JOURNAL OF SOLID STATE CHEMISTRY **102**, 465–479 (1993)

# Phenomenology of Polymorphism

## II. Criteria for Overall (*p, T*) Monotropy: Applications to Monochloroacetic Acid and to Hydrazine Monohydrate

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Received January 24, 1992; in revised form July 13, 1992; accepted July 14, 1992

The most general case of monotropy, (*p,T*) overall monotropy, is described by taking both pressure and temperature variables into account as high-pressure enantiotropy, which involves a high-pressure stable domain for a room-pressure metastable solid modification, cannot be a priori excluded. Criteria for ascertainment of overall monotropy are established by comparing the melting curve slope of the stable form with those of the solid-to-solid transition curves concerned with it and of the fusion curves of the metastable varieties. These comparisons allow also to unambiguously discern between overall monotropy and high-pressure enantiotropy. In applying such criteria the use of straight lines for describing melting and transition equilibria is retained. Their slopes are then calculated by means of the Clapeyron equation also in the case high-pressure results lack, as illustrated by two examples on monochloroacetic acid and hydrazine monohydrate, respectively, whose monotropic behaviour is not only critically accounted for, but also extended to pressures higher than the atmospheric one.

## I. Introduction

The aim of this paper is mainly to define from a thermodynamic point of view the conditions of existence of a "true," i.e., overall monotropy, which involves the stability of a unique phase over the whole pressure–temperature (*p, T*) domain. As can be ascertained by referring to Lehmann's description in 1888 (*1*), the term "monotropy" can be applied, in the study of dimorphism, to the transition of a solid phase $S_2$ toward a solid phase $S_1$ when temperature increases, without the reverse phenomenon ever being observed when temperature decreases. The phase $S_2$ is then described as monotropic, and it is customary to observe two melting points corresponding to each of these two phases. Conversely, the term "enantiotropy" is used in the case where the $S_1$–$S_2$ phase transition turns out to be reversible. To take fully into account the phenomena of monotropy and enantiotropy it is necessary to consider both pressure and temperature variables, as may be argued from Figs. 1 to 4, where, in several cases there represented, a high-pressure stable modification appears. It is to be mentioned that some of these figures had formerly been drawn at the beginning of the century by Bakhuis Roozeboom (*2*). However, one of them (here re-

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0022-4596/93 $5.00

ported as Fig. 4A) seems to have been forgotten since it could not be found in any later books or papers. We show here that this figure actually accounts for "overall monotropy" as defined by Deffet (*3*).

For a sake of simplification both melting and transition curves are represented, according to Oonk's approach (*4*), by straight lines in the same way as in our previous work (*5*). From an experimental point of view this assumption might be proved to be well founded up to high pressure (200 MPa), in particular for organic compounds (*6–10*). At higher pressures, however, this approximation may reveal to be arbitrary, as we point out hereafter in a significant example on $As_2Te_3$. The stable–metastable (metastable–supermetastable) alternation rule on the two-phase equilibrium curves built around stable (metastable) triple points, as already quoted by Oonk (*4*) and extended by us (*5*), is again used for this representation of dimorphism. Figure 1 illustrates the case in which the $S_1$–$S_2$ equilibrium is always stable, whatever the pressure and temperature are, while Fig. 2 represents that in which this equilibrium is stable only at the lowest pressures and becomes metastable at the highest pressures. In other words, in Fig. 2 a low-pressure enantiotropy and a high-pressure monotropy are both represented, of which the phase diagram of sulfur constitutes a well-known similar example. On the other hand, Fig. 3 shows the occurrence of a high pressure stable $S_2$-phase; it can be argued that this phase may appear in turn as monotropic or enantiotropic with respect to $S_1$, depending on the ranges in which the variables are considered. For instance, in Fig. 3B the straight line aa′ describes enantiotropic phase behavior when pressure varies at fixed temperature and the straight line bb′ an analogous phase behavior when temperature varies at a constant pressure higher than that of the $S_1S_2l$ triple point, i.e., $p(S_1S_2l)$. Conversely, the straight line cc′ describes monotropic phase behavior when temperature varies at a constant pressure lower than $p(S_1S_2l)$.

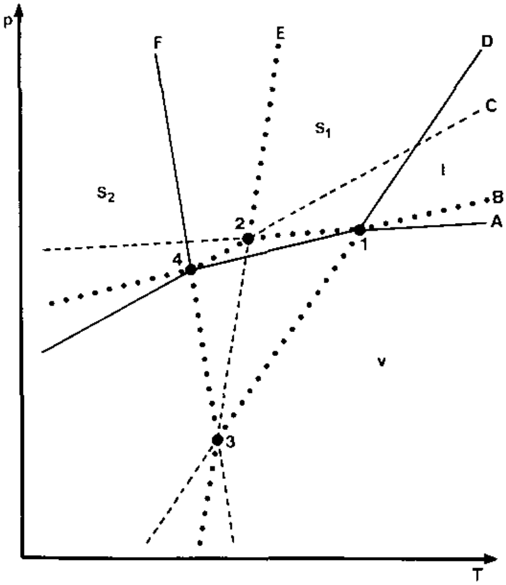

FIG. 1. ($p$, $T$) diagram of overall enantiotropy, with two stable triple points, $S_1lv(1)$ and $S_1S_2v(4)$, and two metastable triple points, $S_2lv(2)$ and $S_1S_2l(3)$. Equilibrium curves: l–v (A); $S_1$–v (B); $S_2$–v (C); $S_1$–l (D); $S_2$–l (E); and $S_1$–$S_2$ (F). (—) Stable equilibrium; (●●●) metastable equilibrium; (---) supermetastable equilibrium. The same numbering and lettering are used also in Figs. 2 to 4.

Several experimental cases reported in the literature may be identified as this kind of behavior. In particular we recently presented one concerning $As_2Te_3$ (*11*), whose metastable $\beta$-form at ordinary pressure is supposed to become stable under high pressure. The slope of the $\alpha$–$\beta$ ($p$, $T$) equilibrium curve ($\alpha$ is the stable variety) is negative, as well as the value of the volume change $\Delta V_{\alpha \rightarrow \beta}$, showing that the $\beta$-form is the denser one. Nevertheless, in this case, where we deal with pressures higher than 700 MPa, the straight-line approximation previously discussed fails. In effect, if ($p$, $T$) data concerning the $\alpha(S_1)$-l and the $\beta(S_2)$-l equilibrium curves (*12, 13*) are interpolated by means of a linear law, one can find that the latter straight line is steeper

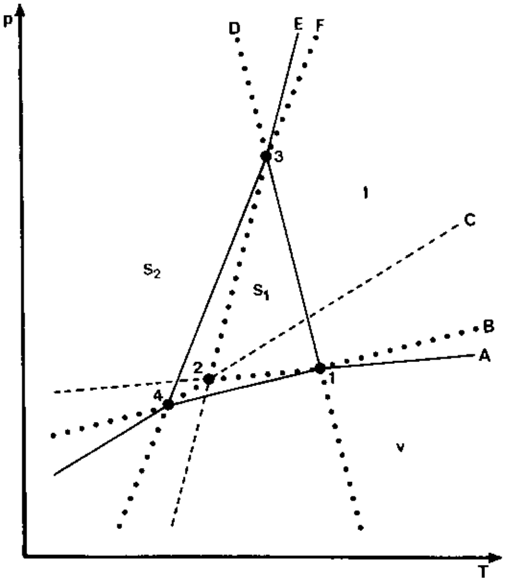

FIG. 2. ($p$, $T$) diagram of low-pressure enantiotropy, with three stable triple points, $S_1$lv(1), $S_1S_2$l(3), and $S_1S_2$v(4). The $S_1S_2$l triple point (3) is located at a pressure higher than that of the l–v curve.

than the former one; consequently, such an interpolation cannot be applied, in this case, to account for the melting point of the $\beta$-form necessarily being located at a temperature lower than that of the $\alpha$-variety at ordinary pressure, as shown in the diagram of Fig. 3B.

