High-pressure properties inferred from normal-pressure properties

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Abstract
From the stable and metastable normal-pressure phase equilibria involved in two-component systems sharing compounds of the series $CCl_{4-n}Br_n$, $n = 0, \ldots, 4$, several thermodynamic properties concerning non-experimentally available phase transitions have been determined. To do so, the well-established concept of crossed isodimorphism has been considered to involve the isomorphism relationships between the low-temperature monoclinic phases as well as, for both rhombohedral and face-centred cubic, orientationally disordered phases appearing in the compounds of the series. On the basis of such relations, the thermodynamic properties of the two-phase equilibria are extrapolated as a function of mole fraction to the pure compounds for which the involved transitions do not exist at normal pressure. The obtained thermodynamic properties are used to build up the topological pressure–temperature phase diagrams of the compounds of the series. The results are compared with the experimental pressure–temperature phase diagrams obtained by means of density measurements as a function of pressure and temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Molecular substances composed of nearly spherical molecules exhibit orientationally disordered (OD) phases, below the liquid state, where the molecules are long range translationally ordered in an almost symmetrical lattice but have rotational freedom [1, 2]. This intermediate state is commonly referred as the plastic crystalline state and these substances are known as plastic crystals or orientationally disordered crystals. Among these materials halogenomethane compounds, $CCl_{4-n}Br_n$, $n = 0, 1, 2, 4$ are prototypical examples of substances displaying such OD states [3–19].

In spite of the similarity of the halogenomethane molecules, the polymorphic behaviour at normal pressure, i.e. in equilibrium with its vapour, is known to be quite different [7, 9, 14, 17]. Thus, as far as CCl_4 is concerned, it crystallizes to an OD face-centred-cubic (FCC) phase and

upon further cooling to another OD phase, the symmetry of which is rhombohedral (R) [9, 15, 20–22]. If the cooling is halted when the FCC phase is formed, this phase melts again without passing back through the R phase, while when the R phase is heated a new melting point several degrees higher than that of the FCC phase is obtained. This behaviour implies that, at least at normal pressure, the FCC phase is metastable and behaves monotropically with respect to the R phase. In figure 1(a) we show the Gibbs energies as a function of temperature (at constant pressure) for a compound displaying such a behaviour involving three phases, α, β and L. Figure 1(b) shows the behaviour for which the α and β phases behave enantiotropically, which implies that at the transition temperature substance B's β form can be converted into the form α, and vice versa [23].

Some remarks about the consequences of both behaviours concerning metastable temperatures should be noted. For the
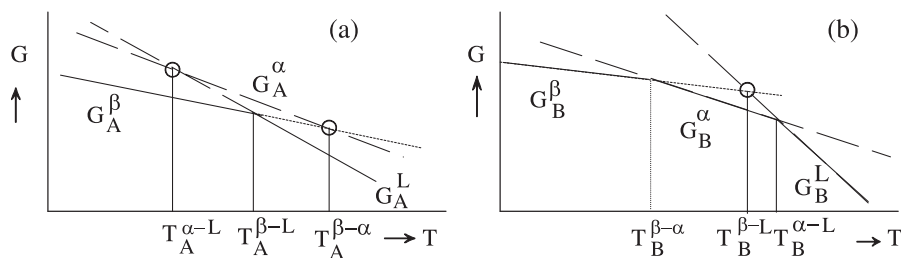
Figure 1. Schemas of the Gibbs energy curves as a function of temperature, for a given pressure, for pure compounds displaying a monotropic (a) and enantiotropic (b) relationship between the α and β phases. Continuous and dashed lines depict stability or metastability, respectively, and open circles indicate the metastable melting or transition points.

enantiotropic behaviour (figure 1(b)), it is to be noticed that if the α form did not exist β would melt at a lower temperature than α ($T_B^{\alpha-L}$), i.e., at the metastable melting point of β ($T_B^{\beta-L}$). As for the pure compound described in figure 1(a), A's α form is invariably metastable, at the considered pressure, with respect to β, and the melting temperature of the α form ($T_A^{\alpha-L}$) is lower than that of the stable β form ($T_A^{\beta-L}$), in such a way that the transition temperature between both polymorphs ($T_A^{\beta-\alpha}$) is always located in the stability domain of the liquid phase, for the given pressure. The fact that the α phase is invariably metastable for the whole temperature range for a given pressure does not means that it cannot exist. The case previously described for the OD FCC phase of CCl_4 is one of the best examples where the metastable phase makes its physical appearance. The same behaviour has been found for compounds of the methylchloromethane series $(CH_3)_{4-n}CCl_n$ for $n = 2, 3$ [20–22, 24]. In other cases the metastable phase has an overall virtual status, but its properties can be computed or obtained by extrapolation from the properties of the mixed crystals. In some other cases, the metastable character (that is to say, the monotropic or enantiotropic behaviour) changes with pressure. As for the case of CCl_4 the pressure–temperature phase diagram has been previously determined and clearly shows that the monotropic character of the OD FCC phase is retained when the pressure changes (the so-called case of 'overall monotropy') [25]. The topological reason for such behaviour comes from the comparison of the slopes ($\frac{dT}{dP}$) of the melting curves for the R and FCC phases: the equilibrium melting curves (FCC–L and R–L) diverge and would have crossed at negative pressure (at the [R + FCC + L] triple point). Figure 2(a) sketches such behaviour.

