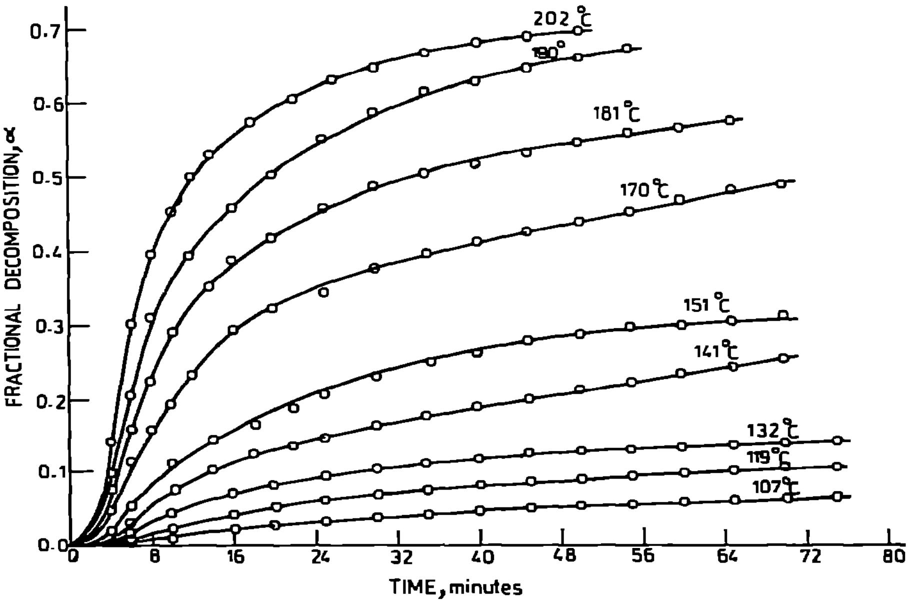


Fig. 1. Thermal decomposition curves of rubidium fluoroperoxozirconate.

INTRODUCTION

Work on thermal and photo-decomposition of the fluoroperoxo species of transition metals has already been described [1—5]. This paper covers the isothermal decomposition of the solid compounds $M_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$, where M = Rb^+ or Cs^+.

EXPERIMENTAL

The compounds were prepared as described earlier [3], except for one modification. During the preparation [6] the Zr : F mole ratio was kept at 1 : 3 instead of 1 : 7. The solids were ground, dried over phosphorus pentoxide, and characterised by analysis, IR, and powder diffraction studies. Samples were homogenized by sieving to below 150 μm.

The constant volume apparatus is the same as described earlier [1—3].

RESULTS

$Rb_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$

The decomposition of this solid was carried out at nine temperatures in the range 107—202°C and α—time data are plotted in Fig. 1. It is seen that