A result similar to that illustrated in Fig. 3B was likely obtained by Bridgman (*14*) in the case of the dimorphism of acetamide, whose high-pressure $S_2$-phase density is higher than that of the $S_1$-phase all along the transition curve under pressure.

Represented in Fig. 3A is the opposite case: the slope of the $S_1$–$S_2$ ($p$, $T$) curve is positive, as well as the value of the volume change $\Delta V_{S_1 \rightarrow S_2}$, since the $S_1$-form is the denser one. An example of this type, derived from an experimental investigation on carbon dioxide by Tammann (*15*), was exhaustively discussed by Bakhuis Roozeboom (*16*) in his pioneer work with regard to triple points classification.

## II. High-Pressure Enantiotropy or Overall Monotropy

In this section we define the conditions of existence of overall monotropy and compare them with those characterizing high-pressure enantiotropy, some examples of which are illustrated in Figs. 3. In the case of high-pressure enantiotropy we could notice the existence of two stable solid domains related to the phases $S_1$ and $S_2$, respectively, and the presence of two stable triple points, $S_1$lv and $S_1S_2$l, the latter being situated at high pressures.

In the case of monotropic dimorphism (Fig. 4), the existence of a unique stable region, $S_1$, is accompanied by that of a unique stable triple point, $S_1$lv. However, the ($p$,$T$) diagrams of Figs. 3 and 4 show several similarities which are to be referred to the common monotropic behavior at ordinary and low pressure. The $S_2$lv triple point is metastable and is located on the metastable extension of the l–v curve at temperatures lower than $T(S_1\text{lv})$. The $S_2$-phase is characterized by sublimation pressures higher than those of the $S_1$-phase at given temperatures, and the $S_1$–v and the $S_2$–v curves cross at the metastable $S_1S_2$v triple point situated in the liquid domain.

Conversely, the $S_1$–l and $S_2$–l curves converge as pressure increases only in the case of high-pressure enantiotropy, while they diverge in the other case, giving rise to a metastable $S_1S_2$l triple point located in the vapor domain, perhaps at negative pressure, as first suggested by Wahl (*17*). The $S_1$–$S_2$ transition curve, linking the $S_1S_2$l and $S_1S_2$v triple points, is in turn metastable or supermetastable over the whole ($p$, $T$) domain in the case of overall monotropy, while it becomes stable under high pressure if a reversible $S_1$–$S_2$ equilibrium is there established between two enantiotropic forms.

In the ($p$, $T$) diagrams for overall monotropy represented in Figs. 4A, B, and C the slopes of the $S_1$–$S_2$ curves are positive, but a negative one (Fig. 4D) can also be expected.

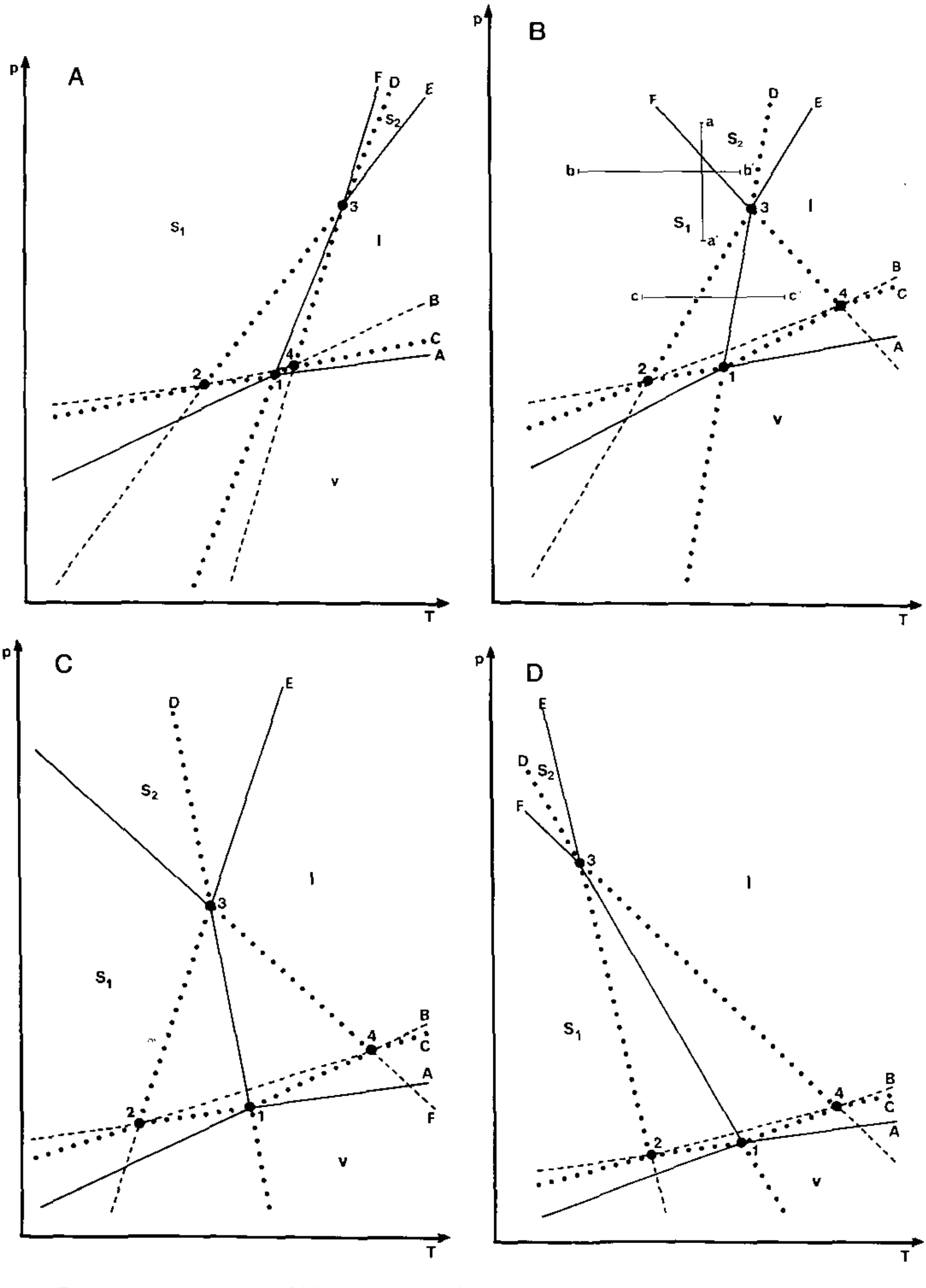

FIG. 3. (*p*, *T*) diagrams of high-pressure enantiotrophy, with two stable triple points, $S_1lv(1)$ and $S_1S_2l(3)$. The $S_1S_2l$ triple point (3) is situated at a pressure higher than that of the l–v curve. (A) The $S_1$–l(D), $S_2$–l(E), and $S_1$–$S_2$(F) curves have positive slopes. (B) The $S_1$–l(D) and $S_2$–l(E) curves have positive slopes, the $S_1$–$S_2$ (F) curve a negative one. (C) The $S_1$–l(D) and $S_1$–$S_2$(F) curves have negative slopes, the $S_2$–l (E) curve a positive one. (D) The $S_1$–l(D), $S_2$–l(E), and $S_1$–$S_2$(F) curves have negative slopes.

