

# Phase Diagrams of Crystalline Adducts Containing Two Volatile Components

MARIO FARINA

*Dipartimento di Chimica Organica e Industriale, Università di Milano, via Venezian 21, I-20133 Milano, Italy.*

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**Abstract.** The phase relationships in binary systems forming a crystalline addition compound are obtained by means of classical thermodynamic arguments for the case in which both components are volatile. This approach can be applied to inclusion compounds and to other low-stability addition compounds existing only in the solid phase. The results are consistent with those already known for clathrates containing a volatile guest and a non-volatile host, and for symmetric systems, such as racemic compounds. The temperature range in which the adduct undergoes a congruent sublimation depends on the ratio of the vapor pressures of the two components. A relation has been found to exist between the properties of the pure components, the melting behavior and the enthalpy of formation of the adduct.

**Key words.** Phase diagrams, solid-liquid equilibria, solid-vapor equilibria, congruent and incongruent vaporization of binary adducts, addition compounds, clathrates, inclusion compounds.

## 1. Introduction

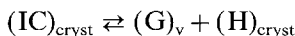
Over the last fifteen years this laboratory has devoted a lot of attention to the theoretical and experimental analysis of the phase diagrams of two-component systems forming crystalline adducts. Two classes of compounds were investigated: clathrates and racemic compounds. In both cases the analysis was extended to the equilibria involving the vapor phase.

The first system taken into consideration was the binary system perhydrotriphenylene (PHTP)/*n*-heptane [1]. PHTP is a very versatile host for the formation of channel-like inclusion compounds with many organic guests of different shape, dimension and chemical constitution [2, 3]: in the case of *n*-heptane the inclusion compound congruently melts at about 120°C, a few degrees lower than the pure host. The analysis of the liquidus curve was carried out on the basis of the Prigogine-Defay equation [4], extended by Haase [5] to binary compounds with a stoichiometric ratio other than 1 ( $AB_n$ ). This approach was applied to a wide series of hydrocarbon guests and to other small molecules of spherical shape [3], and, in a slightly modified form, to the inclusion compound between PHTP and polyethylene [6].

We have shown that the reduced stability of clathrates observed when the chemical constitutions of guest and host differ strongly (in particular when strongly electronegative atoms such as oxygen or fluorine are present in one of the two components), can be accounted for with the same equation provided an interaction parameter – related to the theory of regular solutions – is introduced into the

equation [7]. For a better quantitative agreement between theory and experiment the Margules equations expanded to the cubic term were sometimes used [8].

When one of the two components (usually the guest) is volatile, several mono-variant equilibria involving the vapor phase should be considered: (a) vapor–liquid–solid guest; (b) vapor–solid guest–solid clathrate; (c) vapor–liquid–solid clathrate; (d) vapor–solid clathrate–solid host; (e) vapor–liquid–solid host. Equilibria (c) and (d) deserve special attention: (c) describes the vapor pressure of the saturated solutions in equilibrium with the crystalline adduct, and (d) the vapor pressure of the guest included in the host lattice (in the absence of liquid) [1, 3]. Curve (d) intersects curves (c) and (e) in a quadruple (eutectic or peritectic) point where four phases are present: vapor, liquid, solid clathrate and solid host (a second quadruple point exists in the presence of vapor, liquid, solid clathrate and solid guest, but for most common guests it is located at very low temperature and is generally neglected). From the slope of curve (d) the decomposition enthalpy of the inclusion compound, according to the equation:



was obtained. The inclusion enthalpy related to the reaction:



is calculated by subtracting the preceding value from the vaporization enthalpy of the pure liquid guest [1, 3].

A knowledge of the P–T–x phase diagrams is essential for a correct understanding of the stability and for the prediction of reactivity of the inclusion compounds. An example of the strict connection between these factors can be found in several papers dealing with the polymerization of unsaturated monomers included in PHTP [9–12].

More recently we devoted our attention to binary systems composed of two volatile enantiomers [13, 14]. We described the P–T, T–x and P–x diagrams both when the racemic mixture crystallizes as a conglomerate and as a racemic compound. In spite of the tremendous amount of work carried out on the liquid–solid equilibria (with or without the presence of a solvent) [15], very little is known about the sublimation equilibria of these compounds.

