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Experimental test of rate equations: time evolution of Al, Si ordering in anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$

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Abstract. The kinetic and equilibrium behaviour of the order parameter, Q_{od} , of Al, Si ordering in anorthite has been compared with the results of current rate theories (Ising-type Glauber, Ising-type Kawasaki and Landau-type rate equations). Although all rate equations can be adjusted to fit the time evolution for an accessible small interval of $Q_{\text{od}}(t)$ between 0.76 and 0.88, significant systematic differences were found for the equilibrium behaviour $Q_{\text{od}}(T)$. $Q_{\text{od}}(T)$ is well described by Landau theory but not by Bragg–Williams equations.

The rate laws are rather model-independent for $Q_{\text{od}} > 0.76$, but significant differences are expected for the ordering behaviour of crystals with smaller values of Q_{od} (e.g. < 0.5).

1. Introduction

There are two commonly adopted approaches for analysing kinetic processes of cation ordering in crystals. The first approach assumes that cation ordering can be described quantitatively by Ising models [1–5]. Cation ordering in framework structures almost always produces large spontaneous strains and it is due to the strain-related effective long range correlations that mean field approximations appear justified [6]. In this case, the equilibrium order parameter is expected to follow a Bragg–Williams behaviour while the kinetics should follow the Glauber rate law [7, 8].

Whereas this first approach is, in various forms and guises, the preferred model for most theorists, an alternative approach is often used by experimentalists. This second approach argues that the relevant order parameter or related state variable is a ‘continuously variable function’, even on a local scale, so that the mapping on a simple two-state variable is incorrect [9–11]. More precisely, it is assumed that each kinetic event changing a local state variable by δQ can be infinitesimally small ($\delta Q \ll 1/N$, where N is the number of state variables per unit volume). This condition is not fulfilled in the case of Ising models with $\delta Q = 1/N$. In an n -state Potts model, $\delta Q = 1/nN < 1/N$, numerical simulations have shown that already for $n > 4$ the kinetic behaviour is well approximated by a rate law based on such a continuously variable order parameter [12]. In fact, one might expect intuitively that the case $\delta Q < 1/N$ is always applicable for crystal structures with a large number of intermediate states of ordering within one unit cell (such as in the anorthite structure discussed in this paper). We show below that the rate law is, indeed, well described by a continuously variable order parameter but not by a two-state Ising parameter.

In the similar case of conserved order parameters, the equivalent problem of ‘discrete’ and ‘continuously’ variable state parameters has been analysed ever since the problem was clearly identified by Langer [13]. The mathematical mapping of discrete, atomic state parameters on to a continuously and smoothly variable order parameter via coarse-graining

is essential for the derivation of Cahn–Hilliard-type rate laws [14]. Such coarse-graining hinges on the fact that equilibration on a length scale smaller than the coarse-grained length scale, l , is much faster than the processes which one wants to describe by macroscopic rate laws. Although such an assumption appears to be safe for most spinodal processes in metals, it is not obvious why such a length scale should exist in the case of cation ordering in framework structures.

The second argument against the use of Ising-type models for the quantitative description of cation ordering in framework structures stems from the experimental observation that the excess Gibbs free energy of the equilibrium phase transition is anharmonic in enthalpy but much less so in entropy [15]. This means that the equilibrium behaviour of the order parameter follows a Landau-type behaviour which is, at $T \ll T_c$, quantitatively very different from a Bragg–Williams behaviour (more precisely, the double-well parameter as defined in [16] is much smaller than unity). The kinetic rate law is then determined by [9, 17]

$$\dot{Q} \propto [1 - (\xi_c/\xi)^2 (\sinh \xi \nabla / \xi \nabla)] (\partial G / \partial Q) \quad (1)$$

where G is the excess Gibbs energy, Q is the order parameter and ξ , ξ_c are characteristic lengths. The kinetic operator in the main bracket becomes unity for non-conserved order parameters ($\xi_c = 0$). Let us note here again, that the quantitative time dependence of Q in an n -state Potts model for $n > 4$ is practically indistinguishable from the solution of equation (1) [12].

If we now compare the quantitative predictions of both approaches, i.e. the two-states Ising type and the rate law in equation (1), we find that they are not very different for $T \gtrsim 0.8T_c$ [7, 8]. At lower temperatures, however, we find that both sets of results are different enough to matter for applications of the predicted rate behaviour in material sciences and geology [18–24]. The foremost question is then, which rate law is correct for the description of cation ordering in framework structures. Although the theoretical foundations for either approach seem to be rather clear, it appears that this question has not been approached experimentally.