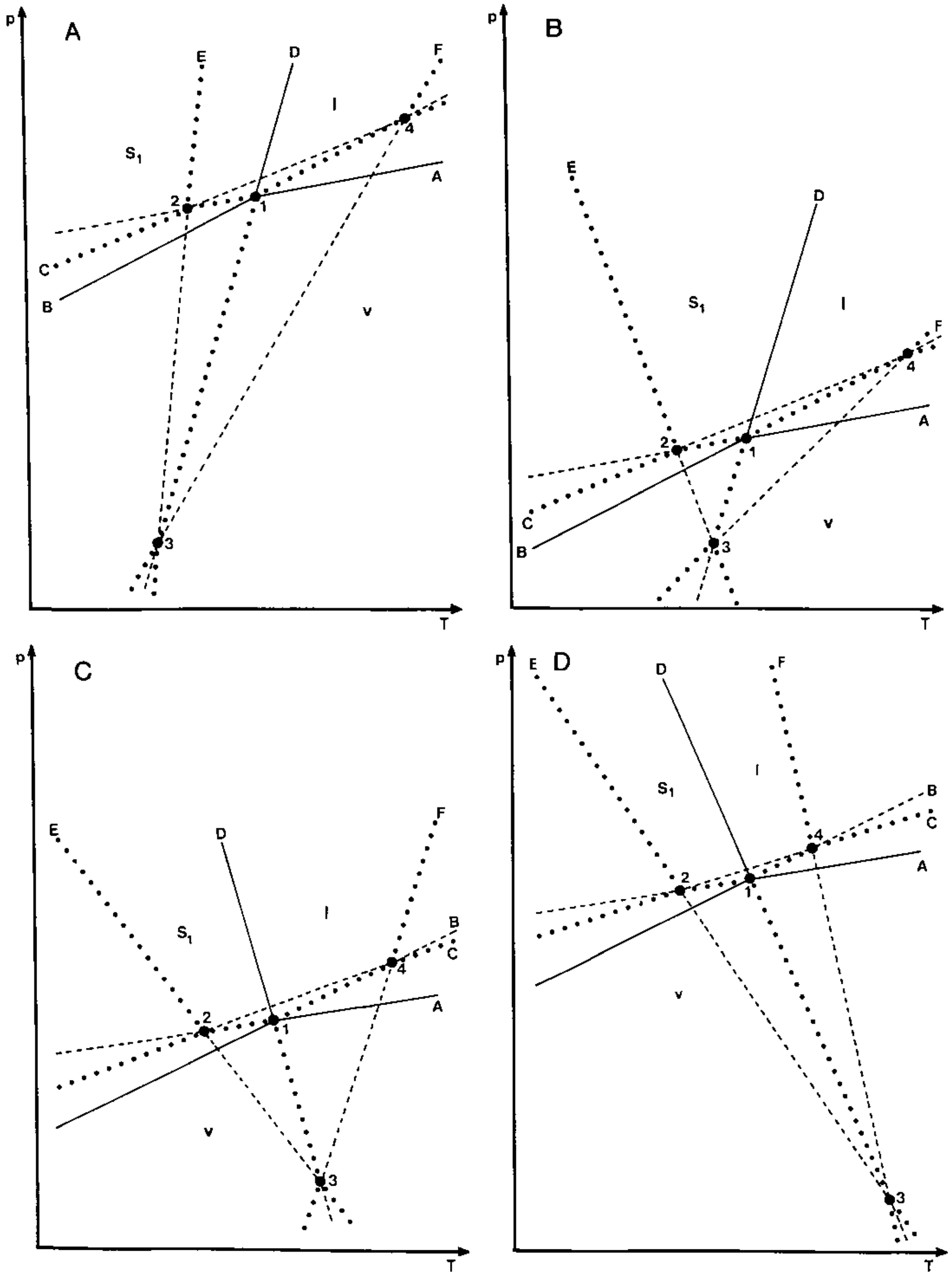

FIG. 4. ($p$, $T$) diagrams of overall monotropy, with only one stable triple point, $S_1lv(1)$, the other three triple points being metastable. As in the case of overall enantiotropy the $S_1S_2l$ triple point (3) is located at a pressure lower than that of the l–v curve. (A) The $S_1$–l (D), $S_2$–l (E), and $S_1$–$S_2$(F) curves have positive slopes. (B) The $S_1$–l(D) and $S_1$–$S_2$(F) curves have positive slopes, the $S_2$–l(E) curve a negative one. (C) The $S_1$–l(D) and $S_2$–l(E) curves have negative slopes, the $S_1$–$S_2$(F) curve a positive one. (D) The $S_1$–l(D), $S_2$–l(E), and $S_1$–$S_2$(F) curves have negative slopes.

This last case implies that the temperature of the $\mathrm{S_1S_2v}$ triple point is lower than that of the $\mathrm{S_1S_2l}$ triple point. For this to be possible, the slopes of the $\mathrm{S_1}$–v and $\mathrm{S_2}$–v sublimation curves should be rather different although the curves are to be located near each other over the ($p$, $T$) surface. It seems quite reasonable to presume that such an eventuality should be only scarcely detected, since it moreover implies volume contraction with increasing temperature for $\mathrm{S_1}$–l, $\mathrm{S_2}$–l, and $\mathrm{S_1}$–$\mathrm{S_2}$ phase transitions, as well.

However, a positive sign of the $dp/dT$ slope of the $\mathrm{S_1}$–$\mathrm{S_2}$ transition curve cannot be used as a mere criterion to state whether an experimentally observed dimorphism is a case of overall monotropy. Conversely, the comparison between the slope of the $\mathrm{S_1}$–l fusion curve of the stable form $\mathrm{S_1}$ and one of the two other curves extending to high pressures, i.e., $\mathrm{S_2}$–l or $\mathrm{S_1}$–$\mathrm{S_2}$, can allow, as we will demonstrate, to immediate discernment between overall monotropy and high-pressure enantiotropy.

In applying such a criterion the use of straight lines to describe melting and transition curves is retained. The $dp/dT$ slopes can then be calculated by means of the Clapeyron equation starting exclusively from thermodynamic and crystallographic data at ordinary pressure on the transformation enthalpy and volume changes.

From the observation of Figs. 3 it can be concluded that the high-pressure enantiotropy is accounted for if one of the following double inequalities is satisfied:

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > 0 \quad \text{(Fig. 3A)} \qquad (1)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > \left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} > 0 \quad \text{(Figs. 3A and 3B)} \qquad (2)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} \quad \text{(Fig. 3B)} \qquad (3)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} \quad \text{(Fig. 3C)} \qquad (4)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} < \left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} < 0 \quad \text{(Figs. 3C and 3D)} \qquad (5)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} < \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} < 0 \quad \text{(Fig. 3D)} \qquad (6)$$

In the same way, the conditions for an overall monotropy to be accounted for are instead

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > 0 \quad \text{(Fig. 4A)} \qquad (7)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} > 0 \quad \text{(Figs. 4A and 4B)} \qquad (8)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} \quad \text{(Fig. 4B)} \qquad (9)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} \quad \text{(Fig. 4C)} \qquad (10)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} < \left(\frac{dp}{dT}\right)_{\mathrm{S_2-l}} < 0 \quad \text{(Figs. 4C and 4D)} \qquad (11)$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{S_1-S_2}} < \left(\frac{dp}{dT}\right)_{\mathrm{S_1-l}} < 0 \quad \text{(Fig. 4D)} \qquad (12)$$

A perfect complementarity can be observed between the two series of inequalities in that there is no common condition accounting both for high-pressure enantiotropy and for overall monotropy.

Conditions for discriminating between the different cases of dimorphism may also be founded upon comparison between the slopes of the $\mathrm{S_2}$–l and $\mathrm{S_1}$–$\mathrm{S_2}$ curves. However, for the sake of better accuracy, it is preferable to deal with data concerning the stable $S_1$–l transition at ordinary pressure and temperature.