In this article we present the equations which govern the phase equilibria of systems where two volatile, ideally miscible components form an  $\text{AB}_n$  crystalline adduct. It will be shown that in particular cases these equations reduce to those already known. A detailed but only qualitative description of analogous systems was reported by Ricci in 1951 [16]. Later on a considerable amount of work was done on the phase diagrams of intermetallic compounds, especially those containing III–V or II–VI group elements [17–20]. As for the inclusion compounds, a large number of papers can be found, but they generally deal with very specific aspects of their phase diagrams and concern systems where the host and guest are mutually immiscible [21–27]. A discussion in classical terms of the vapor–liquid–solid phase diagrams of crystalline adducts formed by two components having a comparable vapor pressure is not readily available, although some material exists in several reviews and conference proceedings [22, 27, 28].

### 2. The Phase Equilibrium Equations

The condensed phase T-x diagram of a two-component system forming a crystalline adduct C (=AB<sub>n</sub>) is reported in Figure 1. This diagram is obtained from Equations (1-3) on the basis of some simple assumptions: complete lack of miscibility of the solid phases, absence of solid metastable phases, instability of the AB<sub>n</sub> adduct in the liquid phase, ideal behavior of the liquid phase, and constancy with temperature of all the transition enthalpies. In particular when dealing with inclusion compounds we assume that the empty host structure is unstable.

$$\text{Curve A-E}_1: \ln x_A = \ln(1-x) = -(L_A/T) + A \tag{1}$$

$$\text{Curve E}_2\text{-B: } \ln x_B = \ln x = -(L_B/T) + B \tag{2}$$

$$\text{Curve E}_1\text{-E}_2: \ln(x_A x_B^n) = \ln(1-x) + n \ln x = -(L_C/T) + C \tag{3}$$

where  $x = x_B$ ,  $A = L_A/T_A$ ,  $B = L_B/T_B$ ,  $C = (L_C/T_C) + n \ln n - (n+1) \ln(n+1)$ .  $T_A$ ,  $T_B$  and  $T_C$  are the melting points of compounds A, B and AB<sub>n</sub>, respectively; AB<sub>n</sub> is considered to be formed of a single molecule. For the sake of simplicity all

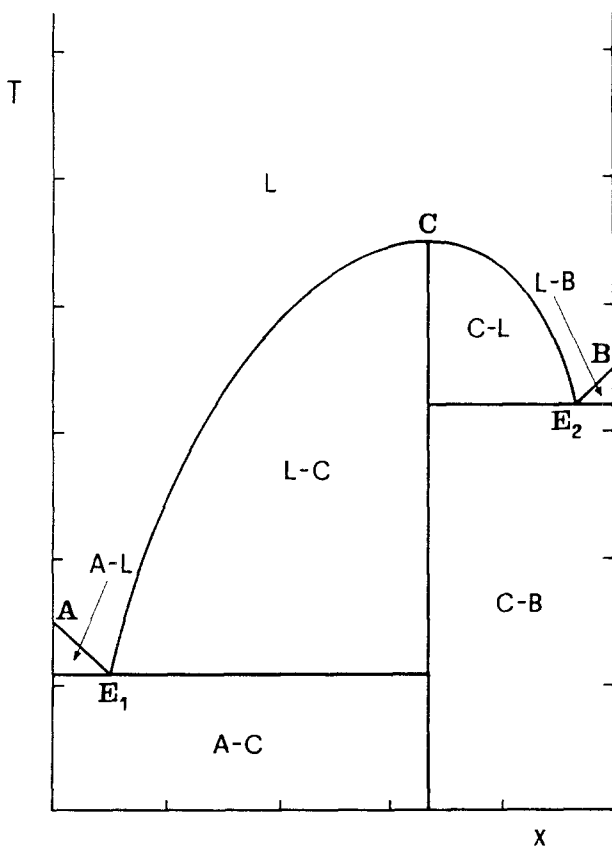


Fig. 1. Calculated condensed phase T-x diagram of a hypothetical AB<sub>2</sub> adduct.  $T_A = 360$  K,  $T_B = 400$  K,  $T_C = 420$  K,  $L_A = 1620$  K,  $L_B = 2000$  K,  $L_C = 6000$  K.

the melting and decomposition enthalpies are written as:  $L_i = \Delta H_i/R$  and expressed in Kelvins. The logarithmic terms in the expression of C derive from the rearrangement of the original Haase equation:

$$\ln(x_A/x_{oA}) + n \ln(x_B/x_{oB}) = -(\Delta H_C/R)(1/T - 1/T_C) \tag{4}$$

noting that  $x_{oA} = 1/(n + 1)$  and  $x_{oB} = n/(n + 1)$ .