Figure 2(b) depicts the case for which the R and FCC behave enantiotropically (the FCC–R transition is then reversible) for pressures lower than the triple point [R + FCC + L], while it would entail a monotropic relationship for pressures higher that the aforementioned triple point. The reader can 'play' with the cases described by figures 2(c) and (d) to establish the pressure domains accounting for the monotropic or enantiotropic relationships between the R and FCC phases.

These examples show that the thermodynamic diagrams shown in figure 1 are not invariably kept as a function of pressure for a given substance. Actually, this implies that the polymorphic behaviour must be described by the influence of both pressure and temperature variables and, unfortunately,

the pressure–temperature phase diagram scenario is not yet a common thermodynamic space in which polymorphism is described, in spite of the huge advances in the technology to produce pressure-dependent experimental devices [26–28].

In the field of polymorphic behaviour, the emphasis is mostly focused on the phases (stable or metastable) appearing exclusively at normal pressure and, unfortunately, the metastability character of a phase (at normal pressure) is frequently confused with the concept of overall monotropy for that phase without any regard to the pressure variable. The implicit reason for such a fundamental error stems from the non-availability of high-pressure devices, which in many cases forces researchers to work under the equilibrium between condensed and vapour phases (the so-called 'normal-pressure conditions'. This should not be confused with atmospheric pressure as is often done!). The purpose of this communication is to show how pressure–temperature phase diagrams can be built up with the data from normal-pressure experiments. Our aim is thus to track down the physical meaning of the phases and the phase transitions, appearing metastable at normal pressure, and how those can become stable in the high-pressure domain, and metastable again on a further increase in pressure. To do this, normal-pressure data will be computed from two-component systems involving the aforementioned halogenomethane compounds. The structure of this paper will be as follows: first, a short review concerning the polymorphic behaviour at normal pressure for the halogenomethane compounds involved in the two-component systems will be presented. Secondly, we will briefly introduce the concept of the crossed isodimorphism, which enables us to rationalize the appearance of metastable phase transitions as well as to give them a physical meaning. Within the same section that concept will be applied to three related two-component systems and, finally, the inference of the topological pressure–temperature phase diagram of some halogenomethane compounds together with a comparison with experimental diagrams will be done.

2. Polymorphism at normal pressure

As for the low-temperature ordered phases of halogenomethanes dealt with in this work, all of them crystallize into a monoclinic structure (space group $C2/c$, $Z = 32$) [8, 14, 17, 29–31]. In addition it has been shown that monoclinic mixed crystals are formed for the whole range of composition [31].
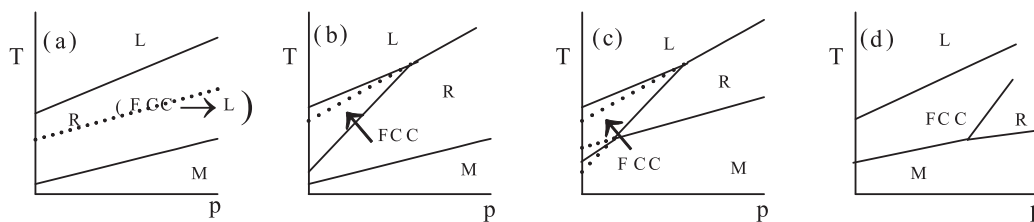
Figure 2. Possible temperature–pressure phase diagrams involving stable (continuous lines) and metastable (dashed lines) two-phase equilibria. L stands for the liquid, R and FCC for the rhombohedral and face-centred cubic OD phases, respectively, and M for the low-temperature monoclinic phase.

Within the OD state the halogenomethanes exhibit a polymorphic nature such that at most two forms are involved: FCC (face-centred cubic), and R (rhombohedral). Under normal-pressure conditions the FCC phase is the high-temperature stable form for $CBrCl_3$, CBr_2Cl_2 and CBr_4, while the R phase is also stable for $CBrCl_3$ and the only OD stable form for CCl_4. The FCC for the latter compound displays a monotropic overall behaviour (then metastable irrespective of pressure) [7, 9, 14, 29].