In the present treatment we have also comprehensively taken into account the fusion processes accompanied by volume contraction. It can be noticed that in most cases where melting occurs accompanied by volume expansion the accounting inequalities reduce to (1), (2), and (3) for high-pressure enantiotropy and to (7) and (8) for overall monotropy.

## III. Application Examples of the Criteria

The criteria defined in the preceding paragraph are applied in this section to establish over the whole $(p, T)$ domain the monotropic nature of the polymorphism of two compounds:

(a) an organic one, monochloroacetic acid;

(b) an inorganic one, hydrazine monohydrate.

### *III. a. Monochloroacetic Acid*

This compound is known to exist in three forms: $\alpha$, $\beta$, and $\gamma$ (*18*, *19*). It should be pointed out that the crystal structure of the metastable $\gamma$-phase has not been solved yet. In the present work the polymorphic behavior of this compound is studied by separately taking into account the $\alpha$–$\beta$, $\alpha$–$\gamma$, and $\beta$–$\gamma$ dimorphic couples, from which a complete trimorphic description can be derived.

Müller (*18*) investigated the volume variation and the enthalpy change at crystallization of each form and also determined the same quantities at the transition from one modification to another (Table I). He showed that both crystallizations and solid-to-solid transitions could occur in a very narrow temperature range (308.35 to 308.85 K), revealing an extended phenomenon of supercooling which was confirmed by the density measurements of Kamaeva (*20*) on the liquid phase. The values of the $dp/dT$ slopes reported in Table I are the results of our application of the Clapeyron equation to Müller's experimental data. The above-established criteria for overall monotropy and high-pressure enantiotropy can then be applied. By alternately referring to the metastable $\beta$- or $\gamma$-variety as the $S_2$-form and to the stable $\alpha$-variety as the $S_1$-form, which we have both dealt with in the preceding paragraph, it turns out that $\beta$- and $\gamma$-modifications should be both monotropic with respect to the $\alpha$-phase. In fact we have:

$$\left(\frac{dp}{dT}\right)_{\beta(S_2)-l} > \left(\frac{dp}{dT}\right)_{\alpha(S_1)-l} > 0$$

and

$$\left(\frac{dp}{dT}\right)_{\alpha(S_2)-l} > \left(\frac{dp}{dT}\right)_{\alpha(S_1)-\beta(S_2)} > 0.$$

On the other hand,

$$\left(\frac{dp}{dT}\right)_{\gamma(S_2)-l} > \left(\frac{dp}{dT}\right)_{\alpha(S_1)-l} > 0$$

and

$$\left(\frac{dp}{dT}\right)_{\alpha(S_1)-l} > \left(\frac{dp}{dT}\right)_{\alpha(S_1)-\gamma(S_2)} > 0.$$

By the way, Körber (*6*) determined the melting points of the stable $\alpha$- and of the metastable $\gamma$-forms up to 1766 and 840 atm, respectively. In both cases $(p, T)$ data up to 864 atm may be accurately interpolated by means of a linear law, as shown in Table II. This result seems to corroborate the assumption made by us in the preceding section, at least up to not too high a pressure. Although very slightly, the slope of the $\gamma$–l curve turns out to be steeper than that of the $\alpha$–l curve, accordingly to the conclusions drawn from the experimental work by Müller.

Timmermans (*21*), however, refers to two different values of these slopes from which it turns out that the $\gamma$-form would become the stable one at pressures higher than 2500

TABLE I

MONOCHLOROACETIC ACID: TEMPERATURES $T$, ENTHALPY CHANGES $\Delta H$, AND VOLUME VARIATIONS $\Delta V$ AT CRYSTALLIZATION OF EACH POLYMORPHIC MODIFICATION ($\alpha$, $\beta$, AND $\gamma$) AND AT THE SOLID-TO-SOLID TRANSITIONS DETERMINED BY MÜLLER (*18*)

| Transition | $T$ (K) | $\Delta H$ ($\mathrm{J \cdot g^{-1}}$) | $\Delta V$ ($\mathrm{cm^3 \cdot g^{-1}}$) | $dp/dT$ ($\mathrm{atm \cdot K^{-1}}$)[a] |
|---|---|---|---|---|
| $\mathrm{l} \rightarrow \alpha$ | 308.65 | −161.08 | −0.09233 | 55.79 |
| $\mathrm{l} \rightarrow \beta$ | 308.55 | −141.42 | −0.07965 | 56.79 |
| $\mathrm{l} \rightarrow \gamma$ | 308.55 | −135.56 | −0.07309 | 59.32 |
| $\beta \rightarrow \alpha$ | 308.35 | −21.34 | −0.01268 | 53.86 |
| $\gamma \rightarrow \alpha$ | 308.85 | −31.80 | −0.01924 | 52.81 |
| $\gamma \rightarrow \beta$ | 308.65 | −8.37 | −0.00656 | 40.79 |

[a] The slopes of the related ($p$, $T$) curves at atmospheric pressure have been calculated by us according to the Clapeyron equation.

atm, referred to by this author as the $\alpha\gamma$l triple point. Since the origin of these data is not clearly specified we have examinated each reference given by Timmermans about monochloroacetic acid, but unsuccessfully. The unique quoted measurements on this compound (*22*) are referred to the fusion of the stable $\alpha$-form and claimed by the author himself, Bridgman, to be approximate. A direct comparison with the steepness of the melting curve of the metastable $\gamma$-form studied by Körber is not allowable since Bridgman performed his measurements at pressures ($p > 6000$ atm) much higher than those of the experimental range investigated by Körber (up to 840 atm).

TABLE II

MONOCHLOROACETIC ACID: CALCULATED PRESSURE VALUES $p_{\mathrm{calc}}$ IN THE REPRESENTATION BY MEANS OF A LINEAR INTERPOLATION OF THE ($p_{\mathrm{exp}}$, $T$) RESULTS AT THE FUSION OF THE STABLE ($\alpha$) AND OF THE METASTABLE ($\gamma$) FORMS REPORTED BY KÖRBER (*6*) UP TO 864 ATM

| Stable phase ($\alpha$) | | | Metastable phase ($\gamma$) | | |
|---|---|---|---|---|---|
| $T_{\mathrm{f}}$ (K) | $p_{\mathrm{exp}}$ (atm) | $p_{\mathrm{calc}}$ (atm) | $T_{\mathrm{f}}$ (K) | $p_{\mathrm{exp}}$ (atm) | $p_{\mathrm{calc}}$ (atm) |
| 334.15 | 1 | −3.49 | 323.15 | 1 | 1.78 |
| 334.35 | 1 | 6.83 | 334.15 | 570 | 571 |
| 339.15 | 260 | 255 | 338.75 | 800 | 809 |
| 347.65 | 700 | 694 | 339.15 | 830 | 830 |
| 349.65 | 800 | 797 | 339.25 | 840 | 835 |
| 351.05 | 864 | 869 | | | |
| $dp/dT = 51.64\ \mathrm{atm \cdot K^{-1}}$<br>$r = 0.9999$<br>$p = 51.64\,T - 17259$ | | | $dp/dT = 51.74\ \mathrm{atm \cdot K^{-1}}$<br>$r = 0.9999$<br>$p = 51.74\,T - 16718$ | | |

On the other hand, the two respective sets of measurements on the stable $\alpha$-form can be satisfactorily correlated by means of an equation for melting curves recently proposed by us for the fusion of $\alpha$-$\mathrm{As_2Te_3}$ (*13*), which is more suitable than a linear law to fit to results obtained at very high pressures (Table III). On account of this result and of that shown in Table II, the occurrence of an overall monotropy of the $\gamma$-form seems to be definitely confirmed.