The vapor pressure of pure liquid components A and B is expressed in its simplest form by the integrated Clausius–Clapeyron equation. Referring to Figure 2, we have:

$$\text{Curve A-A': } \ln P_{AL} = -(V_A/T) + A' \tag{5}$$

$$\text{Curve B-B': } \ln P_{BL} = -(V_B/T) + B' \tag{6}$$

where  $V_A (= \Delta H_{vA}/R)$  and  $V_B (= \Delta H_{vB}/R)$  are in Kelvins and  $A'$  and  $B'$  are numeric constants.

Neglecting the difference in specific heat between the various phases, we can write for solid A and B:

$$\text{Curve A''-A: } \ln P_{AS} = -((L_A + V_A)/T) + A + A' \tag{7}$$

$$\text{Curve B''-B: } \ln P_{BS} = -((L_B + V_B)/T) + B + B' \tag{8}$$

Under the hypothesis of ideal behavior the vapor pressure of any liquid mixture is given by:

$$P = x_A P_{AL} + x_B P_{BL} = (1 - x)P_{AL} + xP_{BL} = P_{AL} + x(P_{BL} - P_{AL}) \tag{9}$$

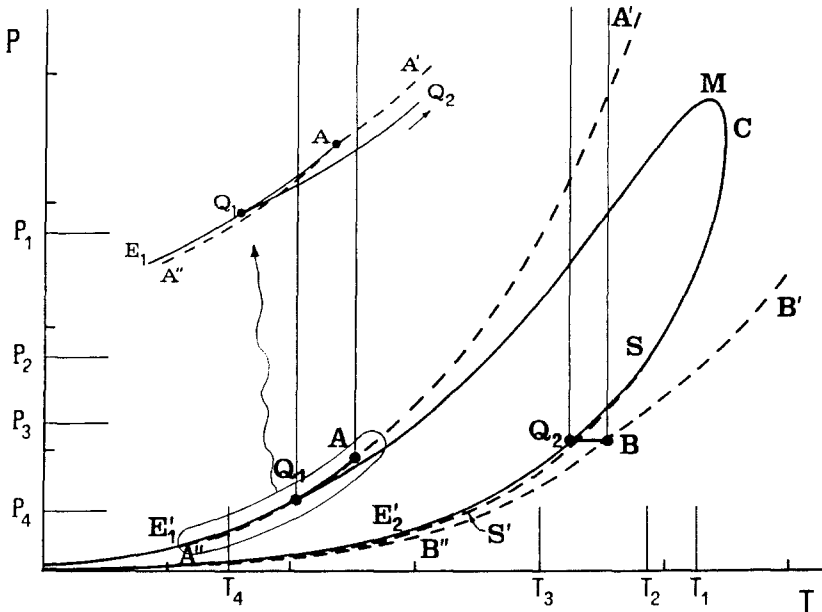


Fig. 2. P–T projection of the solid–liquid–vapor phase diagram of the  $AB_2$  adduct.  $V_A = 5000$  K,  $A' = 20.5$ ,  $V_B = 4700$  K,  $B' = 18.5$ , other parameters as in Fig. 1.

Introducing in (9) the values of  $x$  and  $1 - x$  calculated at a given temperature according to Equations (1-3), we obtain the vapor pressure of the saturated solutions in equilibrium with solid A, B and C, respectively (curves A-Q<sub>1</sub>, Q<sub>2</sub>-B and Q<sub>1</sub>-Q<sub>2</sub>).

