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THERMODYNAMICS AND PHASE DIAGRAM CALCULATIONS IN II-VI AND IV-VI TERNARY SYSTEMS USING AN ASSOCIATED SOLUTION MODEL

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Résumé. — On décrit les propriétés thermodynamiques et les diagrammes T-x de l'équilibre liquide-solide dans les systèmes ternaires II-VI et IV-VI par un modèle de solution régulière associée, dérivé de celui utilisé par Jordan pour le liquide et dans l'hypothèse d'une solution régulière pour le solide. Pour les systèmes pseudo-binaires montrant une miscibilité dans les deux phases et une variation monotone des courbes de liquidus et solidus, on obtient une expression générale, indépendante des interactions dans le liquide. Pour le calcul des diagrammes de phase ternaires, cinq paramètres sont nécessaires : les deux paramètres d'interaction α_1, α_2 et les deux coefficients de dissociation β_1, β_2, obtenus à partir des liquides binaires respectifs, et le paramètre d'interaction W dans le solide, déduit du diagramme pseudo-binaire. On obtient un bon agrément avec les résultats expérimentaux pour les systèmes ternaires : Zn-Cd-Te et Pb-Sn-Te, ainsi que pour les systèmes pseudo-binaires : ZnTe-CdTe, ZnTe-HgTe, ZnSe-ZnTe, CdTe-HgTe, CdTe-CdSe, HgTe-HgSe, PbSe-PbTe, PbTe-SnTe. La théorie est spécialement adaptée au cas où $\beta \simeq 0$ avec α petit. Elle est appliquée à la prévision de la région riche en chalcogènes des systèmes ternaires : Cd-Hg-Te et Cd-Se-Te.

Abstract. — The thermodynamic properties and the T-x phase diagrams for liquid-solid equilibrium in II-VI and IV-VI ternary systems are described by a regular associated liquid solution model derived from that used by Jordan for ZnTe and CdTe and by the regular approximation for the solid solution. For the pseudo-binary systems exhibiting miscibility in both phases and monotonic variation of the liquidus and solidus curves, a general expression is obtained. It is independent of the interactions in the liquid, and is the same as for ideal non associated liquids. In the calculation of the ternary T-x phase diagrams five parameters are needed : the two interaction parameters α_1, α_2, the two coefficients of dissociation, β_1, β_2, obtained from the respective binary liquidus, and the interaction parameter W in the solid, derived from the pseudo-binary phase diagrams. Good agreement with experimental data is obtained for the pseudo-binary systems : ZnTe-CdTe, ZnTe-HgTe, ZnSe-ZnTe, CdTe-HgTe, CdTe-CdSe, HgTe-HgSe, PbSe-PbTe, PbTe-SnTe, and for the ternary systems : Zn-Cd-Te and Pb-Sn-Te. The theory is especially suited for the case $\beta \simeq 0$ and α is small. It is applied to the calculation of the chalcogen-rich part of the ternary systems : Cd-Hg-Te and Cd-Se-Te.

1. **Introduction.** — The development of solution-growth techniques for alloy crystals has created a need for comprehensive and accurate thermodynamic data, especially phase diagrams of liquid-solid equilibria in pseudo-binary and ternary systems. The experimental determination of the phase diagrams including liquidus-solidus tied lines can be prohibitively time-consuming and lead to excessive experimental errors. Attempts have been made at developing models of *liquid* solutions that can provide a general understanding of these systems and can be used to calculate the ternary phase diagram from the more easily determined and more reliable thermodynamic data of binary and pseudo-binary systems.

The large deviations from ideality in the III-V systems led investigators to use liquid solution models (based on the first order approximation of Guggenheim) of increasing complexity to interpret their thermodynamic properties. The expressions derived by Wagner [1] and Vieland [2] for a *pseudo-regular* solution model with an interaction parameter varying linearly with temperature have given good results in some cases [3], [4]. The more general quasi-chemical equilibrium model with temperature-independent interchange energy leads to a satisfactory representation of the binary and ternary phase diagrams for some metallic systems [5] and for combinations of elements

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from group III, IV and V [6], [7], [8]. These approaches generally failed to account for the thermodynamic properties of II-VI and IV-VI systems. In these systems, the larger differences in electronegativity produce more ionic and stronger interactions between unlike atoms, as evidenced by :

— The marked temperature peak of the liquidus near the melting points of binary solutions and near the pseudo-binary composition line in ternary systems : figures 1, 2 and reference [9].

