

# Kinetics of Hydration-Dehydration Reactions Considered As Solid Transformations

A mechanism is proposed for the dehydration-rehydration process in solid inorganic salts, and model rate equations are derived and applied to the observed behavior of potassium carbonate. Quantitative expressions for the effect of pressure on the reaction rates are derived using basic principles from nucleation and heterogeneous phase transformation theory. Model equation predictions agree with experimental dehydration and rehydration rate data at all but extreme pressures. The basic rate equation is also used to interpret the data of Eckhardt and Flanagan (1964) for the effect of pressure on the dehydration of manganous formate dihydrate. The mechanism on which the model equations are based is also consistent with the observed effects of cycling and of high temperature pretreatment on the  $K_2CO_3$  rehydration rate.

M. A. STANISH and

D. D. PERLMUTTER

Department of Chemical Engineering  
University of Pennsylvania  
Philadelphia, PA 19104

## SCOPE

A new mechanistic interpretation is offered for the analysis of the kinetics of gas-solid reactions and applied in detail to the reversible dehydration and rehydration of solid inorganic salts. These processes are considered as solid-solid transformations, and an expression is derived for the intrinsic rate of reaction in terms of the velocity of the movement of the boundary separating the reactant and product phases. The rate dependence on pressure and temperature predicted by the model equations

is compared to those observed for both dehydration and rehydration in experiments with potassium carbonate hydrate and to that reported in the literature for the dehydration of manganous formate dihydrate. In addition, the effects of cycling and of high-temperature pretreatment on the reaction rates of  $K_2CO_3$  are presented, and the ability of the proposed mechanism to account for these effects is discussed.

## CONCLUSIONS AND SIGNIFICANCE

A new mechanistic rate model has been formulated for reversible gas-solid reactions and applied to interpret the dehydration and rehydration kinetics of salt hydrates. Quantitative rate expressions predicting the effects of pressure and temperature were derived using basic principles from nucleation and heterogeneous phase transformation theories. The dehydration model rate equation provides accurate quantitative predictions for the velocity of movement of the  $K_2CO_3 \cdot 3/2H_2O$  dehydration interface at all three temperatures studied. The dehydration equation also provided a close correlation with data from the literature for the dehydration of manganous formate dihydrate.

A comparison of the rehydration model equation with experimental  $K_2CO_3$  particle rehydration rates revealed good agreement of the model with the experimental data for reduced pressures within the range  $1 < (P_{eq}/P) < 2$ . At higher rehydra-

tion pressure, the reaction rates are not controlled by the transformation process at the reaction interface and the model equations are not applicable. Within the range of moderate pressures both above and below the equilibrium pressure, the model effectively describes the rapid decline of both dehydration and rehydration rates as the equilibrium pressure is approached.

The model equations imply that reaction rates depend on the defect structure of the reactant solid. Therefore, the appearance in  $K_2CO_3$  rehydration of induction periods after high-temperature pretreatment and the disappearance of induction periods from the dehydration curve as a consequence of cycling can be attributed to the production and destruction of solid defects: cycling accelerates rates by increasing the concentration of defects, whereas high-temperature pretreatment inhibits rates by destroying defects through annealing.

## INTRODUCTION

The overall rate of reaction of a solid as it transforms from a reactant into a product depends on the interactions between two factors: (1) the rate of movement of the interphase boundary, and (2) the rate of diffusion of reactants and/or products to or from the interphase boundary. The former is characteristic of the particular mechanism of boundary movement, that is, the intrinsic trans-

formation rate; the latter depends on the relative rates of the surface, grain-boundary, and solid-state diffusion processes. The treatment of solid kinetics that follows addresses itself only to the rate of boundary movement. It considers the circumstances in which all diffusional processes are fast relative to the rate of chemical transformation.

Langmuir (1916) gave perhaps the earliest cohesive discussion of the mechanism of solid decompositions and argued that such

reactions occur exclusively at the phase boundary or interface between the reactant and product solids. Although the same mechanism has since become widely accepted for the hydrate dehydration process, there remains disagreement concerning the details of the changes that actually occur at or near the interface. Topley (1932) supposed that the dehydration proceeds by the attainment of some critical energy in a bond, resulting in its breakage and leading to the rearrangement of the immediately neighboring lattice and the escape of the gaseous product. In a subsequent refinement, Topley and Smith (1935) proposed that the reactant and product surfaces are separated by a layer of water molecules that are adsorbed on and polarized by the product solid and that transmit force fields that act upon the reactant lattice. Thus, in this view, the rate of dehydration would depend on the configuration of the adsorbed molecules. Colvin and Hume (1938) disagreed with this position, proposing instead that "the escape of the water molecules from the hydrate lattice results in the production of a short-lived and completely unorganized layer of ions and water molecules."

Cooper and Garner (1940) proposed a model in which the reactant and product solids are separated by a transition layer derived from the reactant phase "by the loss of water either without lattice change or by collapse of the original lattice." The rate of dehydration is then determined by the rate of loss of water across the transition layer, which depends on the thickness of this layer and thus on the rate of crystallization of the product. According to the authors, this rate of crystallization will be a function of the temperature and of the pressure of water vapor. Fichte and Flanagan (1971) differed with most others in assuming that the interface for copper formate tetrahydrate (CFT) dehydration is coherent, i.e., that the reactant and product lattices form a good fit across the interface. Thus the escaping water molecules must diffuse in site-to-site fashion through the anhydride lattice to the external surface.