As for the solid-vapor equilibria, we can distinguish several cases. When the components A and B do not form an addition compound and are not soluble in each other, the total pressure is the sum of that of the pure solids:

$$P = P_{AS} + P_{BS} \quad (10)$$

For a pure AB<sub>n</sub> adduct which undergoes a congruent vaporization:

$$P = P_{AC} + P_{BC} \quad (11)$$

For solid mixtures containing the adduct and an excess of either A or B crystals, we have:

$$\text{Curve } E'_1\text{-Q}_1 \text{ (AB}_n \text{ + A crystals): } P = P_{AS} + P_{BC} \quad (12)$$

$$\text{Curve } E'_2\text{-Q}_2 \text{ (AB}_n \text{ + B crystals): } P = P_{AC} + P_{BS} \quad (13)$$

$P_{AC}$  and  $P_{BC}$  are the partial pressures of A and B in equilibrium with the crystalline adduct. For the pure adduct (Equation 11) they are related to each other through the equilibrium constant  $K$ , whose value is obtained by combining Equations (3), (5) and (6):

$$K = P_{AC}P_{BC}^n = (1 - x)x^n P_{AL} P_{BL}^n \quad (14)$$

$$\ln K = -((L_C + V_A + nV_B)/T) + C + A' + nB' \quad (15)$$

When the adduct shows a congruent evaporation, the composition of the vapor phase corresponds to that of the crystals ( $x_v = n/(n + 1)$ ). By writing  $P_{AC} = P/(n + 1)$  and  $P_{BC} = Pn/(n + 1)$  we obtain:

$$\ln K = \ln P_{AC} + n \ln P_{BC} = (n + 1) \ln P + n \ln n - (n + 1) \ln(n + 1) \quad (16)$$

By comparing Equations (16) and (15) and taking into account the meaning of  $C$ , the relation between sublimation pressure and temperature for the pure adduct is:

$$\ln P = -(((L_C + V_A + nV_B)/T) + ((L_C/T_C) + A' + nB'))/(n + 1) \quad (17)$$

The corresponding curve is shown in Figure 2 (curve S'-S).

For generic mixtures of AB<sub>n</sub> and A or B crystals we should refer to Equations (12) and (13). Along the curve E'<sub>1</sub>-Q<sub>1</sub> we are in the presence of the pure crystalline component A having vapor pressure  $P_{AS}$ . As a consequence:

$$P_{BC} = (K/P_{AS})^{1/n} = \exp(-(((L_C - L_A)/n) + V_B)/T + ((C - A)/n) + B') \quad (18)$$

In the same way, along E'<sub>2</sub>-Q<sub>2</sub>:

$$P_{AC} = K/(P_{BS})^n = \exp(-((L_C + V_A - nL_B)/T) + C + A' - nB) \quad (19)$$

The above reported equations describe the monovariant equilibria existing in the P-T projection phase diagram shown in Figure 2 (the vertical lines correspond to the phase equilibria not involving the gas phase). The triple points of pure

components are indicated as A and B. Two quadruple points  $Q_1$  and  $Q_2$  exist, practically coincident with points  $E_1$  and  $E_2$  of Figure 1, where two solid phases, liquid and vapor, coexist: it should be noted that, as already observed by Ricci [16],  $Q_1$  is located above the vapor pressure curves of the pure components. M is the maximum pressure point and C the maximum temperature point, in practice coincident with point C of Figure 1.

In order to obtain a complete description of the phase equilibria further equations concerning the composition of the vapor phase ( $x_v$ ) should be taken into account. From Equations (7), (8), (9), (11), (14) and (15) the following relationships are obtained:

Vapor phase in equilibrium with the liquid:

$$x_v = xP_{BL}/P = xP_{BL}/(P_{AL} + x(P_{BL} - P_{AL})) \quad (20)$$

Vapor phase in equilibrium with solid A:

$$x_v = 1 - (P_{AS}/P) = 1 - (\exp(-(L_A + V_A)/T) + A + A')/P \quad (21)$$

Vapor phase in equilibrium with solid B:

$$x_v = P_{BS}/P = \exp(-(L_B + V_B)/T) + B + B')/P \quad (22)$$

Vapor phase in equilibrium with the crystalline  $AB_n$  adduct:

$$(1 - x_v)x_v^n = P_{AC}(P_{BC})^n/(P)^{n+1} = K/(P)^{n+1} \quad (23)$$

where  $K$  and  $P$  depend on  $T$  and ultimately on  $x$ .