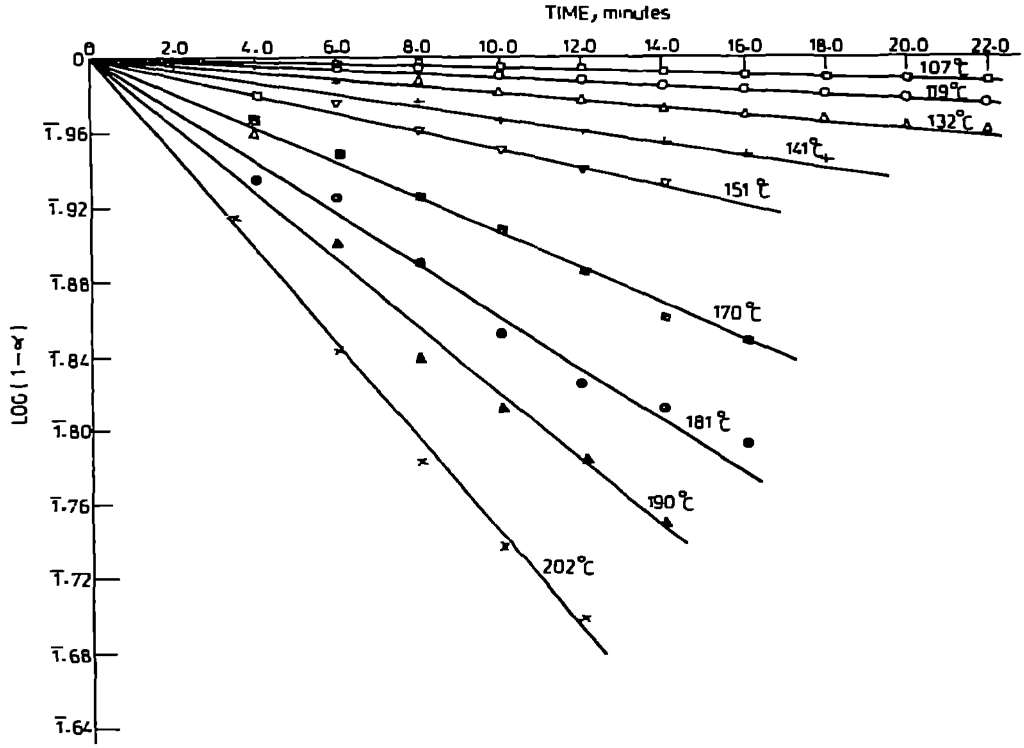


Fig. 2. Plot of $\log(1-\alpha)$ vs. t (unimolecular decay law) for rubidium fluoroperoxozirconate.

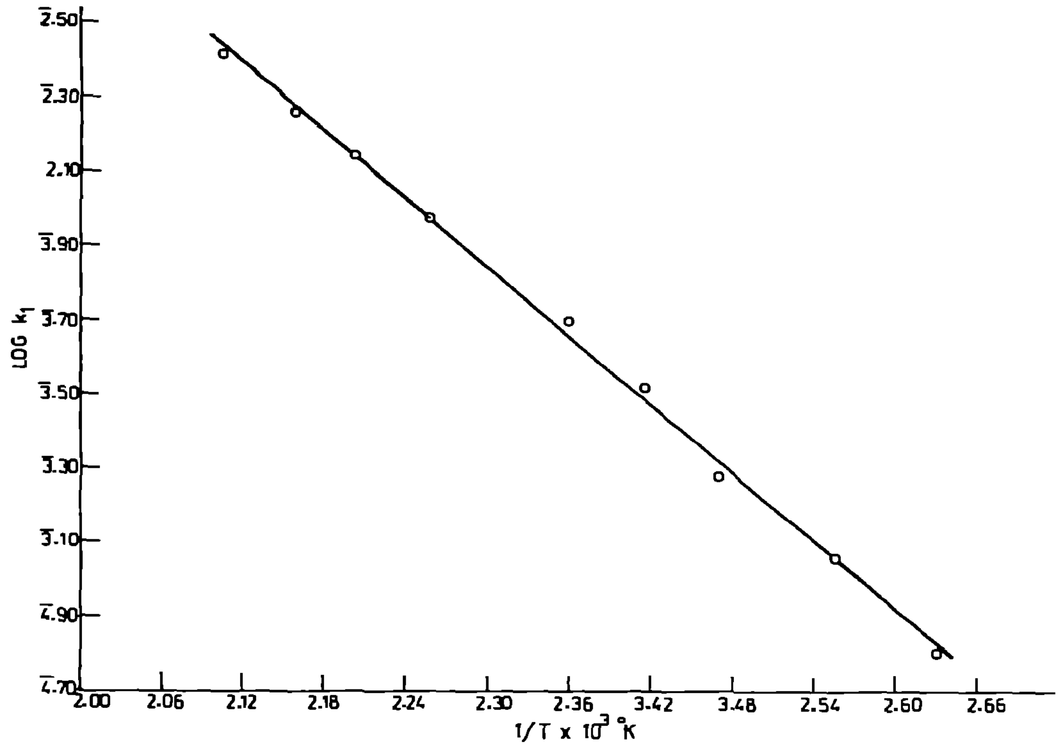


Fig. 3. Arrhenius plot of unimolecular decay law rate constants, i.e. log k_1 vs. $1/T \times 10^3$ (T in units of K), for rubidium fluoroperoxozirconate.