In contrast, the metastable fusion of the $\beta$-form has not as yet been investigated under high pressure. In any case, we can test its overall monotropy, predicted by Müller's investigations, since its melting enthalpy and crystal structure are known. In Tables IV and V crystallographic results at room temperature (*23–25*) as well as several thermodynamic data at the melting points of the $\alpha$- and $\beta$-varieties (*26–28*) are respectively collected. In order to calculate the $dp/dT$ slopes, we have determined the specific volume variations at fusion according to the following procedure:

(a) linear interpolation of the liquid den-

TABLE III

MONOCHLOROACETIC ACID: PRESSURE VALUES $p_{calc}$ IN THE CORRELATION BETWEEN KÖRBER'S (*6*) AND BRIDGMAN'S (*22*) ($p_{exp}$, $T$) MEASUREMENTS AT THE FUSION OF THE STABLE $\alpha$-FORM CALCULATED BY MEANS OF AN INTERPOLATING EQUATION

| Körber (*6*) | | | Bridgman (*22*) | | |
|---|---|---|---|---|---|
| $T$ (K) | $p_{exp}$ (atm) | $p_{calc}$ (atm) | $T$(K) | $p_{exp}$ (atm) | $p_{calc}$ (atm) |
| 334.15 | 1 | −8.57 | 335.68 | 1 | 65.5 |
| 334.35 | 1 | 1 | 412.55 | 6146 | 6070 |
| 339.15 | 260 | 240 | 424.85 | 7297 | 7421 |
| 347.65 | 700 | 709 | 437.75 | 9020 | 8971 |
| 349.65 | 800 | 827 | | | |
| 351.05 | 864 | 912 | | | |
| 361.25 | 1597 | 1575 | | | |
| 363.55 | 1757 | 1736 | | | |
| 363.85 | 1766 | 1757 | | | |

Interpolating equation:[a]

$$p = p_{f,0}\{a[(T/T_{f,0})^c - 1] + b(T/T_{f,0} - 1) + 1\}$$

$a = 374884$ $\quad b = -433838$ $\quad c = 1.2$

$p_{f,0} = 1$ atm $\quad T_{f,0} = 334.35$ K $\quad r = 0.9999$

[a] The equation incorporates the values $p_{f,0}$ and $T_{f,0}$ of one of the data couples for melting at atmospheric pressure reported by Körber.

sity results reported by Kamaeva (deviation <0.03%) and calculation of the supercooled liquid densities by extrapolation at the crystallization temperatures of the $\alpha$- and $\beta$-phases given by Müller;

(b) determination of the densities of the $\alpha$- and $\beta$-phases at the crystallization, accordingly to the volume variations reported by Müller;

(c) determination of the thermal expansivities of the solid phases using the crystallographic data at room temperature (assumed to be 293.15 K) presented by Kanters *et al.* (*23, 24*) and confirmed, as to what concerns the stable $\alpha$-form, by Kalyanaraman *et al.* (*25*);

TABLE IV

MONOCHLOROACETIC ACID: CRYSTAL DATA FOR THE MONOCLINIC $\alpha$- AND $\beta$-FORMS

| | $\alpha$-form | | $\beta$-form |
|---|---|---|---|
| Ref. | (*23*) | (*25*) | (*24*) |
| $a$(Å) | 5.380 | 5.379 | 4.635 |
| $b$(Å) | 19.150 | 19.148 | 12.974 |
| $c$(Å) | 7.860 | 7.859 | 6.686 |
| $\beta$(°) | 109.14 | 109.08 | 107.93 |
| $Z$ | 8 | 8 | 4 |
| $d_{calc}$ (g · cm$^{-3}$) | 1.6407 | 1.6408 | 1.6406 |

(d) estimation of the volumes of the $\alpha$- and $\beta$-forms as well as those of the liquid phase at the two respective melting temperatures, and calculation of the specific volume variations at fusion which are also reported in Table V.

Because of their easiness, calculations are not reported. We merely underline the fair agreement of their final mean results (0.1037 cm$^3$ · g$^{-1}$ for the fusion of the $\alpha$-form and 0.0840 cm$^3$ · g$^{-1}$ for that of the $\beta$-form) with the specific volume variations at crystallization (0.0923 cm$^3$ · g$^{-1}$ for the $\alpha$-form and 0.0797 cm$^3$ · g$^{-1}$ for the $\beta$-form, respectively), as should a priori be expected. Also, Table V shows that, in spite of the strong deviation among the melting enthalpy values respectively found in literature for these two modifications, the $dp/dT$ slopes calculated by means of the Clapeyron equation are always steeper for the fusion of the metastable form than for that of the stable one. This result agrees with the conclusion drawn from Müller's experimental work of an overall monotropy for the metastable $\beta$-phase.

The trimorphism of monochloroacetic acid (Fig. 5) may easily be represented by superimposing the monotropic dimorphism diagrams of the couples $\alpha$–$\beta$ and $\alpha$–$\gamma$ and by taking into account that, from the $dp/dT$ slopes of Table I,

$$\left(\frac{dp}{dT}\right)_{\gamma\text{-l}} > \left(\frac{dp}{dT}\right)_{\beta\text{-l}} > 0$$

and

$$\left(\frac{dp}{dT}\right)_{\beta\text{-l}} > \left(\frac{dp}{dT}\right)_{\beta\text{-}\gamma} > 0.$$

One can notice that the fusion of the $\beta$-form is metastable while that of the $\gamma$-form

TABLE V

MONOCHLOROACETIC ACID: TEMPERATURES $T_f$, ENTHALPY CHANGES $\Delta H_f$, AND SPECIFIC VOLUME VARIATIONS $\Delta V$ AT THE FUSIONS OF THE STABLE ($\alpha$) AND OF THE METASTABLE ($\beta$) FORMS

| Ref. | $T_f$ (K) | $\Delta H_f$ ($J \cdot g^{-1}$) | $V_{l,f}$ ($cm^3 \cdot g^{-1}$)[a] | $V_{S,f}$ ($cm^3 \cdot g^{-1}$)[b] | $\Delta V$ ($cm^3 \cdot g^{-1}$) | $dp/dT$ ($atm \cdot K^{-1}$)[c] |
|---|---|---|---|---|---|---|
| Stable phase ($\alpha$) | | | | | | |
| (*26*) | 334.15 | 203.66 | 0.7268 | 0.6231 | 0.1037 | 58.01 |
| (*26*) | 334.15 | 177.10 | 0.7268 | 0.6231 | 0.1037 | 50.44 |
| (*27*) | 334.45 | 207.56 | 0.7270 | 0.6232 | 0.1038 | 59.01 |
| (*28*) | 334.35 | 129.95 | 0.7269 | 0.6232 | 0.1037 | 36.99 |
| Metastable phase ($\beta$) | | | | | | |
| (*26*) | 329.15 | 199.24 | 0.7235 | 0.6395 | 0.0840 | 71.12 |
| (*26*) | 329.15 | 169.57 | 0.7235 | 0.6395 | 0.0840 | 60.53 |
| (*27*) | 329.35 | 199.55 | 0.7236 | 0.6397 | 0.0839 | 71.24 |
| (*28*) | 329.15 | 146.94 | 0.7235 | 0.6395 | 0.0840 | 52.45 |

[a] The specific volumes of the liquid phase at melting, $V_{l,f}$, have been calculated by linear interpolation of the experimental results by Kamaeva (*20*).

[b] The specific volumes of the solid phases at melting, $V_{S,f}$, have been calculated according to the procedure designed in Section III.a of the text.

