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Kinetics and Mechanism of the Transformation of Vaterite to Calcite

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The transformation of vaterite to calcite was investigated systematically. The transition temperature and the energetics of the transformation were determined from differential thermal curves. The variations of lattice constants and crystallite size, accompanying the transformation were studied by X-ray diffractometry. The kinetics of transformation were investigated in the temperature range 460—490°C. The kinetic data were analysed with the help of three separate solid-state models.

Anhydrous calcium carbonate is known to exist in three crystalline modifications—calcite, aragonite, and vaterite. All the three modifications could be prepared synthetically. Calcite is the stable form of calcium carbonate at ordinary pressure and temperature. Aragonite and vaterite are metastable modifications which transform to calcite on heating. Although the transformation of aragonite to calcite has been studied by several investigators, the only kinetic study on the transformation of anhydrous vaterite to calcite appeared to be the dilatometric investigation of Pruna *et al.*[1] However, there were quite a few investigations of the transformation of vaterite in contact with mother liquor. Here again there was considerable controversy regarding the transformation product. Lucas[2] reported that in the presence of mother liquor, vaterite was transformed to calcite and no aragonite was formed. On the other hand according to Faivre and Wallaeys,[3] both aragonite and calcite were formed by the transformation of nascent vaterite in contact with mother liquor. More recently Bischoff[4] has studied the transformation of vaterite to aragonite in aqueous medium in the presence of magnesium ions.

Owing to the incomplete and often conflicting information existing in the literature regarding the transformation of vaterite, a systematic investigation of the transformation of anhydrous vaterite was carried out. Apart from the kinetics of transformation, the effect of thermal treatment on the cell constants and crystallite sizes was followed from the stage of preparation to well beyond the transformation temperature. The kinetic data were analysed with the help of standard solid state models and the most appropriate model was indicated.

Experimental

Preparation of Vaterite.[5] A solution of 50 g potassium carbonate in 700 ml distilled water and containing 300 ppm sodium hexametaphosphate was heated to 60°C and the solution stirred briskly with a magnetic stirrer. 0.1 M calcium chloride solution was added at an average rate of 0.5 ml min^{-1} till 200 ml of the solution were mixed. The crystals of vaterite were filtered off on a sintered glass crucible, washed thoroughly with distilled water and dried by washing with alcohol and ether. The anhydrous vaterite was preserved in a tightly stoppered bottle in a desciccator.

DTA of Vaterite. Differential thermal curves of known weights of vaterite and quartz were obtained on the Shimadzu-Recording DTA apparatus type DT-2A. Ignited alumina was the reference material. The sample and the reference material were uniformly packed into platinum containers which rest on Pt-Pt 10% Rh thermocouples. A heating rate of 12.5°C min^{-1} was employed.

High Temperature Thermostat. The thermostatic unit consisted of a nichrome-wound electrical tubular furnace, placed vertically. Kinetic studies were performed by dropping 20—25 mg of the vaterite sample into 6 mm *i.d.* fused silica tubes situated in the thermostat. The silica tubes rested

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[1] M. Pruna, R. Faivre, and C. Chaudron, *Bull. Soc. Chim. Fr.*, V, **16**, D205 (1949).

[2] G. Lucas, *Bull. Soc. Fr. Mineral. Cristallogr.*, **70**, 185 (1947); *Chem. Abstr.*, **42**, 6708c (1948).

[3] R. Faivre and R. Wallaeys, *C. R. Acad. Sci. Paris.*, **231**, 285 (1950).

[4] J. L. Bischoff, *Amer. J. Sci.*, **266**, 80 (1968).

[5] J. D. C. McConnell, *Mineral Mag.*, **32**, 535 (1960).

in an alloy steel cylindrical block situated midway in the furnace and insulated from the ends of the furnace by means of fire-clay plugs. Temperature was measured by means of a chromel-alumel thermocouple inserted in a fused silica sheath and inserted in a hole at the centre of the alloy steel block. The thermocouple was previously calibrated against melting and fusion points of standard solids. Furnace temperature was monitored by a Tinsley Vernier Potentiometer and controlled by means of a Sunvic energy regulator and variac auto-transformer. Recorded temperatures are believed to be accurate to ±2°C. Experimental runs were terminated by quickly removing the silica tube from the steel block at predetermined time intervals followed by immediate quenching in cold water. The quenched samples were analysed to determine the fractions of calcite and vaterite present in them.

