ELSEVIER

Thermochimica Acta 259 (1995) 103-109

thermochimica
acta

Crystallisation of 1-carvone under adiabatic conditions[☆]

J.C. van Miltenburg*, J.P. van der Eerden, H.A.J Oonk, H.E. Gallis

Department of Interfaces and Thermodynamics, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands

Received 22 July 1994; accepted 7 December 1994

Abstract

The crystallisation of 1-carvone was followed under adiabatic conditions. In separate experiments, the enthalpy curves of the sample and the vessel were measured with the sample in the liquid state and with the sample in the solid state. From these data the growth speed as a function of temperature is calculated.

Keywords: Adiabatic calorimetry; Carvone; Crystal growth

1. Introduction

If the temperature ranges for optimal nucleation and crystallisation are separated, a melt can be supercooled till the glass transition temperature. Crystallisation then often occurs during the reheating of the sample. We performed this kind of experiment in an adiabatic calorimeter (cal V [1]) with a sample of 1-carvone. The crystallisation process starts very slowly at about 179 K and can be followed by the apparatus.

For the determination of the growth kinetics from an undercooled melt, most experiments reported in the literature are performed under isothermal conditions. This implies that in order to get data about the temperature dependence of the growth process, several experiments at different temperatures have to be made. The method used in this report, however, does give in one measurement the possibility to calculate the growth rate as a function of temperature. We also found that following the

---

[☆] Presented at the 13th International Symposium on Chemical Thermodynamics, Clermont-Ferrand, France, 17-22 July 1994.

* Corresponding author.

SSDI 0040-6031(95)02272-4

crystallisation under adiabatic conditions can show the formation of metastable crystals [2].

The time scale of these experiments is not within the possibilities offered by differential scanning techniques; a complete crystallisation of the sample studied took about 24 h. Scanning through this region with a heating rate of about one degree per minute will force the crystallisation and less accurate data are obtained.

2. Experimental

The sample (in this case 7.815 g) is enclosed in a gold-plated vessel. This vessel is surrounded by shields which are controlled at the temperature of the vessel. High vacuum insures further isolation. A liquid-nitrogen container and a liquid-helium container are built into the cryostat. Fast cooling in the order of 1 K min^{-1} is obtained by breaking the vacuum in the calorimeter space with a pressure of 1000 Pa of helium. This heat-exchange gas is pumped off before the measurements are started.

When measuring specific heats one can get an internal precision (deviation from a smooth curve) of about 0.02%; absolute accuracy is estimated to be 0.2%. Measurements are made with the intermittent method: energy is supplied to the sample container for a certain time (say 600–1000 s), then the temperature is followed for about 1000 s. After each stabilisation period the "drift" of the temperature $\mathrm{d}T/\mathrm{d}t$ in the second half of the stabilisation period is calculated. When no special effects, like crystallisation, occur, the heat exchange between the calorimeter vessel and the surroundings is $C(\mathrm{d}T/\mathrm{d}t)$, with C being the total heat capacity of the vessel and its contents. This heat exchange as measured in the empty sample container experiments is reproducible to within 5 μW, so when a special effect takes place in the vessel we calculate the enthalpy increment between two stabilisation temperatures as the electrical energy supplied to the vessel and the integral of the heat exchange as calculated from the empty sample container experiment.

In the first run, the enthalpy increment of the vessel was measured from the glass to the liquid-phase region. During this measurement, crystallisation took place, and from the temperature drift in the stabilisation period, we obtained a very good indication where the first effects start. Then the sample was recooled, heated till crystallisation took place, kept for 24 h in the crystal state close to the melting point, and then cooled till about 80 K. Then the second run was made on the crystallised substance and was again continued into the liquid state. The enthalpy in the liquid state should be the same at the same temperature in the liquid state and, by shifting one of the enthalpy curves till they overlap in the liquid state, we arrive at the enthalpy curves as shown in Fig. 1. These curves represent the enthalpy of the total system, i.e. the vessel and its contents. Normal practice in adiabatic calorimetry is to subtract the values of the empty container, but here, following a constant enthalpy path during crystallisation in the third experiment (see below), we need the enthalpy values of the total system. In the third experiment, the sample was cooled below the glass transition temperature and then heated to the temperature where in the first run we found the first indication that crystallisation had started. Normal measuring procedure was stopped and the tem-