Uncertainty also exists in the interpretation of the dependence of dehydration and rehydration rates on water vapor pressure. The theory most commonly used to account for the effect of water vapor on dehydration rates was first developed for the reversible decomposition of carbonates by Spencer and Topley (1929). In this model, the reaction interface consists of reactive sites that become blocked by adsorption of the product gas. If the forward decomposition rate is proportional to the fraction of unoccupied sites and the reverse reaction rate is proportional to the fraction of occupied sites, and the adsorption process is described by the Langmuir isotherm, then the net rate of decomposition per unit area,  $r$ , is given as a function of the pressure,  $P$ , by

$$r/r_0 = (P_{eq} - P)/(P_{eq} + KP) \quad (1)$$

where  $r_0$  is the rate in a vacuum,  $P_{eq}$  is the equilibrium vapor pressure, and the coefficient  $K$  is a constant at the specified temperature. Equation 1 may be rearranged to the form:

$$(r_0 - r) = k_2 r_0 P / (P + k_3) \quad (2)$$

where  $k_2 = (K + 1)/K$  and  $k_3 = P_{eq}/K$ .

Several equivalent forms of Eqs. 1 and 2 have been applied to dehydration kinetics, all based on the assumption that water vapor acts as an inhibitor by forming an adsorbed layer in the reaction zone and that this adsorption obeys Langmuir's isotherm. Anous et al. (1951) reported for example that the dehydration of chrome alum obeyed the kinetic expectation of Eq. 2. Acock et al. (1946) found the ratio  $[P/(r_0 - r)]$  to be linear with pressure for experiments with ammonium alum, a result again consistent with Eq. 2. Similarly, Gardet et al. (1976) obtained linearity of the ratio  $[(P_{eq} - P)/r]$  against  $P$  for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  dehydration in water vapor, as expected from Eq. 1.

Ball and Norwood (1973) investigated the vapor rehydration of hexagonal  $\text{CaSO}_4$  and discovered that the conversion was best described by a square-root-of-time dependence. Assuming that rehydration occurs only on surfaces covered by at least a monolayer of adsorbed water and using the BET relationship to describe this adsorption, the authors derived an expression relating the observed

rate constant,  $k_{obs}$ , to the true rate constant,  $k_1$ , the pressure,  $P$ , and the vapor pressure of pure water,  $P^*$ , at the specified temperature:

$$k_{obs} = k_1(P/P^*)/(1 - P/P^*) \quad (3)$$

Their data obeyed Eq. 3 to a temperature of about 375 K, above which it was assumed that the BET derivation no longer held.

As an alternative and a departure from this Langmuirian adsorption-based standpoint, the problem can be approached from the theory of nucleation and phase transformations. This is the viewpoint taken in this analysis of the kinetics of dehydration-rehydration reactions in general and of experimental measurements for the  $\text{K}_2\text{CO}_3$ -water system in particular.

## SOLID-SOLID TRANSFORMATIONS

The free energy of formation of a nucleus in a heterogeneous solid-solid transformation may be formulated as in Chadwick (1972):

$$\Delta G = -A\Delta G_v + B\gamma_i + C\epsilon - \Delta G_D \quad (4)$$

where  $\Delta G_v$  is the bulk free energy change,  $\gamma_i$  is the interfacial energy,  $\epsilon$  is the strain energy arising from the difference in the volumes of the two phases, and  $\Delta G_D$  is the energy of any defect consumed by the nucleus. Since the interfacial energy varies with area whereas the bulk and strain energies vary with volume, the total free energy must go through a maximum ( $\Delta G_c$ ) at some critical size, effectively forming an energy barrier to nucleation. Nuclei are initially formed by thermal fluctuations; only those fluctuations with energy sufficient to overcome the free energy barrier will produce stable nuclei.

Following Christian (1975) there exists within a solid undergoing a heterogeneous solid-solid transformation an assembly of nuclei with a dynamic distribution of sizes given by

$$N_j = N_t \exp(-G_j/kT) \quad (5)$$

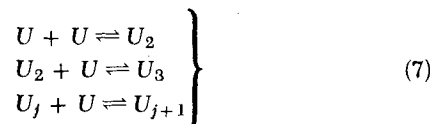
where  $N_t = N_0 + \sum_j jN_j$  is the total number of elements in the assembly and  $\Delta G_j$  is the free energy of formation of a nucleus containing  $j$  elements, from Eq. 4. The size of any given nucleus is continually changing due to the addition or loss of elements via thermal fluctuations. If the overall rate of addition is greater than that of loss, there is a net growth of nuclei through the population described by Eq. 5, resulting in a net production of stable nuclei. The detailed mathematical derivation of this production rate is also presented in Christian (1975); the important final result for this rate is given in Becker-Döring theory by:

$$I = \frac{N_t \nu S_c}{j_c} \left[ \frac{\Delta G_c}{3\pi kT} \right]^{1/2} \exp(-\Delta g/kT) \exp(-\Delta G_c/kT) \quad (6)$$

where  $S_c$  is the number of elements in the surface of the nucleus of critical size,  $j_c$  is the number of elements contained in its volume, and  $\Delta G_c$  is the corresponding free energy of formation.