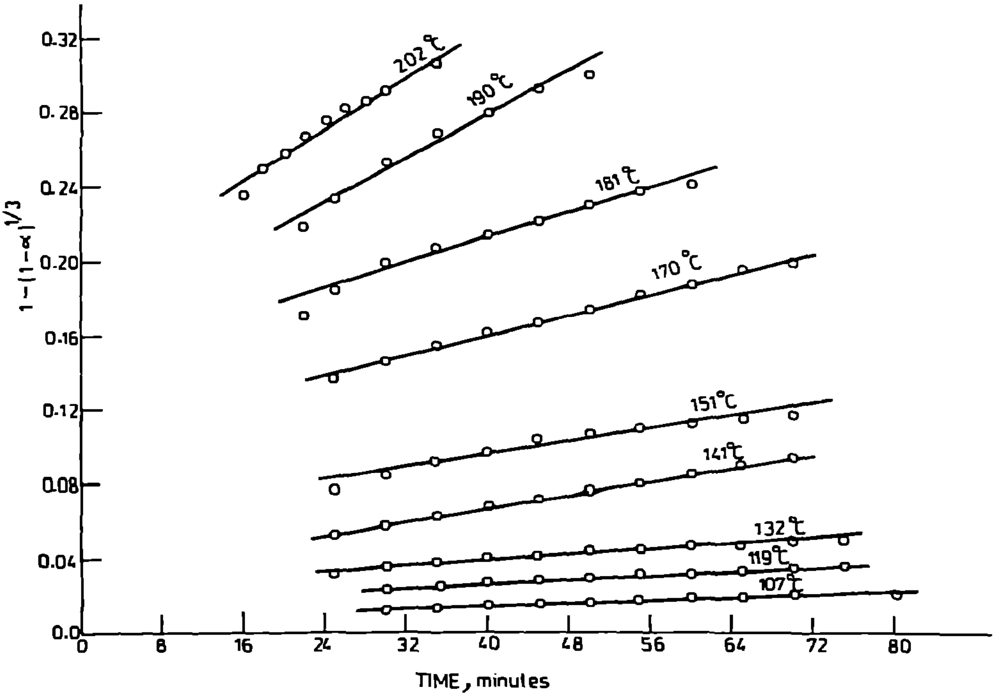


Fig. 4. Plot of $1-(1-\alpha)^{1/3}$ vs. t (contracting volume equation) for rubidium fluoroperoxozirconate.

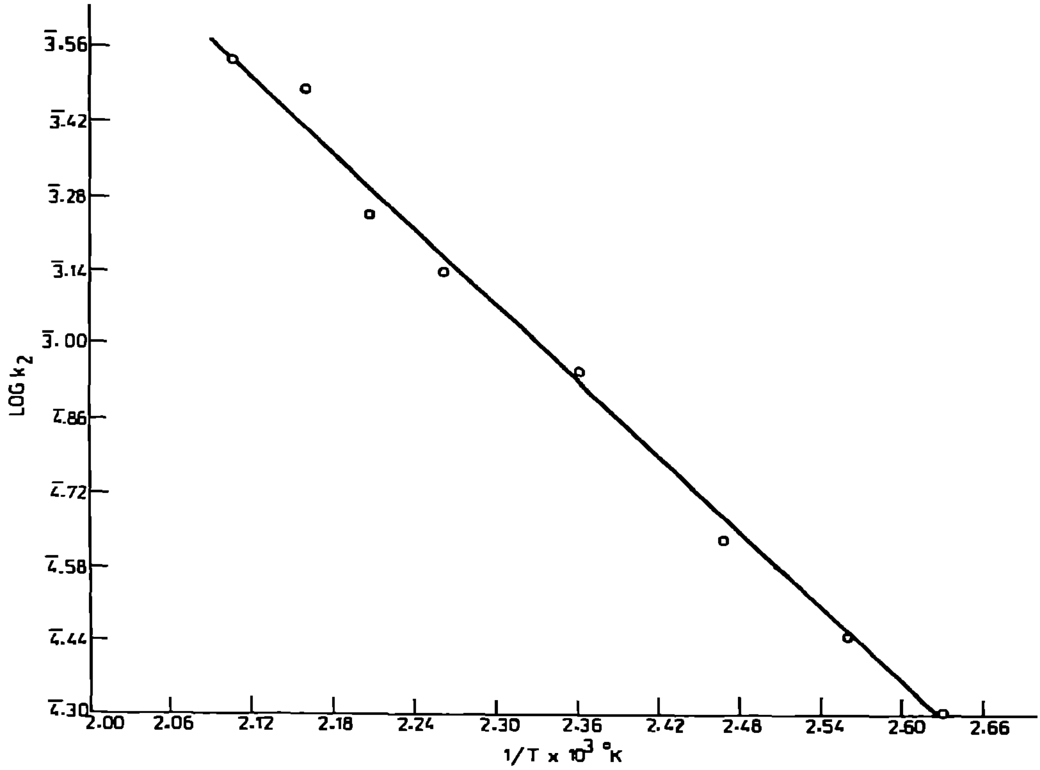


Fig. 5. Arrhenius plot of contracting volume rate constants, i.e. log k_2 vs. $1/T \times 10^3$ (T in units of K), for rubidium fluoroperoxozirconate.

