graphie wird das Dimethylsulfoxid bei gleicher Temperatur im Hochvakuum abdestilliert; zur Titration wird ein aliquoter Teil (0,5 ml) der Lösung mit 8 ml H_2O verdünnt. – Resultate: Bei 60° nach 30 Min.: ca. $^1/_3$ umgelagert; nach 4 Std.: noch Spuren Ausgangsmaterial; nach 10 Std.: Ausgangsmaterial ganz verschwunden; bei 40° nach 10 Std.: noch Spuren Ausgangsmaterial. Das Hauptprodukt der Umlagerung ist dünnschichtchromatographisch identisch mit **18** nach a), die Bildung eines Nebenproduktes tritt bei 60° stärker in Erscheinung (ca. 5–10%) als bei 40°. DC.: Hauptprodukt: *h*/0,37; *i*/0,20 (Ninh. –, Tol. +, Ind. +). Nebenprodukt: *h*/0,52; *i*/0,36 (Ninh. –, Tol. +, Ind. +). Reste von Dimethylsulfoxid: *h*/0,60; *i*/0,58 (Ninh. –, Tol. + +, Ind. –).

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120. Lattice Energy, Lattice Constant, and Thermodynamic Properties of γ-Al_2O_3

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(15. IV. 70)

Zusammenfassung. Basierend auf bekannten thermodynamischen Daten von α-Al_2O_3 (Korund) und der Phasenumwandlung α-$Al_2O_3 \rightarrow \gamma$-$Al_2O_3$ werden eine Reihe von Konsequenzen für die Natur der γ-Phase diskutiert. Es wird gezeigt, dass die Annahme einer unterkühlten Flüssigkeit für die γ-Phase mit zuverlässigen Daten schwer verträglich ist. Andererseits sind diese Daten konsistent mit einer ungeordneten kubischen Struktur der γ-Phase, die für alle Temperaturen bis zum Schmelzpunkt des α-Al_2O_3 in Bezug auf dieses als thermodynamisch unstabil betrachtet werden kann. Die bisher bekannten Daten der Phasenumwandlung $\gamma \rightarrow \alpha$ weisen insgesamt auf einen kinetisch kontrollierten Prozess hin, obwohl sie wechselseitig nicht konsistent sind. Es wird der *Coulomb*-Anteil der Gitterenergie von γ-Al_2O_3 numerisch berechnet und eine Gitterkonstante von 7,883 Å (25 °C) für die ungeordnete spinellartige γ-Al_2O_3 Struktur aus thermodynamischen Daten abgeleitet.

1. Introduction. – Whereas the chemical thermodynamics [1] [2] [3] and crystal structure [4] [5] of α-Al_2O_3 have been the subject of numerous investigations, only scanty reliable information is available on γ-Al_2O_3. In particular there are few thermodynamic data for the pure γ-phase. For the phase transition $\alpha \longrightarrow \gamma$ only the transition enthalpy ΔH° has been published [2]. Recently *Yokokawa* & *Kleppa* [6] have reported direct measurements of the solution enthalpy of γ-type aluminium oxide and therefrom derived a phase transition enthalpy of 5.3 kcal/mole at 978 K. This value disagrees widely with values given by *Kubaschewski* & *Evans* [2], who consider as a most probable value $\Delta H^\circ_t = 20.6$ kcal/mole at 1273 K. Still another value $\Delta H^\circ_t = 11.0$ kcal/mole at 1473 K is given in JANAF Tables [7]. *Das* & *Fulrath* [8] studied the nucleation of a solid phase by fast cooling of powdered Al_2O_3 molten in a torch. Mainly from X-ray investigations these authors assigned this phase to have γ-structure. No further information concerning the kinetics of γ-phase formation seems to be available. It is known, however, that in the *Verneuil* crystal-growing technique part of the Al_2O_3 powder is not used in the formation of the crystal, but is found in the furnace as a fine powder, whose structure is believed to be of γ-type. It should further be pointed out that some contradictory data concerning the structure of γ-Al_2O_3 have been published [8] [9] [10], assigning to this phase a cubic (spinel-type) [9] [10] or alternatively a supercooled liquid structure [8], with essentially different densities. In the subsequent sections the available thermodynamic data are discussed with respect to their consistency. Furthermore, it is shown that the γ-phase may be assumed to be a solid, spinel-like phase, which, however, may be unstable up to the melting point of α-Al_2O_3. The observed phase transition points may therefore be assumed to be kinetically controlled.