## APPLICATION TO REACTION KINETICS

The reaction of interest is to be modeled as propagated via growth step formation at the reaction interface. These steps consist of new product phase material formed from the reactant phase via thermal fluctuations and may contain many unit cells in a three-dimensional assembly. Formally, the growth steps may be described as clusters of fundamental transformation units, each unit being the smallest group of atoms within the lattice of the reactant phase that is able to simultaneously rearrange itself to form a new group having the lattice structure of the product phase. The units form growth steps by the sequential binary combination processes:



Growth steps of all sizes exist in numbers that depend on the energy constraints governing their stability. Analogous to Eq. 4 for the free energy of a nucleus in a heterogeneous phase transformation, the free energy of formation of a growth step containing  $n_s$  moles of solid may be formulated as:

$$\Delta G_s = \Delta G_m n_s + \gamma_i \psi_A n_s^{2/3} + \epsilon_s n_s - \Delta G_D \quad (8)$$

where  $\Delta G_m$  is the molar free energy of transformation and  $\psi_A$  is an area shape factor for interfacial energy. This expression includes the terms for free, interface, strain, and defect (interphase boundary) energies, respectively. An expression for the free energy of an interphase growth step may be derived from Eq. 8 by neglecting the strain energy term and combining the interphase boundary defect and interface energy terms, both of which depend on the surface area of the step. The result is:

$$\Delta G_s = \Delta G_m n_s + (\gamma_i \psi_A - \gamma_D \psi_D) n_s^{2/3} \quad (9)$$

where  $\gamma_D$  is the interphase boundary energy and  $\psi_D$  is the appropriate area shape factor. The critical size of the growth step is obtained by differentiating Eq. 9 with respect to  $n_s$ , setting that result equal to zero, and solving for  $n_s$ . The final result is:

$$n_s^* = [2\psi/3(-\Delta G_m)]^3 \quad (10)$$

where  $\psi \equiv (\gamma_i \psi_A - \gamma_D \psi_D)$ . Substitution of Eq. 10 into Eq. 9 gives the free energy of a critical growth step:

$$\Delta G_s^* = 4\psi^3/27(\Delta G_m)^2 \quad (11)$$

The formation of growth steps is analogous to the formation of nuclei in the Becker-Döring theory. Adapting the results of that theory, Eqs. 10 and 11 may be substituted in Eq. 6 to obtain the rate of generation of stable growth steps. After rearrangement, the result is:

$$I_s = k_U T^{-1/2} \exp(-\epsilon_U/kT) \exp\left[-\frac{4\psi^3}{27kT(\Delta G_m)^2}\right] \quad (12)$$

where

$$k_U \equiv (N_U \psi^{1/2} \psi_U \nu_U) / [3(\pi k)^{1/2}] \quad (13)$$

in terms of  $N_U$ , the total number of fundamental transformation units;  $\psi_U$ , a shape factor for the number of units on the surface of a critical growth step;  $\nu_U$ , the frequency factor; and  $\epsilon_U$ , the activation energy for the transfer of one unit to a growth step.

The interphase boundary consists on one side of the product phase and on the other of a reactant phase containing a random distribution of growth steps. The growth steps exist in a dynamic state of continual generation, growth, and decay brought about by thermal fluctuations. Equation 12 gives the rate at which growth steps become large enough that because of energy constraints, they can no longer return to their original state by means of thermal fluctuations. As the stable growth steps continue to enlarge, each must at some point leave the reactant lattice to join the product phase: i.e., it must cross the interphase boundary. Formally, this occurs at that size for which the steady-state distribution function vanishes, in the most general case a function of temperature and pressure; however, since it need not be explicitly defined in Becker-Döring theory, a constant value  $s = s_o$  is assumed as a matter of convenience.

The net rate of reaction is given by the product of  $s_o$  and the rate of generation of stable growth steps. For dehydration,

$$\Delta G_m = \frac{3}{2} NkT \ln(P/P_{eq}) \quad (14)$$

From Eqs. 12 and 14 the net rate of conversion of transformation units is:

$$\dot{U}_d = k_U s_o T^{-1/2} \exp(-\epsilon_U/kT) \exp\{-\Upsilon/T^3[\ln(P/P_{eq})]^2\} \quad (15)$$

and the corresponding reaction rate is

$$-\dot{r} = k_o T^{-1/2} \exp(-\epsilon_U/kT) \exp\{-\Upsilon/T^3[\ln(P/P_{eq})]^2\} \quad (16)$$

where

$$\Upsilon \equiv 16\psi^3/243N^2k^3 \quad (17)$$

and the new rate constant  $k_o = k_U s_o V_U$  gives the rate of reaction in terms of the velocity of movement of the interphase boundary ( $V_U = \text{m}^3$  per transformation unit). In the special case of dehydration in a vacuum  $P = 0$ , and Eq. 16 reduces to

$$-\dot{r}_o = k_o T^{-1/2} \exp(-\epsilon_U/kT) \quad (18)$$

For rehydration,  $\Delta G_m = 3/2NkT \ln(P_{eq}/P)$ , and from Eq. 12, the rate of rehydration is:

$$\dot{r} = k'_o T^{-1/2} \exp(-\epsilon'_U/kT) \exp\{-\Upsilon'/T^3[\ln(P_{eq}/P)]^2\} \quad (19)$$

where  $k'_o$ ,  $\epsilon'_U$ , and  $\Upsilon'$  are defined analogously to  $k_o$ ,  $\epsilon_U$ , and  $\Upsilon$  but have different values.

## RESULTS AND DISCUSSION

Experiments were performed with J. T. Baker Chemical Co. reagent grade materials, obtained either as  $\text{K}_2\text{CO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$  or as anhydrous  $\text{K}_2\text{CO}_3$ , separated by sieving into relatively narrow particle size ranges. The reaction behavior of samples weighing 5 to 10 mg was observed in a Dupont model 951 Thermogravimetric Analyzer (TGA) connected to a vacuum pump and to a water vapor pressure control system. Sample temperature was maintained by the TGA furnace and measured by a chromel-alumel thermocouple placed adjacent to the sample pan. The output of this thermocouple and the weight of the salt sample were recorded as functions of time. Manipulation of the temperature and pressure during these experiments has been described previously (Stanish and Perlmutter, 1983, 1984).