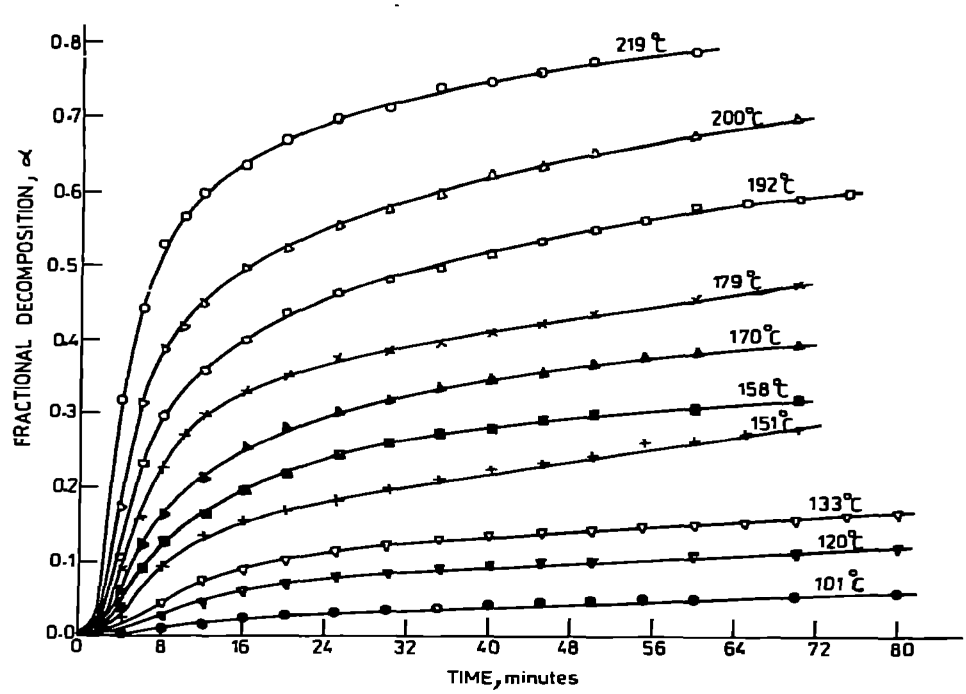


Fig. 6. Thermal decomposition curves of caesium fluoroperoxozirconate.

