

equation always under a cube root, and under either the  $\ln$  or the  $\tan^{-1}$  so that the expression is very insensitive to any error in  $\alpha$ . It is perhaps significant that the point corresponding to the start of the hydration ( $\alpha = 0.012$ ) is the worst fitting one.

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<sup>1</sup> De Boer, J. H. (ed.), *Reactivity of Solids*, 280 (Elsevier, 1961).

<sup>2</sup> Schiller, K., *J. App. Chem.*, **12**, 135 (1962).

<sup>3</sup> Schiller, K., *J. App. Chem.*, **13**, 572 (1963).

<sup>4</sup> Schiller, K., *J. App. Chem.*, **14**, 209 (1964).

<sup>5</sup> Birss, F. W., and Thorvaldson, T., *Canad. J. Chem.*, **33**, 870 (1955).

I FEEL that Schiller may be under some misapprehension regarding our previous work. The differential equation, the solution of which forms my complete equation for the hydration of calcium sulphate hemihydrate, was derived from one developed earlier to account for the self-acceleration of the reaction<sup>1-6</sup> by the inclusion of a term allowing for processes leading to the decay of the rate. Contrary to Schiller's statement (preceding communication), I have not modified my views, but have expressed them more completely in mathematical terms. The differential equation resembles one quoted by Schiller<sup>7</sup> but not derived precisely from a model. The equation mentioned by Schiller is well known for dealing with the formation and growth of nuclei of a solid product (for example, see ref. 8), and he has not tested to what extent a solution describes experimental observations in the particular system. The differences between the two equations are highly significant.

My replies to Schiller's four objections are as follows:

(1) If needles grow exclusively along the long axis and plates in two dimensions parallel to their planes the surface area is approximately proportional to mass, the approximation being better the smaller the unchanging dimensions. This is the condition for the growth of gypsum in my theoretical model, and its aptness for the accelerated and unmodified reaction is borne out by the experimental results. Schiller considers only growth in three dimensions, when a two-thirds relationship will apply as discussed earlier<sup>8</sup>. However, my model is theoretically possible, and in my opinion provides a better basis for interpreting the rate of the accelerated and unmodified reactions than does one assuming growth in three dimensions. The model leading to a two-thirds relationship between the mass and surface area of the system of growing gypsum crystals may be better for interpreting the more complex reaction occurring in the presence of inhibitors which tend to result in equi-axial crystals of gypsum, as we have suggested already<sup>9</sup>.

(2) I am aware of the questions of under-saturation and super-saturation raised by Schiller<sup>4</sup>, but they do not appear to complicate the matter seriously as shown by the accord between experimental results and a theory which ignores them. The probable reason for this is that a steady state regarding concentration gradients will be set up in the kinetically important parts of the system before much hemihydrate has been hydrated. This situation can result from the low solubility of calcium sulphate and the fact that by far the greater part of it in the system is solid.

(3) The difference in power index between my differential equation and that quoted by Schiller makes a considerable difference so far as the first half of the reaction is concerned, and particularly regarding nucleation, as Schiller admits in his third objection. The implication that "there will be no hydration unless some gypsum is present" is in accord with the heterogeneous nature of nucleation in the system. As explained elsewhere<sup>6</sup>, the population of seeding nuclei results in gypsum being present in effect at the

beginning of the reaction, although the hemihydrate need contain no gypsum as such.

(4) The mathematical argument that the expression  $F(\alpha)$  is insensitive to error is incorrect.  $F(\alpha)$  is a function of a single variable, and will respond (unless it is constant) equally to any variation in  $\alpha$  whether this is due to error in measurement or to a real change in the system.

Schiller obtains the differential equation<sup>7,10</sup> to which he refers by a considerable approximation from another equation derived from a mechanism that he develops in the series of papers quoted. In them, Schiller treats an equation (No. 11, ref. 9) as the true outcome of his method. I have tested his equation No. 11 with results obtained from the isothermal hydration of calcium sulphate hemihydrate and find that it does not represent them very well. Schiller uses the increase in temperature of the system to test his equation. It is true that we have shown theoretically and experimentally<sup>2-6</sup> that the courses of the adiabatic and isothermal reactions are not very different for the accelerated and unmodified reactions (but not for the inhibited reaction<sup>6</sup>); but it is nevertheless desirable that equations that are derived for isothermal conditions or on the assumption that the temperature coefficient is small should be tested with data from isothermal hydration, and this Schiller has not done.

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<sup>1</sup> Ridge, M. J., *Nature*, **204**, 70 (1964).

<sup>2</sup> Ridge, M. J., *Austral. J. App. Sci.*, **9**, 163 (1958).

<sup>3</sup> Ridge, M. J., *Austral. J. App. Sci.*, **10**, 218 (1959).

<sup>4</sup> Ridge, M. J., *Rev. Pure App. Chem.*, **10**, 243 (1960).

<sup>5</sup> Ridge, M. J., and Surkevicus, H., *J. App. Chem.*, **11**, 420 (1961).

<sup>6</sup> Ridge, M. J., and Surkevicus, H., *J. App. Chem.*, **12**, 246 (1962).

<sup>7</sup> Schiller, K., in *Reactivity of Solids*, edit. by de Boer, J. H., et al., 280 (Elsevier, Amsterdam, 1961).

<sup>8</sup> Erofeev, B. V., in *Reactivity of Solids*, edit. by de Boer, J. H., et al., 273 (Elsevier, Amsterdam, 1961).

<sup>9</sup> Ridge, M. J., and Surkevicus, H., *Austral. J. App. Sci.*, **11**, 385 (1960).

<sup>10</sup> Schiller, K., *J. App. Chem.*, **12**, 135 (1962).

### Thermal Decomposition of Irradiated Strontium Azide

MAGGS<sup>1</sup> showed that the isothermal decomposition of strontium azide is characterized by a marked induction period during which no appreciable volume of gas is liberated. This is followed by a period of acceleration during which an exponential relationship:

$$\log p = k_1 t + c_1 \quad (1)$$

is obeyed.

Garner and Reeves<sup>2</sup> obtained a better fit of the  $p/t$  plots using the power law:

$$p^{1/n} = k_2 t \quad (2)$$

where  $n = 3$ . They also studied the effect of pre-irradiation of the azide by ultra-violet light and found: (i) that agreement with the power law (with  $n = 3$ ) improved, (ii) the induction period was shortened, and (iii) the values of  $k_2$  increased, as the times of pre-irradiation increased. Maggs<sup>1</sup> also studied the effect of the emission from radium on the rate of decomposition. The radium was kept in a glass phial adjacent to the surface of the azide during evacuation of the apparatus and also during the decomposition. At 109.5°C the induction period was halved, and  $k_1$  increased three-fold after an initial evacuation for 15-16 h.

Sviridov<sup>3</sup> found that strontium azide pre-irradiated in air at room temperature for 1 min by X-rays (25 kV and 14 m.amp) decomposed at 126°C at a greatly increased rate. In 20 min, 30 per cent decomposition occurred,