### Dehydration Rates

For comparison of experiment to theory it is simplest to begin by correlating available vacuum dehydration data following the form of Eq. 18. Using the rates reported for  $\text{K}_2\text{CO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$  crystals by Stanish and Perlmutter (1983, Figure 6), a least-squares fit yields the activation energy  $\epsilon_U = 1.54 \times 10^{-19}\text{J}$  (with a standard deviation  $\sigma = 0.05 \times 10^{-19}\text{J}$ ) and the rate constant  $k_o = 6.65 \times 10^8 \text{ m} \cdot \text{K}^{1/2}/\text{s}$ .

In order to extend the analysis to dehydrations in a water vapor atmosphere, it is convenient to combine Eqs. 16 and 18 in the form

$$-\ln(\dot{r}/\dot{r}_o) = \Upsilon/T^3[\ln(P/P_{eq})]^2 \quad (20)$$

to emphasize the linearity to be expected between the LHS and the grouping  $1/T^3[\ln(P/P_{eq})]^2$ . This prediction is tested in Figure 1 by using the experimental dehydration rates previously reported

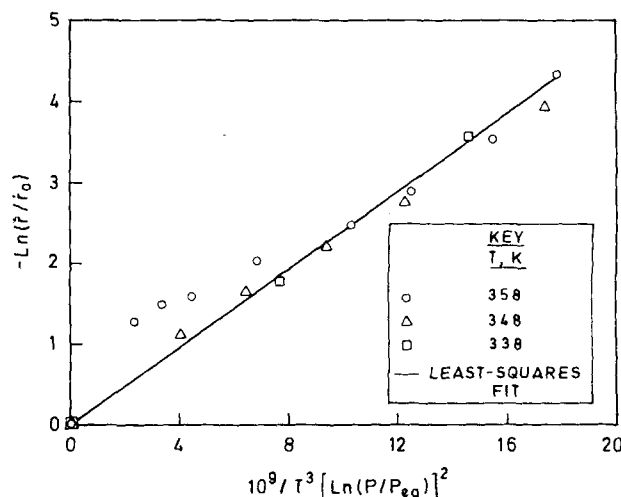


Figure 1. Dehydration rates for  $\text{K}_2\text{CO}_3 \cdot \frac{3}{2}\text{H}_2\text{O}$  on coordinates suggested for linearity by Eq. 20. Straight line is the least-squares fit.

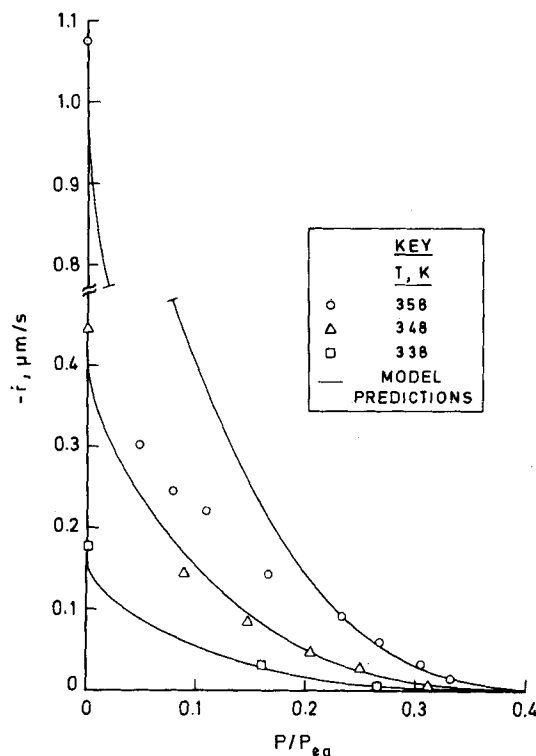


Figure 2. Model predictions of dehydration rates at different temperatures compared with experimental results.

for  $\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  at three different temperatures (Stanish and Perlmutter, 1983, Figure 5). Using the least-squares criterion, the best straight line through the origin gives the results  $\bar{T} = 2.40 \times 10^8 \text{K}^3$  (with a standard deviation  $\sigma = 0.08 \times 10^8 \text{K}^3$ ) for  $\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

Having estimated each of the needed parameters, it is feasible to use Eq. 16 to predict dehydration rates at different temperatures and pressures. The results of such computations are shown in Figure 2 together with the experimental data at the same conditions. The model is especially effective at predicting the lower dehydration rates at all three temperatures; both model and experiment indicate that the rate becomes very small at pressures well below the equilibrium value. The same model and analysis were also applied to interpret other dehydration data from the literature for which no quantitative theory has yet been developed. Eckhardt and Flanagan (1964) reported an investigation of the dehydration of manganese formate dihydrate (MFD), including the effect of water vapor pressure on the rate constant for dehydration. The behavior is quite similar to that of  $\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  in that the rate is very strongly inhibited by small pressures of water vapor. The reported activation energy  $\epsilon_U = 1.20 \times 10^{-19} \text{J}$ ; vapor pressure data (Eckhardt et al., 1971) were employed to compare the predictions of this model to the reported rate data using the following convenient form of Eq. 16:

$$F(k', T) = \ln k' + \frac{1}{2} \ln T + (\epsilon_U/kT) \\ = \ln k_o - \bar{T}/T^3 [\ln(P/P_{eq})]^2 \quad (21)$$

The transformation model is shown in Figure 3 to fit the reported pressure dependence very closely. As was the case for  $\text{K}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , the steep decline in rate observed at low pressures is described well by the model.