— The occurrence of liquid immiscibility [9], [10] reported in a number of binary liquid solutions containing atoms from groups II, IV or VI, as expected by Jordan [11] for ZnTe and as discussed in the classical paper of Hume-Rothery and Anderson [12].

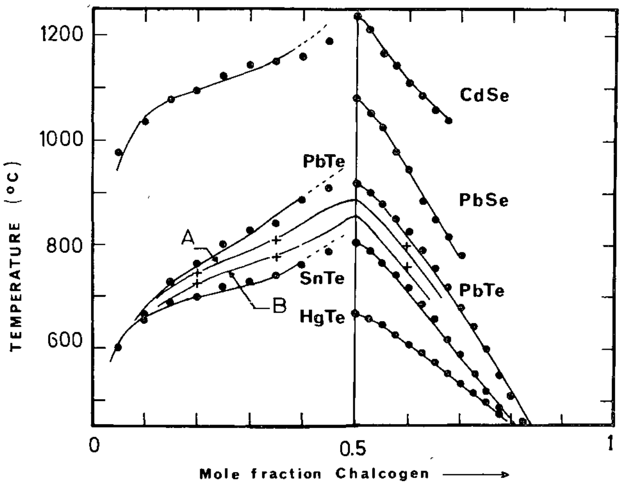

FIG. 1. — Liquidus of some II-VI and IV-VI binary compounds. ● : experimental data. Solid lines : calculated curves from the binary form of eq. (20). Monotectics are no considered. A and B : liquidus isopleths of the ternary system Pb-Sn-Te for the constant Pb/Sn ratios 0.71/0.29 and 0.4/0.6 respectively.

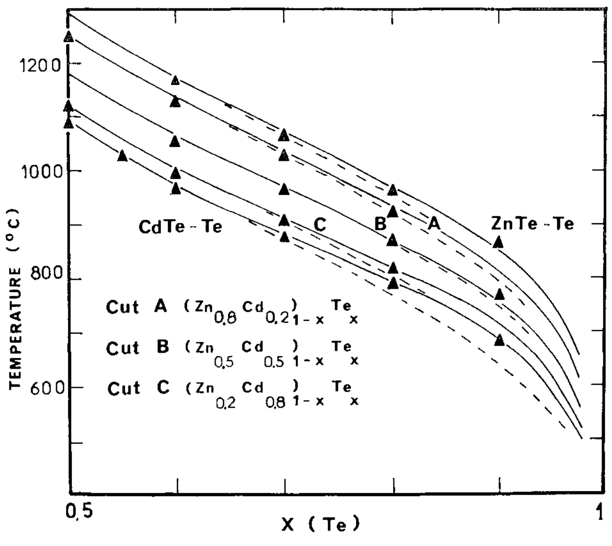

FIG. 2. — Liquidus isopleths at constant Zn/Cd ratios on the Te-rich side of the ternary system Zn-Cd-Te. ▲ : experimental data of Steininger, Strauss and Brebick (ref. [15]). Solid lines : calculated curves with the values of α and β of table I, dashed lines : calculated with $\alpha = \beta = 0$.

These two features result from the two kinds of atom having such a strong tendency to mix at a particular composition that the free energy (G) falls, producing an inflexion in the $G(x)$ curve (x = composition). Both the regular and the quasi-chemical model are based on the assumption that the energy of the solution is a function of the number of atom pairs of different type, and they fail to differentiate between metal-rich and chalcogen-rich solution. Since the real lines are highly asymmetrical (Fig. 1) more sophisticated models are needed, which take into account the difference in the binding energies of the various types of atoms.

The surrounded atom model [13], an extension of the quasi-chemical equilibrium model, could be used. Its basic entity is an atom with all its nearest neighbours, rather than atom pairs. Approximations should be made to reduce the number of parameters involved for the ternary systems (¹). This model is still not practical for the calculation of ternary phase diagrams nor the non-random two-liquid model [14].

Postulating the existence of stable complexes in the liquid state, Jordan [11] has developed an essentially thermodynamic treatment for associated solutions without considering in detail the nature of the bonds involved. It is the aim of this paper to generalize this model to ternary systems and to give a method for the calculation of ternary phase diagrams in the case of systems involving congruently melting II-VI and IV-VI compounds and exhibiting pseudo-binary systems with a miscibility in both phases and monotonic variations of the liquidus and solidus curves.