Crystallographic properties characterizing both low-temperature and OD phases have been previously reported as a function of temperature, and those values enable us to obtain volume variations at the transition temperatures [8, 14, 17, 24]. The melting and transition temperatures, as well as their associated enthalpy and volume changes, are collected in table 1.

3. Two-component systems

Although the details of the experimental procedures used to determine the two-component phase diagrams have been widely described in previous works [12, 13, 20–22] for our purpose here it is expedient to consider the phase diagram shown in figure 3, in which three phases, α, β and γ, are involved.

For the two-component phase diagram represented in figure 3, referred to as crossed isodimorphism [23], the form α is the low-temperature stable phase for component A, and the form β is the low-temperature stable phase for component B (β is metastable for A and α is metastable for B). The stable phase diagram can be looked upon as the stable result of two crossing loops: $[\alpha + \gamma]$ and $[\beta + \gamma]$. The two crossing loops imply a stable three-phase equilibrium $[\alpha + \beta + \gamma]$, which, in the case of figure 3, is peritectoid (the eutectoid case can be analysed by means the same procedure). The metastable transition temperatures ($T_A^{\beta \to \gamma}$ and $T_B^{\alpha \to \gamma}$) would have the physical meaning described in figure 1.

The three two-component phase diagrams shared by CCl_4, $CBrCl_3$ and CBr_2Cl_2 are shown in figure 4 [12, 34]. As for the $CCl_4 + CBr_2Cl_2$ and $CCl_4 + CBrCl_3$ diagrams, the stable OD form for mole fractions lower than the peritectic invariant is the OD R phase. Accordingly, the phase behaviour shown by these binary combinations of CCl_4 with each of the other two compounds is in agreement with the concept referred to as crossed isodimorphism (shown in figure 3). It means that, in the high-temperature region of the upper loops, the OD R phase
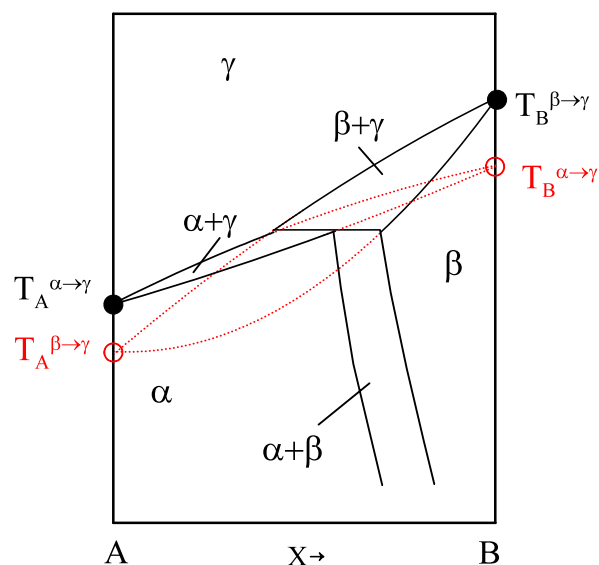

Figure 3. Two-component phase diagram illustrating the concept of crossed isodimorphism. Solid and dashed curves represent stable and metastable behaviour, respectively. Open circles represent the so-called metastable transition points.

is stable for component A (CCl_4) in the A + B two-component system and the OD FCC phase is stable for component B (CBr_2Cl_2 and $CBrCl_3$), R being metastable with respect to the FCC phase. Interestingly, a common characteristic of the two systems is that the metastable extension of the [FCC + L] equilibrium (dashed lines) exists, whereas the other, [R + L], does not. Such behaviour is a consequence of the monotropic behaviour of the FCC melting for a large concentration domain, in such a way that the [FCC + L] metastable equilibrium could be experimentally determined from $X = 0$ (CCl_4) up to the peritectic point for both $CCl_4 + CBr_2Cl_2$ and $CCl_4 + CBrCl_3$ two-component systems.

The concept of crossed isodimorphism has been also applied to the low-temperature equilibria involving the low-temperature monoclinic phase (M).

With the procedure described, the metastable melting or transition points can be determined by simple extrapolation of the two-phase equilibria, as is shown in figure 4. In addition to the melting and transition temperatures, all the enthalpy changes as a function of the concentration were simultaneously determined by means of differential scanning calorimetry (figure 5). These data provide the enthalpy change for the

Table 1. Temperatures and enthalpy and entropy changes associated with the phase transitions of CCl_4, $CBrCl_3$ and CBr_2Cl_2. The stable and metastable transitions are denoted by superscripts (s) and (m), respectively. M refers to the low-temperature monoclinic ($C2/c$) phase and R and FCC for the rhombohedral and face-centred cubic OD phases.