X-Ray Diffraction Technique. X-Ray diffraction photographs of the heat-treated samples were taken using Rich Seifert X-ray unit with filtered copper radiation. 114.6 mm dia. Philips Debye-Scherrer Camera and a cylindrical specimen 0.3 to 0.5 mm dia. were employed. Bragg angles in the range 30—60°θ for the different reflections of vaterite and calcite were measured. The data were subjected to Cohen's[6] least-squares refinement and cell constants were calculated. By measuring the line broadening of the (104) reflection of calcite and (112) reflection of vaterite, the crystalline sizes were calculated using Scherrer[7] equation.

X-Ray powder diffraction photographs of the kinetic samples were taken in a 57.3 mm dia. Philips Debye-Scherrer Camera. Densitometer records of the (104) reflection of calcite and (110), (112), and (114) reflections of vaterite were obtained, employing photovolt transmission density unit and the multiplier photometer model 520-M. In this model full-scale deflection in the most sensitive range corresponds to 0.01 microlumen. The relation[8] between the intensity and fraction of calcite in the mixture was found to be

$$f_c = \frac{I_{104(c)}}{I_{110(v)} + I_{112(v)} + I_{104(c)} + I_{114(v)}} \qquad (1)$$

Employing Eq. (1), the fraction of calcite in the kinetic samples was calculated.

Results and Discussion

The differential thermal curve for the sample of vaterite is shown in Fig. 1. The small exothermic peak with the peak temperature of 567°C is attributed to the transformation of vaterite to calcite. The heat of transformation ΔH was calculated by comparison with the peak of $\alpha \rightleftharpoons \beta$ transition in quartz. ΔH was found to be 145 cal mol^{-1}. E_a for the transformation using the method of Borchardt and Daniels[9] was found to be 120 kcal mol^{-1}.

The variation of unit cell volume of calcite and vaterite with temperature is shown in Fig. 3. There is a small contraction in the lattice prior to transformation. The variation of crystallite size with temperatures is represented in Fig. 2. There is a considerable decrease in the crystallite size of vaterite around the transformation temperature.

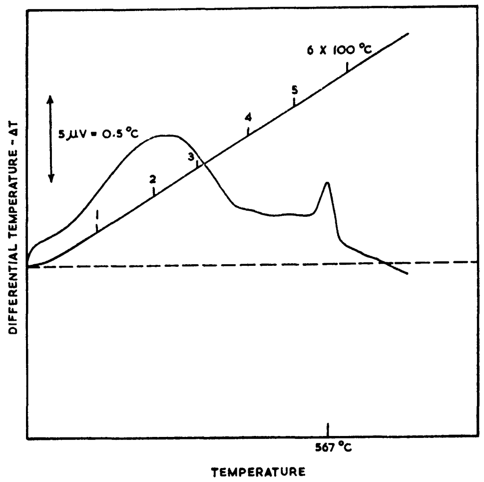

Fig. 1. Differential thermal curve of vaterite.

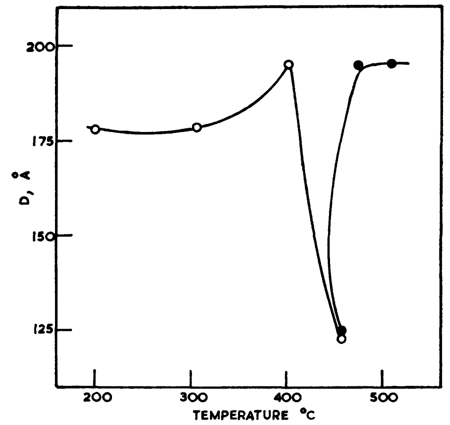

Fig. 2. Variation of the crystallite size of varite-calcite with temperature.