2. Thermodynamics of the $\alpha \rightarrow \gamma$-phase transition. – 2.1. Thermodynamic data available from the literature for α- and γ-Al_2O_3 are collected in Table I. The question then arises which of the following two alternatives is compatible with these data:

a) the γ-phase is considered as a supercooled liquid;
b) the γ-phase is a disordered cubic crystalline phase.

The following discussion of this question is based on *Kubaschewski*'s [2] and NBS [1] data. It will be shown that the other data [6] [7] lead to unreasonable conclusions. 2.1.a. If the γ-phase is assumed for the moment to be a supercooled liquid, then the thermodynamic data in Table I should be reinterpreted as shown by Table II: Now the transition effects ΔG°_t and ΔH°_t take the role of fusion effects. In order to reach further conclusions, a number of assumptions must be made. The specific heat of α-Al_2O_3 is experimentally known over the whole temperature range from 200 K to 2300 K [11]. From this an average *Debye* temperature $\theta_D \approx 540$ K may be calculated. Also from heat capacity data it is seen that the T^3-law is valid with good approximation in the interval from 0 K to 100 K. If now the same θ_D and the same interval of validity of the

Table I. *Known thermodynamic data about the α- and γ-phase of Al_2O_3*

Thermodynamic property	α-phase	γ-phase
Enthalpy of formation: ΔH_f^0 (298K) [kcal/mole]	– 399.09 a)	– 384.84 a)
Gibbs energy of formation: ΔG_f^0 (298K) [kcal/mole]	– 376.77 a)	
Entropy S^0 (298K) [cal · mole^{-1} · deg^{-1}]	12.186 a)	
Heat capacity C_p^0 (298K) [cal · mole^{-1} · deg^{-1}]	18.88 a)	
Enthalpy of fusion: ΔH_{fus}^0 [kcal/mole]	26.0 b)	
Phase transition enthalpy $\Delta H_t^0(T)$ [kcal/mole]	20.6 (T = 1273K) b) 11.0 (T = 1473K) c) 5.3 (T = 978K) d)	

a) According to NBS Circular 500, Part I [1].
b) According to *Kubaschewski & Evans* [2].
c) According to JANAF Thermochemical Tables [7].
d) According to *Yokokawa & Kleppa* [6].

T^3-law are assumed for the γ-phase, then one may approximate $\Delta C_p^0 = C_p^{0\gamma} - C_p^{0\alpha}$ as follows:

$$\begin{aligned} \Delta C_p^0 &= a \cdot T^3 && T \leqslant 100\text{K} \\ \Delta C_p^0 &= A \cdot T + B && 100\text{K} \leqslant T \leqslant T_0 \\ \Delta C_p^0 &= C \cdot T + D + E/T^2 && T \geqslant T_0 \end{aligned} \tag{1}$$

where a, A, B, C, D, E are empirical constants. Applying well known thermodynamic formulae [12] for the process

$$-\ \alpha\text{-}Al_2O_3(s) + \gamma\text{-}Al_2O_3(l) = 0 \tag{2}$$

and choosing $T_0 = 300\,\text{K}$, one obtains from the data in Table II:

Table II. *Interpretation of known thermodynamic data required by the assumption of a supercooled liquid*

Temperature [K]	$\Delta G_t^0 = \Delta G_{fus}^0$ [kcal/mole]	$\Delta H_t^0 = \Delta H_{fus}^0$ [kcal/mole]
2293 (m.p.)	0	26.0
1273	–	20.6
298	–	14.25

$$a = 6.9282\ 10^{-7}\ \text{cal/mole/deg}^4$$
$$A = 2.0785\ 10^{-2}\ \text{cal/mole/deg}^2$$
$$B = -1.3856\ \text{cal/mole/deg}$$
$$C = -1.9267\ 10^{-3}\ \text{cal/mole/deg}^2$$
$$D = 8.8345\ \text{cal/mole/deg}$$
$$E = -3.0660\ 10^5\ \text{cal}\cdot\text{deg/Mole}$$
$$\Delta H_t^0(0) = 13.688\ \text{kcal/mole}$$