Transition	T (K)	ΔH (kJ mol⁻¹)	ΔS (J mol⁻¹ K⁻¹)	Δv^{RX} ($p = 0.1$ MPa) (cm³ mol⁻¹)	Δv^{HP} ($p = 0.1$ MPa) (cm³ mol⁻¹)	$(dT/dp)^{CC}$ (K MPa⁻¹)	$(dT_c/dp)^{exp}$ (K MPa⁻¹)	Ref.
				CCl_4				
$M^S \to R^S$	227.6	—	—					[15]
	225.35	4.581	20.33					[33]
	225.70(1)	4.631(20)	20.52					[32]
	225.9	4.68	20.72	4.68(37)		0.225	0.205	[34]
$R^S \to L^S$	250.2						0.381	[15]
	250.3	2.515	10.05					[33]
	250.53(1)	2.562	10.23		—			[32]
	250.3	2.52	10.06	5.08(51)		0.505		[34]
$FCC^m \to L^m$	245.8	—	—				0.303	[15]
	246.01(1)	1.830(70)	7.44					[32]
	245.8	1.82	7.42	3.34(41)	—	0.45		[34]
$R^m \to FCC^m$	262.9[b]	0.69[b]	2.64[b]					[34]
	258.0[a]	0.66[a]	2.57[a]					[13]
				$CBrCl_3$				
$M^S \to R^S$	238.1	4.58	19.23	4.31(40)	4.20(55)[a]	0.218	0.217(9)	[14]
	238.19	4.618	19.40					[7]
$R^S \to FCC^S$	260.3	0.52	1.98	1.41(30)	1.41(12)[a]	0.714	0.61(4)	[14]
	259.34	0.527	2.03					[7]
$FCC^S \to L^S$	267.1	2.03	7.61	2.72	2.82(14)[a]	0.357	0.38(1)	[14]
	267.9	2.032	7.59					[7]
$R^m \to L^m$	265.7[a]	2.55[a]	9.58[a]	—	3.65(43)[a]	0.380	0.35(1)	[14]
	265.5[a]	2.55[a]	9.59[a]					[34]
				CBr_2Cl_2				
$M^S \to FCC^S$	258.8	5.22	20.19	6.03(31)	—	0.299(30)	0.320(32)	[17]
	258.8	5.431	21.06					[7]
$M^S \to R^m$	262.0[a]	4.80[a]	18.32[a]	—	4.05(24)[a]	0.221(24)	0.208(5)	[17]
$FCC^S \to L^S$	293.7	2.30	7.82	2.86(13)	2.75(17)[a]	0.365(44)	0.303(20)	[17]
	294.4	2.308	7.89					[7]
$R^m \to FCC^S$	243.6[a]	0.436[a]	1.79[a]	—	1.19(9)[a]	0.666(113)	0.681(32)	[17]
$R^m \to L^m$	280.7[a]	2.36[a]	8.40[a]	—	2.89(35)[a]	0.344(65)	0.380(21)	[17]

[a] Values obtained from the extrapolation of experimental values of two-component systems or pressure–temperature phase diagrams.

[b] Values obtained from fundamental thermodynamics (see text).

stable and experimentally available metastable equilibria. On the basis of equation:

$$\Delta H^{\alpha \to \gamma}(X) = \Delta H^{\alpha \to \beta}(X) + \Delta H^{\beta \to \gamma}(X) \qquad (1)$$

which assumes that the contribution of the specific heats for the enthalpy changes can be neglected, the enthalpy change for the non-experimentally available transitions can be also obtained. Inspection of figure 5 immediately leads to the conclusion that the data for the three systems are mutually consistent and enable us to get coherent enthalpy changes for the virtual metastable melting or transition points corresponding to the pure compounds. In particular, it is to be noticed that the enthalpy changes for the metastable transitions of CBr_2Cl_2 extrapolated from two independent two-component phase diagrams nicely converge at the same values [12].

All the thermodynamic melting and transition numerical data at normal pressure (both for stable and metastable points) have been assembled in table 1.

With the data obtained we have performed a coherent and unifying thermodynamic assessment of the involved equilibria for the ensemble of the two-component systems by means of the so-called EGC method or Oonk method [23, 35].

Details concerning the thermodynamic formalism of the Oonk method used to perform the thermodynamic assessment of the two-component systems have been described in detail elsewhere [35]. Here we only recall the calculated two-phase equilibria for those systems giving rise to the extrapolated melting or transition points by means of the dotted red lines in figure 4.

