JOURNAL OF SOLID STATE CHEMISTRY **98**, 366–378 (1992)

Phenomenology of Polymorphism (I): Pressure–Temperature Representation of Trimorphism. General Rules. Application to the Case of Dimethyl 3,6-Dichloro-2,5-Dihydroxyterephthalate

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Received July 25, 1991; in revised form December 11, 1991

Trimorphism is presented in the form of a topological description as the capability of a chemical substance to exist under five aggregation states: three crystalline solid forms, the liquid, and the vapor. The general rules to construct the corresponding (p, T) diagram and to locate the 10 triple points are given and discussed. Several theoretical diagrams are presented in the case in which one deals with only three stable triple points. An example of application is given for the dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate. Hierarchies of stability among the three forms are inferred qualitatively as a function of increasing pressure and, quantitatively, also in domains of temperatures lower than those investigated by other authors in a previous experimental work. These stability hierarchies show a great sensitivity to the choice of an enthalpy change value, with respect to another of the same quantity, in determining the slopes of the two-phase equilibrium curves. © 1992 Academic Press, Inc.

1. Introduction

One of the main problems related to polymorphism is to establish a hierarchy of stability among different crystalline varieties of a given chemical compound. Stability is related to free enthalpy G though, very often, in terms of an exclusive change as a function of temperature.

Lehmann (*1, 2*) a century ago discriminated between two features of polymorphism, enantiotropy and monotropy, by merely founding upon optical investigations with varying temperature, without taking into account the pressure variable (in particular, that of the vapor of the investigated substances). On the other hand, it is well known that free enthalpy not only depends on temperature but also on pressure, which implies that every variation of G as a function of temperature should be experimentally correlated to a constant pressure. In practice, this procedure is hardly ever respected. Furthermore, the lowest vapor-pressure criterion proposed by Ostwald (*3, 4*) remains scarcely used since vapor-pressure measurements are only seldom performed; in its turn, the lowest volume criterion is not always ascertained, as we demonstrate in the following.

In this paper we present:

(a) a description of trimorphism founded upon two simple rules which are usually recognized. The former is of paramount importance as to the construction of the (p, T) diagram by locating the triple points, whose

0022-4596/92 $5.00

number depends on that of the polymorphic modifications (they are 10 in the case of trimorphism). The latter allows us to establish all along the two-phase equilibrium curves the ranges of stability and metastability, which are separated by the triple points previously located. Hence, hierarchies of stability (and also of metastability) among the solid varieties of a trimorphic substance all over the (p, T) region and the domains of the stable phases can be inferred. To this purpose, several theoretical diagrams are illustrated and discussed;

(b) an example showing that, by means of the Clapeyron equation, the combined use of crystallographic and thermodynamic results may allow us to build up, at least in a semiquantitative way, the (p, T) diagram of the studied trimorphic substance. According to the sample sealing features inherent to the thermodynamic method (differential scanning calorimetry) employed by other authors, we refer to the melting points of the three varieties as $S_i$lv triple points and to the solid–solid transitions points as S_iS_jv triple points, where S_i(or S_j), l, and v represent solid, liquid, and vapor phases, respectively. The aforementioned rules being applied, the other triple points are located by determining the intersection points between the curves describing the related two-phase equilibria, whose slopes are estimated by using the Clapeyron equation. A stability hierarchy degree which is respectful of fundamental thermodynamics and, if it exists, the stability range are therefore inferred for each modification as functions of temperature. Both of them are proved to change whether the enthalpy variation value associated with a solid–solid transition is taken from two different sources.

2. General Rules

Riecke (*5*) stated that the number of triple points in the (p, T) diagram of a body capable of existence under n polymorphic varieties is equal to that, C, of the distributions into groups of $p = 3$ phases of the ensemble of the $n + 2$ phases of the diagram:

$$C = \frac{(n+2)!}{p!\,(n+2-p)!}.$$

In the case of trimorphism ($n = 3$) this formula leads us to predict 10 triple points. If the three solid modifications of the body, its liquid phase, and its vapor phase are named S_1, S_2, S_3, l, and v, respectively, these ten triple points are

(1) S_1lv (4) S_1S_2l (7) S_1S_2v (10) $S_1S_2S_3$
(2) S_2lv (5) S_1S_3l (8) S_1S_3v
(3) S_3lv (6) S_2S_3l (9) S_2S_3v

(the same numbering is used on the drawings to account for them).

Triple points cannot be all stable and, on the other hand, they are located in the phase diagram of trimorphism according to the following rules:

(a) the three polymorphic forms must share the same vapor–liquid equilibrium curve in the (p, T) diagram; we suggest this rule actually defines true polymorphism;

(b) the extensions of the two-phase equilibrium curves are built around the triple points as shown in Fig. 1, as quoted by Oonk (*6*), according to a stable–metastable alternation if the invariant point is stable (Fig. 1A), to a metastable–supermetastable alternation if the invariant point is metastable (Fig. 1B), or even to a supermetastable–hypermetastable alternation if the invariant point is supermetastable (Fig. 1C).

From these two fundamental rules it may be consequently argued that the melting triple points, necessarily located along the vapor–liquid equilibrium curve, are characterized by a stability which decreases as temperature lowers (Fig. 2). This last statement elucidates the well-known rule according to which the most stable form exhibits the highest "melting temperature."