In section 2 the general equations of liquidus and solidus are given in the case of ternary associated solutions. In section 3 an approximate expression is obtained in the case of regular associated liquid solutions assuming a regular solution for the solid. In section 4 the interaction energies in the solid phase (the only parameter needed in the model) are derived from experimental data for all II-VI and IV-VI pseudo-binary systems for which data are available. The comparison of calculations with experimental data is made for the Zn-Cd-Te and Pb-Sn-Te systems for which experimental data about ternary diagrams are available. Particular attention was paid to the first one because of the thorough study of Steininger, Strauss and Brebrick [15] and because the Zn-Te and Cd-Te liquidus curves (which cannot be described by assuming regular or ideal behaviour in the liquid) have been calculated [11] in good agreement with experimental results by the use of the regular associated solution model. In section 5 some implications

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(1) Six binary parameters are used to describe an excess thermodynamic function of melting for the ternary non-associated systems : BRION, B., et *al.* *J. Chem. Phys.* **66** (1969) 1238 ; **67** (1970) 1745.

of the model are discussed and an application to the case of the ternary systems : Cd-Hg-Te, Cd-Te-Se is made.

2. **General equations for liquid-solid equilibrium in ternary regular associated solutions.**

— 2.1 LIQUID-SOLID EQUILIBRIUM. — The ternary phase diagram is calculated by using the conditions for equilibrium between a ternary liquid solution A, B, C, and the pseudo-binary solid solution AC-BC. No departure from stoichiometry is assumed in the solid. The liquid solution is postulated to be constituted by two binary associated solutions A, C, AC(L) and B, C, BC(L) corresponding to the two association reactions :

$$\begin{aligned} \mathrm{AC(L)} &\rightleftarrows \mathrm{A(L)} + \mathrm{C(L)}\,, \\ \mathrm{BC(L)} &\rightleftarrows \mathrm{B(L)} + \mathrm{C(L)}\,. \end{aligned} \qquad (1)$$

There are no complexes AB(L). Let there be five species in equilibrium in the liquid, monomers A, B and C and associated molecules AC and BC. n_{A}, n_{B}, n_{C}, n_{AC}, n_{BC} are the corresponding number of moles. The *total* number of moles of A, B, C, in the combined and uncombined states are n_1, n_2, n_3. One can express n_1, n_2, n_3 in terms of n_{A}, n_{B}, n_{C}, n_{AC}, n_{BC} :

$$\begin{aligned} n_1 &= n_{\mathrm{A}} + n_{\mathrm{AC}} \\ n_2 &= n_{\mathrm{B}} + n_{\mathrm{BC}} \\ n_3 &= n_{\mathrm{C}} + n_{\mathrm{AC}} + n_{\mathrm{BC}}\,. \end{aligned} \qquad (2)$$

Using the atom fractions x_i of the ternary components and the mole fraction x_j of the species, one can write :

$$n_1 + n_2 + n_3 = \frac{n_i}{x_i} \qquad i = 1, 2, 3 \qquad (3)$$

$$n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}} + n_{\mathrm{AC}} + n_{\mathrm{BC}} = \frac{n_j}{x_j}$$

$$j = \mathrm{A, B, C, AC, BC} \qquad (4)$$

and

$$\sum_i x_i = \sum_j x_j = 1\,. \qquad (5)$$

Prigogine and Defay [16] have shown that the gross chemical potentials of components i, μ_i are equal to the chemical potentials of the corresponding uncombined (monomeric) species in the actual associated solution ; hence one can write

$$\mu_1 = \mu_{\mathrm{A}}\,, \quad \mu_2 = \mu_{\mathrm{B}}\,, \quad \mu_3 = \mu_{\mathrm{C}}\,. \qquad (6)$$

The activities of the components i and the activities of the actual monomeric species A, B, C, a_{A}, a_{B}, a_{C} are related by

$$a_1 = \gamma_1 x_1 = \gamma_{\mathrm{A}} x_{\mathrm{A}} = a_{\mathrm{A}} \qquad (7)$$

and the two corresponding equations obtained with 2, 3 and B, C, respectively, where the γ_i' s are the gross activity coefficients of components i and γ_{A}, γ_{B}, γ_{C} are the activity coefficients of the monomeric species A, B and C, all referred to the pure liquid standard states.