Since, however, $\Delta G_t^0(T_f) = 0$, where T_f means the melting temperature, it follows that $\Delta S_t^0(0\,\text{K}) = -3.9812$ cal/mole/deg. This means $S^{0\gamma}(0) < S^{0\alpha}(0)$, which contradicts the fact that crystalline α-Al_2O_3 should have a higher degree of order than supercooled molten γ-Al_2O_3. Therefore the assumption of a supercooled liquid structure for the γ-phase is hardly defendable.

2.1.b. If the γ-phase is considered as a disordered cubic crystalline phase, the data listed in Table I should be interpreted as shown by Table III. Equation (2) now has to be replaced by the two processes

Table III. *Interpretation of known thermodynamic data required by the assumption of a disordered cubic crystalline phase*

Temperature [K]	ΔG_t^0	ΔG_{fus}^0	ΔH_t^0	ΔH_{fus}^0 [a]
2293	–	0	–	26.0
1273	0	–	20.6	–
298	–	–	14.25	–

[a] In units of kcal/mole.

$$-\alpha(s) + \gamma(s) = 0\,, \tag{3'}$$

and

$$-\alpha(s) + \alpha(l) = 0\,, \tag{3''}$$

since now the data reported are assigned to the $\alpha \longrightarrow \gamma$ phase transition (3'), and to the fusion of α-Al_2O_3 (3"), respectively. Making the same assumption concerning ΔC_p as in section 2.1.a one obtains three equations using the values of $\Delta H_t^\circ(T)$ at $T = 298$ K and 1273 K, and the value of $\Delta G_t^\circ(T)$ at $T = 1273$ K (other values of the phase transition temperature have also been used in the calculations!). Including the four conditions for continuity of ΔC_p and its derivative with respect to T at $T = 100$ K and $T = T_0$, one has now seven equations, but eight unknowns. In order to proceed further, we may compute $\Delta S_t^\circ(0)$ by statistical mechanics, using the *Boltzmann* formula $S^{\circ\gamma}(0) = k \cdot \ln\Omega$ for the configurational entropy of the γ-phase. The structure of the latter was reported as a defect spinel structure [10], in which $21^1/_3$ of the available 24 cation sites are occupied statistically. One obtains then

$$S^{\circ\gamma}(0) = k \ln \binom{[2\,N_L \cdot 9/8}{2\,N_L} = 1.56 \text{ cal/mole/deg.}$$

Using $S^{\circ\alpha}(0) = 0$ the reaction entropy $\Delta S_t^\circ(0)$ of the process (3') is obtained:

$$\Delta S_t^\circ(0) = +1.56 \text{ cal/mole/deg.}$$

Table IV. *Thermodynamic values obtained from the assumption of a crystalline γ-phase*

Phase transition temperature	1273K	1500K	1750K
a [cal/mole/deg^4]	$1.019 \cdot 10^{-6}$	$6.850 \cdot 10^{-7}$	$3.69 \cdot 10^{-7}$
A [cal/mole/deg^2]	$3.056 \cdot 10^{-2}$	$2.056 \cdot 10^{-2}$	$1.107 \cdot 10^{-2}$
B [cal/mole/deg]	$-2.038 \cdot 10^{+0}$	$-1.371 \cdot 10^{+0}$	$-7.384 \cdot 10^{-1}$
C [cal/mole/deg^2]	$-1.109 \cdot 10^{-2}$	$-1.716 \cdot 10^{-3}$	$-7.169 \cdot 10^{-3}$
D [cal/mole/deg]	$1.671 \cdot 10^{+1}$	$8.653 \cdot 10^{+0}$	$1.020 \cdot 10^{+0}$
E [cal/mole·deg]	$-5.623 \cdot 10^{+5}$	$-3.007 \cdot 10^{+5}$	$-5.274 \cdot 10^{+4}$
$\Delta H_t^\circ(0)$ [kcal/mole]	$1.342 \cdot 10^{+1}$	$1.369 \cdot 10^{+1}$	$1.395 \cdot 10^{+1}$

Consequently, using the same type of reasoning as in section 2.1.a one obtains the data listed in Table IV.