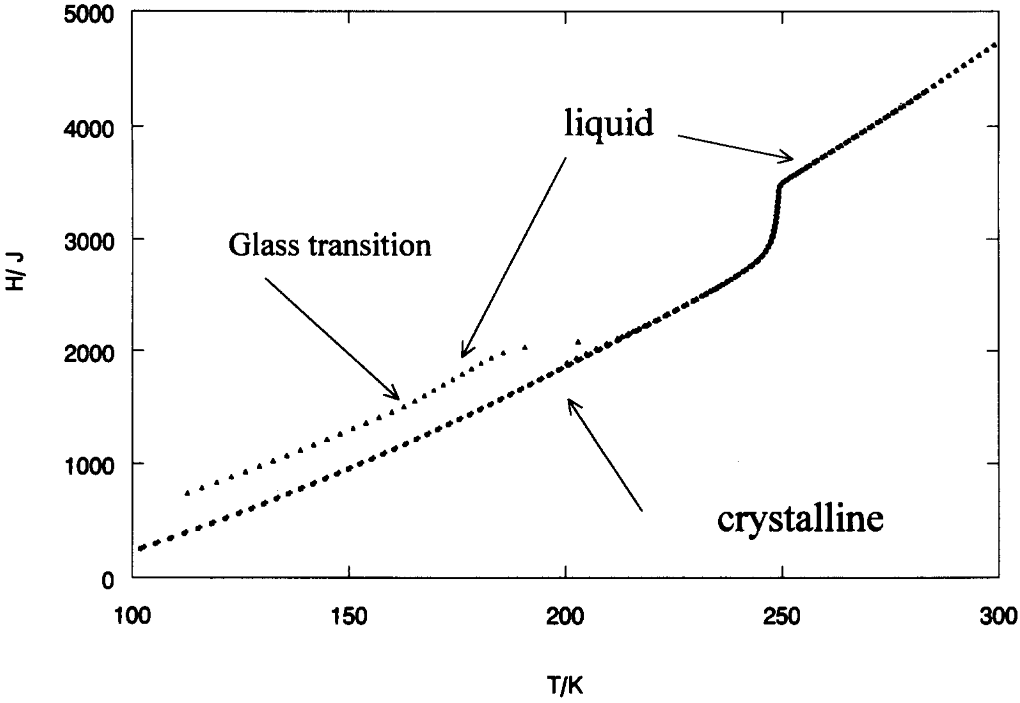

Fig. 1. The experimental enthalpy curves of the vessel and the compound, showing the enthalpies of the glass state, the undercooled liquid, the crystalline state and the liquid.

perature of the sample was followed while the shields were regulated. The temperature–time curve is given in Fig. 2. As we are not supplying energy to the vessel and the shield regulation system is working, the total enthalpy of the vessel and its contents is constant and the energy released by the crystallisation process is used to increase the temperature.

3. Theory

We know from the crystallisation behaviour of this compound that the temperature ranges for optimal nucleation and for growth are separated. So we assume that when the crystallisation process starts, N crystallisation nuclei have been formed and that they start to grow. At the start of the crystallisation at T_0 the enthalpy difference between the liquid and the solid phase is ΔH. For simplicity (and close to reality over this short interval), we have taken the enthalpy curves to be straight lines. The change in volume of the solid formed with time can be given as

$$dV_s/dt = (1 - V_s/V_t)(dV_E/dt) \quad (1)$$

Here V_s is the volume of the solid formed, V_E is the volume the solid would occupy without coalescence of the growing particles, and V_t is the total volume of solid after