Alternatively, the composition of a hypothetical liquid phase is calculated through Equations (1–3) and then converted into the vapor composition by using Equations (9) or (20).

Figure 3 represents the  $P$ – $x$  projection of the same system described in Figure 2. The two lines correspond to the liquid and vapor compositions in equilibrium with the solid phases. At point S the gas phase has composition  $x_v = n/(n + 1)$ , coincident with that of the pure  $AB_n$  adduct. Its meaning will be discussed in the following section.

### 3. Isobaric and Isothermal Diagrams

Some typical  $T$ – $x$  isobaric diagrams are reported in Figure 4. They refer to the same system used for calculating the  $P$ – $T$  projection shown in Figure 2. Referring to this figure, when the pressure exceeds that of point M, no interaction exists between the vapor and the solid phase. As a consequence, the condensed phase diagram reported in Figure 1 is representative of such a situation. Figure 4a shows the  $T$ – $x$  diagram for a value of pressure intermediate between M and S: an incongruent sublimation of the adduct is observed, with the formation of a vapor phase richer in A and a liquid richer in B. When the pressure is lower than that of point S the  $V$ – $C$  equilibrium curve shows a maximum at a composition corresponding to that of the pure addition compound (Figure 4c), indicating the presence of a congruent sublimation point. Point S therefore represents the ceiling point for the congruent sublimation of the adduct. The temperature and pressure of this point

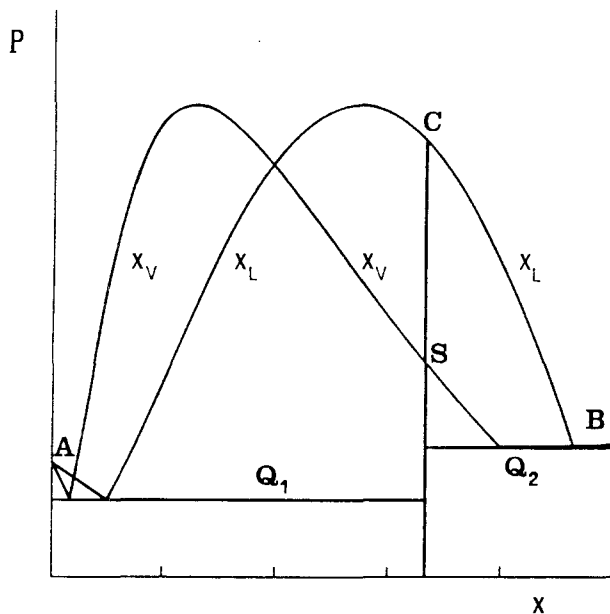


Fig. 3. P-x projection of the same  $AB_2$  adduct described in Figures 1 and 2.

correspond to those at which the intersection of the vaporus curve of the V-L equilibrium (Equation 20) with the C-V equilibrium (Equation 23) occurs at  $x_v = n/(n + 1)$  (Figures 3 and 4b). Below point S the vapor pressure of the pure adduct follows Equation (17).

Comparison of Figures 4a, b and c shows a continuous decrease of the region at which the liquid phase can exist. When the pressure is low enough (Figure 4d) the liquid disappears and the only phases to be considered are the three solid compounds (A, B and  $AB_n$ ) and vapor.

Similar remarks can be made for the isothermal P-x diagrams. At a temperature higher than  $T_C$  the only equilibrium to be considered concerns vapor and liquid. By decreasing temperature we observe the incongruent vaporization of solid  $AB_n$  in Figure 5a, the ceiling temperature for congruent sublimation in Figure 5b, the congruent sublimation of the adduct in Figure 5c. In all cases the liquid phase is present in the high-pressure region. The boundary lines for liquid-solid equilibria are drawn as vertical lines, thus neglecting the influence of pressure on such equilibria. This approximation can be accepted in view of the small value of  $dT/dP$  and the limited range of pressure taken into consideration in the present study. Finally, at temperatures lower than  $Q_1$  the liquid disappears and the diagram shows the presence of solid and vapor phases only (Figure 5d).