2.2. The question now arises why we have used only the two values of $\Delta H_t^o(T)$ at $T = 298\,K$ and $1273\,K$, although further values at $T = 978\,K$ and $1473\,K$ have also been published [6] [7]. However, if these values are analyzed in the same way one is led to unreasonable values and temperature dependences of the thermodynamic functions ΔC_p^o, ΔH_t^o, ΔG_t^o, as well as ΔS_t^o. These unreasonable results arise both for the assumption of a supercooled liquid and for the assumption of a crystalline γ-phase. In Figures 1a–c the thermodynamic functions ΔC_p^o, ΔH_t^o and ΔG_t^o obtained from different choices of experimental data are plotted. It may easily be seen from these plots that the values we have taken as reliable give by far the most plausible results. The above discussion of the reliability of the different ΔH_t^o data does not depend significantly on the assumptions made for $\Delta C_t^o(T)$. Other assumptions, such as $\Delta C_p^o = C \cdot T + D + E/T^2 + F \cdot \ln(T)$ for $T \geq T_0$ have been used, providing essentially the same results.

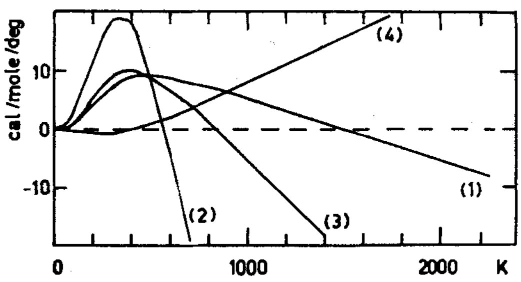

Figure 1a: $\Delta C_p^o(T)$

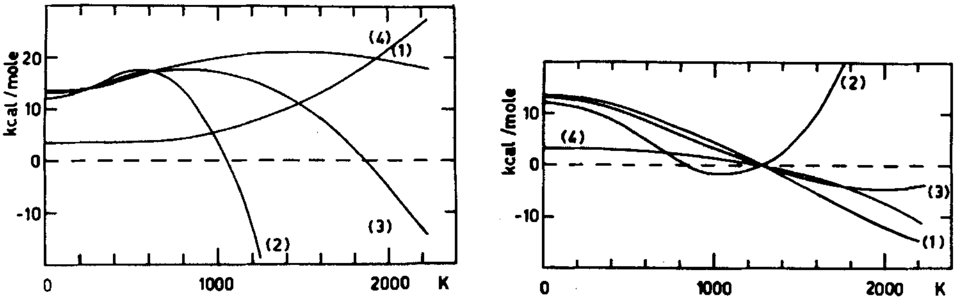

Figure 1b: $\Delta H_t^o(T)$ Figure 1c: $\Delta G_t^o(T)$

Figure 1. *Comparison of thermodynamic functions $\Delta C_p^o(T)$, $\Delta H_t^o(T)$ and $\Delta G_t^o(T)$ obtained from using different sets of $\Delta H_t^o(T)$-values*

1 ΔH_t^o – values at T = 298K and 1273K used [1] [2].

2 ΔH_t^o – values at T = 298K and 978K used [1] [6].

3 ΔH_t^o – values at T = 298K and 1473K used [1] [7].

4 ΔH_t^o – values at T = 978K and 1473K used [6] [7].

T_t has been chosen to be 1273K for all curves plotted here.