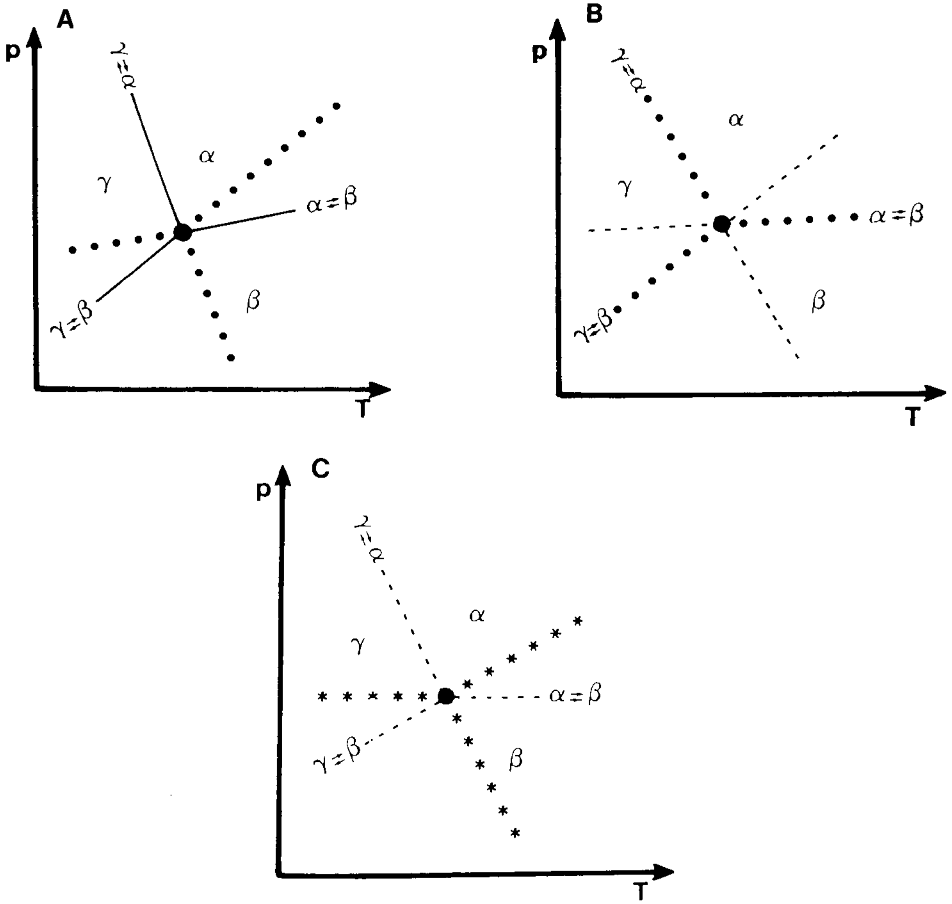

FIG. 1. Extensions of two-phase equilibrium curves built around a stable (A), metastable (B), or supermetastable (C) triple point concerning the α, β, γ forms of a pure solid substance: ——, stable equilibrium; ●●●●, metastable equilibrium; ----, supermetastable equilibrium; ****, hypermetastable equilibrium.

Nevertheless, in this description one effectively deals with melting triple points.

Thus, the problem of the (*p*, *T*) representation of polymorphism reduces to a mere building exercise which consists in locating the other seven triple points and in predicting the different likely cases, which will mainly depend on the slopes of the two-phase equilibrium curves as well as on their differences. For the sake of simplification these curves are represented by straight lines in the same way as Oonk's were (*6*).

3. Construction of the (*p*, *T*) Diagram

A. Triple Points with the Liquid Phase

As shown above for the S_1lv, S_2lv, and S_3lv triple points (Fig. 2), the S_1lv, S_1S_2l, and S_1S_3l triple points sharing the S_1 and l phases will be located on the same curve which describes the (*p*, *T*) conditions of the $S_1 \leftrightarrow$ l equilibrium. Similarly, the S_2lv, S_1S_2l, and S_2S_3l triple points will be located on the $S_2 \leftrightarrow$ l equilibrium curve, and the S_3lv, S_1S_3l, and S_2S_3l triple points on the $S_3 \leftrightarrow$ l curve.

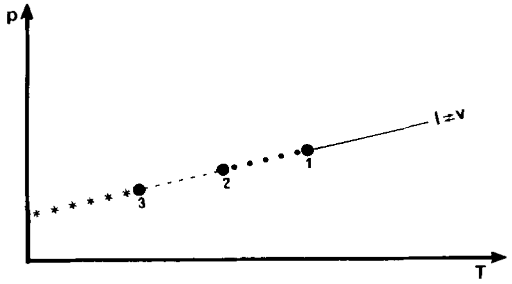

FIG. 2. Hierarchy of stability of the melting triple points of three polymorphs in the (p, T) diagram of the corresponding pure substance. $S_1lv(1)$, stable; $S_2lv(2)$, metastable; and $S_3lv(3)$, supermetastable.

Figure 3 shows an example of positioning of the S_1S_2l, S_1S_3l, and S_2S_3l triple points and illustrates that each two-phase equilibrium curve necessarily meets three triple points.

B. Triple Points with the Vapor Phase

For symmetry reasons, the S_1S_2v, S_1S_3v, and S_2S_3v triple points will be positioned in the same way as those involving the liquid phase, as shown in Fig. 4. This figure also materializes the Ostwald rule according to which the most stable form exhibits the lowest vapor pressure p.

More precisely, it shows the case for which $p(S_1) < p(S_2) < pS(_3)$, i.e., that related to a stable S_1-form and to two metastable S_2- and S_3-forms, S_3 being more metastable than S_2.