#### 4. Discussion

The phase diagrams of several hypothetical  $AB_n$  compounds were calculated using Equations (1-23), introducing the appropriate numerical values for the different cases. Any variation in the vapor pressure of one of the components, e.g. that of B,

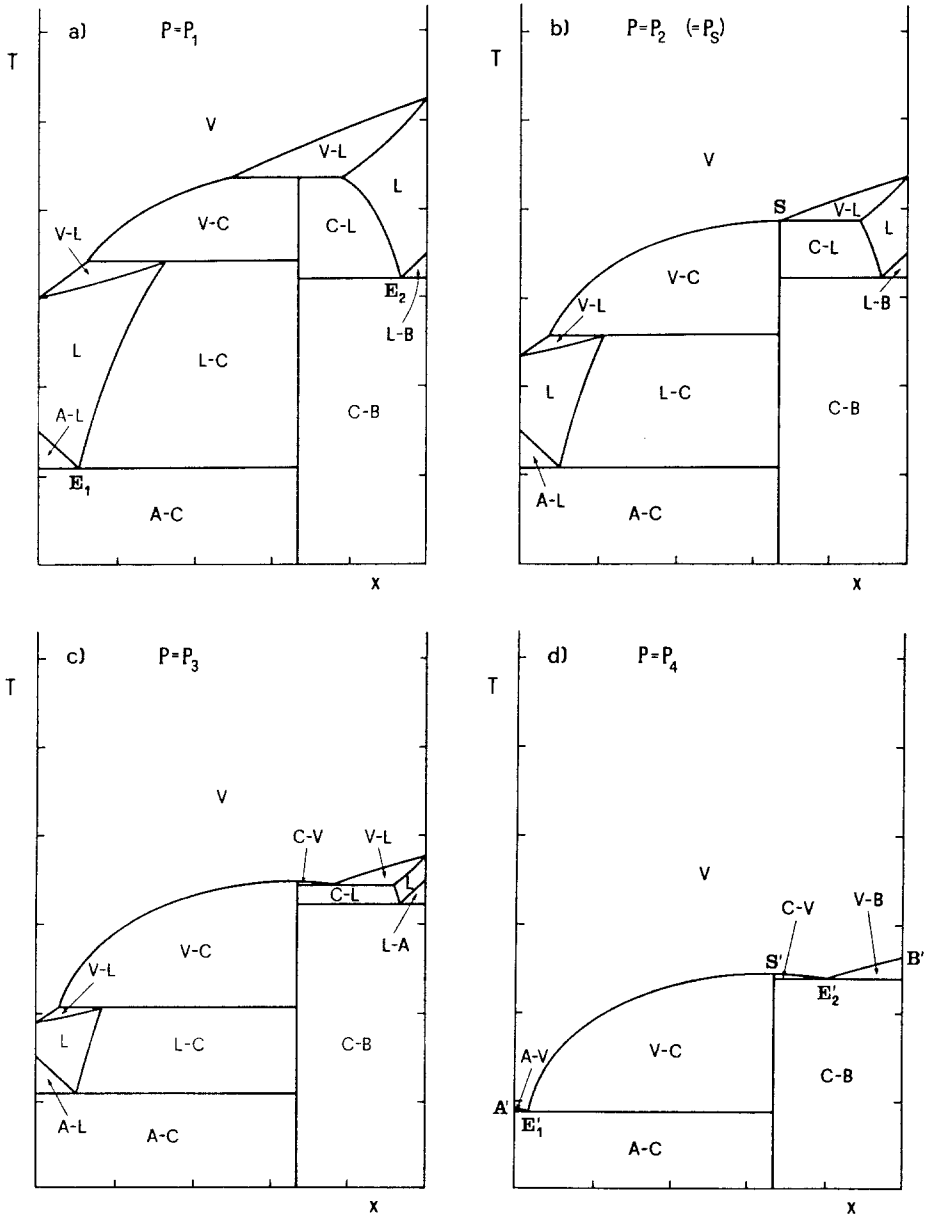


Fig. 4. Isobaric sections of the solid-liquid-vapor phase diagram of the AB<sub>2</sub> adduct. The corresponding pressures are indicated in Fig. 2.

