

## Reply to comments of Cook and Dryden on: Dimerization of impurity-vacancy dipoles in alkali halides\*

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Cook and Dryden do not point out any flaws in our analysis, but simply restate their case. We do not believe there are any flaws. We assume that the processes governing the initial rate of decay of the dipoles are association to form dimers, and dissociation *only*, neglecting the formation and dissociation of trimers. Neglect of the latter implies a range of validity to the solution of the equation, which we show to be  $n_i/n_0 > 1/3$ . We work out the consequences of these assumptions, and obtain a theory which is in excellent agreement with experiment, in its range of validity.

We will first treat the comments on our paper by Cook and Dryden, hereafter referred to as I, and then the evidence they present for their point of view. They state that our work is equivalent to "curve fitting." Since the only arbitrary parameters are the rate constants, which are not known *a priori* by Cook and Dryden or by us, our theory is no more and no less "curve fitting" than theirs.

Next, they question the application of our theory to "limited data." We have applied the analysis to four different I-V dipole systems in our paper,<sup>1</sup> with varying initial concentrations and temperatures. Good agreement between theory [according to Ref. 1, Eq. (11)], and experiment is obtained right up to the plateau region of the curves in every case. In each case there are plenty of experimental points before the plateau is reached. Further, in another paper<sup>2</sup> we apply our theory to the I-V dipole decay results in KCl:Ba<sup>++</sup> at a series of temperatures. We now have at least nine different experiments that show excellent agreement with our theory. We do not consider this "limited data."

Cook and Dryden imply that we make much of the "back reaction." *Indeed we do.* It is the whole point of our analysis. They seem surprised that "they (meaning us) seem to have failed to realize that the back reaction has always been considered in work from this laboratory." While the back reaction is included by Dryden and Symons and Kemp from the same laboratory (Refs. 14 and 4 of I) in theories that assume trimer formation and dissociation and formation of more complex aggregates, nowhere in the published literature to our knowledge do Dryden and Cook (or anyone else) show attempts at applying a simple dimer formation-dissociation theory in the initial stages of dipole decay to their experiments, as we have done. Indeed, in almost every instance where the back reaction is mentioned, it is later ignored. See, for example, their comments after

Eq. (2) of I. The same is true of Refs. (3) and (5)-(8) of I which they quote in support of their contention of trimer formation. Dimer formation and dissociation and trimer dissociation is ignored in every case. Trimer formation alone is considered, and the results analyzed according to Eq. (2) of Ref. 1 (not used by us). From Ref. 1, Fig. 2. we see that agreement with experiment assuming *either* dimer or trimer *formation only* can be obtained over limited ranges of time. (Compare this with the excellent straight lines that we obtain right up to the plateau in every case with our theory.)

We will *not* quote the results of Harris and Jackson (Ref. 10 of I), who determine the kinetics to be of *second* order in LiF:Mg to support *our* contention of dimer formation and dissociation because these authors also use the procedure outlined above, which we believe to be incorrect. However, we should like to quote the theoretical results of Naberhius and Fong (Ref. 9 of I). Using minimization of the free energy, they found that extensive dimer formation should occur through wide ranges of temperature and concentrations with trimer formation being of negligible significance except at very high concentrations, which are outside the concentration ranges normally used in I-V dipole kinetic experiments.

Cook and Dryden worry that we ignore the most important part of their evidence, the concentration dependence of the rate constant. We agree with Eq. (1) of I for formation and dissociation of one type of *n*-mer only. We also agree with Eq. (2) of I, which shows the rate constant to be concentration dependent. We *disagree* with the neglect of the second term (back reaction) in Eq. (2) of I. Neglecting the back reaction is equivalent to denying the existence of a plateau in the decay curves, which is contrary to experiment. The plateau is simply a result of the formation-dissociation equilibrium (rate of formation of dimers = rate of dissociation). In those experiments where plateaus

are not observed, insufficient decay time is available at the particular temperature used for the equilibrium to be established. Here, the formation rate exceeds the dissociation rate over the complete decay time. However, in this case as well, without *a priori* knowledge of the relative values of the rate constants  $k_1$  and  $k_2$  both processes must be considered effective from  $t=0$  on, i. e. throughout the decay, and must be included in the analysis

Inserting the values of  $a$  and  $b$  into Ref. 1, Eq. 11 we see that the time of decay to any fractional concentration is a function not only of the initial concentration  $n_0$ , but also of the plateau level  $n_s$ . This disagrees with Cook and Dryden's contention that the half-life in this case (dimer formation and dissociation) is proportional only to the reciprocal of the concentration. To put this more physically: If the back reaction is included for both (a) formation and dissociation of dimers, and (b) formation and dissociation of trimers, then the dipole decays in each case are slower than for formation only. This has the effect of lengthening the time required to reach any fractional concentration (for any initial concentration) from

that obtained theoretically by omitting the back reaction. Thus in Cook and Dryden's  $t_{1/2}$  versus concentration graph (where they omit the back reactions) the theoretical curves should slope more towards the  $t_{1/2}$  axis, removing the agreement between experiment and theory for third-order formation only. Whether second order would then agree or not will depend on the relative values of the dimer rate constants for formation and dissociation. In other words, we do not consider their half-life versus concentration test to be adequate to decide between second and third-order kinetics if the back reaction is omitted in the theory for both cases.

To summarize, what we seem to have here are two different sets of basic assumptions, ours and Cook and Dryden's. The consequences of these assumptions seem to be correctly determined by both groups. Our model has the simple advantage that second order makes more sense, especially in the initial stages of decay. Only further measurements and the test of time will show which of the theories is correct. We are confident of the outcome.

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<sup>1</sup>S. Unger and M. M. Perlman, Phys. Rev. B 10, 3692 (1974).

<sup>2</sup>S. Unger and M. M. Perlman, Phys. Rev. B 12, 809 1975.