C. Positioning of the $S_1S_2S_3$ Triple Point

This point is to be found at the crossing of the $S_1 \leftrightarrow S_2$, $S_2 \leftrightarrow S_3$, and $S_1 \leftrightarrow S_3$ curves. Each one meets two other triple points with two solid phases; for instance, S_1S_2l and

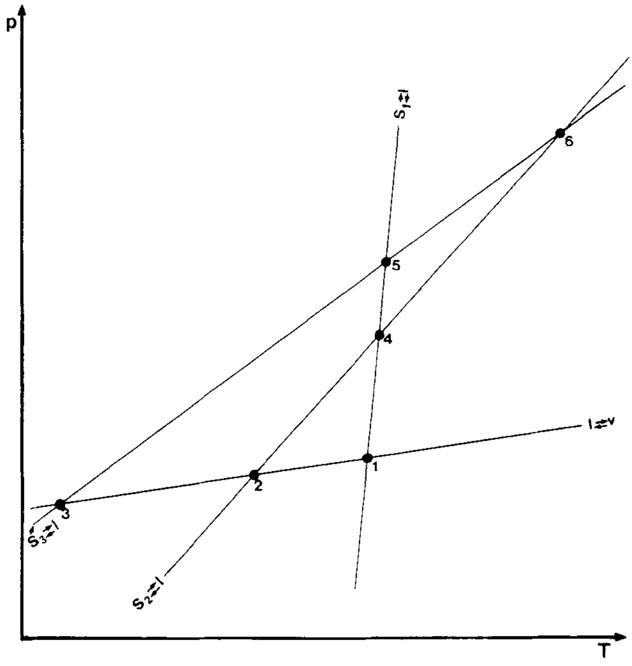

FIG. 3. Location of the triple points involving the liquid phase. The related positioning of $S_1S_2l(4)$, $S_1S_3l(5)$, and $S_2S_3l(6)$ triple points depends on the slopes of the $S_i \leftrightarrow l$ curves as well as on their differences.

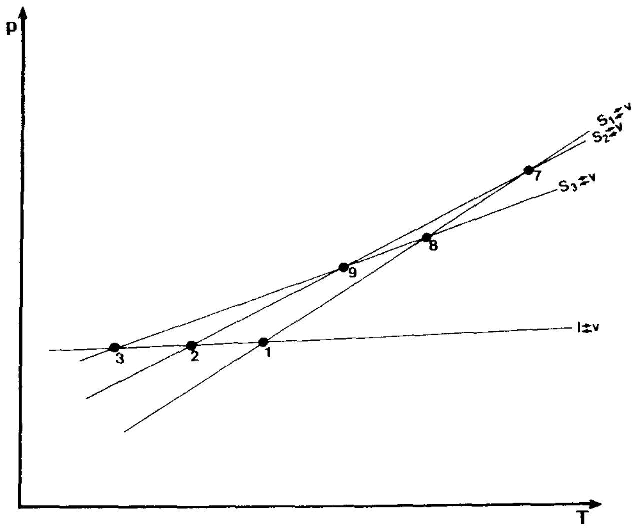

FIG. 4. Location of the $S_1S_2v(7)$, $S_1S_3v(8)$, and $S_2S_3v(9)$ triple points involving the vapor phase.

S_1S_2v triple points are located on the $S_1 \leftrightarrow S_2$ curve.

D. Conclusion

The (p, T) diagram of trimorphism is to be built around the $l \leftrightarrow v$ equilibrium curve since the group of the three melting S_ilv triple points is to be located on the unique $l \leftrightarrow v$ curve as shown in Fig. 2. Moreover, the two ternary groups of triple points S_iS_jl and S_iS_jv give rise to two triangles whose vertices are linked two by two by three $S_i \leftrightarrow S_j$ curves. The tenth triple point, $S_1S_2S_3$, is located at the crossing point of these three $S_i \leftrightarrow S_j$ curves (see, for example, Fig. 5D).

However, this topological description does not take into account the second rule (Fig. 1), which will now be used for the following representations of some theoretical (p, T) diagrams.

4. Some Theoretical Diagrams

The examples given in Figs. 5A, 5B, 5C, and 5D illustrate a case for which there are only three stable triple points, namely the S_1lv, S_1S_2v and S_2S_3v ones.

These examples exhibit some common features and some differences:

—each S_i-polymorph is stable in a given (p, T) region and each $S_i \leftrightarrow v$ curve is stable in a given T-range.

—the slope of the stable melting curve is positive in the three examples. This is not the case for the stable $S_i \leftrightarrow S_j$ curves. Although they diverge as pressure increases,