The isostructural relationship between the low-temperature monoclinic phases of the halogenomethane compounds $CBr_{4-n}Cl_n$ ($n = 0, \ldots, 4$) has been analysed before and the continuous formation of mixed crystals was clearly demonstrated for the whole composition range [31]. It then follows that such phases are also isomorphous, so as for the thermodynamic assessment, only one Gibbs function is needed. In addition, it has been demonstrated that the fractional occupancy of the halogen atoms fully controls the lattice dimensions, inde-
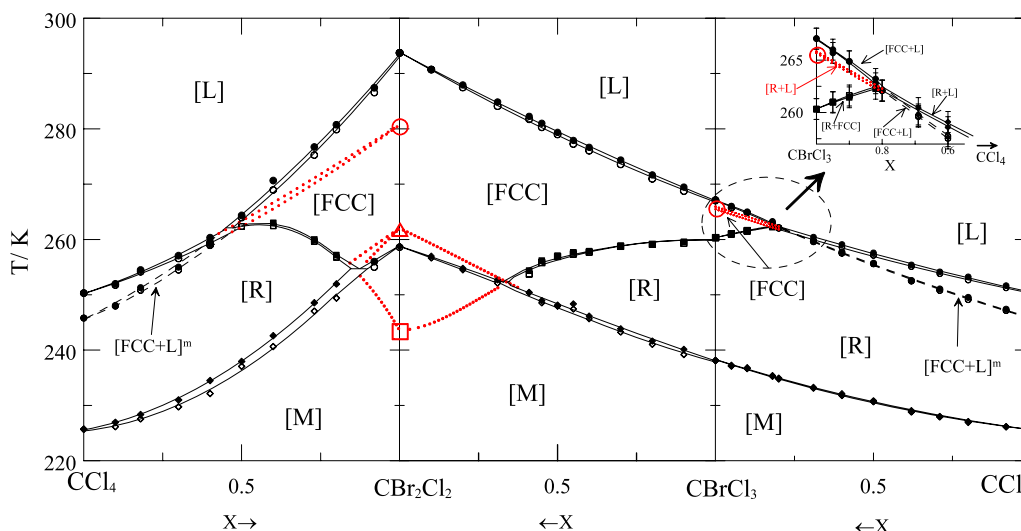
Figure 4. Experimental two-component phase diagrams sharing halogenomethane compounds. Continuous lines are for the stable two-phase equilibria, dashed lines are the experimental metastable [FCC + L]^m equilibria and dotted red lines are for the extrapolated equilibria from the thermodynamic assessment. Melting or transition metastable points for pure components CBr$_2$Cl$_2$ and CBrCl$_3$ are denoted by red circles (R–L), triangle (M–R) and square (R–FCC).
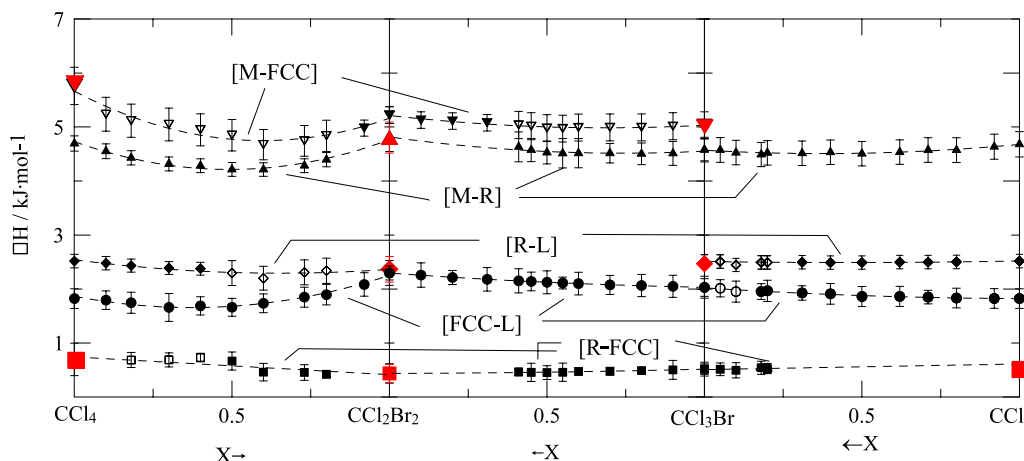

Figure 5. Experimental enthalpies (full symbols) monoclinic to R or to FCC (triangles), for the melting of R (diamonds) and the melting of FCC (circles) and R to FCC transition (squares) as a function of the concentration. Empty symbols are obtained by equation (1). Red symbols correspond to the values obtained by extrapolation or by equation (1).

pendently of the dipole–dipole or dipole–induced dipole interactions that can appear as a function of the halogen composition [31].

