the three values determined for anion tracer diffusion by Oishi and Kingery (152 ± 25, 110 ± 15 and about 60 kcal.mole^{-1} respectively). If this set of values is accepted, the following conclusions must be drawn:

(1) Paladino and Kingery's value for cation tracer diffusion in polycrystalline alumina (114 ± 15 kcal.mole^{-1}) must represent extrinsic cation diffusion in the presence of excess oxygen vacancies ($Q_{c2} = 130 \pm 3$ kcal.mole^{-1}),

(2) Oishi and Kingery's value for anion tracer diffusion in polycrystalline alumina (110 ± 15 kcal.mole^{-1}) represents intrinsic oxygen diffusion ($Q_a = 115 \pm 4$ kcal. mole^{-1}),

(3) Oishi and Kingery's value for anion tracer diffusion in single-crystal alumina (152 ± 25 kcal.mole^{-1}) represents extrinsic anion diffusion in the presence of excess cation vacancies ($Q_{a1} = 150 \pm 5$ kcal.mole^{-1}), and

(4) their observed lower-temperature value for anion tracer diffusion in both types of sample (about 60 kcal.mole^{-1}) represents extrinsic anion diffusion in the presence of a fixed concentration of anion vacancies ($Q_{ma} = 63 \pm 17$ kcal.mole^{-1}).

In Figure 4, lines with gradients appropriate to the calculated activation energies are superimposed on the experimental data for tracer diffusion. It is seen that a good fit is obtained in all cases.

It must be remembered that the calculations in this section have been made assuming that the vacancy concentrations in alumina are predicted by the conventional thermodynamic theory of Schottky defects, that the changes in activation energy brought about in the pressure-sintering experiments are caused by the introduction of extrinsic vacancy concentrations in the manner suggested, and for no other reason, and that the activation energies for the movement of the ionic species are essentially unaffected by the presence of small amounts of impurity. The way in which it has been found possible to correlate the calculated values with published results for tracer diffusion lends some confidence to the calculations.

The conclusion that the activation energy for aluminium ion diffusion in polycrystalline alumina observed by Paladino and Kingery (114 ± 15 kcal.mole^{-1}) was that for extrinsic cation diffusion in the presence of excess oxygen vacancies could presumably be checked by aluminium tracer measurements using alumina doped in such a way as to induce an excess concentration of cation vacancies, when a low activation energy (< 36 kcal.mole^{-1}) should be observed, according to the present calculations.

The conclusions concerning the meaning of the diffusion coefficients measured by anionic tracer diffusion lead to some interesting speculations. According to OISHI and KINGERY,[11] there was definite evidence that the observed anion tracer diffusion in their polycrystalline samples took place by grain-boundary diffusion (argued from the observation that the apparent diffusion coefficient decreased with time, i.e. with depth of penetration from the surface). If this is so, the implication is that intrinsic oxygen diffusion occurred in grain-boundary regions. However, extrinsic (class 1) diffusion was observed for their single-crystal samples, with diffusion coefficients at least an order of magnitude lower than for intrinsic diffusion. It is probable that

diffusion within the grains of the polycrystalline samples would follow the same mechanism as that within the single-crystal samples, so that an immediate explanation is obtained for the preferential grain-boundary diffusion in the polycrystals.

That intrinsic diffusion was observed in grain-boundary regions implies either that the trace impurities giving rise to excess cation vacancies were repelled from the grain boundaries, or that these impurity ions associated with dislocations in the boundary regions so that they no longer caused anomalous vacancy concentrations (being no longer free to distribute themselves randomly within the lattice). The latter suggestion also offers an explanation of why intrinsic ionic diffusion should be observed with undoped alumina in the present pressure-sintering experiments at temperatures below 1400°C, when extrinsic diffusion might be expected. The alumina grains undergoing pressure-sintering are likely to contain high concentrations of dislocations because of the stresses to which they are subjected, and if association readily occurs between trace-impurity ions and dislocations, this could explain why intrinsic diffusion can be observed at such low temperatures.

The calculations in the present section imply that the oxygen tracer diffusion measurements of Oishi and Kingery with single-crystal specimens (Figure 4, plot G) represent extrinsic class 1 diffusion at temperatures above about 1650°C and extrinsic class 2 diffusion at lower temperatures, although some samples exhibited extrinsic class 1 behaviour at temperatures as low as about 1500°C. In particular, samples annealed in air at 1900°C before diffusion coefficients were measured at lower temperatures (below about 1650°C) gave results which indicated extrinsic class 1 behaviour (i.e. the points fell on the 150 kcal.mole^{-1} plot). It might not be expected that a set of samples should exhibit both types of extrinsic diffusion (according to the temperature range) with no evidence of intrinsic diffusion, but it is possible that the samples contained different types of impurities which gave rise to both cation and anion vacancies, in different concentrations. If this is so, the results suggest that, at temperatures above 1650°C, the excess concentration of cation vacancies controlled the diffusion behaviour, while the impurity-controlled concentration of anion vacancies could be ignored at these temperatures. As the temperature was reduced below about 1600°C, it would appear that the concentration of anion vacancies was prevented from falling below the value fixed by the presence of the appropriate impurity ions, so that extrinsic class 2 diffusion was observed. It appears that annealing at high temperature can cause either a reduction in the concentration of these latter impurity ions, or their association with lattice defects such as dislocations, so that extrinsic class 1 diffusion can be extended to lower temperatures. The samples were reported to contain traces of magnesium and calcium (which may cause anion vacancies), silicon (which may cause cation vacancies), and may have contained anionic impurities which were not sought for during analysis.

From Equation 3(a) (where $z_a = 2$ and $z_c = -3$), D_M controlled by oxygen diffusion should be a little more than twice the tracer diffusion coefficient. If the higher-temperature part of plot F in Figure 4 is accepted as representing intrinsic oxygen diffusion, it is seen that

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