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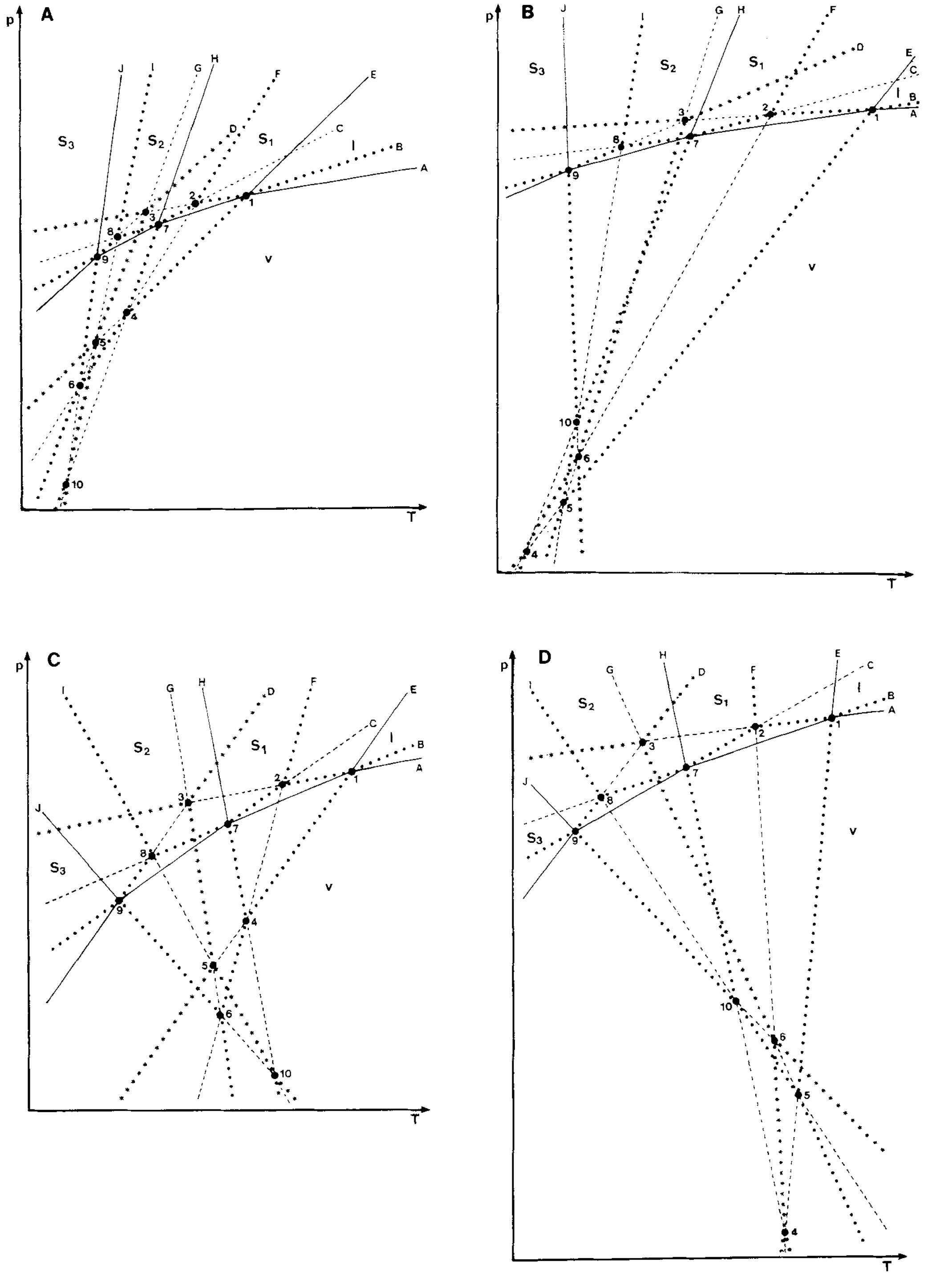
FIG. 5. (p, T) diagrams of trimorphism with three stable triple points: $S_1lv(1)$, $S_1S_2v(7)$, and $S_2S_3v(9)$. Equilibrium curves: $l \leftrightarrow v$, (A); $S_1 \leftrightarrow v$, (B); $S_2 \leftrightarrow v$, (C); $S_3 \leftrightarrow v$, (D); $S_1 \leftrightarrow l$, (E); $S_2 \leftrightarrow l$, (F); $S_3 \leftrightarrow l$, (G); $S_2 \leftrightarrow S_1$, (H); $S_3 \leftrightarrow S_1$, (I); and $S_3 \leftrightarrow S_2$, (J). (A) The $S_i \leftrightarrow S_j$ curves have positive slopes. The $S_1S_2S_3$ triple point (10) is supermetastable. (B) The $S_i \leftrightarrow S_j$ curves have alternatively negative and positive slopes. The $S_1S_2S_3$ triple point (10) is metastable. (C) The $S_i \leftrightarrow S_j$ curves have negative slopes. The $S_1S_2S_3$ triple point (10) is supermetastable. (D) With respect to Fig. 5C, the slope of the $S_1 \leftrightarrow l$ curve is more positive and, consequently, the $S_1S_2S_3$ triple point (10) becomes metastable.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it can be observed that they have positive slopes in Fig. 5A, negative ones in Fig. 5C, and that Fig. 5B represents an intermediate case.

It is to be noted that Fig. 5D also shows a case with positive melting slope for $S_1 \leftrightarrow$ 1 equilibrium. However, the difference between Figs. 5C and 5D is due to the position of the S_1S_2l, S_1S_3l, and S_2S_3l triple points with respect to the $S_1S_2S_3$ one. In Fig. 5C, the pressure at $S_1S_2S_3$ triple point is lower than those of the S_1S_2l, S_1S_3l, and S_2S_3l triple points, while in Fig. 5D, it is higher. A negative slope for $S_1 \leftrightarrow$ l curve would not induce any topological change in Fig. 5D provided that the $S_1 \leftrightarrow$ l, $S_1 \leftrightarrow S_2$, and $S_1 \leftrightarrow S_3$ stable curves diverge with increasing pressure.

Whatever the case is, the application of the rule illustrated in Fig. 1 leads to the following stability hierarchy for the three melting triple points: S_1lv stable, S_2lv metastable, S_3lv supermetastable, in agreement with Ostwald rule. This fact may account for the scarcity of polymorphs with three "melting points." From the topological construction of the cases displayed in Figs. 5A to 5D, we may draw the following observations:

(a) the S_1S_3v triple point always turns out to be metastable;

(b) the S_1S_2l, S_1S_3l, S_2S_3l, and $S_1S_2S_3$ triple points can alternatively be metastable or supermetastable, as shown in Table I.

TABLE I

HIERARCHIES AMONG GROUPS OF NONSTABLE TRIPLE POINTS IN SOME EXAMPLES OF TRIMORPHISM REPRESENTED BY MEANS OF (p, T) DIAGRAMS IN FIGS. 5A, 5B, 5C, AND 5D, RESPECTIVELY. THE COMMON STABLE TRIPLE POINTS ARE THE S_1lv, S_1S_2v, AND S_2S_3v ONES.

Figure	Metastable triple points	Supermetastable triple points
5A	S_2lv, S_1S_3v S_1S_2l, S_2S_3l	S_3lv, S_1S_3l $S_1S_2S_3$
5B	S_2lv, S_1S_3v S_1S_3l, $S_1S_2S_3$	S_3lv, S_2S_3l S_1S_2l
5C	S_2lv, S_1S_3v S_1S_2l, S_2S_3l	S_3lv, S_1S_3l $S_1S_2S_3$
5D	S_2lv, S_1S_3v S_1S_3l, $S_1S_2S_3$	S_3lv, S_2S_3l S_1S_2l