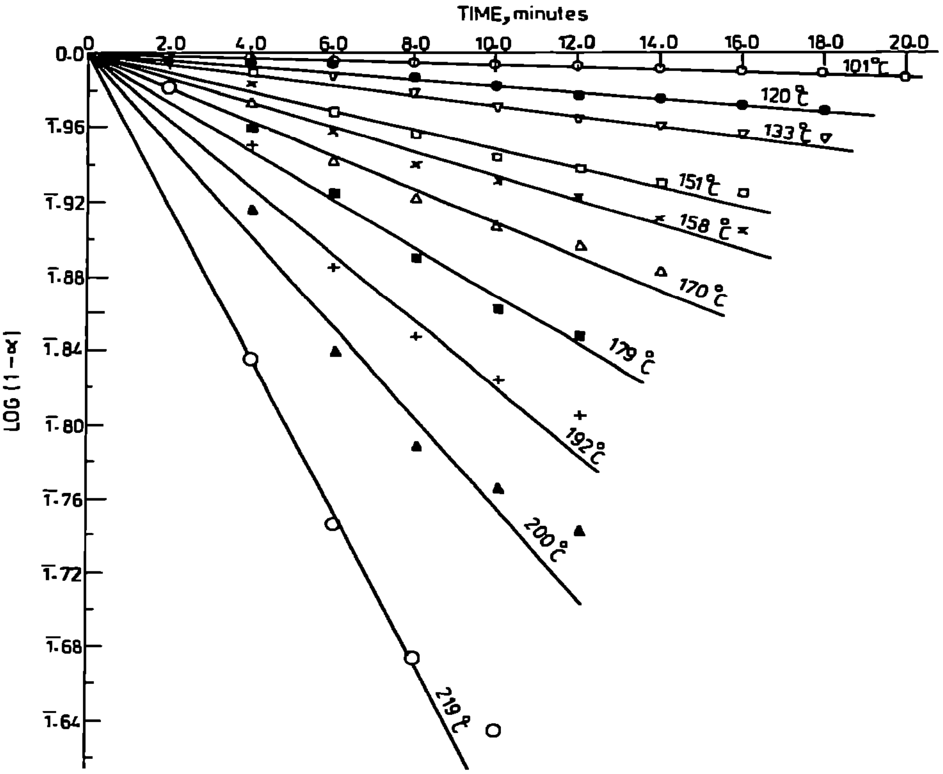


Fig. 7. Plot of log $(1 - \alpha)$ vs. t (unimolecular decay law) for caesium fluoroperoxozirconate.

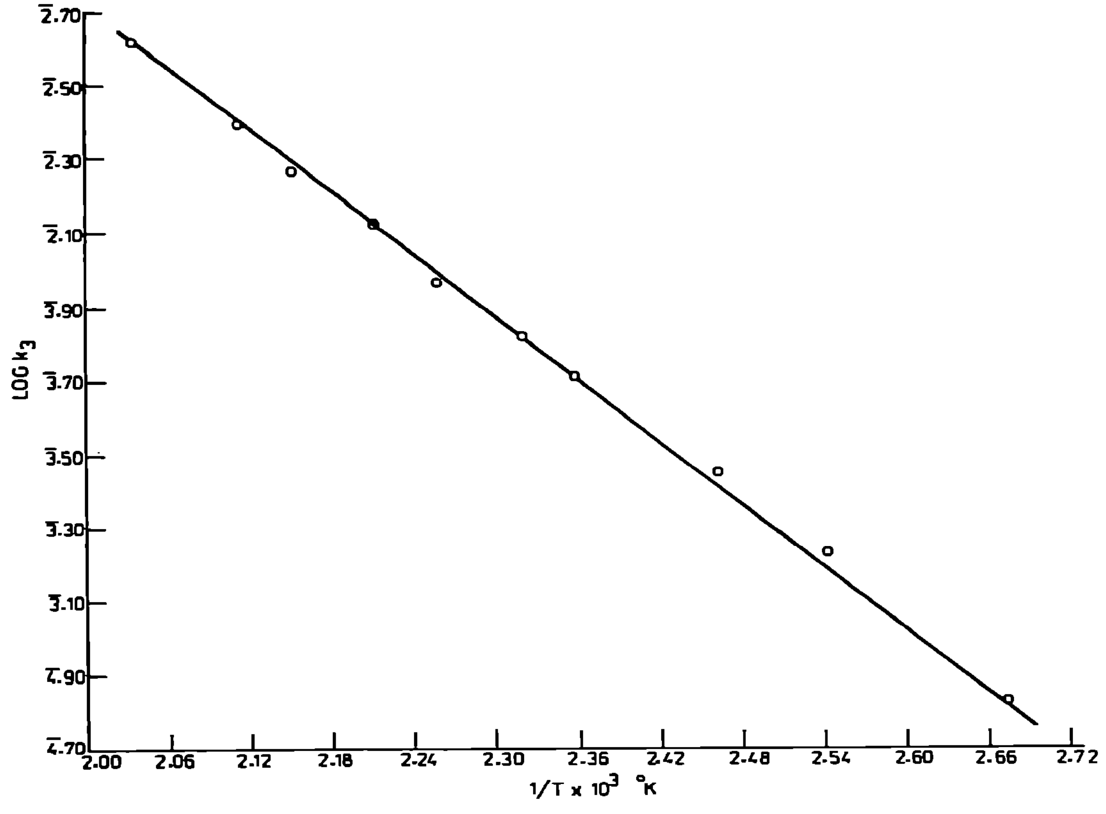


Fig. 8. Arrhenius plot of unimolecular decay law rate constants, i.e. $\log k_3$ vs. $1/T \times 10^3$ (T in units of K), for caesium fluoroperoxozirconate.