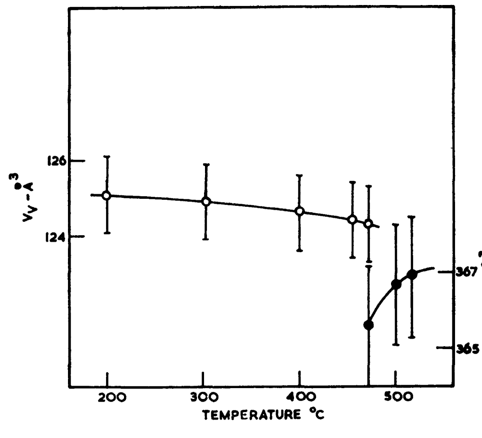

Fig. 3. Variation of lattice constants of vaterite-calcite with temperature.

The experimental results on the transformation rate studies over the temperature range 460—490°C are shown in Figs. 4 and 5. The extent of transformation of vaterite to calcite as a function of time under isothermal conditions is shown in Fig. 4, while in Fig. 5 the conversion of vaterite to calcite as a function of temperature at different times is shown. All the curves in Fig. 5 intersect the temperature axis at 450°C. This can be taken as the point where the rate of trans-

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[6] M. U. Cohen, *Rev. Sci. Instrum.*, **6**, 68 (1935); **7**, 155 (1936).

[7] P. Scherrer, *Göttinger Nachrichten*, **21**, 98 (1918).

[8] M. Subba Rao, Ph. D. thesis, submitted to the Indian Institute of Science (1969).

[9] H. J. Borchardt and F. Daniels, *J. Amer. Chem. Soc.*, **79**, 41 (1957).

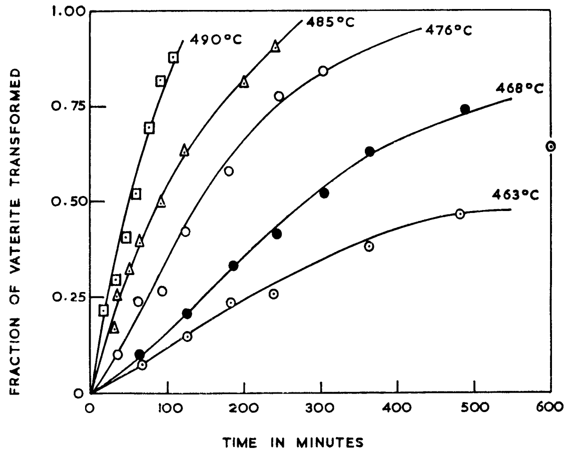

Fig. 4. Conversion of vaterite to calcite as a function of time at different temperatures.

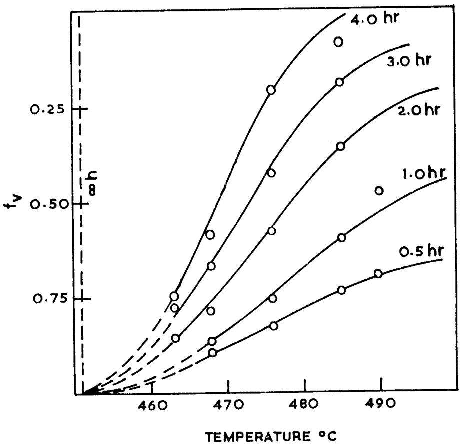

Fig. 5. Conversion of vaterite as a function of temperature for different times.

formation is immeasureably slow, *i.e.*, it takes infinite time.

The transformation curves in Fig. 4, exhibit short acceleratory periods. The kinetic data have been analysed with the help of three models (1) Avrami's[10] equation, (2) Honig's[11] order-disorder theory as applied to diffusionless transitions in solids and (3) Mampel's[12] equation. The relation derived by Avrami[10] includes the interaction between grains of the new phase during transformation. The approximate form of the Avrami rate equation is

$$1 - \alpha = \exp(-kt^n) \qquad (2)$$

where α is the fraction of vaterite transformed to calcite in time 't'. A plot of $\log_{10}\ln(1/1-\alpha)$ against $\log_{10}t$ should give a straight line with 'n' as the slope. Figure 6 shows that the kinetic data on the transformation of vaterite to calcite comply reasonably well with equation (2). The slopes of the lines vary from 1.38 to 1.46 with an average value of 1.42. This value is midway between 4/3 and 3/2. The value of 4/3 gives