[c] The $dp/dT$ values represent the slopes of the two melting curves at atmospheric pressure.

is supermetastable, according to the metastable–supermetastable alternation rule. The metastability hierarchy between the nonstable forms does not change with increasing pressure since the $\beta\gamma l$ triple point is situated at a very low or, perhaps, negative pressure.

### *III. b. Hydrazine Monohydrate*

Two crystalline forms of this compound are known: a stable trigonal variety (T) and a metastable cubic modification (C), respectively (*29–32*). The crystallographic and thermodynamic data on these two forms are collected in Tables VI and VII, respectively.

The absolute value of the measured enthalpy change for the C → T transformation on cooling ($-42\ J \cdot g^{-1}$) (*32*) rather well agrees with that calculated for the conceivable reverse transformation T → C on heating ($40\ J \cdot g^{-1}$), by taking into account the experimental value of the melting enthalpy change $\Delta H_{T \to l}$ ($180\ J \cdot g^{-1}$) (*33*) as well as that of the crystallization enthalpy of C ($-140\ J \cdot g^{-1}$) (*32*), and assuming that

$$\Delta H_{T \to C} = \Delta H_{T \to l} + \Delta H_{l \to C}.$$

This assumption is well founded since it will be proved that these three transitions may occur in a narrow temperature range (from 215 to 222 K). From this, it can be deduced that the entropy of the T → C transformation should be unambiguously positive.

At this stage, we have to put aside the hypothesis according to which the C-phase would be the stable one at low temperatures (we would be dealing with the case of overall enantiotropy already illustrated in Fig. 1). If this occurred, the C → T transition would be accompanied by an endothermic effect on heating, contrarily to what is shown by Foulon *et al.* (*32*), whose experimental work does indicate that the reverse transition is associated with such an effect on an increase in temperature.

Also, their measurements of the cell parameters show that the T → C transition, if

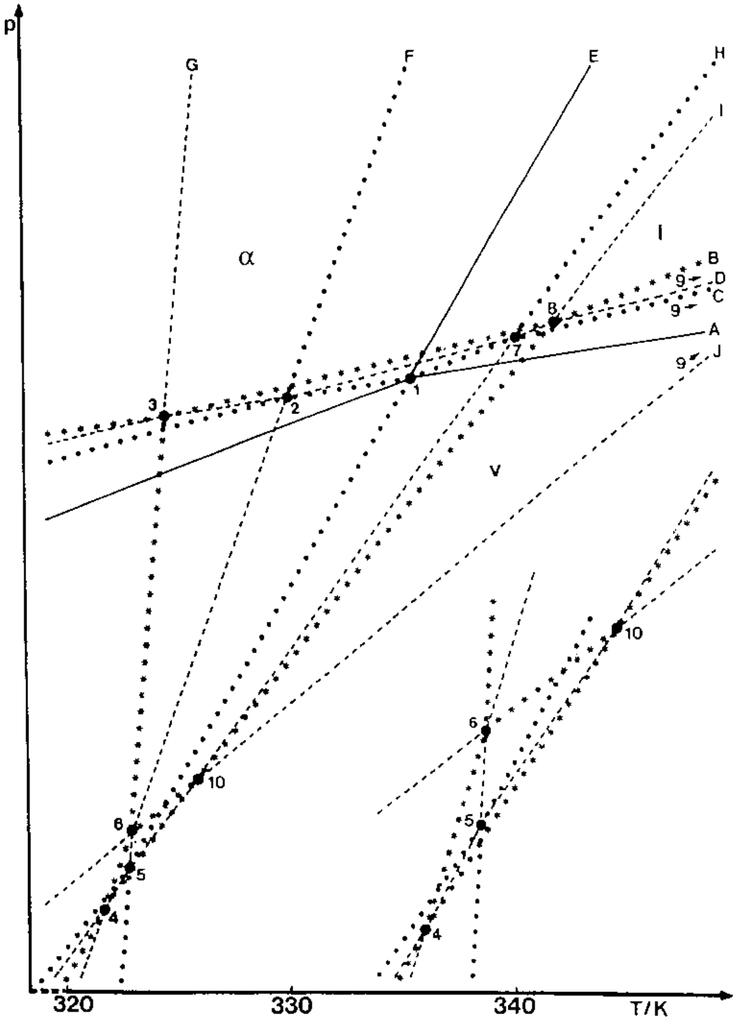

FIG. 5. (*p*, *T*) diagram of the monotropic trimorphism of monochloroacetic acid, with only one stable triple point, α-l-v(1). Other triple points are β-l-v (2); γ-l-v (3); α-β-l (4); α-γ-l (5); β-γ-l (6); α-β-v (7); α-γ-v (8); β-γ-v (9); α-β-γ (10). Equilibrium curves: l–v (A); α–v (B); β–v (C); γ–v (D); α–l (E); β–l (F); γ–l (G); α–β (H); α–γ (I); β–γ (J). (—) Stable equilibrium; (•••) metastable equilibrium; (---) supermetastable equilibrium; (***) hypermetastable equilibrium.

it occurred, should be characterized by a positive volume change. In fact, the specific volume of the T-form is equal to 0.9109 $cm^3 \cdot g^{-1}$ and to 0.9220 $cm^3 \cdot g^{-1}$ at 130 and 206 K, respectively, while for the other variety it is 0.9333 $cm^3 \cdot g^{-1}$ at 212 K, this last value being in rather good agreement with that which can be drawn from the crystallographic study by Zocchi *et al.* (*30*) (0.9292 $cm^3 \cdot g^{-1}$ at about 213 K). In contrast, the specific volume value of the stable T-form at 108 K estimated from the structural data by Liminga *et al.* (*29*) (0.9023 $cm^3 \cdot g^{-1}$) is not satisfactorily correlated to the results reported by Foulon *et al.* (*31*, *32*) at higher temperatures. The conclusion drawn from

TABLE VI

HYDRAZINE MONOHYDRATE: CRYSTAL DATA FOR THE TRIGONAL T-FORM AND THE CUBIC C-FORM

| | T-form | | | C-form | |
|---|---|---|---|---|---|
| Ref. | *(29)* | *(32)* | *(31)* | *(30)* | *(31)* |
| $T$ (K) | 108 | 130 | 206 | 213 | 212 |
| $a$ (Å) | 4.873 | 4.896 | 4.905 | 6.76 | 6.77 |
| $c$ (Å) | 10.94 | 10.941 | 11.034 | — | — |
| $Z$ | 3 | 3 | 3 | 4 | 4 |
| $d_{\text{calc}}$ ($\text{g} \cdot \text{cm}^{-3}$) | 1.1083 | 1.0978 | 1.0846 | 1.0762 | 1.0715 |

this set of experimental data is reinforced by the result of a recent crystallographic simulation study performed by Foulon *et al.* *(31)* which shows a small volume contraction of about 1% at the C → T "transition."

Since the metastable C-variety appears to be the less dense one, we may exclude the conclusion that we are to be dealing with a case of high-pressure enantiotropy such as those illustrated in Figs. 3B, C, and D, or with the case of overall monotropy of Fig. 4D. Consequently, for hydrazine monohydrate it is necessary to discern only between the case of high-pressure enantiotropy of Fig. 3A and those of overall monotropy of Figs. 4A, B, and C.

TABLE VII

HYDRAZINE MONOHYDRATE: TEMPERATURES $T_f$ AND $T_c$ AND ENTHALPY CHANGES $\Delta H_f$ AND $\Delta H_c$ FOR MELTING (f) OF THE T-FORM AND CRYSTALLIZATION (c) OF THE C-FORM, AND THE SAME QUANTITIES FOR THE C → T TRANSITION, $T_{C \to T}$ AND $\Delta H_{C \to T}$

| Modification | C-form | T-form |
|---|---|---|
| $T_f$ (K) | — | 222 |
| $T_c$ (K) | 218 | — |
| $\Delta H_f$ ($\text{J} \cdot \text{g}^{-1}$) | — | 180 |
| $\Delta H_c$ ($\text{J} \cdot \text{g}^{-1}$) | −140 | — |
| $T_{C \to T}$ (K)[a] | 215 | |
| $\Delta H_{C \to T}$ ($\text{J} \cdot \text{g}^{-1}$) | −42 | |

[a] For a cooling rate of the DSC investigation equal to 0.1 $\text{K} \cdot \text{min}^{-1}$.