In the solid state the chemical potentials in the solid phase are given by

$$\begin{aligned} \mu_{\mathrm{AC}}^{S}(T) &= \mu_{\mathrm{AC}}^{S,0}(T) + RT \operatorname{Log} \gamma_{\mathrm{AC}}^{S}\, y \\ \mu_{\mathrm{BC}}^{S}(T) &= \mu_{\mathrm{BC}}^{S,0}(T) + RT \operatorname{Log} \gamma_{\mathrm{BC}}^{S}(1 - y) \end{aligned} \qquad (8)$$

where $\mu_{\mathrm{AC}}^{S,0}$ is the chemical potential of the pure compound AC, and y is the mole fraction of compound AC in the solid solution. At equilibrium

$$\begin{aligned} \mu_{\mathrm{AC}}^{S}(T) &= \mu_{\mathrm{A}}(T) + \mu_{\mathrm{C}}(T) \\ \mu_{\mathrm{BC}}^{S}(T) &= \mu_{\mathrm{B}}(T) + \mu_{\mathrm{C}}(T)\,. \end{aligned} \qquad (9)$$

Using the method of Vieland [2] the chemical potential of the pure compound AC may be determined in terms of the chemical potentials of the stoichiometric liquid, $\mu_{\mathrm{A}}^{*}(T)$ and $\mu_{\mathrm{C}}^{*}(T)$, the entropy of fusion ΔS_1, the melting temperature T_1 for the compound AC, and ΔC_{p}, the difference in specific heat between the compound and its supercooled liquid, by considering the total change in chemical potential as the compound AC at $T < T_1$ is heated to the melting temperature, melted, and the resulting stoichiometric liquid supercooled to T. The resulting expression is :

$$\mu_{\mathrm{AC}}^{S,0}(T) = \mu_{\mathrm{A}}^{*}(T) + \mu_{\mathrm{C}}^{*}(T) - \Delta S_1 . [T_1 - T] +$$

$$+ \Delta C_{\mathrm{p}} \left[T_1 - T - T \operatorname{Log} \frac{T_1}{T} \right] \qquad (10)$$

$\mu_{\mathrm{BC}}^{S,0}$ may be expressed similarly, T_2, ΔS_2 being the temperature and entropy of fusion of the compound BC. Neglecting the small terms in ΔC_{p}, the equilibrium eq. (9) may be combined with eq. (8), (10), to give :

$$\begin{aligned} y\gamma_{\mathrm{AC}}^{S} &= \frac{a_{\mathrm{A}}\, a_{\mathrm{C}}}{a_{\mathrm{A}}^{*}\, A_{\mathrm{C}}^{*}} \exp \frac{\Delta S_1}{R} \left(\frac{T_1}{T} - 1 \right) \\ (1 - y)\, \gamma_{\mathrm{BC}}^{S} &= \frac{a_{\mathrm{B}}\, a_{\mathrm{C}}}{a_{\mathrm{B}}^{*}\, a_{\mathrm{C}}^{*}} \exp \frac{\Delta S_2}{R} \left(\frac{T_2}{T} - 1 \right). \end{aligned} \qquad (11)$$

In the associated solution, the activities are related to the equilibrium constants K_1, K_2 for the association reactions (1) according to :

$$\begin{aligned} K_1 &= \frac{a_{\mathrm{A}}\, a_{\mathrm{C}}}{a_{\mathrm{AC}}} = \frac{x_{\mathrm{A}}\, x_{\mathrm{C}}}{x_{\mathrm{AC}}} \frac{\gamma_{\mathrm{A}}\, \gamma_{\mathrm{C}}}{\gamma_{\mathrm{AC}}} = K_1^{i} \frac{\gamma_{\mathrm{A}}\, \gamma_{\mathrm{C}}}{\gamma_{\mathrm{AC}}} \\ K_2 &= \frac{a_{\mathrm{B}}\, a_{\mathrm{C}}}{a_{\mathrm{BC}}} = \frac{x_{\mathrm{B}}\, x_{\mathrm{C}}}{x_{\mathrm{BC}}} \frac{\gamma_{\mathrm{B}}\, \gamma_{\mathrm{C}}}{\gamma_{\mathrm{BC}}} = K_2^{i} \frac{\gamma_{\mathrm{B}}\, \gamma_{\mathrm{C}}}{\gamma_{\mathrm{BC}}} \end{aligned} \qquad (12)$$

where a_{AC}, a_{BC} and γ_{AC}, γ_{BC} are the activities and activity coefficients of the complexes and K^{i} the values of K in the ideal model. Then :

$$\frac{a_{\mathrm{A}}\, a_{\mathrm{C}}}{a_{\mathrm{A}}^{*}\, a_{\mathrm{C}}^{*}} = \frac{a_{\mathrm{AC}}}{a_{\mathrm{AC}}^{*}} \quad \text{and} \quad \frac{a_{\mathrm{B}}\, a_{\mathrm{C}}}{a_{\mathrm{B}}^{*}\, a_{\mathrm{C}}^{*}} = \frac{a_{\mathrm{BC}}}{a_{\mathrm{BC}}^{*}}\,. \qquad (13)$$