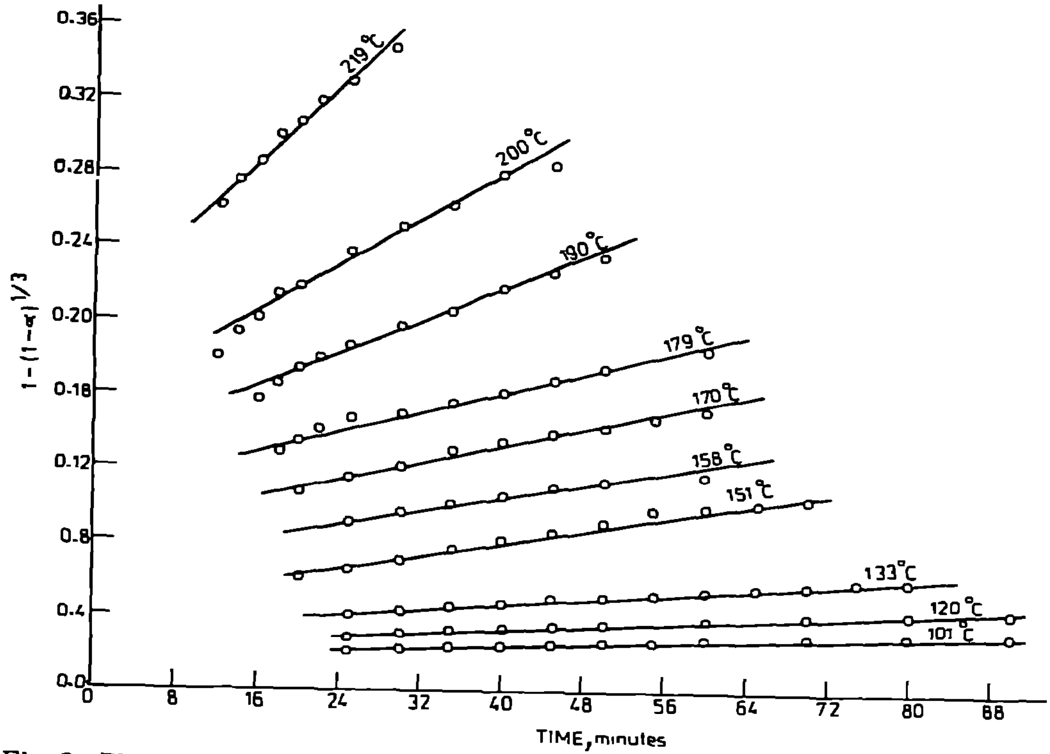


Fig. 9. Plot of $1-(1-\alpha)^{1/3}$ vs. t (contracting volume equation) for caesium fluoroperoxozirconate.