As for the OD phases, the symmetry differences between the R and FCC lattices imply the existence of a demixing region when they are involved. This is the case for the two-component diagrams considered in this work. The existence of continuous mixed crystals for the whole concentration range implies the establishment of an isomorphism relationship, as is the case for the R mixed crystals between CCl$_4$ and CBrCl$_3$ compounds [34]. It implies that any physical parameter (as lattice parameters) should evolve continuously with the mole fraction. Figure 6 displays, as an example, the continuous variation of the R lattice parameters over the whole concentration range at 243.2 K. As far as the metastable (at normal pressure) R phase of CBr$_2$Cl$_2$ is concerned, the

crystallographic properties can be revealed by means of the analysis of R mixed crystals as a function of composition. Figure 6 shows the variation of the R lattice parameters, a^R and α^R as a function of the concentration at 243.2 K for the CCl$_4$ + CBr$_2$Cl$_2$ system [12]. By assuming the existence of a metastable R phase for the CBr$_2$Cl$_2$ compound, it can be inferred that a 'virtual' continuous series of mixed crystals in the R phase would give rise to an isomorphism relationship and, thus, the lattice parameters for such a metastable phase at normal pressure can be inferred quite accurately. Following the same procedure at different temperatures, as well as for several mixed crystals with molar fractions distributed along the possible concentration range, the inference of a set of lattice parameters, and thus volume values, for the metastable phases becomes feasible.
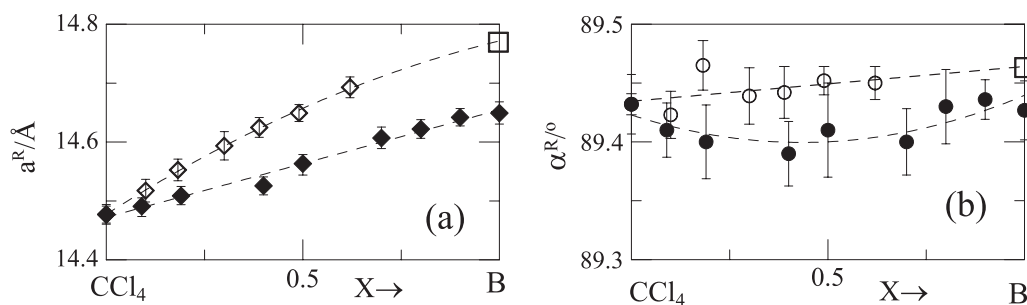
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Figure 6. Rhombohedral lattice parameters (a^R (a) and α^R (b)) as a function of the concentration for the systems $CCl_4 + B$, $B = CBrCl_3$ (full symbols) [34] and $B = CBr_2Cl_2$ (empty symbols) [12] at 243.2 K. Squares correspond to the extrapolated rhombohedral lattice parameters for CBr_2Cl_2 at 243.2 K.
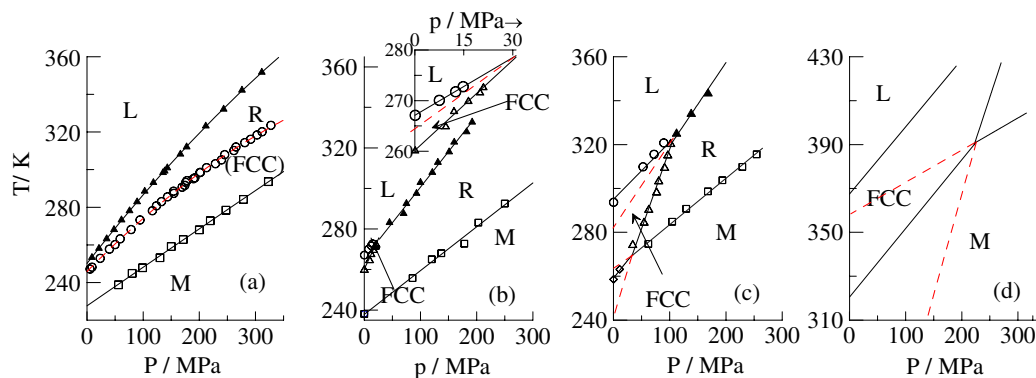

Figure 7. Experimental pressure–temperature phase diagrams for the compounds (a) CCl_4 (courtesy of Dr Maruyama) [15], (b) $CBrCl_3$ [14], (c) CBr_2Cl_2 [17] and (d) the schema for that of CBr_4 according to Bridgmann [42]. The inset corresponds to a magnification of the low-pressure domain of the p–T phase diagram involving the R, FCC and L phases for $CBrCl_3$. Red lines correspond to the extrapolation of the two-phase equilibria at normal pressure, in order to obtain the transition or melting temperatures to be compared with those obtained from the assessment of the two-component phase diagrams at normal pressure (see table 1) and to the metastable FCC + L equilibrium for CCl_4.