considerably affects some features of the diagram. For instance, provided that  $P_B$  is lower than  $P_A$ , point S shifts upward if  $P_B$  increases and downward in the opposite case. When  $P_B$  equals  $P_A$  the adduct undergoes a congruent sublimation at any temperature and S coincides with C. By successively decreasing  $P_B$ , S can move below  $Q_2$ . In the last instance S corresponds to the intersection point of curves V-B



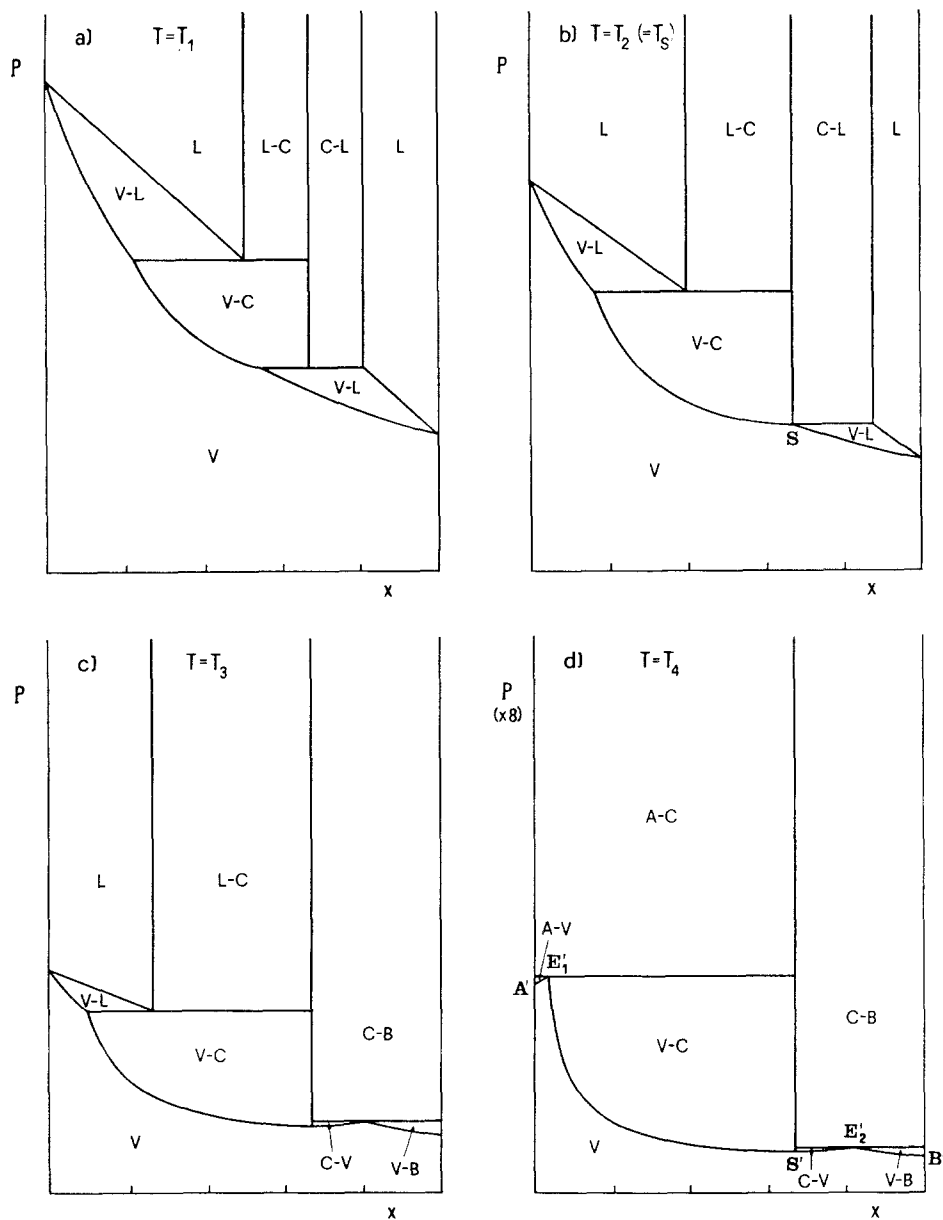


Fig. 5. Isothermal sections of the solid-liquid-vapor phase diagram of the  $AB_2$  adduct. The corresponding temperatures are indicated in Fig. 2.