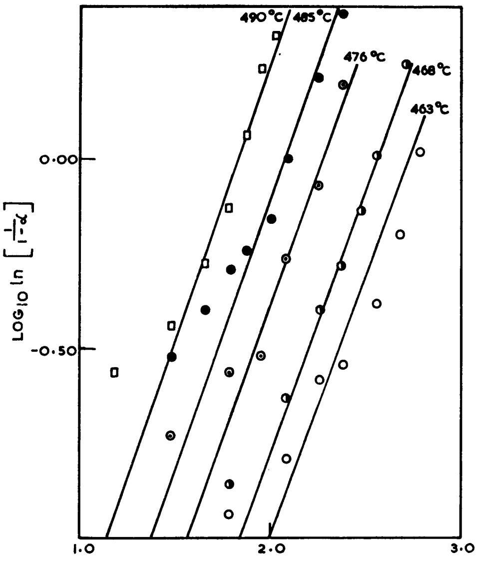

Fig. 6. Avrami plots of the vaterite-calcite transformation data.

a better fit and n is found to be 4/3 in the transformation of aragonite to calcite (communicated to the Indian Journal of Chemistry) which is analogous to the transformation of vaterite to calcite. Hence, the slope is approximated to 4/3 here too. From the slopes of the plots of $-\ln(1-\alpha)^{3/4}$ *vs.* t, a value for the activation energy is extracted and it is found to be 85 kcal mol^{-1}.

In the theory proposed by Honig,[11] a solid undergoing a transformation is represented by the change in the lattice units which transform from an initial state to a final state by two different ways, *i.e.*, a nucleation process and a propagation process. Through application of the methodology of order-disorder theory, Honig[11] has derived the following generalised rate equation.

$$-\frac{1}{k_n}\cdot\frac{d\alpha_0}{dt} = \alpha_0 + \frac{Zk_p}{k_n}\left\{\frac{-1+[1+4(C-1)\alpha_0(1-\alpha_0)]^{1/2}}{2(C-1)}\right\} \qquad (3)$$

In the present transformation α_0 is the fraction of vaterite remaining at time 't', C is a parameter indicating the tendency towards phase aggregation, k_p and k_n are the rate constants for the propagation and nucleation mechanisms respectively. For large values of C the generalised rate equation may be integrated to obtain

$$Zk_p(t-t_0)/(C-1)^{1/2} = \cos^{-1}(2\alpha_0-1) \qquad (3a)$$

Honig has evaluated C as $(1+k_p/k_n)^2$, and thus Eq. (3a) takes on the approximate form

$$Zk_n(t-t_0) = \cos^{-1}(2\alpha_0-1) \qquad (4)$$

where Z is the coordination number of a site in the lattice under consideration and t_0 is an arbitary constant evaluated by curve fitting.

Figure 7 shows that the vaterite→calcite transformation data fit Eq. (4) fairly well. The slope of the lines gives the value of Zk_n. The variation of Zk_n with temperature is shown in Fig. 8.

The value of the exponent in the Avrami's equation (*i.e.*, n=4/3) suggests that the kinetics of the trans-

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[10] M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940).

[11] J. M. Honig in kinetics of high-temperature processes. Kingery (ed.) (John Wiley & Sons, Inc., New York, 1959), Chap, 25.

[12] K. L. Mampel, *Z. Phys. Chem.*, **A187**, 43, 235 (1940).

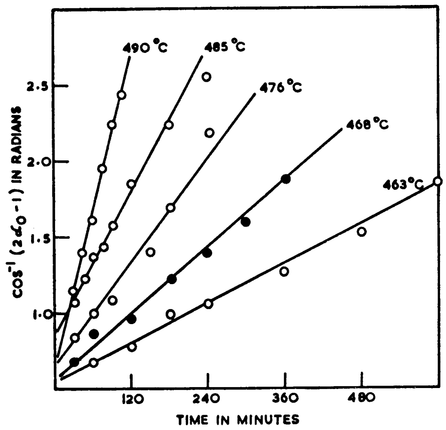

Fig. 7. Order-disorder plots of vaterite-calcite transformation data.