The reason for the lack of previous experimental studies is the fact that only very few materials allow such studies. This is because cation ordering (e.g. Al, Si in feldspars) is very slow at low temperatures where the order parameter is large. In order to avoid studies on time scales of many years, virtually all studies so far have concentrated on the kinetic behaviour at high temperatures (e.g. $T \gtrsim 0.9T_c$) where the differences between the predictions of various models are very small.

In our present study we have used a new system, $\text{CaAl}_2\text{Si}_2\text{O}_8$, in which the T_c of Al, Si ordering, described by the order parameter Q_{od} may be as high as $\simeq 2800$ K [25]. The ordering at $0.5 T_c \approx 1400$ K is still fast enough to be followed experimentally which allows us to test the two models. The disadvantage of this material is, however, that no uniform starting material with less than 75% order could be produced so far. Our study is therefore limited to changes of Q_{od} between 0.76 and 0.88. We show in this paper from the simultaneous refinement of equilibrium and kinetic data that we can reject the Ising/Glauber models whereas we find good agreement with the second type of behaviour related to time dependent Landau theory.

2. Experimental details

Crystalline anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, was produced from glass of the same composition as described in detail by Carpenter [25]. The samples were annealed at high temperatures for sufficiently long times that a homogeneous degree of Al, Si order, with antiphase domains

coarser than 3000 Å, was generated (16 days at 1673 K and 3 days at 1808 K) [25]. The degree of order was determined from lattice constants via the empirical relationship [26]:

$$Q_{od} = 10.1\sqrt{\epsilon_s} \quad (2)$$

where ϵ_s is the spontaneous strain obtained from room temperature lattice parameter data. Lattice parameters were refined from $\text{CaAl}_2\text{Si}_2\text{O}_8$ powder diffraction lines measured with a focussing Guinier camera (Huber). The standard deviations (1σ) were typically of the order of 0.002 Å for a , b , c , 0.02° for α , 0.01° for β and 0.01° for γ . This leads to a relative error in Q_{od} of 2%.

For the kinetic runs, the powdered starting material with $Q_{od} = 0.76$ was packed into platinum foil and heated for various amounts of time at 1673 K, 1473 K and 1273 K, respectively. The equilibrium values of Q_{od} in the temperature interval between 1000 K and 1700 K and the excess enthalpies for the samples were published previously [25]. We include for our calculations only data obtained on synthetic samples at $T \leq 1670$ K because there is doubt that samples prepared at higher temperature might contain larger defect concentrations, possibly due to premelting effects.

We argue below that the new determination of the relevant Landau-type energy as based on the simultaneous refinement of equilibrium and kinetic data leads to similar values for a first-order (2–4–6) potential as derived from equilibrium data alone [25]. The difference between first-order, tricritical and second-order transitions is somewhat marginal, however, and we include refinements for all models in order to show the internal consistency in all cases.

3. Analysis and results

The experimental results are shown in figures 1 and 2. They are compared with the following models (in the case of anorthite Q is to be replaced by Q_{od}):

(a) Ising/Glauber

$$Q = \tanh((T_c/T)Q) \quad (3)$$

$$\dot{Q} = -(1/\tau)[Q - \tanh((T_c/T)Q)] \quad (4)$$

$$H = -\frac{1}{2}k_B T_c Q^2 \quad (5)$$

$$G = \frac{1}{2}k_B T[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q)] - \frac{1}{2}k_B T_c \quad (6)$$

$$G_{kin} = -k_B T[(T/T_c)\ln[\cosh((T_c/T)Q)] - \frac{1}{2}Q^2] \quad (7)$$

(b) Ising/Kawasaki

$$Q = \tanh((T_c/T)Q) \quad (8)$$

$$\dot{Q} = -(1/\tau)[2Q/(Q^2 + 1) - \tanh(2QT_c/T)] \quad (9)$$

$$H = -\frac{1}{2}k_B T_c Q^2 \quad (10)$$

$$G = \frac{1}{2}k_B T[(1+Q)\ln(1+Q) + (1-Q)\ln(1-Q)] - \frac{1}{2}k_B T_c \quad (11)$$