(Equation 22) and C-V (Equation 23) when the vapor composition equals that of the crystalline adduct ( $x_v = n/(n + 1)$ ). In other words, the sublimation curve of the adduct intersects the  $E_2-Q_2$  curve at S.

In this respect crystalline racemic compounds and the majority of the known inclusion compounds represent two extreme cases: in the former, due to symmetry

reasons,  $P_A$  equals  $P_B$  at any temperature ( $P_D = P_L$ ) and the crystalline DL compound has a definite sublimation pressure in the entire range of existence of the solid phase [14]. In the latter the vapor pressure of the host (B) is generally negligible with respect to the guest (A) and the clathrate cannot show a congruent sublimation. For intermediate cases the location of point S depends on the  $P_A/P_B$  ratio; the more this ratio differs from 1, the lower is the ceiling temperature for the congruent sublimation. The seemingly indefinite behavior of addition compounds was recognized long ago in the field of binary semiconductors [20] and the so called three-temperature technology was developed for the production of such materials in the case of incongruently evaporating systems [29].

Equations (18) and (19) show the connections existing between the thermodynamic parameters of the various phase transitions. From (19) Equation 24 is obtained:

$$E_A = L_C + V_A - nL_B \quad \text{and} \quad A'' = C + A' - nB \quad (24)$$

From (18):

$$E_B = ((L_C - L_A)/n) + V_B \quad \text{and} \quad B'' = ((C - A)/n) + B' \quad (25)$$

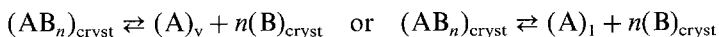
By subtracting the terms related to the vapor phase, Equations (24) and (25) transform into:

$$D_A = E_A - V_B = L_C - nL_B \quad \text{and} \quad A^* = A'' - A' = C - nB \quad (26)$$

and

$$D_B = E_B - V_A = (L_C - L_A)/n \quad \text{and} \quad B^* = B'' - B' = (C - A)/n \quad (27)$$

$E_A$  and  $A''$  on one side, as well as  $D_A$  and  $A^*$  on the other, are the enthalpic and entropic factors of the decomposition reaction of the adduct into solid and vapor, or solid and liquid respectively:



$E_B$ ,  $B''$ ,  $D_B$  and  $B^*$  are defined in an analogous way. For clathrates,  $-E_A$  and  $-D_A$  represent the enthalpy of inclusion referred to one mole of guest in the vapor or liquid state respectively.

$D_A$ ,  $D_B$  and the related entropic factors can be obtained in two independent ways: from vapor pressure measurements or from calorimetric or thermometric experiments on the condensed phases. According to Equation (13), the evaluation of  $D_A$  from vapor pressure experiments requires two series of measurements, one concerning pure B (curve B'-B), the other a mixture of B and  $AB_n$  (curve  $E_2-Q_2$ ). The experimental procedure is greatly simplified when  $P_B$  is negligible. Under such a condition, along  $E_2-Q_2$   $P$  coincides with  $P_{AC}$ : as a consequence  $E_A$ , and hence  $D_A$ , can be obtained directly from the slope of the curve.

It should be stressed that the formation of a crystalline addition compound or a clathrate does not necessarily imply an enthalpic stabilization. As already pointed out for racemic compounds [15], and confirmed in the case of PHTP inclusion compounds [3], the formation of an  $AB_n$  adduct can occur even when  $D_A$  is zero or slightly negative. The driving force in this case is entropic in nature. At the molecular scale in the case of PHTP/cyclohexane and PHTP/dioxane this entropic stabilization was attributed to the orientation disorder of the nearly spherical guest molecules inside the channels [3].

From an experimental point of view very little is known about  $AB_n$  adducts containing two components with comparable volatility. This fact arises both from the difficulty of finding suitable systems and of measuring very low vapor pressures. In the field of inclusion compounds we believe that useful information could derive from the study of the system formed by PHTP (a saturated  $C_{18}H_{30}$  hydrocarbon) and a linear hydrocarbon guest chosen in the range between  $C_{16}$  and  $C_{24}$ .

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