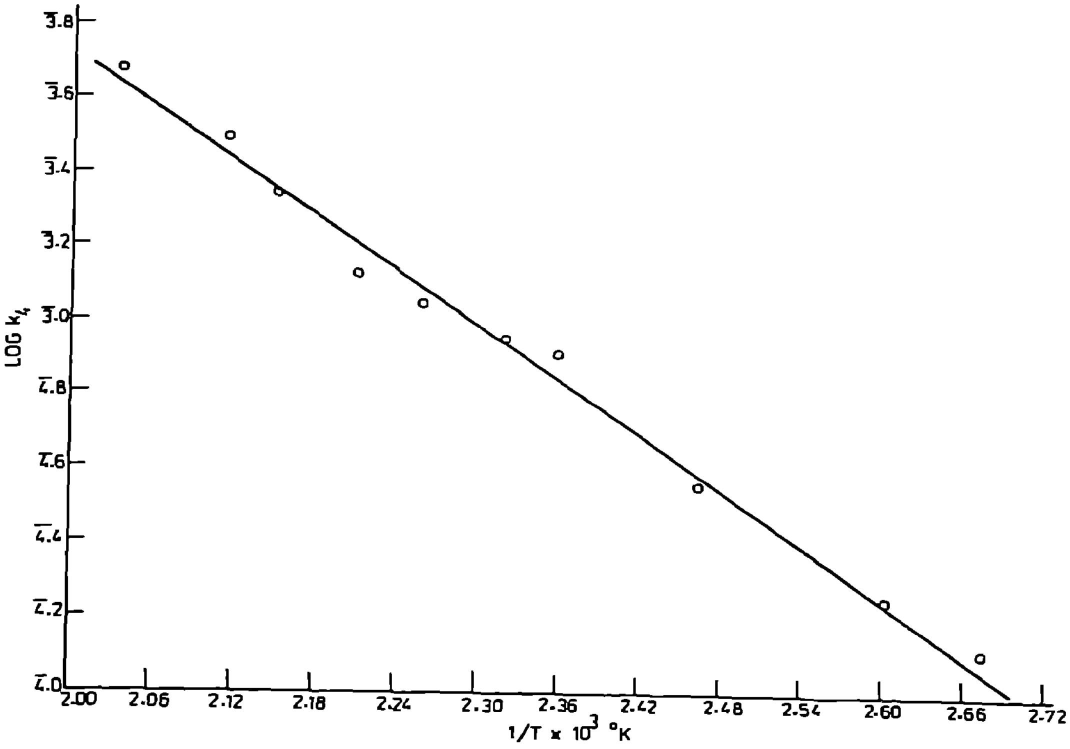


Fig. 10. Arrhenius plot of contracting volume equation rate constants i.e. log k_4 vs. $1/T \times 10^3$ (T in units of K), for caesium fluoroperoxozirconate.

the induction period and acceleratory region are absent. The rate of decomposition is greatest at the beginning of the reaction, i.e. the reaction is deceleratory throughout the course of decomposition. Values of α ranged from 0.06 to 0.70 in this temperature range. The initial stage of decomposition is best described by a unimolecular decay law, see Fig. 2. The activation energy of the process, deduced from an Arrhenius plot, Fig. 3, is 14.0 kcal $mole^{-1}$. The later stages obey a contracting volume equation, Fig. 4. Similarly the activation energy from an Arrhenius plot, Fig. 5, is 10.9 kcal $mole^{-1}$.

$Cs_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$

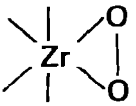
The isothermal decomposition of this compound was studied in the temperature range 101—219°C and α—time data are plotted in Fig. 6. As for the rubidium analogue, the rate of decomposition is greatest at the beginning of the reaction and then decreases with time at all temperatures. The minimum and maximum α values in this temperature range are 0.06 and 0.79. The initial stage of decomposition is adequately described by a unimolecular decay law, see Fig. 7. The activation energy from an Arrhenius plot, Fig. 8, is 12.9 kcal $mole^{-1}$. The later stages of decomposition obey a contracting volume equation, Fig. 9. From the Arrhenius plot, Fig. 10, the activation energy is 11.2 kcal $mole^{-1}$.

DISCUSSION

This paper completes the isothermal decomposition studies for two sets of solid fluoroperoxozirconates of alkali metals with the molar compositions $M_3Zr_2(O_2)_2F_7 \cdot x\,H_2O$ and $M_2Zr_2(O_2)_2F_6 \cdot 2\,H_2O$. Results on the first set have been described earlier [1,3]. The salient findings on the second group of solids are summarized below.

The shapes of the α—time plots for all the compounds are similar. The initial part of the decomposition is described by a unimolecular decay law, indicating rapid or instantaneous nucleation followed by rapid surface growth. The later stages of decomposition obey a contracting volume equation, which implies that the surface has been completely transformed into product and the reaction interface is moving towards the centre of the compound particles. The activation energies obtained are listed in Table 1.

These activation energies compare well with an earlier set [3]. Uniformly low and comparable activation energies suggest that the rate-determining step is the same for all these solids. It is probable, as proposed earlier [3], that the first step in the peroxide decomposition of these solids is breaking of the metal—peroxide bond and release of strain within the system



It was seen during photo-decomposition studies on these solids [4,5] that the only photo-excitable species is the peroxo group, which subsequently

TABLE 1

Activation energies

$M_2Zr_2(O_2)_2F_6 \cdot 2H_2O$ species	Activation energies (kcal $mole^{-1}$)	
	Unimolecular decay law	Contracting volume equation
Potassium [2]	13.6	6.9
Rubidium	14.0	10.9
Caesium	12.9	11.2

undergoes decomposition and oxygen is evolved. Lattice water remains unaffected during photolysis. Note that, unlike other systems where the metal undergoes reduction during photolysis or thermal decomposition [7], zirconium(IV) in all these solids is unlikely to be reduced to zirconium(III) under the conditions used. Hence it may be inferred that, both for thermal and photo-decomposition, the interaction between the peroxo groups leads to the formation of oxygen and oxide ion accompanied by extensive lattice rearrangement:

$$O_2^{2-} \rightarrow (O_2^{2-})^* \text{ excited state}$$
$$(O_2^{2-})^* + O_2^{2-} \rightarrow O_2 + 2\,O^{2-}$$

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