2.2 ACTIVITY OF THE COMPLEXES. — Combining the eq. (2), (3), (4), (5), we obtain :

$$\begin{aligned} x_{\mathrm{A}} &= x_1(1 + x_{\mathrm{AC}} + x_{\mathrm{BC}}) - x_{\mathrm{AC}} \\ x_{\mathrm{B}} &= x_2(1 + x_{\mathrm{AC}} + x_{\mathrm{BC}}) - x_{\mathrm{BC}} \\ x_{\mathrm{C}} &= x_3(1 + x_{\mathrm{AC}} + x_{\mathrm{BC}}) - x_{\mathrm{AC}} - x_{\mathrm{BC}} \,. \end{aligned} \tag{14}$$

We introduce the degrees of dissociation d_1 and d_2 corresponding to AC and BC respectively :

$$d_1 = \frac{n_{\mathrm{A}} + n_{\mathrm{C}}}{n_1 + n_3}, \qquad d_2 = \frac{n_{\mathrm{B}} + n_{\mathrm{C}}}{n_2 + n_3}.$$

Expressing the d's in terms of x_j and using the eq. (14) to eliminate x_{A}, x_{B}, x_{C} we obtain finally :

$$\begin{aligned} x_{\mathrm{AC}} &= \frac{2(1-d_1)(1-x_2)-(1-d_2)(1-x_1)}{3-(1-d_2)(1-x_1)-(1-d_1)(1-x_2)} \\ x_{\mathrm{BC}} &= \frac{2(1-d_2)(1-x_1)-(1-d_1)(1-x_2)}{3-(1-d_2)(1-x_1)-(1-d_1)(1-x_2)} \,. \end{aligned} \tag{15}$$

It is now necessary to obtain the expressions of d_1 and d_2 in terms of x_1, x_2, x_3. This can be done by introducing the particular values β_1, β_2 of the parameters of dissociation d_1, d_2 of the respective binary stoichiometric liquids AC, BC. We have, rewriting (13) ;

$$\begin{aligned} \gamma_{\mathrm{A}}\,\gamma_{\mathrm{C}}[x_1(1 + x_{\mathrm{AC}} + x_{\mathrm{BC}}) - x_{\mathrm{AC}}] \times & \\ \times \frac{x_3(1 + x_{\mathrm{AC}} + x_{\mathrm{BC}}) - x_{\mathrm{BC}} - x_{\mathrm{AC}}}{x_{\mathrm{AC}}\,\gamma_{\mathrm{AC}}} &= \\ = \gamma_{\mathrm{A}}^*\,\gamma_{\mathrm{C}}^*\,\beta_1^2[1 - \beta_1^2]^{-1}\,\gamma_{\mathrm{AC}}^{*-1} . & \end{aligned} \tag{16}$$

The left hand side of this equation expresses K_1 by use of eq. (14), the right hand side corresponds to the particular value of K_1 for the stoichiometric liquid AC ($x_2 = x_{\mathrm{B}} = x_{\mathrm{BC}} = 0$, $x_1 = x_3 = 0.5$). A corresponding equation is obtained for BC by replacing the subscripts 1 by 2 and A by B. (We have assumed K only temperature-dependent.) The resolution of the system allows, in principle, to obtain x_{AC} and x_{BC} in terms of the variables x_1, x_2, x_3 and of the two parameters β_1 and β_2. This calculation is, however, neither straightforward nor very practical. An approximation is needed, and will be made in section 3.

In the regular approximation the expressions of the five activity coefficients γ_j with the quadratic formalism for the five component systems considered are unknown and would involve interaction parameters which are not available. The eq. (13) avoids the use of a_{A}, a_{B}, a_{C}, but it is necessary to know a_{AC} and a_{BC}. Approximate expressions can be obtained for $\gamma_{\mathrm{AC}}^{\mathrm{L}}$ and $\gamma_{\mathrm{BC}}^{\mathrm{L}}$ with the following requirements :

— For the binary liquid it should give the expression $\exp[1 - 4\,x(1 - x)]\,\dfrac{\alpha}{2\,RT}$ obtained by Jordan [11].