$$G_{kin} = -k_B T[(T/2T_c)\ln[\cosh(2QT_c/T)] - \ln(Q^2 + 1)] \quad (12)$$

(c) Landau model

$$Q = ((T_c - T)/T_c)^{1/2} \quad \text{second-order} \quad (13)$$

$$Q = ((T_c - T)/T_c)^{1/4} \quad \text{tricritical} \quad (14)$$

$$Q = -B/2C + \sqrt{B^2/4C^2 - (A/C)(T - T_c)} \quad \text{first-order} \quad (15)$$

$$\dot{Q} = -(1/\tau k_B T) \partial G / \partial Q \quad (16)$$

$$H = -\frac{1}{2} A T_c Q^2 + \frac{1}{4} B Q^4 + \frac{1}{6} C Q^6 \quad (17)$$

$$G = G_{\text{kin}} = \frac{1}{2} A (T - T_c) Q^2 + \frac{1}{4} B Q^4 + \frac{1}{6} C Q^6. \quad (18)$$

In each case τ is an activated time constant $\tau = \tau_0 \exp(E_a/kT)$. The Kawasaki rate law for a conserved order parameter is unrealistic for the process of Al, Si ordering but is included for comparison with the Glauber rate law in order to test if local correlations are significant.

The two Ising-related models contain as adjustable parameters the time constant τ_0 , the activation energy E_a , the enthalpy of solution H_{soln}^0 for $Q_{\text{od}} = 0$ and the transition temperature T_c . In addition, the Landau-type model contains, instead of T_c , the coefficients of the Landau potential A , B and C , from which T_c can be calculated by scaling $Q_{\text{od}} = 1$ at $T = 0$ K. We have tested three forms of the Landau potential, namely for a second-order ($C = 0$), tricritical ($B = 0$) and first-order ($B < 0$, $C > 0$) phase transition. We will see below that the effect of such changes on the rate law was very small when the free parameters were fitted to the available experimental data.

For each model all the parameters were determined simultaneously by minimizing the objective function $F(\tau_0, E_a, H_{\text{soln}}^0, T_c, A, B, C)$

$$F = \chi^2 = f_{Q_{\text{kin}}} + f_{Q_{\text{eq}}} + f_{H_{\text{soln}}} \quad (19)$$

consisting of three least squares functions of the form

$$f_j = \sum_i \frac{1}{N_j} \left(\frac{y_i^{\text{obs}} - y_i^{\text{calc}}}{y_i^{\text{obs}}} \right)^2 \quad (20)$$

where N_j is the number of datapoints in each data set. The total number of independent datapoints is 53. The value for χ^2 is given in table 1.

Table 1. Parameters of the five models defined in equations (3)–(18). The number of parameters fitted to 53 independent datapoints is 4 (Ising), 5 (Landau tricritical, second-order) and 6 (Landau first-order). The value of T_c in the Landau models is given for comparison but is not a fitted parameter (but results from the values of A , B , C). The values of χ^2 can be compared directly because the number of fitted parameters (i.e. 4, 5, 6) is always small compared with the number of independent observations (i.e. 53).

	Ising		Landau		
	Glauber	Kawasaki	1st-order	Tricritical	2nd-order
τ_0^{-1} (h^{-1})	1.950×10^{13}	2.048×10^{13}	2.266×10^{11}	1.063×10^{11}	4.242×10^{10}
E_a (kJ mol^{-1})	390.4	373.0	377.6	369.8	361.1
H_{soln}^0 (kJ mol^{-1})	-39.65	-39.63	-30.83	-26.13	-14.69
T_c (K)	2200	2200	(2325)	(3477)	(6146)
A ($\text{kJ mol}^{-1} \text{K}^{-1}$)	—	—	4.067×10^{-2}	3.873×10^{-2}	3.647×10^{-2}
B (kJ mol^{-1})	—	—	-107.6	—	224.2
C (kJ mol^{-1})	—	—	202.2	134.7	—
χ^2	0.227	0.228	0.057	0.057	0.057