4. Topological and experimental pressure–temperature phase diagrams

The experimental information from the two-component phase diagrams at normal pressure, i.e. in equilibrium with the vapour phases, together with that obtained from the thermodynamic assessment, which in turns confirms thermodynamic coherence of the data, can be used to build up the topological pressure–temperature phase diagrams. For such a construction only general rules on the basis of fundamental thermodynamics must be considered [36–38], and the most important concerns that each triple point is the crossing point of three two-phase equilibrium curves, in such a way that their metastable extensions alternate with their more stable counterparts.

CCl_4 has been widely studied by many experimental methods [9, 15, 32–34]. Although the pressure–temperature phase diagram was published early [39–41], it has been revisited recently [15]. In addition, many two-component systems sharing CCl_4 have been published to date and a common characteristic of all of them is that the metastable extension of the [FCC + L] equilibrium exists (as for the $CCl_4 + CBr_2Cl_2$ system depicted in figure 4), confirming that the monotropy of the FCC phase with respect to the R phase behaves similarly when molecularly mixed crystals are formed [12, 13, 20–22, 24, 34]. There are enough data obtained

for the two-component systems to build up the topological phase diagram. It appears that, due to the overall monotropy of the FCC phase, the [R + FCC + L] triple point is located in the negative pressure domain and thus the pressure–temperature phase diagram must definitely correspond to that depicted in figure 2(a) or, in other words, the schema depicted in figure 1(a) holds irrespective of the pressure. Figure 7(a) shows the experimental pressure–temperature phase diagram recently reported [15] and is virtually identical to that topologically constructed.

As far as the $CBrCl_3$ compound is concerned, a simple inspection of figure 4 shows that transition or melting temperatures, from or to the stable or metastable phases, are ordered as $T^{FCC-L} > T^{R-L} > T^{R-FCC} > T^{M-R}$. The R to L being, in this case, a metastable melting point at normal pressure. The value of T^{R-L} ($p = 0.1$ MPa) for $CBrCl_3$ is the temperature at which the R phase would melt if the FCC phase did not exist (see $T_B^{\beta-L}$ in figure 1(b)). As can be easily seen, the order of the temperatures at normal pressure corresponds to the pressure–temperature phase diagram sketched in figure 2(b). The assigned topology can be confirmed by calculation of the two-phase coexistence lines (using the Clausius–Clapeyron equation and the values listed in table 1) and comparing the results to those obtained from the pressure–temperature phase diagram (figure 7(b))
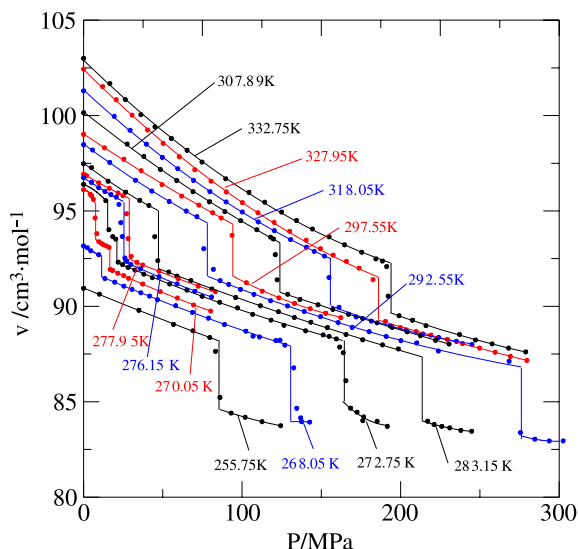
Figure 8. Molar volume as a function of pressure for several isotherms for CBrCl$_3$ [34].

Figure 9. Molar volume as a function of temperature at normal pressure for CBr$_2$Cl$_2$ obtained by means of x-ray (open symbols) and neutron (full symbols) diffraction [17]. The inset panel depicts the values of the normal-pressure molar volumes of the high-pressure rhombohedral phase obtained by extrapolation at $p = 0.1$ MPa from the isotherms measured as a function of pressure, while the red point corresponds to the volume obtained from extrapolation as a function of molar fraction for the CCl$_4$ + CBr$_2$Cl$_2$ two-component system at 243.2 K (see figure 6).

deduced from the experimental pressure–volume–temperature diagram (figure 8).