The melting point of the stable T-form has been determined to be 222 K by van Ekeren *et al.* *(33)*. Since the metastable C-variety is, by the way, monotropic with respect to the stable one at least at the lowest pressures, its melting point is necessarily situated at a lower temperature. So, in spite of the phenomenon of supercooling, we have assumed the temperature of crystallization of the C-variety (218 K) *(32)* to correspond to its fusion temperature. As for the C → T transition temperature, we have chosen that, 215 K, observed with the lowest cooling rate (0.1 $\text{K} \cdot \text{min}^{-1}$) and the highest transformation rate (100%) in the experimental differential scanning calorimetric (DSC) investigation by Foulon *et al.* *(32)*. In their communication, an exhaustive study of the C → T transition temperature variation as a function of the cooling rate is reported in a graph. This temperature is shown to decrease until about 196 K as cooling rate increases to 50 $\text{K} \cdot \text{min}^{-1}$.

In order to estimate the specific volumes of the solid phases at their transformation temperature and at their respective fusion temperatures, the following procedure was adopted:

(a) determination of the thermal expansivity $\alpha_T$ of the stable T-form by means of the couple of specific volume values at different temperatures available from the crystallographic study by Foulon *et al.* and estimation of the specific volume of this phase at 215 and 222 K;

(b) assuming the thermal expansivity of the C-form to be roughly the same as that of the stable form, estimation of the specific volume of the former at 215 K and at fusion (218 K).

The results of these calculations are

$$\alpha_T = 1.46\ 10^{-4}\,\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{K}^{-1},$$

$$V_{T,215} = 0.9232\,\text{cm}^3 \cdot \text{g}^{-1},$$

$$V_{T,222} = 0.9242\,\text{cm}^3 \cdot \text{g}^{-1}$$

for the trigonal phase;

$$V_{\mathrm{C},215} = 0.9337\ \mathrm{cm^3 \cdot g^{-1}},$$
$$V_{\mathrm{C},218} = 0.9341\ \mathrm{cm^3 \cdot g^{-1}}$$

for the cubic phase.

The calculated volume contraction (1.12%) at 215 K in passing from the C-form to the T-one on cooling is in very good agreement with that computed by crystallographic simulation (about 1%). As to what concerns the specific volume of the liquid phase at the two melting temperatures, neither experimental values nor extended sets of measurements at room temperature allowing suitable extrapolations at these lower temperatures have been found in the literature. Specific volumes of hydrazine monohydrate have been determined at 294.15 K by Curtius and Schulz (*34*) (0.9704 to 0.9709 $\mathrm{cm^3 \cdot g^{-1}}$), at 283.15 K by Dito (*35*) (0.9551 $\mathrm{cm^3 \cdot g^{-1}}$), and at 273.15 K by Semishin (*36*) (0.954 $\mathrm{cm^3 \cdot g^{-1}}$). These experimental values are exploited in the following application of the criteria for high-pressure enantiotropy or overall monotropy.

Application of the criteria for high-pressure enantiotropy implies the double inequalities

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{-}C(S_2)}} > \left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{-}l}} > 0$$

and

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{-}l}} > \left(\frac{dp}{dT}\right)_{\mathrm{C(S_2)\text{-}l}} > 0$$

to be verified by application of the Clapeyron equation. Let us then consider, to begin, the double inequality related to the melting phenomena. We obtain, for the fusion of the T-form, the results

$$\Delta H_{\mathrm{f}} = 1776.7\ \mathrm{atm \cdot cm^3 \cdot g^{-1}}\ (180\ \mathrm{J \cdot g^{-1}})$$
$$T_{\mathrm{f}} = 222\ \mathrm{K}$$
$$V_{\mathrm{S,f}} = 0.9242\ \mathrm{cm^3 \cdot g^{-1}}$$

$V_{\mathrm{l,f}}$ unknown,

and, for that of the C-form, the results

$$\Delta H_{\mathrm{f}} = 1381.7\ \mathrm{atm \cdot cm^3 \cdot g^{-1}}\ (140\ \mathrm{J \cdot g^{-1}})$$
$$T_{\mathrm{f}} = 218\ \mathrm{K}$$
$$V_{\mathrm{S,f}} = 0.9341\ \mathrm{cm^3 \cdot g^{-1}}$$

$V_{\mathrm{l,f}}$ unknown,

where $\Delta H_{\mathrm{f}}$, $T_{\mathrm{f}}$, $V_{\mathrm{S,f}}$, and $V_{\mathrm{l,f}}$ are the enthalpy change, the temperature, and the specific volumes of the solid and liquid phases at fusion, respectively. Since the melting temperature values are very close one may, in the application of the Clapeyron equation, refer to the unknown specific volume $V_{\mathrm{l,f}}$ at the mean temperature (220 K). By application of the second condition for high-pressure enantiotropy we may write

$$\frac{1776.7}{222(V_{\mathrm{l,f}} - 0.9242)} > \frac{1381.7}{218(V_{\mathrm{l,f}} - 0.9341)} > 0 \quad (\mathrm{atm.K^{-1}})$$

from which it turns out that the double inequality is satisfied only for

$$V_{\mathrm{l,f}} > 0.9718\ \mathrm{cm^3 \cdot g^{-1}}.$$

This result reveals that the hypothesis of a high-pressure enantiotropy is not consistent since such values of specific volume are characteristic of the liquid phase at temperatures higher than 293.15 K, as previously shown, and not at 220 K as assumed.

So unmistakable a result fully justifies the approximation made for its calculation. High-pressure enantiotropy is excluded also by comparison of the slope of the T–l melting curve with that of the C–T transition curve for which the results are available

$$\Delta H_{\mathrm{t}} = -414.51\ \mathrm{atm \cdot cm^3 \cdot g^{-1}}\ (-42\ \mathrm{J \cdot g^{-1}}),$$
$$T_t = 215\ \mathrm{K},$$
$$\Delta V_t = -0.0105\ \mathrm{cm^3 \cdot g^{-1}},$$

where $\Delta H_t$, $T_t$, and $\Delta V_t$ are the enthalpy change, the temperature, and the specific volume variation at the transformation. In fact, we should obtain

$$\frac{-414.51}{215(-0.0105)} > \frac{1776.7}{222(V_{l,f} - 0.9242)} > 0 \quad (\mathrm{atm} \cdot \mathrm{K}^{-1}),$$

but this double inequality would be satisfied only if

$$V_{l,f} > 0.9678\ \mathrm{cm}^3 \cdot \mathrm{g}^{-1}.$$

It could equally be demonstrated that the condition for high-pressure enantiotropy remains unsatisfied whichever $T_t$ temperature value belonging to the occurrence range (215 to 196 K) of the C → T transition is considered.

Conditions for overall monotropy are thus necessarily satisfied. The only point to be elucidated remains the choice among the cases illustrated in Figs. 4A, B, and C, respectively.