2.3. In the previous sections of this paper it was supposed that the phase equilibrium temperature T_t is approximately 1273 K. The question arises, however, whether $T_t = 1273$ K is really a transition point or merely a kinetically controlled pseudo-transition point. From *Kubaschewski*'s data [2] it is only evident that $T_t = 1273$ K is the lowest temperature at which the γ to α transformation has been experimentally observed. On the other hand it is known that the crystals grown by the *Verneuil* process are always of the α-type. This leads to the suggestion that the γ-phase may be unstable for all temperatures below the melting point T_f of the α-phase. By using either expansion for $\Delta C_p^o(T)$ with the set of data considered as reliable, one obtains acceptable characteristics for ΔC_p^o in the whole interval $1273\,K \leqslant T_t \leqslant T_f$. In Figures 2a–b the plots of $\Delta C_p^o(T)$ and of $\Delta H_t^o(T)$ for different values of T_t as parameter are shown. The data as shown in Table III have been used for these calculations. It may be seen from these plots that the most reasonable $\Delta C_p^o(T)$ and $\Delta H_t^o(T)$ curves are obtained if T_t is in the interval $1500\,K \lesssim T_t \gtrsim 1800\,K$.

The fact that only the α-phase is obtained from the *Verneuil* process does not, however, rule out the possibility that $T_t < T_f$. Nevertheless, it seems rather unlikely that at temperatures near or above 2000 K an unstable phase could exist during time intervals typically used in the *Verneuil* growth of α-sapphire.

3. Lattice energy of α- and γ-Al_2O_3. – 3.1. *Seitz* [13] gives the *Madelung* constant for the coulombic contribution U_{coul}^{α} to the lattice energy of the α-modification:

$$\alpha^{(\alpha)} = 45.825\,,$$

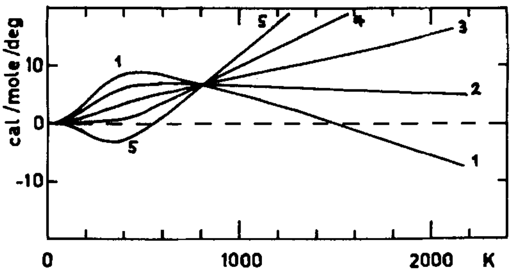

Figure 2a: $\Delta C_p^o(T)$

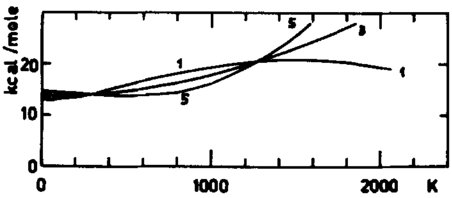

Figure 2b: $\Delta H_t^o(T)$

Figure 2. *Thermodynamic functions $\Delta C_p^o(T)$ and $\Delta H_t^o(T)$ for different phase equilibrium temperatures T_t (γ-phase taken as crystalline phase, values of Kubaschewski [2] and NBS [1] used)*

1 $T_t = 1273$K
2 $T_t = 1500$K
3 $T_t = 1750$K
4 $T_t = 2000$K
5 $T_t = 2250$K

where $\alpha^{(\alpha)}$ is defined by $U^{\alpha}_{\text{coul}} = N_L \cdot \alpha^{(\alpha)} \cdot e_+ \cdot e_-/l$ and l is the cube root of the molecular volume. Since the lattice constants of this structure are known with great accuracy [4] [5], namely [5] $a = 4.7590$ Å, $c = 12.991$ Å, one obtains at 298 K

$$U^{\alpha}_{\text{coul}} = -(4362.86 \pm 0.35)\ \text{kcal/mole}$$

The error in U^{α}_{coul} was estimated by taking an upper limit of the experimental errors reported for the lattice constants.