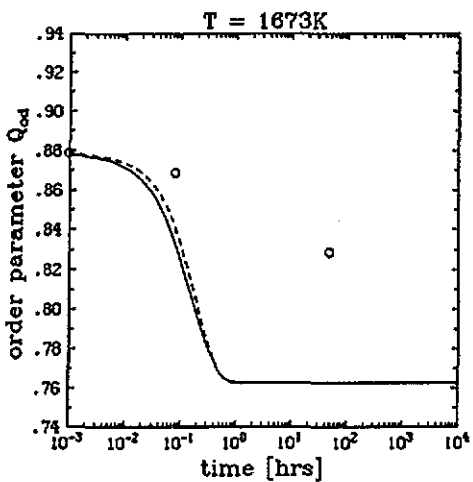
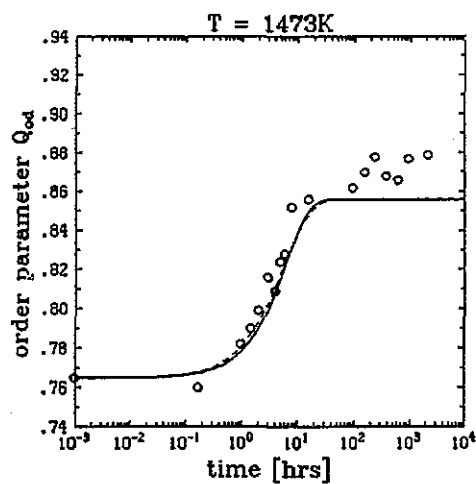
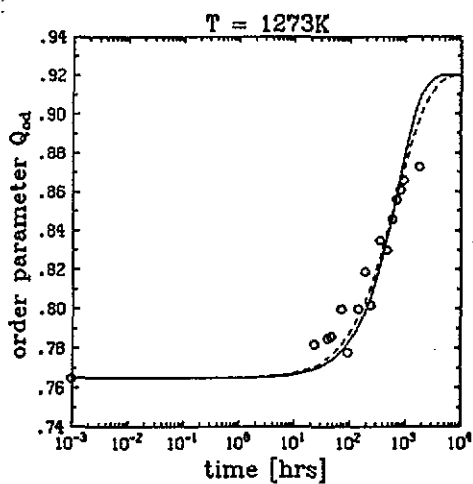
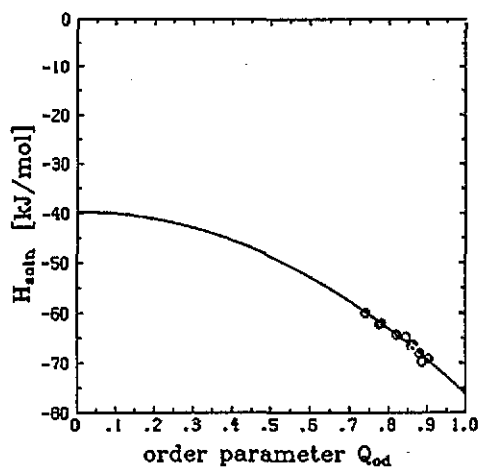
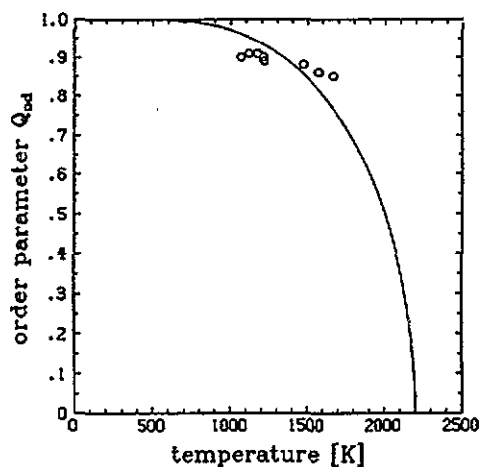


Figure 1. Experimental data and calculated curves using the parameter values given in table 1 for the Ising/Glauber model (solid line) and Ising/Kawasaki model (dashed line): equilibrium order parameter $Q_{od}(T)$, enthalpy of solution H_{soln} as a function of the order parameter (data from [25]), time evolution of the order parameter for isothermal annealing at 1273 K, 1473 K and 1673 K.