To achieve this, it should be necessary to know whether the two fusions occur with volume expansion or, instead, whether one (the C-form) or both modifications melt with volume contraction. To this purpose, no information is provided by literature sources. In the first case, in which the specific volume of the liquid phase at the melting temperature of the C-form has to be greater than or equal to 0.9341 $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$, the case of overall monotropy is that illustrated in Fig. 4A. In fact one obtains

$$\left(\frac{dp}{dT}\right)_{\mathrm{C(S_2)\text{–}l}} > \left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}} > 0,$$

and

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}} > \left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}C(S_2)}} > 0.$$

In the second case, for a liquid specific volume smaller than 0.9341 $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$ at 218 K and greater than or equal to 0.9242 $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$ at 222 K, overall monotropy is that of Fig. 4B, where the slope of the metastable $\mathrm{C(S_2)}$–l curve is negative.

The following double inequalities are satisfied:

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}} > \left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}C(S_2)}} > 0,$$

and

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{C(S_2)\text{–}l}}.$$

In the third case, related to a liquid specific volume smaller than 0.9242 $\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$ at 222 K, overall monotropy is illustrated in Fig. 4C where the slopes of the stable $\mathrm{T(S_1)}$–l and of the metastable $\mathrm{C(S_2)}$–l curves are both negative. The double inequalities are

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}C(S_2)}} > 0 > \left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}}$$

and

$$\left(\frac{dp}{dT}\right)_{\mathrm{T(S_1)\text{–}l}} < \left(\frac{dp}{dT}\right)_{\mathrm{C(S_2)\text{–}l}} < 0.$$

Nevertheless, it is meaningful to underline the capability of this approach to come to unambiguous conclusions about the nature of polymorphism even when sets of results at room pressure are partially incomplete, as in this last example. Hydrazine monohydrate, together with $\alpha,\beta$-dibromopropionic acid investigated by Wahl (*17*) and *o*-nitrotoluene, *o*-toluidine, *n*-cetyl iodide, ethyl stearate, and veratrole studied by Deffet (*7*, *8*), can be thought of, to our knowledge, as one of the examples unambiguously related to the (*p*, *T*) diagram for the fourth type of dimorphism illustrated in Fig. 4A, formerly reported by Bakhuis Roozeboom (*37*) but always forgotten since.

## IV. Concluding Remarks

The method discussed in this paper for discriminating between types of dimorphism (and trimorphism) may be of useful predictive interest in the case where experimental results on melting and solid-to-solid transition curves under pressure are lacking. It involves a simple step to gather data from heterogeneous sources and to deal with them in a comprehensive way.

Finally, by merely obtaining of atmospheric-pressure results one can predict polymorphic features up to higher pressures, provided the straight-line approximation in describing equilibrium curves always holds.

This method is not, in any case, intended to eliminate high-pressure measurements since, owing to this kind of experiment, it is easier to evaluate its relevance in studying and classifying polymorphic behaviors.

## Acknowledgment

The authors are indebted to Mrs. Ollitrault-Fichet for the careful drawing of the figures.

## References

1. O. LEHMANN, "Molekularphysik," Vol. 1, p. 193, Engelmann, Leipzig (1888).
2. H. W. BAKHUIS ROOZEBOOM, "Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," Vol. 1, pp. 183, 185, 187, 189, Vieweg, Braunschweig (1901).
3. L. DEFFET, "Répertoire des composés organiques polymorphes," p. 9, Desoer, Liège (1942).
4. H. A. J. OONK, "Phase Theory," pp. 49–54, Elsevier, Amsterdam (1981).
5. R. CÉOLIN, S. TOSCANI, V. AGAFONOV, AND J. DUGUÉ, *J. Solid State Chem.* **98,** 366 (1992).
6. F. KÖRBER, *Z. Phys. Chem.* **82,** 45 (1913).
7. L. DEFFET, *Bull. Soc. Chim. Belg.* **44,** 97 (1935).
8. L. DEFFET, *Bull. Soc. Chim. Belg.* **49,** 223 (1940).
9. T. TAKAGI, *Mem. Fac. Ind. Arts Kyoto Tech. Univ. Sci. Technol.* **25,** 51 (1976).
10. P. FIGUIÈRE, A. H. FUCHS, M. GHELFENSTEIN, AND H. SZWARC, *J. Phys. Solids* **39,** 19 (1978).
11. S. TOSCANI, J. DUGUÉ, R. OLLITRAULT-FICHET AND R. CÉOLIN, *Thermochim. Acta* **186,** 247 (1991).
12. V. A. KIRKINSKII AND V. G. YAKUSHEV, *Izv. Akad. Nauk SSSR Neorg. Mater.* **10,** 1431 (1974).
13. S. TOSCANI, J. DUGUÉ, AND R. CÉOLIN, *Thermochim. Acta* **196,** 191 (1992).
14. P. W. BRIDGMAN, *Proc. Amer. Acad.* **52,** 91 (1916).
15. G. TAMMANN, *Wied. Ann.* **68,** 571 (1899).
16. H. W. BAKHUIS ROOZEBOOM, Ref. (2), pp. 187–188.
17. W. WAHL, *Z. Phys. Chem.* **84,** 179 (1914).
18. R. MÜLLER, *Z. Phys. Chem.* **86,** 177 (1914).
19. M. AUMERAS AND R. MINANGOY, *Bull. Soc. Chim. Fr.*, 110 (1948).
20. L. M. KAMAEVA, *Zh. Fiz. Khim.* **30,** 645 (1956).
21. J. TIMMERMANS, "Les constantes physiques des composés organiques cristallisés," pp. 430 and 424, Masson, Paris (1953).
22. P. W. BRIDGMAN, *Phys. Rev.* **3,** 153 (1914).
23. J. A. KANTERS AND G. ROELOFSEN, *Acta Crystallogr. B* **32,** 3328 (1976).
24. J. A. KANTERS, G. ROELOFSEN, AND T. FEENSTRA, *Acta Crystallogr. B* **32,** 3331 (1976).
25. B. KALYANARAMAN, J. L. ATWOOD, AND L. D. KISPERT, *J. Chem. Soc. Chem. Commun.* 715 (1976).
26. J. TIMMERMANS, Ref. (21), p. 482.
27. J. TIMMERMANS AND L. DEFFET, "Le polymorphisme des composés organiques," p. 31, Gauthier–Villars, Paris (1939).
28. R. C. WEAST (ED.), "Handbook of Chemistry and Physics," 59th ed. CRC Press, West Palm Beach, FL (1978).
29. R. LIMINGA AND I. OLOVSSON, *Acta Crystallogr.* **17,** 1523 (1964).
30. M. ZOCCHI, W. R. BUSING, R. D. ELLISON, AND H. A. LEVY, *Acta Crystallogr.* **15,** 803 (1962).
31. M. FOULON, J. C. DAMIEN, M. MULLER, AND Y. GUINET, Communication PS-08.08.34 to the 15th Meeting of the International Union of Crystallography, Bordeaux, July 19–28, 1990 and *Acta Crystallogr. A* **46** supplement, C-348 (1990).
32. M. FOULON, Y. GUINET, M. MULLER, AND H. FONTAINE, Communication to the 2nd Meeting on "Disorder in Molecular Solids," 3rd Session, Garchy, France, June 24–27, 1991.
33. P. J. VAN EKEREN, H. A. J. OONK, Y. GUINET, M. FOULON, M. FERRIOL, AND M. T. COHEN-ADAD, *in* "Comptes rendus des dix-septièmes journées d'étude des équilibres entre phases," pp. 151–155, Oonk, Utrecht, April 3–4, 1991.
34. T. CURTIUS AND H. SCHULZ, *J. Prakt. Chem.* **42,** 521 (1890).
35. J. W. DITO, *Proc. Sect. Sci. K. Akad. Wet. Amsterdam,* **4,** 756 (1902).
36. V. I. SEMISHIN, *J. Gen. Chem. USSR* **8,** 654 (1938).
37. H. W. BAKHUIS ROOZEBOOM, Ref. (2), p. 189.