3.2. In order to obtain the lattice energy U^{γ}_{coul} of the γ-phase, some assumptions for the γ-structure have to be made. To be correct, U^{γ}_{coul} should be calculated as an ensemble average in the sense of the *Ising* problem. In order to avoid such a calculation, we take as a basis a spinel structure in which all cation sites are occupied, but with cations whose charge is reduced by the factor 8/9, so that positive and negative charges are compensated. Denoting the vectors in the unit cell by x_i for the aluminium sites, and by y_j for the oxygen sites, we have to calculate lattice sums of the following type:

$$\psi_{\text{Al}} = \frac{e_0}{a} \sum_{u_k} \left\{ \sum_{i=1}^{34} \frac{Z_i}{|x_i + u_k|} - \sum_{j=1}^{32} \frac{2}{|y_j + u_k|} \right\}. \tag{8}$$

Here u_k denotes the vector of the unit cells. From the potentials ψ_{Al} and ψ_{O} one obtains the lattice energy of the γ-phase according to

$$U^{\gamma}_{\text{coul}} = \frac{3 \cdot N_L \cdot e_0^2}{a} \left\{ \frac{a}{e_0}\, \psi_{\text{Al}} - \frac{a}{e_0}\, \psi_{\text{O}} \right\}. \tag{9}$$

The formulas for the potential (8) have to be evaluated numerically. In the actual calculation the lattice sum was taken over a cube of $5a$ edge length. In order to obtain an estimate of errors, this sum was compared with the sum over a $3a$ cube. This gave an estimated upper error limit of $0.6 \cdot 10^{-4}$ for the *Madelung* constant obtained from a $5a$ cube. If we put

$$U^{\gamma}_{\text{coul}} = -\alpha^{(\gamma)} \cdot \frac{e_0^2}{a} \cdot N_L \tag{10}$$

the *Madelung* constant $\alpha^{(\gamma)}$ of the γ-structure is

$$\alpha^{(\gamma)} = 88.470 \pm 0.060\,. \tag{11}$$

From $\Delta U^{\circ}_{t} = \Delta H^{\circ}_{t} = \Delta G^{\circ}_{t}$ at 0 K, and from

$$\Delta U^{\circ}_{t}(0) = \Delta U(0) + \frac{45}{8} \cdot R\,[\theta^{\alpha}_{D} - \theta^{\gamma}_{D}]\,, \tag{12}$$

where $\Delta U(0) = U^{\gamma}_{\text{lattice}} - U^{\alpha}_{\text{lattice}}$, we get, neglecting the zero point energy term,

$$U^{\gamma}_{\text{lattice}} = \Delta U^{\circ}_{t}(0) + U^{\alpha}_{\text{lattice}}\,. \tag{13}$$

Calculation of the lattice energies $U^{\gamma}_{\text{lattice}}$ and $U^{\alpha}_{\text{lattice}}$ was made approximately, using the equation

$$U_{\text{lattice}} = U_{\text{coul}} \cdot (1 - 1/n)\,. \tag{14}$$

For n the value 7.0 has been selected for both the α and the γ phase. Repulsion exponents for oxides are usually chosen in the interval $6 \leqq n \leqq 9$ [13]. From (13) U_{lattice} may now be calculated, from which in turn by (14) and (10) the lattice constant of the γ-phase is evaluated. This value does not depend strongly on the value of T_t

used in the calculations. It is $a_\gamma = 7.8831$ for $T_t = 1500$ K. Only very little reliable information on a_γ seems to be available; experimental values given by different authors differ by as much as 1%. In Table V the results for $T_t = 1273$ K, 1500 K and 1750 K, respectively, are collected together with published data. It will be seen that the lattice constant of the γ-phase derived from thermodynamic data, assuming a disordered cubic structure, lies well within the uncertainty of experimental values. As is evident from the derivation of a_γ given above, its value depends on the repulsion coefficient n, but very little on the value of the phase transition temperature T_t.

Table V. *Lattice energies and lattice constants of* α-Al_2O_3 *and* γ-Al_2O_3

Phase	Lattice energy [kcal/mole]	Lattice constants [Å]
α	–4362.86	$a_0 = 4.7590$[a]
		$c_0 = 12.991$ [a]
		$a = 7.88 \ldots 7.94$[b]
γ	–4349.44	$a = 7.8826$[c]
	–4349.17	$a = 7.8831$[d]
	–4348.91	$a = 7.8836$[e]

[a] According to reference [5].

[b] According to different authors [8] [9].

[c] This work ($T_t = 1273$K).

[d] This work ($T_t = 1500$K).

[e] This work ($T_t = 1750$K).

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