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COMMENTS AND ADDENDA

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Kinetics of aggregation of divalent cation impurities in alkali halides: Comments on a paper by Unger and Perlman

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Deductions made in a recent paper by Unger and Perlman about the kinetics of aggregation in doped alkali halides are discussed and the experimental basis for deciding on the order of the aggregation process is restated.

A number of years ago we reported[1,2] that the first stage of aggregation of impurity-ion–vacancy pairs in divalent-cation doped alkali halides proceeds by third-order kinetics. This was confirmed by several other workers.[3–8] Owing no doubt to the uncommon occurrence of third-order kinetics, several attempts[9–11] have been made to show that our analysis of the data was incorrect and that, in fact, the process goes by a second-order reaction. A common feature of these attempts is that they ignore the most important part of the evidence, namely, the concentration dependence of the rate constant, and they proceed to analyze data limited to one concentration for each system by curve fitting alone.

One of us has already drawn attention (see Ref. 12, Fig. 2) to the difficulty within present experimental accuracy in distinguishing by curve fitting alone between second- and third-order kinetics including the back reaction, where equilibrium occurs before half the dipoles disappear. Indeed, we agree with Unger and Perlman that it is possible to fit a curve for second-order decay with back reaction to our experimental results where equilibrium occurs early in the reaction. Equally, it is possible to fit a curve for third-order decay with back reaction. Surprisingly, Unger and Perlman seem to have failed to realize that the back reaction has always been considered in work from this laboratory (see particularly Refs. 4 and 14).

To find the order of reaction it is necessary to use a classic kinetic test, namely, the concentration dependence of the rate constant. In view of the latest discussion by Unger and Perlman it seems desirable to reemphasize this point. The necessary theory may be found in most Physical Chemistry texts (see, for example, Ref. 13).

A reaction in which n impurity-ion–vacancy pairs (dipoles) combine to form an n-mer may be expressed by the equation

$$\frac{dx}{dt} = -k_1 x^n + k_2 x_n , \tag{1}$$

where x is the concentration of dipoles and x_n the concentration of n-mers. If we examine a series of crystals containing the same impurity ion in different concentrations c, and rewrite Eq. (1) in terms of the fraction p of dipoles remaining after time t, we obtain

$$\frac{dp}{dt} = -k_1 c^{n-1} p^n + k_2 (1-p) = -k_1^1 p^n + k_2 (1-p) , \tag{2}$$

from which it can be seen that the rate constant for aggregation k_1^1 is proportional to c^{n-1}. Under conditions such that equilibrium occurs for only a small fraction of dipoles remaining, it is obvious that the second term can be neglected in comparison to the first for most of the reaction and that the time taken to reach any fractional concentration will be a measure of k_1^1. The concentration dependence of the half-life of the reaction $t_{1/2}$ mea-

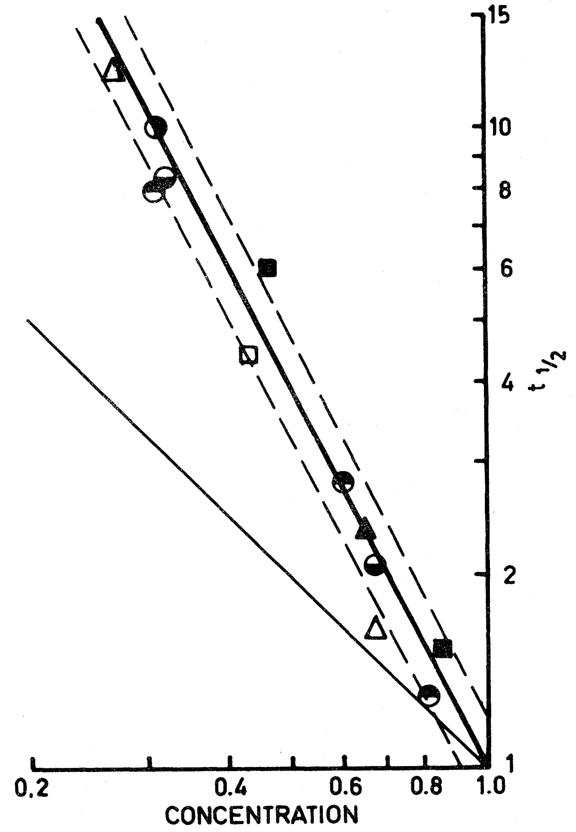

FIG. 1. Half-life of the forward reaction $t_{1/2}$ plotted as a function of the initial concentration of impurity-ion vacancy pairs, the symbols represent: ◒◓, KCl:Sr^{2+}; ◑, KCl:Pb^{2+}; ▲, NaCl:Mn^{2+}; △, NaCl:Ca^{2+}; and ■□, LiF:Mg^{2+}. Both $t_{1/2}$ and concentration are plotted in reduced form relative to the highest concentration for which data are available at the particular aggregation temperature. The thicker line has a slope of -2, the thinner a slope of -1, and the dashed lines represent ±10% in the concentration about the line of slope -2. For those systems in which two symbols are used these symbols refer to different temperatures.

sured simply by finding the time required for half the dipoles to disappear, can then be used to determine the order of the reaction.

In systems where equilibrium occurs earlier in the reaction, which is where more than a small fraction of dipoles remain at equilibrium, the above result can be used and $n = 3$ substituted in Eq. (2). Equation (2) can then be solved for different ratios of k_1^1 to k_2 and the solutions fitted to the experimental points to give k_1^1 and an equivalent $t_{1/2}$, i.e., the half-life of the forward reaction. Obviously $t_{1/2}$ determined this way will be less than the time taken for half the dipoles to disappear.

It is worth noting that using our procedure it was not necessary to assume any reaction order *a priori*. Because the concentration dependence follows a power law, determination of the correct reaction order does not require great accuracy in estimating half-lives. Indeed, if we had assumed a second-order reaction with a back reaction in those cases where the back reaction had to be considered, the experimental points would have been reasonably well fitted and the half-lives determined in this way would not have differed greatly from those obtained using the correct third order and would have been adequate for determination of the correct reaction order by finding their concentration dependence. The test has been applied to data from another laboratory and third-order kinetics demonstrated.[12]

Since our original demonstration of third-order kinetics, we have made measurements on many other systems. The results are collected in Fig. 1, in which the half-lives and concentrations for any system at one fixed temperature are plotted in reduced form relative to the highest concentration for which data were available. Lines of slope -1 and -2 have been drawn through the origin and it is clear that as we reported years ago the kinetics are third, not second order.

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