#### Rehydration Rates

The kinetics of dehydration rates are fundamentally different from those obtained for rehydration, in that the shrinking core behavior that so well described the former is not observed for the

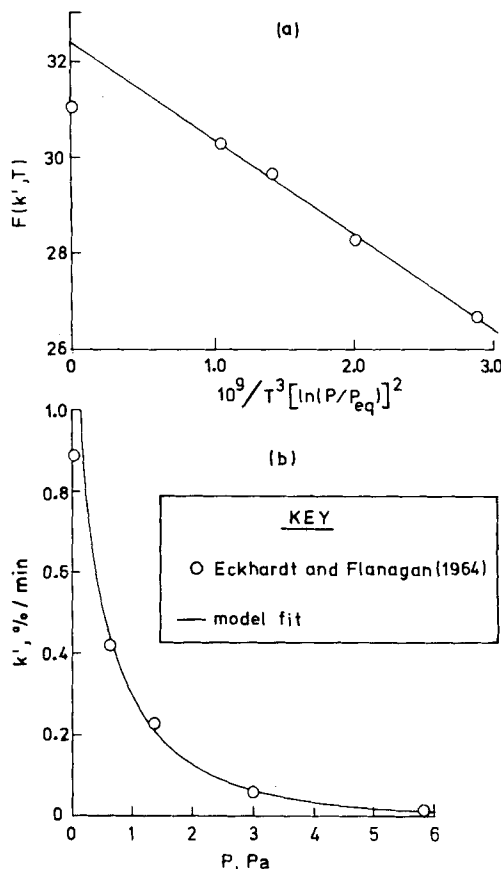


Figure 3. Interpretation of dehydration data of Eckhardt and Flanagan (1964): (a) linearity test according to Eq. 21; (b) model prediction of rate constants compared to experimental results.

latter. This means in effect that the interface movement that was a suitable metric for dehydration is not available for rehydration. As an alternative it is convenient to use the slope of the linear portion of the rehydration conversion-time curve to characterize the rate by defining the relative average rate (RAR) between 40 and 60% conversion. In terms of this definition Eq. 19 for rehydration may be rewritten in the form:

$$\ln(\text{RAR}) = \ln k'_o - \frac{1}{2} \ln T - \epsilon'_U/kT - \bar{T}'/T^3 [\ln(P_{eq}/P)]^2 \quad (22)$$

suggesting the linearity test used on the coordinates of Figure 4(a). The data points on this figure are from the previous report of Stanish and Perlmutter (1984). The slope and intercept of the straight line yield  $\bar{T}' = 1.91 \times 10^7 \text{K}^3$  and  $[\ln k'_o - 1/2 \ln T - \epsilon'_U/kT] = 1.30$ . Having evaluated these parameters at 333 K, Eq. 22 can be used to predict the rehydration pressure dependence. The results of such a computation are shown in Figure 4(b) together with the experimental results. As was the case for the dehydration data, the model equation closely follows the observed pressure effect at pressures relatively near the equilibrium value. In the range  $1 < (P/P_{eq}) < 2$ , the model correctly predicts that the rate function is convex to the reduced-pressure axis. However, for  $(P/P_{eq}) > 2$ , the model predicts that the relative rate should asymptotically approach  $\text{RAR} = 3.67$ , whereas experiment shows that the rate of rehydration becomes proportional to pressure for  $(P/P_{eq}) > 3$  (Stanish and Perlmutter, 1984).

This inconsistency is not unexpected. According to Eq. 10, the critical growth step size varies inversely with the cube of the free energy of transformation. However, real growth steps must be of finite size; certainly none can be smaller in size than one transformation unit. Therefore, at high enough pressures (large free energy of transformation), the model equations no longer have physical

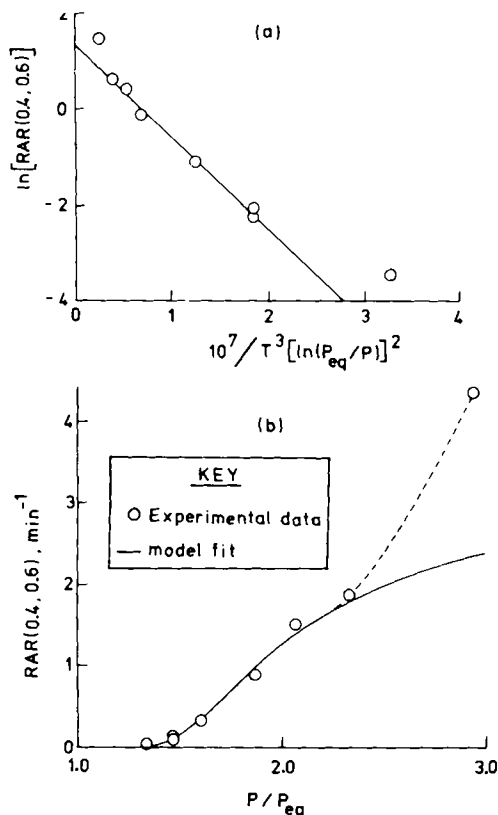


Figure 4. Rehydration rates for  $K_2CO_3$ : (a) linearity test according to Eq. 22; (b) model prediction of rates compared to experimental results.

meaning, indicating that the reaction rate is no longer limited by the rate of growth step formation.

#### Role of Solid-Phase Properties

Characteristic rehydration-dehydration cycling behavior is presented in Figure 5, taken from the data reported by Stanish and Perlmutter (1984) for  $K_2CO_3$ , showing that both the forward and reverse reactions are accelerated by cycling. The primary effect occurs after the first cycle; in addition, the induction and acceleration periods observed in the first-cycle dehydration and rehydration are eliminated in the second and later cycles. Induction periods in gas-solid reactions are usually attributed to the slow nucleation of the product phase and the subsequent acceleration to the increasing interfacial area between the reactant and product phases as the latter grows. The absence of induction may then be taken as evidence of very rapid or instantaneous nucleation. The behavior shown in Figure 5 thus suggests that cycling influences the reactivity of the solid phase itself, as indicated by the relative rate of nucleation. In drawing this inference it should be noted that diffusional effects are insufficient to alone account for the rate changes produced by cycling (Stanish and Perlmutter, 1984) and cannot account for the elimination of the induction periods.