5. Example of Application

A. Previous Works and Previous Conclusions

Formerly referred to by Hantszch (*7*) and much more recently by Byrn *et al.* (*8*) as a case of dimorphism, in this section we deal, as a matter of fact, with the trimorphism of the dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate as proved by the crystallographic and thermodynamic investigations recently reported in literature by Dunitz and coworkers (*9, 10*). The authors pointed out that the three varieties, named Y, W, and LY, are conformational polymorphs in which an ester group is approximately in the plane of the benzene ring (Y), nearly perpendicular to it (W), or in an intermediate orientation (LY). From single-crystal studies they have drawn the molecular volumes of the three modifications as a function of temperature while, by means of differential scanning calorimetry (DSC), they have measured the enthalpy changes ΔH of a series of transitions occurring between the varieties. In particular they have detected:

(a) the transformation of Y into W, occurring over the temperature range between about 375 and 415 K to which an average enthalpy change value of 1.7 kJ mol^{-1} was assigned (it must be underlined that this transition had already been previously investigated by Byrn *et al.* (*8*) who instead measured an enthalpy variation of 2.56 kJ mol^{-1});

(b) the transformation of LY into W between 360 and 380 K ($\Delta H \cong 2.5$ kJ mol^{-1}). Occasionally, they have also detected an aleatory transformation of LY into Y;

(c) the melting of the W-form at around 455 K as well as that metastable of Y 20 degrees below.

From this thermodynamic study they have deduced the following hierarchies of stability:

(a) Y > LY > W (the sign > means "more stable than") at room temperature and below;

(b) W > Y > LY above 360 K.

They have then concluded that there is no temperature at which the form LY is the most stable one.

In the following paragraphs W, Y, and LY forms are shown to correspond to the S_1, S_2, and S_3 solid modifications of the theoretical diagrams, respectively.

B. Our Remarks

Since the DSC studies are performed on samples in sealed-off containers, it may be assumed that the solid–solid transformations occur under their saturating vapor pressure. Consequently, the corresponding thermal effects have to be connected to the solid–solid (or liquid)–vapor triple points. Hence we have drawn the following remarks:

(1) the "melting" of W at 455 K is to correspond to the stable W–l–v triple point;

(2) the "melting" of Y at 435 K is to correspond to the metastable Y–l–v triple point;

(3) since Y endothermally transforms into W at 408 K (see Section 5C), i.e., at $T < 435$ K, the corresponding thermal effect is to be related to the Y–W–v triple point, as shown in Fig. 6, with respect to the rule of alternating stable and metastable curves;

(4) similarly, the endothermal transformation of LY into W observed at 357 K (see Section 5C) is to correspond in fact to the metastable LY–W–v triple point;

(5) the LY–W–v triple point is located on the W ↔ v curve. Since the thermal effect related to the LY → W transformation was found to be endothermal, the LY ↔ v curve is consequently to be situated at pressures lower (when $T < 357$ K) or higher (when $T > 357$ K) than those of the W ↔ v curve.

Moreover, as the molecular volumes of the three modifications have been measured over a wide range of temperature (*9*), we have coupled these data with the thermodynamic ones (*10*) to estimate the dp/dT slopes values of some equilibrium curves and to locate at least semiquantitatively the LY–Y–W and the LY–Y–v triple points.

Consequently, the LY–l–v triple-point temperature (398 K) has been directly drawn from the following (p, T) diagram construction, as it must represent the abscissa of the intersection point between the LY ↔ v and the l ↔ v equilibrium curves.

C. Location of the W–Y–LY Triple Point

As a matter of fact, we have first calculated the values of the dp/dT derivatives of the Y ↔ W and LY ↔ W equilibria. From reported DSC curves we have estimated the onset temperatures of the Y → W and the LY → W transitions to be 408 and 357 K, respectively. At the same time we have interpolated the molecular volume values for the three forms by means of a parabolic function of temperature, that is to say,

$$V = a_0 + a_1T + a_2T^2.$$

Coefficients a_0, a_1, and a_2 are reported in Table II for each modification. Consequently, by means of the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V},$$

we have calculated the values of the derivatives for the two named equilibria. We have obtained 11.53 atm K^{-1} for the Y ↔ W equilibrium and 17.62 atm K^{-1} for the LY ↔ W one.