As for the CBr$_2$Cl$_2$ compound it can be seen from the two-component systems depicted in figure 4, that the order of the phase transition temperatures is $T^{\text{FCC–L}} > T^{\text{R–L}} > T^{\text{M–R}} > T^{\text{M–FCC}} > T^{\text{R–FCC}}$. Such an order topologically matches that shown in figure 2(c). The experimental pressure–temperature phase diagram shown in figure 7(c) agrees perfectly with the topological one, and values collected in table 1 demonstrate the agreement. It should be pointed out that the case of CBr$_2$Cl$_2$ is definitely different from that of CBrCl$_3$ because the OD R phase does not make a 'real' physical appearance at normal pressure. Figure 9 shows the molar volumes of the M, FCC and L phases at normal pressure for CBr$_2$Cl$_2$. As an inset, the extrapolated molar volume at normal pressure for the high-pressure OD R phase for each measured isotherm is shown as a function of temperature. It is clearly seen that the value obtained from the analysis of the variation of the lattice parameters as a function of the mole fraction at 243.2 K (see empty symbols in figure 6) lies on the curve obtained by fitting of molar volumes as a function of temperature obtained from the extrapolation at normal pressure. This validates the data and by extension the method.

Thus, detailed data and coherent thermodynamic analyses of two-component systems can provide much more information than that typically obtained (as excess properties of the mixed crystals). In particular, for the pure components taking part in the two-component system. This topological method, based on fundamental thermodynamics can also be used to get information about the intermediate phases appearing in two-component systems, as has been shown in some n-alkane systems [43, 44]. Moreover, topology and isodimorphism relationships provide information about the nature of the high-pressure phases even when they do not exist at normal pressure. As an example we have shown the existence of an OD high-pressure *rhombohedral* phase for the halogenomethane CBr$_2$Cl$_2$.
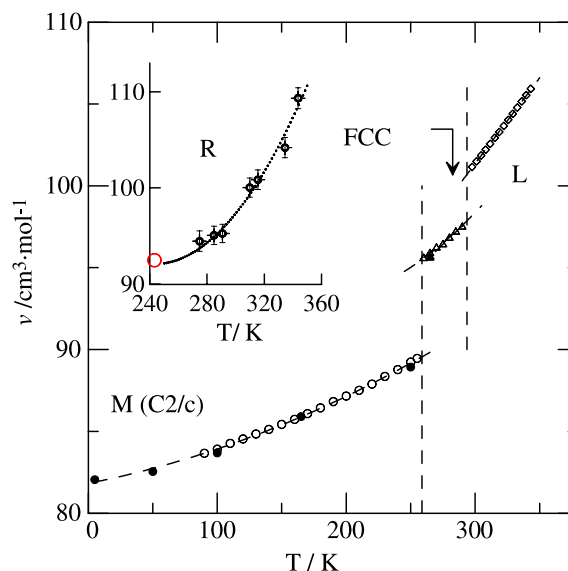
To conclude this section we would like to point out the existence of a high-pressure phase for CBr$_4$ as determined by Bridgmann long ago (figure 7(d)). Although the symmetry of such a phase has not yet been determined, the studies we are carrying out on two-component systems formed from members of the series of halogenomethane compounds (CBr$_{4-n}$Cl$_n$, $n = 0, \ldots, 4$), together with the establishment of the p versus T phase diagram, will elucidate whether such a phase corresponds to a rhombohedral phase which exists for the other members of the series at normal pressure (CCl$_4$ and CBrCl$_3$) or at high but moderated pressure (CBr$_2$Cl$_2$). This would avoid the extreme densification conditions which lead to dramatic changes in the chemical and physical properties.

5. Conclusions

The halogenomethane compounds, in spite of their simple molecular structure, exhibit a number of solid–solid phase transitions. In particular, their globular molecular shape induces, for all the members of the series, high-temperature or high-pressure orientationally disordered (OD) or plastic phases, mainly due to the freedom for reorientational processes. The small changes in the molecular size or symmetry (T_d for CCl$_4$ and CBr$_4$, C$_{3v}$ for CBrCl$_3$ and C$_{2v}$ for CBr$_2$Cl$_2$) induced by changing one of the halogen atoms, produces a fine-tuning in the stability of the different phases.

The polymorphism of CBrCl$_3$ and CBr$_2$Cl$_2$ has been studied by several experimental methods, many of them concerning physical properties at normal pressure. This restriction prevents a unified description of the overall

polymorphic behaviour of the halogenomethane series. By means of a careful analysis in the pressure–temperature space, the polymorphic behaviour of all the members of the series acquire a physical global coherence, and stresses that the pressure is as relevant a parameter as the temperature, in spite of the experimental limitations that pressure imposes. In this paper we clearly point out that crucial missing information of the pressure–temperature phase behaviour can be obtained, even at normal pressure, by means of a careful experimental analysis and detailed thermodynamic assessment of two-component systems determined at normal pressure (i.e., for condensed phases in equilibrium with the vapour phase).

Acknowledgments

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