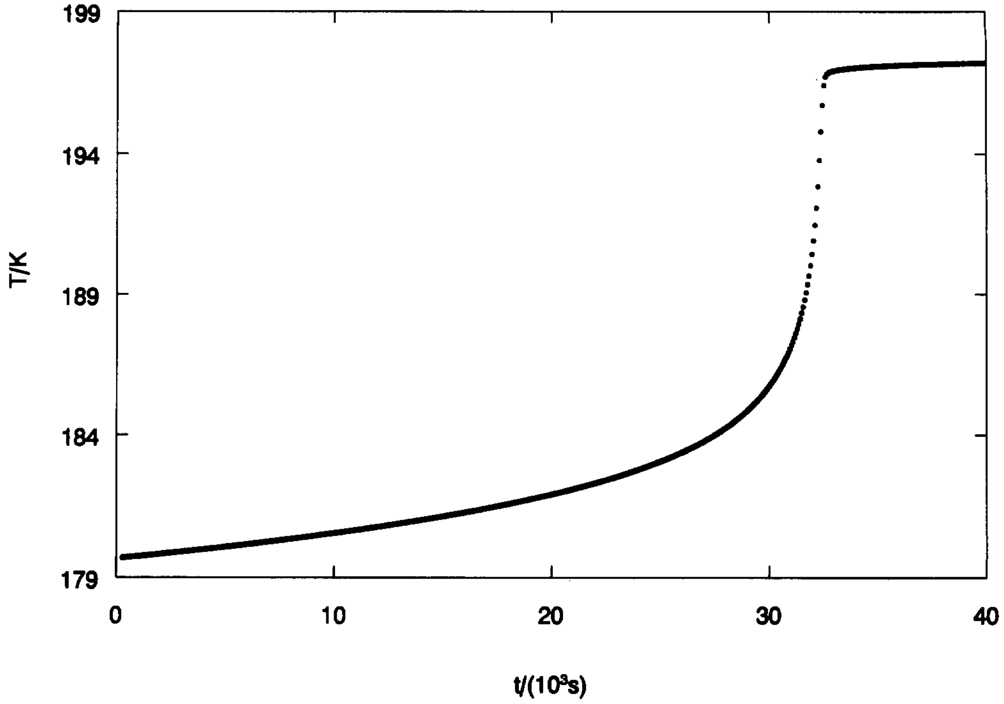

Fig. 2. The temperature vs. time curve during crystallisation under adiabatic conditions.

crystallisation. The factor $(1 - V_s/V_t)$ gives the chance that growth takes place in the liquid phase. At time $t = 0$, the enthalpy of the system is H_0. The amount of solid formed at temperature T is given by

$$V_s = \frac{(H_l - H_0)}{(H_l - H_s)} V_t \tag{2}$$

The subscript l refers to the liquid phase, s to the solid phase, and H_l and H_s are the enthalpies at the actual temperature T respectively. If we denote the heat capacity of the vessel filled with liquid by α and when filled with solid by β, and assume that they are independent of temperature then we may write

$$\begin{aligned} H_l &= H_0 + \alpha(T - T_0) \\ H_s &= H_0 - \Delta H + \beta(T - T_0) \end{aligned} \tag{2a}$$

Substituting these relations in Eq. (2)

$$V_s = \frac{\alpha(T - T_0)}{\Delta H + (\alpha - \beta)(T - T_0)} V_t \tag{3}$$

$$\frac{\mathrm{d}V_s}{\mathrm{d}t} = \frac{\mathrm{d}V_s}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\alpha \Delta H V_t}{[\Delta H + (\alpha - \beta)(T - T_0)]}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

From Eq. (1) we find

$$\frac{\mathrm{d}V_\mathrm{s}}{\mathrm{d}t}=\frac{\mathrm{d}V_\mathrm{E}}{\mathrm{d}t}\frac{\Delta H-\beta(T-T_\mathrm{o})}{\Delta H+(\alpha-\beta)(T-T_\mathrm{o})} \tag{5}$$

Combining Eqs. (4) and (5) gives

$$\frac{\mathrm{d}V_\mathrm{E}}{\mathrm{d}T}=\frac{\alpha\Delta H V_\mathrm{t}}{[\Delta H+(\alpha-\beta)(T-T_\mathrm{o})]\,[\Delta H-\beta(T-T_\mathrm{o})]} \tag{6}$$

Integrating this function and assuming that the volume of the nuclei can be neglected, $V_\mathrm{E}(t=0)=0$, we get

$$V_\mathrm{E}=V_\mathrm{t}\ln\left[\frac{\Delta H+(\alpha-\beta)(T-T_\mathrm{o})}{\Delta H-\beta(T-T_\mathrm{o})}\right] \tag{7}$$

Assuming that the crystals are growing as spherical particles of radius r

$$V_\mathrm{E}=N\tfrac{4}{3}\pi r^3 \tag{8}$$

and surface of the "free" growing particles A_E is

$$A_\mathrm{E}=N4\pi r^2=(36N\pi)^{1/3}\,V_\mathrm{E}^{2/3} \tag{9}$$

For the growth speed G we find

$$G=\frac{\mathrm{d}r}{\mathrm{d}t}=\frac{\mathrm{d}V_\mathrm{E}}{\mathrm{d}t}\frac{1}{(36N\pi)^{1/3}(V_\mathrm{E})^{2/3}} \tag{10}$$

From Eqs. (6) (multiplied by the experimental $\mathrm{d}T/\mathrm{d}t$) and (7), we calculated $GN^{1/3}$ (see Fig. 3) as a function of temperature. As the density of the compound is very close to unity, we took for V_t the mass of the sample.