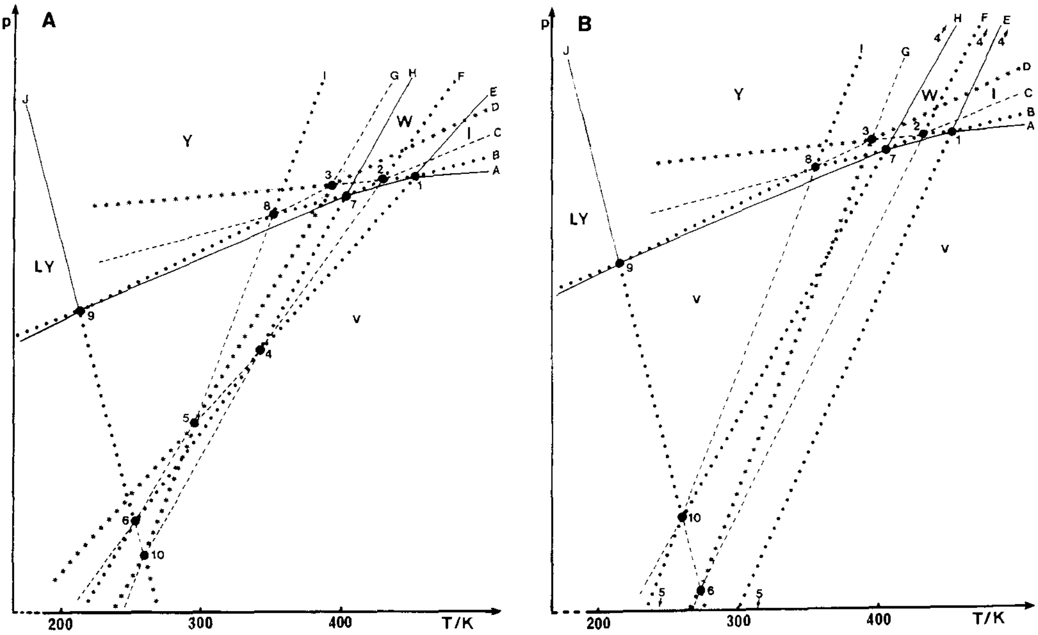

FIG. 6. (p, T) diagrams with three or four stable triple points able to represent the trimorphism of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate. Equilibrium curves: l ↔ v, (A); W ↔ v, (B); Y ↔ v, (C); LY ↔ v, (D); W ↔ l, (E); Y ↔ l, (F); LY ↔ l, (G); Y ↔ W, (H); LY ↔ W (I); and LY ↔ Y, (J). Triple points: W–l–v, (1); Y–l–v, (2); LY–l–v, (3); W–Y–l, (4); W–LY–l, (5); Y–LY–l, (6); W–Y–v, (7); W–LY–v, (8); Y–LY–v, (9); and W–Y–LY, (10). (A) Diagram accounting for case (a) in Section 5E and for the general (p, T) representation of Fig. 5B; three stable triple points: W–l–v(1), W–Y–v(7) and Y–LY–v(9). According to Fig. 5B, the slope of the W ↔ l melting curve was arbitrarily taken less positive than those of the Y ↔ W and LY ↔ W curves. As the following ones, this diagram was drawn from thermodynamic results reported in Ref. (*10*). (B) Diagram representing case (b) in Section 5E; four stable triple points: W–l–v(1), W–Y–v(7), Y–LY–v(9), and W–Y–l(4); the W–LY–l triple point (5) is metastable at pressure lower than that of the l ↔ v curve and the slope of the w ↔ l curve is positive. (C) Diagram representing case (c) in Section 5E. Consequently, with respect to Fig. 6B, the W–LY–l triple point (5) is metastable at pressure higher than that of the l ↔ v curve. (D) Diagram representing case (c′) in Section 5E. The only difference with respect to Fig. 6C consists in the negative slope of the W ↔ l curve. (E) (p, T) diagram drawn from thermodynamic results reported in Refs. (*10*) and (*8*); three stable points: W–l–v(1), W–Y–v(7), and W–Y–LY(10) (see Fig. 7). The same choice as that in Fig. 6A was made as to what implies the slope of the W ↔ l curve with respect to that of the Y ↔ W and LY ↔ W curves.

So, taking into account this result, the thermal location of W and Y meltings and the rules discussed above, a (p, T) diagram can be derived for the studied compound.

Y–W–v, LY–W–v, and LY–Y–v triple points are all situated at pressures which are reasonably expected at very low values, very near to zero; so their coordinates are $p \approx 0$ and $T = T_{x \leftrightarrow y}$, where $T_{x \leftrightarrow y}$ is the temperature of transformation of the generic form x into the y one. The lines respectively passing through the LY–W–v and the Y–W–v triple points represent the LY ↔ W and Y ↔ W equilibria which, according to their different slopes, have to intersect at