Evidence of enhanced reactivity in cycled material also appears in Figure 6. The rehydration behavior shown for the "partial cycle" case is that of a sample of uncycled material that has been hydrated to only 27.2% conversion and then fully dehydrated once more. As shown, this material rehydrates rapidly to approximately 27% conversion, at which point the rate decreases suddenly.

Pretreatment of  $K_2CO_3$  particles at elevated temperatures was also found to affect the rate of subsequent rehydration. This phenomenon is illustrated in Figures 7 and 8 for samples previously dehydrated in vacuum at 353 K and then heated to various temperatures in different atmospheres for varying lengths of time. Heating of the anhydrous  $K_2CO_3$  to higher temperatures was found to have the greatest effect on the subsequent rehydration when the treatment was carried out in atmospheres of oxygen or air. The

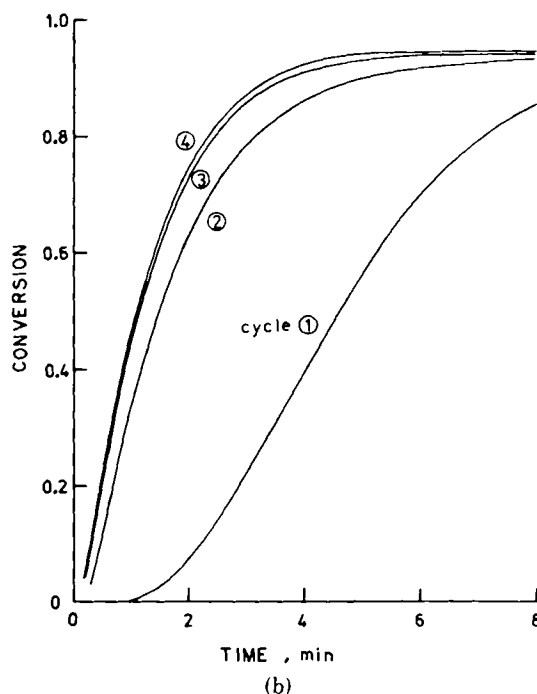
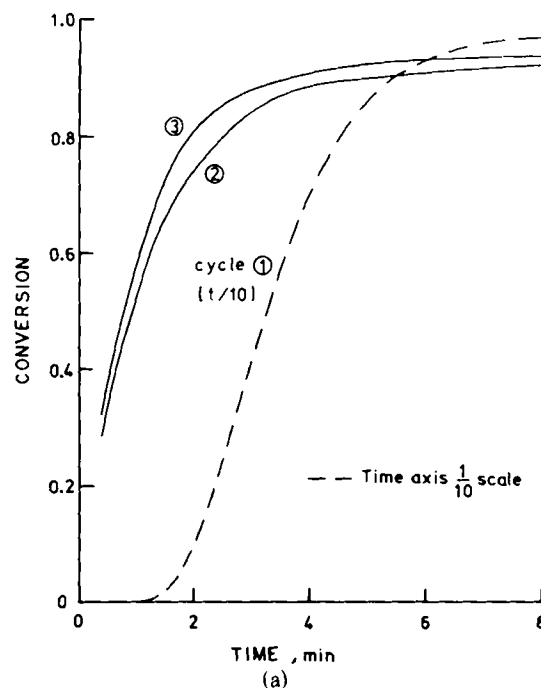


Figure 5. (a) Effect of cycling on  $K_2CO_3 \cdot 3/2H_2O$  dehydration ( $-170 + 200$  mesh) at  $T = 353$  K and  $P = 1,500$  Pa; intermediate hydrations at  $T = 333$  K and  $P = 2,300$  Pa. The first cycle time scale is  $10\times$  larger than the scale shown; (b) effect of cycling on  $K_2CO_3$  hydration ( $170 + 200$  mesh) at  $T = 333$  K and  $P = 2,300$  Pa; intermediate dehydration at  $T = 353$  K and  $P = 1,500$  Pa.

effect was substantially less pronounced, but still quite measureable, after heating in nitrogen or in a vacuum. As shown in Figure 8, the magnitude of the effect is dependent on both the duration and the temperature of heating; thus what occurs during the heating period must be a temperature-activated rate process.

Perhaps the most significant change in the rehydration behavior as a result of heat treatment is the appearance of induction periods that vary with the temperature and the duration of the prior heating. These would not be expected if the rate inhibition were due solely to an increased resistance to mass transfer within the solid as a result of rearrangement of pore size distribution.

Since they are normally associated with slow nucleation, the

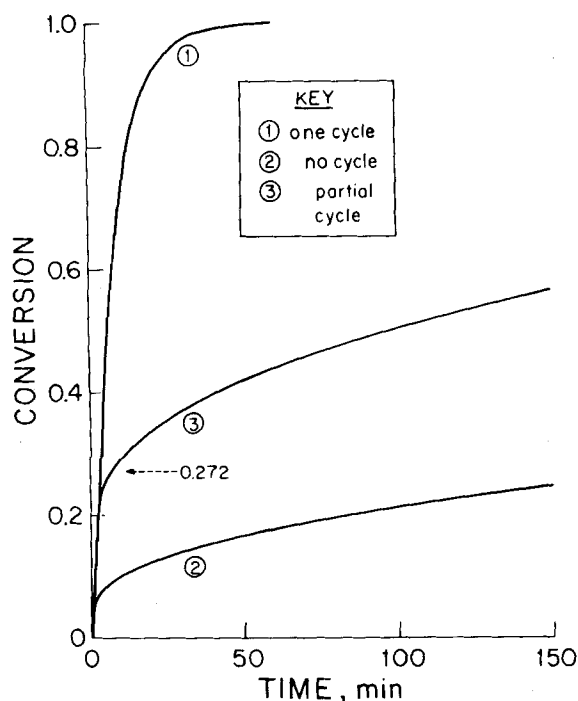


Figure 6. Effect of prior cycling on rehydration kinetics.