4. Discussion

The growth speed G is derived directly from the experimental data. The assumption that N is constant during the crystallisation process is supported by another experiment where we cooled the sample from the liquid phase down to 179 K and followed the temperature change. In that case, where no nucleation at low temperature had taken place, it took about 70000 s before a measurable temperature rise started. G seems to be an exponentional function of T. This is not unreasonable as we might assume an Arrhenius-like behaviour. G will, however, also depend on the undercooling and we tried to fit the experimental data to the form

$$GN^{1/3}=A(T_\mathrm{fus}-T)\exp\left(-\frac{B}{RT}\right) \tag{11}$$

with $T_\mathrm{fus}=249.5$ K being the melting point. The values found by the fitting procedure are $A=8.89\times10^{23}\ \mathrm{m\,s^{-1}\,K^{-1}}$ and $B=113494\ \mathrm{J\,mol^{-1}}$. The fit is given in Fig. 3 by the broken line.

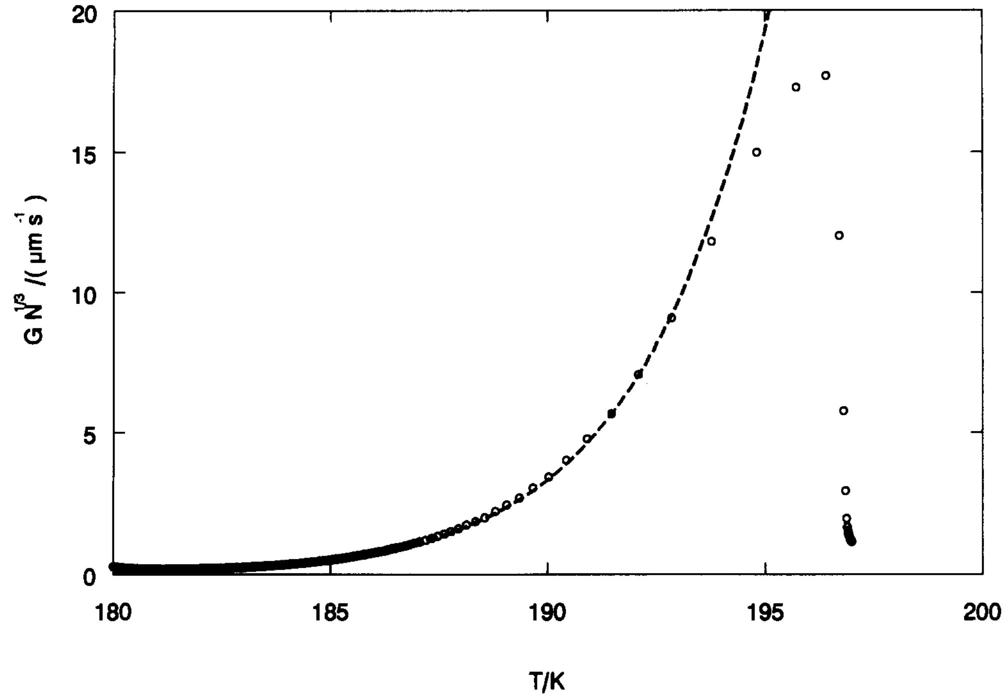

Fig. 3. The calculated growth function $N^{1/3}$ G as a function of temperature. The fit is given by the broken line.

It should be kept in mind that small variations of T_0 and ΔH do have a severe influence on the form of dV_E/dt and V_E at the beginning and the end of the crystallisation process, thus making the exact determination of the function G in those regions difficult. The fit given was made between 0.2 V_t and 0.8 V_t. The value of B does seem very high compared to the melting enthalpy of the compound (11700 J mol^{-1}), whereas for instance in the growth of silicon Chernov [3] assumes that this value should be smaller than the fusion enthalpy.

We feel, however, that this method of finding the growth curve is promising and should be further investigated.

5. Conclusion

An experimental method for following the crystallisation of a compound under adiabatic conditions is described. The mathematical analysis of the temperature–time curve is given. Assuming spherical crystal growth, the growth curve is calculated as a function of temperature. The growth curve has been fitted to a form containing the difference between the actual temperature and the melting point of the crystalline phase and an activation energy.

References

[1] J.C. van Miltenburg, G.J.K. van den Berg and M.J. van Bommel, J. Chem. Thermodyn., 19 (1987) 1129.

[2] J.C. van Miltenburg, J.P. van der Eerden, N. Lebrun and M. Foulon, XX^e JEEP, Bordeaux 1994 (ISBN2-9504481-5-1) p. 63..

[3] A.A. Chernov, Modern Crystallography III, Crystal Growth, Solid State Sciences 36, Springer-Verlag, Berlin, 1984.