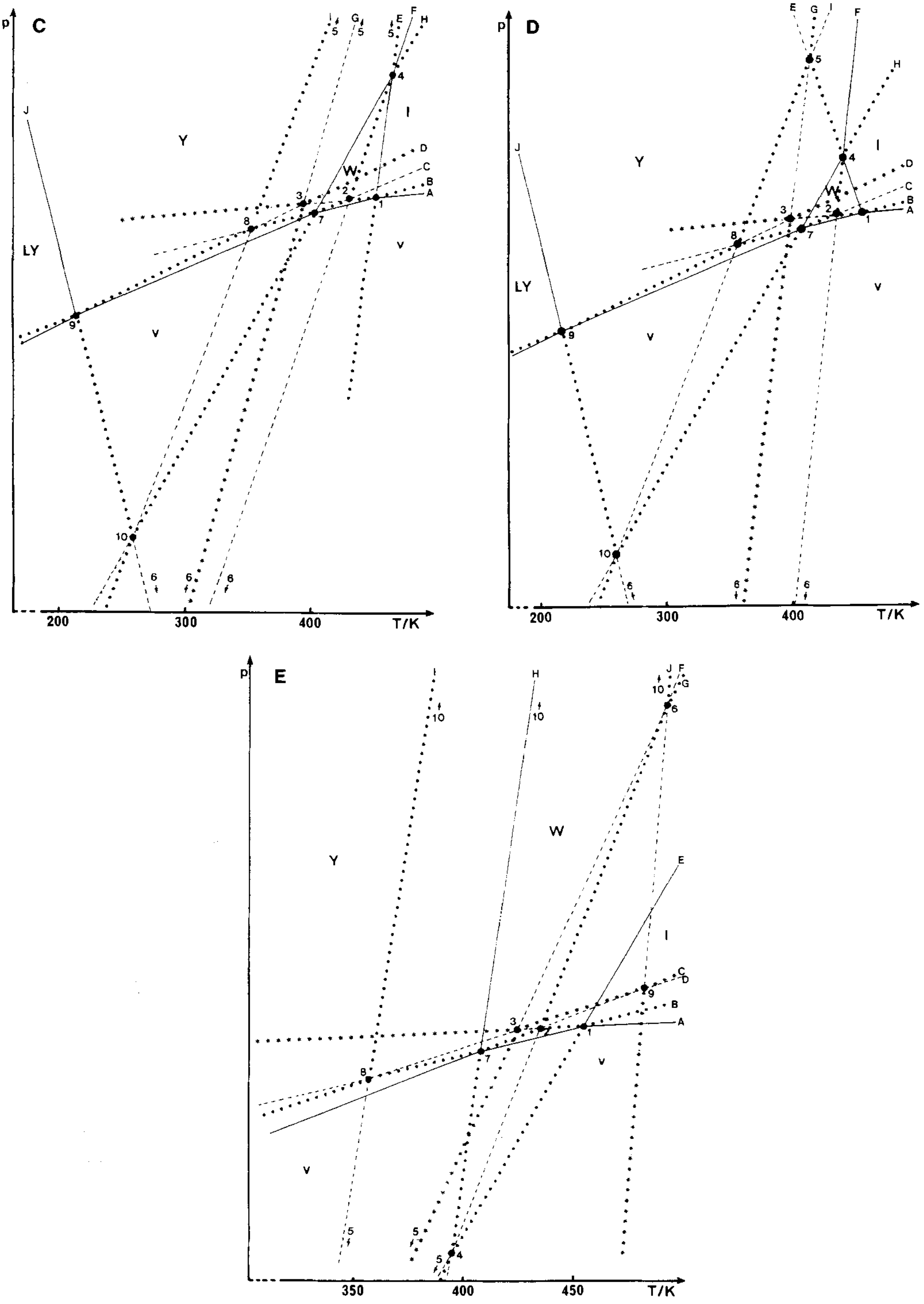

FIG. 6—*Continued*

TABLE II

COEFFICIENTS a_0, a_1, AND a_2 OF THE PARABOLIC EQUATION, $V = a_0 + a_1T + a_2T^2$, USED TO INTERPOLATE THE VOLUMETRIC RESULTS GIVEN IN REF. (9)

Modification	a_0 ($\mathrm{cm^3 \cdot mol^{-1}}$)	a_1 ($\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$)	a_2 ($\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-2}}$)
W	165.83	0.0191	1.8×10^{-5}
Y	160.16	0.0106	5.2×10^{-5}
LY	161.94	0.0563	5.6×10^{-5}

another triple point W–Y–LY ($S_1S_2S_3$). Its temperature may be obtained by solving the following system:

$$(p/\mathrm{atm}) = 11.53\,[(T/K) - 408]$$

$$(p/\mathrm{atm}) = 17.62\,[(T/K) - 357].$$

Hence $T = 260$ K.
At this triple point one may state that

$$\Delta H_{\mathrm{LY}\to\mathrm{Y}} = \Delta H_{\mathrm{LY}\to\mathrm{W}} + \Delta H_{\mathrm{W}\to\mathrm{Y}},$$

where ΔH are transformation enthalpy changes. Then, by substituting the experimental values we have obtained

$$\Delta H_{\mathrm{LY}\to\mathrm{Y}} = 0.8 \text{ kJ mol}^{-1}.$$

D. Location of the LY–Y–v Triple Point

By means of interpolating equations on respective molecular volumes we have estimated that the transition LY → Y is accompanied with a negative volume change ($\Delta V_{\mathrm{LY}\to\mathrm{Y}} = -0.78$ cm^3 mol^{-1}) and, consequently, dp/dT turns out to be negative and equal to -39.9 atm K^{-1}.

Since the LY ↔ Y equilibrium curve has to pass through the W–Y–LY triple point, the LY → Y transformation temperature proves to be 217 K.

E. Conclusions

At this stage, the only uncertainty in the (p, T) phase-diagram construction remains the lack of a complete set of thermodynamic data on the fusion curve of the W-form. Anyway, four likely cases are envisageable for the slope of the W ↔ l curve with respect to those of the LY ↔ W and of the Y ↔ W curves:

$$\text{(a)}\quad \left(\frac{dp}{dT}\right)_{\mathrm{LY}\leftrightarrow\mathrm{W}} > \left(\frac{dp}{dT}\right)_{\mathrm{Y}\leftrightarrow\mathrm{W}} > \left(\frac{dp}{dT}\right)_{\mathrm{W}\leftrightarrow\mathrm{l}} > 0;$$

$$\text{(b)}\quad \left(\frac{dp}{dT}\right)_{\mathrm{LY}\leftrightarrow\mathrm{W}} > \left(\frac{dp}{dT}\right)_{\mathrm{W}\leftrightarrow\mathrm{l}} > \left(\frac{dp}{dT}\right)_{\mathrm{Y}\leftrightarrow\mathrm{W}} > 0;$$

$$\text{(c)}\quad \left(\frac{dp}{dT}\right)_{\mathrm{W}\leftrightarrow\mathrm{l}} > \left(\frac{dp}{dT}\right)_{\mathrm{LY}\leftrightarrow\mathrm{W}} > \left(\frac{dp}{dT}\right)_{\mathrm{Y}\leftrightarrow\mathrm{W}} > 0;$$

and

$$\text{(c}'\text{)}\quad \left(\frac{dp}{dT}\right)_{\mathrm{LY}\leftrightarrow\mathrm{W}} > \left(\frac{dp}{dT}\right)_{\mathrm{Y}\leftrightarrow\mathrm{W}} > 0 \quad \text{and}$$

$$\left(\frac{dp}{dT}\right)_{\mathrm{W}\leftrightarrow\mathrm{l}} < 0.$$

All these cases are to be referred to the (p, T) diagram drawn in Fig. 5B, which predicts a metastable $S_1S_2S_3$ (W–Y–LY) triple point. Nevertheless, in case (a) (Fig. 6A) the W–Y–LY triple point turns out to be supermetastable. In the other cases, the metastability of the W–Y–LY triple point is acknowledged but, instead, the W–Y–l (S_1S_2l) triple point results to be a high-pressure stable one (Figs. 6B to 6D). In its turn, the W–LY–l (S_1S_3l) triple point is alternatively metastable at lower (case (b)) or at higher (cases (c) and (c′)) pressure than that of the l ↔ v curve at the same temperature.

According to the common features in Figs. 5B, 6A, 6B, 6C, and 6D concerning the LY ↔ Y, LY ↔ W and Y ↔ W equilibria, the range of stability of each modification can be defined at least as a function of temperature. It turns out that LY is stable at temperature below 217 K, Y between 217 and 408 K, and W between 408 and 455 K.

Moreover, from these figures the following hierarchy of stability may be inferred:

$T < 217$ K	LY > Y > W
217 K < 357 K	Y > LY > W
357 K < 408 K	Y > W > LY
$T > 408$ K	W > Y > LY.