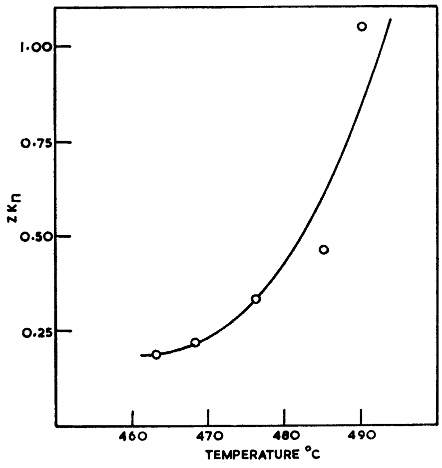

Fig. 8. Variation of Zk_n with temperature.

formation might depend on the interfacial area between the two solids. If the rate of a reaction depends on the area of the interface between the two solids, it can be represented by a 2/3 power law.

The 2/3 power law, *i.e.*, $dx/dt=kx^{2/3}$ can be reduced to the more familiar form

$$1-(1-\alpha)^{1/3} = kt \tag{5}$$

where α is the fraction transformed in time 't'.

Equation (5) is the familiar contracting volume model, which has been employed to explain the kinetics of thermal decomposition of solids.

Figure 9 shows a few representative plots of the vaterite→calcite transformation data using Eq. (5). Two different linear portions can be recognised on each of the plots. From the slopes of these plots activation energies have been calculated. The values of E_a are 85 kcal mol^{-1} and 95 kcal mol^{-1} respectively for each of the two regions.

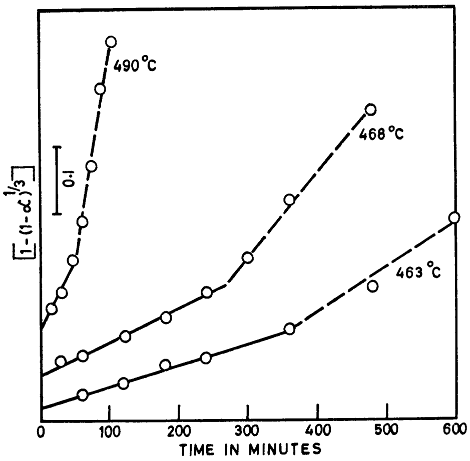

Fig. 9. Plots of $[1-(1-\alpha)^{1/3}]$ *vs.* time for the transformation of vaterite to calcite.

Equation (5) is equivalent to one of the limiting forms of Mampels[12] equation. In the Mampel[12] model $k=v/r$ where v is the rate of advance of the interface and r is the radius of the particle.

Considering the powder as composed of a large number of isotropic spheres of uniform radius, Mampel derived a general expression for the fraction decomposed, from probability considerations, taking into account the possibility of the overlapping of the zones of decomposition spreading out from neighbouring nuclei. The general expression reduces to simpler forms for three special cases: (i) for small values of t, α is proportional to t^4, (ii) for intermediate periods Eq. (5) gives a close approximation, and (iii) for the final period the reaction tends towards unimolecular law. Mampel has shown that the limits of the three periods are largely determined by the ratio r/v. For very fine powders practically the whole of the reaction follows the unimolecular law. For particles of intermediate size the reaction is represented reasonably well by Eq. (5).

In the present transformation Eq. (5) has been used to explain both the acceleratory and deceleratory kinetics. The slopes of the plots are different for the two regions. There is a break up of particles during the transformation. The particles are probably not reduced to fine powders. It is perhaps this change in the particle size which is responsible for the change in the slope.

Hence, Eq. (5) based on nucleation on the surface and progress of the reaction by interfacial growth is found to explain the complete course of the reaction. Further, in none of the kinetic samples, aragonite phase was detected. In the transformation of anhydrous vaterite to calcite, aragonite is not an intermediate phase.

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