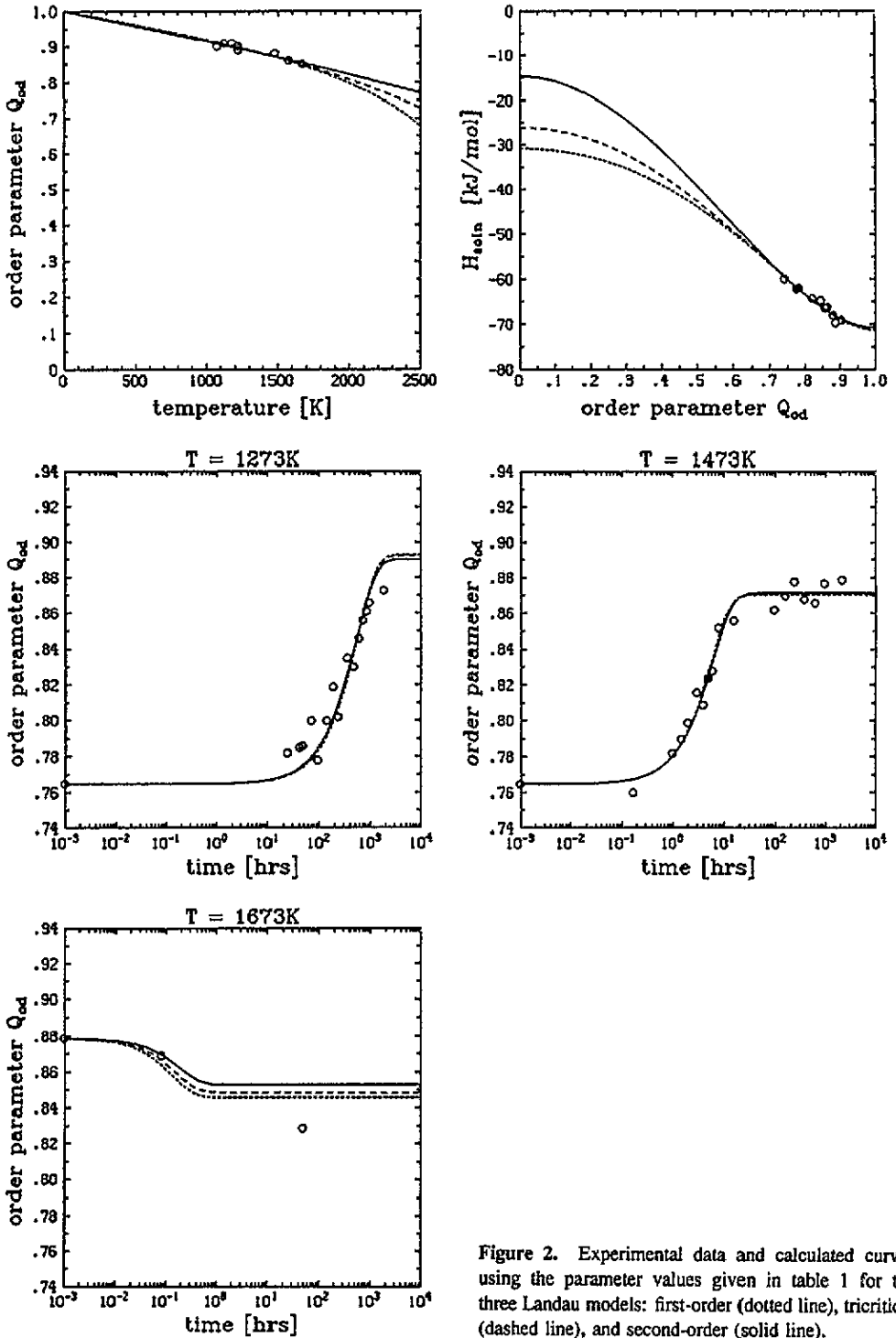


Figure 2. Experimental data and calculated curves using the parameter values given in table 1 for the three Landau models: first-order (dotted line), tricritical (dashed line), and second-order (solid line).

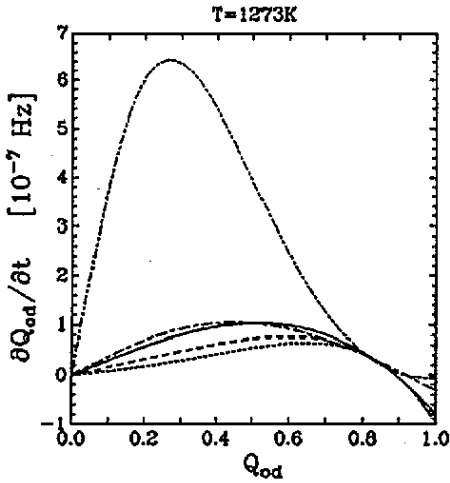


Figure 3. Calculated change of the order parameter, $\partial Q_{od}/\partial t$, at a constant annealing temperature $T = 1273$ K plotted as a function of the order parameter for the different models. Curves from top to bottom at $Q_{od} = 0.2$: Ising/Kawasaki, Ising/Glauber, Landau second-order, tricritical, and first-order. All curves coincide in the order parameter range around $Q_{od} = 0.8$ where experimental data are available.