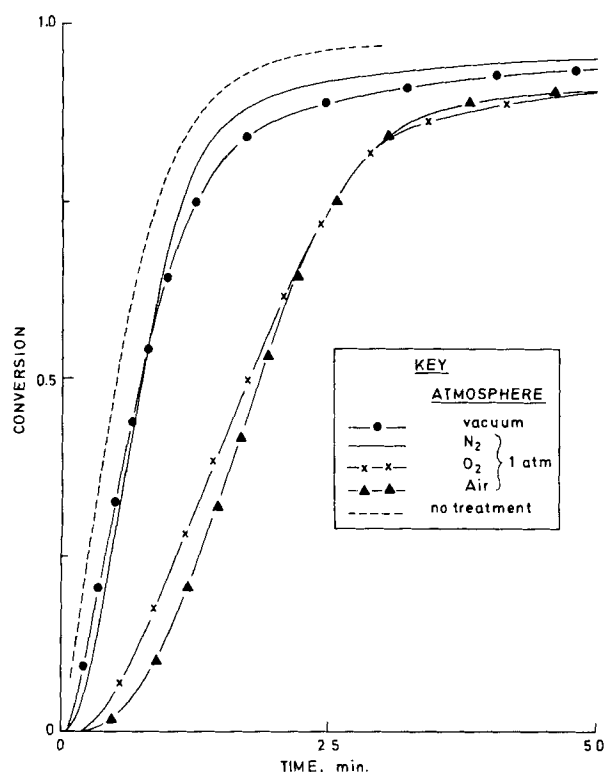


Figure 7. Effect of pretreatment on rehydration kinetics for samples annealed at 563 K for 40 minutes.

induction periods suggest that the heat treatment decreases the intrinsic reactivity toward water vapor of the anhydrous solid phase. Near one-half the absolute melting temperature, a solid may begin to recrystallize via a grain-growth process (Chadwick, 1972). Since the melting temperature of  $K_2CO_3$  is 1,164 K, such a process could become significant at about 582 K, which is within 60 K of the heating temperatures for which changes in rehydration reactivity were observed. Thus the temperature at which these changes take place suggests that a recrystallization or grain-growth process

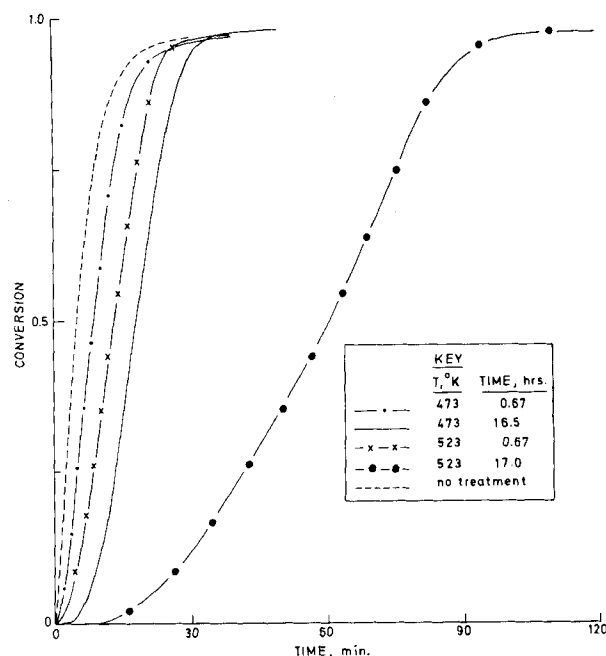


Figure 8. Effect of thermal pretreatment on rehydration kinetics for samples heat treated in air.

is responsible; observed differences in the rate of rehydration of heat-treated particles indicate that oxygen enhances the process.

Since the volume or molar free energy of transformation is a fixed thermodynamic quantity at a given temperature and pressure and the interfacial- and strain energies are in general determined by the relationships between the lattice structures of the two solids involved in the transformation, the primary variable in the free energy of formation of growth steps (and thus in the rate of reaction) is the defect energy. Changes in the defect structure of a solid could alter the rate of transformation and thus change the intrinsic reactivity. If heat treatment causes grain coarsening or recrystallization, the intrinsic reactivity may be decreased because fewer lattice defects and grain boundaries are available as sites for growth step formation. On the other hand, a process that produces defects in the lattice structure, such as perhaps dehydration-rehydration cycling, could increase the intrinsic reactivity since growth-step formation is favored at defect sites.

#### ACKNOWLEDGMENT

This research was supported by the U.S. Department of Energy through the Solar Energy Research Institute under Contract No. DE-FG02-80CS-84051-A002.

#### NOTATION

- $A$  = nucleus size, mol
- $B$  = nucleus surface area,  $m^2$
- $C$  = characteristic nucleus size for strain, mol
- $\Delta G$  = free energy change, J
- $\Delta G_m$  = molar free energy of transformation, J/mol
- $\Delta G_s^*$  = free energy of formation of a critical growth step, J
- $\Delta g$  = activation energy for addition of one element to a nucleus, J
- $I$  = nucleation rate,  $s^{-1}$
- $j_c$  = number of elements contained in a nucleus of critical size
- $K$  = rate coefficient, dimensionless