The hierarchy of stability of the different forms established by Richardson *et al.* (*10*) is acknowledged only between 217 and 357 K and above 408 K, where the Y-form and the W-form are respectively the most stable ones. However, the LY-variety appears to be the most stable one at low temperature. The LY ↔ W equilibrium ($S_3 \leftrightarrow S_1$) results, in turn, to be metastable and located in the range of stability of the Y(S_2)-variety. Furthermore, the criterion of the least volume, already put critically under discussion by Richardson *et al.* (*10*), appears unexpectedly belied at low temperature where the Y-form is always the densest one.

Nevertheless, it must be pointed out that building up a diagram requires accurate experimental results (in particular from calorimetric studies) for its features to allow unambiguous conclusions. To make an example, if we used the enthalpy change value for the Y → W ($S_2 \rightarrow S_1$) transformation reported by Byrn *et al.* (2.56 kJ mol^{-1}) (*8*), we would obtain a positively sloped Y ↔ W equilibrium curve (17.64 atm K^{-1}) slightly sharper than the LY ↔ W one and, consequently, a W–Y–LY($S_1S_2S_3$) triple point situated at high pressure.

Assuming that the equation

$$\Delta H_{\mathrm{LY}\rightarrow\mathrm{Y}} = \Delta H_{\mathrm{LY}\rightarrow\mathrm{W}} + \Delta H_{\mathrm{W}\rightarrow\mathrm{Y}}$$

also holds far from W–Y–LY triple point, and the enthalpy changes ΔH to be roughly independent on temperature and on pressure, from experimental values on enthalpy changes of the LY ↔ W and of the W ↔ Y transitions one finds that $\Delta H_{\mathrm{LY}\rightarrow\mathrm{Y}}$ is equal to -0.06 kJ mol^{-1}. Consequently, the LY ↔ v curve is to be located at pressures higher than those of the Y ↔ v curve. More precisely, the metastable LY ↔ v equilibrium is situated between the stable Y ↔ v and the supermetastable W ↔ v equilibria at $T <$ 357 K since, according to the endothermal LY ↔ W transformation at 357 K, the LY ↔ v curve is situated at pressures lower than those corresponding to the W ↔ v curve at T < 357 K.

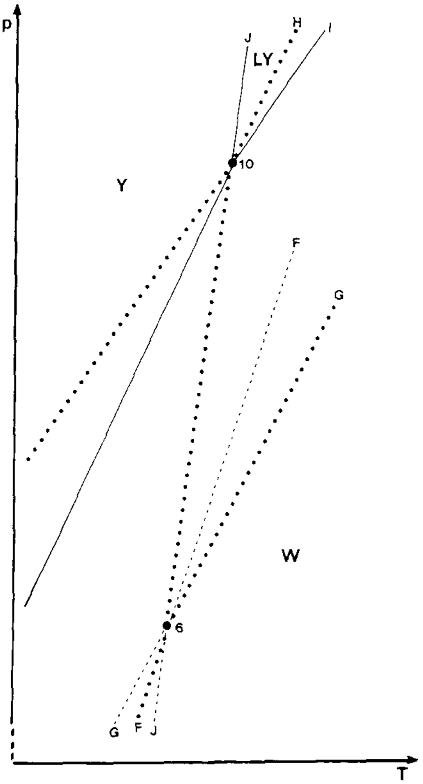

Fig. 7. Extension of the Y ↔ LY, Y ↔ l, LY ↔ l, Y ↔ W, and LY ↔ W equilibrium curves in diagram 6E toward higher pressure; the Y–LY–l(6) and W–Y–LY(10) triple points are metastable and stable, respectively.

Moreover, the same choice as that in Fig. 6A was made here as to what implies the slope of the W ↔ l curve with respect to that of the Y ↔ W and LY ↔ W curves.

The (p, T) diagram of Fig. 6E can then be derived; one can note that the LY–Y–v triple point is necessarily located at a temperature $T_{\mathrm{LY-Y-v}}$ higher than that of the melting of the high-temperature stable W-form. The LY–l–v triple point temperature is instead equal to 425 K. LY-modification appears to be a monotropic variety in the presence of the two enantiotropic Y- and W-forms.

From the same figure the hierarchy of stability can be inferred,

$$\begin{array}{rl} T < 357\ \mathrm{K} & \mathrm{Y} > \mathrm{LY} > \mathrm{W} \\ 357\ \mathrm{K} < T < 408\ \mathrm{K} & \mathrm{Y} > \mathrm{W} > \mathrm{LY} \\ 408\ \mathrm{K} < T < T_{\mathrm{LY-Y-v}} & \mathrm{W} > \mathrm{Y} > \mathrm{LY} \\ T > T_{\mathrm{LY-Y-v}} & \mathrm{W} > \mathrm{LY} > \mathrm{Y}, \end{array}$$

that exhibits no temperature range at ordinary pressure along which the LY-form is the most stable one. This result agrees with the hierarchy established by Richardson *et al.* (*10*) with the only exception the narrow 357–408 K range in which the Y-form remains the most stable one.

On the other hand, if one deals with the high-pressure extensions of the LY ↔ W, Y ↔ W, LY ↔ l, Y ↔ l and Y ↔ LY equilibria in Fig. 6E, it can be shown that the LY-form may be expected as a high-pressure stable variety (Fig. 7). According to the alternation rule, the supermetastable Y ↔ LY equilibrium should become metastable at pressures higher than that of the LY–Y–l triple point and successively stable beyond the W–Y–LY triple point, as well as the LY ↔ W equilibrium. So, the two equilibrium curves would delimitate a domain of stability for the LY-form.

The here-reported building examples of a (p, T) trimorphic diagram, which lead to discordant conclusions if two different experimental values of the same quantity are respectively taken into account, should represent a double spur: on one hand to increase low-temperature investigations and on the other to enhance studies of the high-pressure features of polymorphism.

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