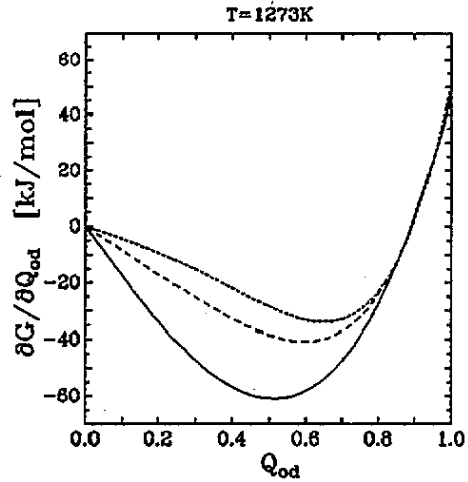


Figure 4. Kinetic driving force $\partial G/\partial Q_{od}$ at $T = 1273$ K calculated with the parameters given in table 1 for the three Landau potentials: first-order (dotted line), tricritical (dashed line), and second-order (solid line).

Starting with some trial values for the parameters, $f_{Q_{od}}$ has been calculated by solving the differential equation for \dot{Q} for all the kinetic data using a Runge–Kutta method. $f_{Q_{od}}$ has been determined from the equilibrium data. $f_{H_{soln}}$ follows from the relation between the excess enthalpy H and the measured enthalpy of solution H_{soln}

$$H(Q_{od}) = H_{soln}^0 - H_{soln}(Q_{od}) \quad (21)$$

where H_{soln}^0 is the value for $Q_{od} = 0$.

The objective function F was then minimized with respect to all parameters using a Nelder–Mead downhill simplex method [27]. The strategy in trying to find the global minimum of F has been described for a similar problem in [23]. The resulting sets of parameters are listed in table 1.

The theoretical curves and experimental data are compared for each model in figure 1, for the Ising models and in figure 2 for the Landau models. In each case, the figures show the equilibrium curve $Q_{od}(T)$, the heat of solution H_{soln} as a function of the order parameter and the time evolution of the order parameter at 1273 K, 1473 K and 1673 K, respectively.

By inspection of the systematic deviations between the observed and calculated parameters it is clear that only the Landau-type models coincide with the experimental results. The disagreement with the Ising-type models is not so much in the rate behaviour but the temperature dependence of Q_{od} in thermodynamic equilibrium. The apparent independence of the rate law with respect to the model assumptions is somewhat accidental, however. It is essentially due to the small interval of $Q_{od}(t)$ which could be covered in the experiment. This point is illustrated in figure 3 where $\partial Q_{od}/\partial t$ is plotted as a function of Q_{od} using the fitted values for the parameters. At values of $Q_{od} \approx 0.8$, i.e. in the experimental region, all curves roughly coincide and similar rate behaviour is expected for all models. At lower values of Q_{od} , the Kawasaki rate law becomes very efficient and

much faster rates are expected for this model than for the others, which in turn do not differ significantly. The equilibrium behaviour, on the other hand, does show significant differences between the Ising and Landau model with good agreement between experimental and theoretical results for the Landau case only.

We finally comment on the possible variations between the three Landau potentials tested. All three potentials have the same slopes $\partial G/\partial Q_{od}$ for Q_{od} in the experimental region (figure 4). Equally, the calculated values of the enthalpy of solution H_{soln} are virtually identical and so is the equilibrium curve $Q_{od}(T)$ for $0.7 < Q_{od} < 0.9$. A distinction between the three Landau potentials based on the experimental data is therefore not possible.

In order to distinguish between these potentials, $\partial G/\partial Q_{od}$ has, in addition to the data presented here, to be known at much lower values of Q_{od} , say 0.5. For this value the rate of ordering would change by a factor of 5 between the first-order and the second-order behaviour. This would make an experimental distinction between them rather easy. Unfortunately no such structural states could be produced as yet and we find that for realistic values of Q_{od} , all three Landau potentials reproduce the experimental observations very well.

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