$k$	= Boltzmann constant, J/K
$k'$	= rate constant, %/min
$k_o$	= rate constant, $\text{m} \cdot \text{K}^{1/2}/\text{s}$
$k_1$	= rate constant, $\text{min}^{-1}$
$k_2$	= rate constant, dimensionless
$k_3$	= rate constant, Pa
$k_U$	= rate constant, $\text{K}^{1/2}/\text{m}^2 \cdot \text{s}$
$N$	= Avogadro's number, molecules/mol
$N_j$	= number of nuclei of size $j$
$N_t$	= total number of units in assembly
$N_U$	= number of transformation units in assembly per unit area of interface, $\text{m}^{-2}$
$n_s$	= number of moles in a growth step
$n_s^*$	= number of moles in a critical growth step
$P$	= pressure, Pa
$P^*$	= vapor pressure of pure water, Pa
$RAR$	= relative average rate of rehydration, $\text{min}^{-1}$
$r$	= decomposition rate, $\text{mol}/\text{m}^2 \cdot \text{s}$
$r_o$	= decomposition rate in vacuum, $\text{mol}/\text{m}^2 \cdot \text{s}$
$\dot{r}$	= interface velocity, $\text{m}/\text{s}$
$\dot{r}_o$	= interface velocity in vacuum, $\text{m}/\text{s}$
$S_c$	= number of elements in the surface of a critical nucleus
$s_o$	= number of transformation units in a growth step when it crosses the reaction interface
$T$	= temperature, K
$\dot{U}$	= rate of conversion of transformation units, $\text{m}^{-2} \cdot \text{s}^{-1}$
$V_U$	= volume of a transformation unit, $\text{m}^3$

#### Greek Letters

$\gamma$	= surface energy, $\text{J}/\text{cm}^2$
$\epsilon$	= strain energy, $\text{J}/\text{mol}$
$\nu$	= vibrational frequency, $\text{s}^{-1}$
$\sigma$	= standard deviation from least-squares correlation
$\psi$	= surface energy shape factor, $\text{J}/\text{mol}^{2/3}$
$\psi_A$	= area shape factor for interfacial energy, $\text{m}^2/\text{mol}^{2/3}$
$\psi_U$	= shape factor for number of units on a critical growth step, $\text{mol}^{-2/3}$
$\psi_D$	= area shape factor for interphase boundary defect energy, $\text{m}^2/\text{mol}^{2/3}$

#### Subscripts

$c$	= critical
$D$	= defect
$d$	= dehydration

$eq$	= equilibrium
$i$	= interfacial
$j$	= size of $j$
$obs$	= observed
$s$	= growth step
$U$	= transformation unit
$v$	= bulk

#### LITERATURE

- Acock, G. P., W. E. Garner, J. Milsted, and H. J. Willavoys, "The Dehydration of Ammonium, Potassium, and Some Mixed Alums," *Proc. R. Soc.*, **189**, 508 (1946).
- Anous, M. M. T., R. S. Bradley, and J. Colvin, "The Rate of Dehydration of Chrome Alum," *J. Chem. Soc.*, 3348 (1951).
- Ball, M. C., and L. S. Norwood, "Studies in the System Calcium Sulphate/Water. Part 4: Rehydration of Hexagonal  $\text{CaSO}_4$ ," *J. Chem. Soc., Farad. Trans. I*, **69**, 169 (1973).
- Chadwick, G. A., *Metallography of Phase Transformations*, Crane, Russak & Co., New York (1972).
- Christian, J. W., *The Theory of Transformation in Metals and Alloys. Part I*, Pergamon Press, Oxford (1975).
- Colvin, J., and J. Hume, "The Dehydration of Salt Hydrates," *Trans. Farad. Soc.*, **34**, 969 (1938).
- Cooper, J. A., and W. E. Garner, "The Dehydration of Crystals of Chrome Alum," *Proc. R. Soc., A*, **174**, 487 (1940).
- Eckhardt, R. C., P. M. Fichte, and T. B. Flanagan, "Kinetics of Rehydration of Crystalline Anhydrides-Manganous Formate," *Trans. Farad. Soc.*, **67**, 1143 (1971).
- Eckhardt, R. C., and T. B. Flanagan, "Anisotropic Solid-State Reaction," *Trans. Farad. Soc.*, **60**, 1289 (1964).
- Fichte, P. M., and T. B. Flanagan, "Kinetics of Dehydration of Single Crystals of Copper Formate Tetrahydrate," *Trans. Farad. Soc.*, **67**, 1467 (1971).
- Gardet, J. J., "The Dehydration Kinetics of Calcium Sulphate Dihydrate. Influence of the Gaseous Atmosphere and the Temperature," *Chem. Concr. Res.*, **6**, 697 (1976).
- Langmuir, I., "The Constitution and Fundamental Properties of Solids and Liquids. Part I: Solids," *J. Amer. Chem. Soc.*, **38**, 2221 (1916).
- Spencer, W. Devonshire, and B. Topley, "Chemical Kinetics of the System  $\text{Ag}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{O} + \text{CO}_2$ ," *J. Chem. Soc.*, **124**, 2633 (1929).
- Stanish, M. A., and D. D. Perlmutter, "Kinetics and Transport Effects in the Dehydration of Crystalline Potassium Carbonate Hydrate," *AIChE J.*, **29**, 806 (Sept., 1983).
- Stanish, M. A., and D. D. Perlmutter, "Rate Processes in Cycling a Reversible Gas-Solid Reaction," *AIChE J.*, **30**, 56 (Jan., 1984).
- Topley, B., "The Mechanism and Molecular Statistics of the Reaction  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$ ," *Proc. R. Soc.*, **A136**, 413 (1932).
- Topley, B., and M. L. Smith, "Kinetics of Salt Hydrate Dissociations:  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{MnC}_2\text{O}_4 + 2\text{H}_2\text{O}$ ," *J. Chem. Soc.*, **321** (1935).

Manuscript received October 11, 1982; revision received June 16, and accepted July 1, 1983.