— On the pseudo-binary line ($x_3 = x_2 + x_1 = 0.5$) the boundary conditions are $\gamma_{\mathrm{AC}}^{\mathrm{L}} \to 1$ and $\gamma_{\mathrm{BC}}^{\mathrm{L}} \to 1$.

These expressions are :

$$\begin{aligned} \gamma_{\mathrm{AC}}^{\mathrm{L}} &= \exp\left\{\alpha_1\,\frac{1 - 4\,x_3(x_1 + x_2)}{2\,RT}\right\} \\ \gamma_{\mathrm{BC}}^{\mathrm{L}} &= \exp\left\{\alpha_2\,\frac{1 - 4\,x_3(x_1 + x_2)}{2\,RT}\right\} . \end{aligned} \tag{17}$$

The coefficients α_i are obtained from the corresponding binary liquid. They involve K_i and the interchange energies for specific pairwise interactions ω_{AC} and $\omega_{\mathrm{A,AC}}$, $\omega_{\mathrm{C,AC}}$ (the two latter are presumed to be equal) for α_1, and $\omega_{\mathrm{B,C}}$, $\omega_{\mathrm{B,BC}} = \omega_{\mathrm{C,BC}}$ for α_2. If one or the two binary solutions is completely dissociated ($K = \infty$, $\beta = 1$), α is identified with the interaction parameter of a classical regular binary solution.

3. Ternary liquidus-solidus equations. — 3.1 APPROXIMATE SOLUTION. — The use of (17) to express γ_{AC} and γ_{BC}, and (15) to explicit x_{AC}^* and x_{BC}^* gives :

$$\begin{aligned} \frac{a_{\mathrm{AC}}}{a_{\mathrm{AC}}^*} &= x_{\mathrm{AC}}\,\frac{1+\beta_1}{1-\beta_1}\exp\frac{\alpha_1}{2\,RT}\,[1 - 4\,x_3(x_1+x_2)] \\ \frac{a_{\mathrm{BC}}}{a_{\mathrm{BC}}^*} &= x_{\mathrm{BC}}\,\frac{1+\beta_2}{1-\beta_2}\exp\frac{\alpha_2}{2\,RT}\,[1-4\,x_3(x_1+x_2)] \,. \end{aligned} \tag{18}$$

It is now necessary to know x_{AC} and x_{BC}. We are principally interested in the very associated solutions where $\beta \ll 1$. This is generally the case for the considered systems (Table I). Then, the second member of eq. (16) vanishes and the solution of this system is :

$$x_{\mathrm{AC}} = \frac{x_1}{x_3}, \qquad x_{\mathrm{BC}} = \frac{x_2}{x_3}. \tag{19}$$

Using (19), in eq. (18) and rewriting (11), assuming the solid solution to be regular (i. e. $\Delta G^{xs} = Wy(1-y)$), we obtain the system for the ternary liquidus and solidus surfaces :

$$\begin{aligned} y\exp\left\{\frac{W}{RT}(1 - y)^2\right\} &= \frac{1+\beta_1}{1-\beta_1}\,\frac{x_1}{x_3}\exp\frac{\Delta S_1}{R}\left(\frac{T_1}{T} - 1\right)\exp\left\{\frac{\alpha_1}{2\,RT}[1 - 4(x_1 + x_2)\,x_3]\right\} \\ (1 - y)\exp\left\{\frac{W}{RT}\,y^2\right\} &= \frac{1+\beta_2}{1-\beta_2}\,\frac{x_2}{x_3}\exp\frac{\Delta S_2}{R}\left(\frac{T_2}{T} - 1\right)\exp\left\{\frac{\alpha_2}{2\,RT}[1 - 4(x_1 + x_2)\,x_3]\right\} . \end{aligned} \tag{20}$$

TABLE I

Coefficient of dissociation β of the stoichiometric liquid and interaction parameter α obtained in the approximation of the regular associated solution from experimental liquidus data of the figures 1 *and* 2

Sub-system	ZnTe -Te	ZnTe -Zn	CdTe -Te	CdTe -Cd	HgTe -Te	PbTe -Te	PbTe -Pb	SnTe -Te	SnTe -Sn	PbSe -Se	CdSe -Se	CdSe -Cd
α kcal/mol	1.9	17	1.7	10.9	0.0	— 6.2	5.5	— 3	8.5	— 9.4	7.8	12
β	0.00	0.065	0.00	0.055	0.04	0.04	0.14	0.04	0.10	0.00	0.02	0.12

For the binary boundary, these equations become the approximate equation of the liquidus given by Jordan [11] and can be used to determine α and β by fitting the experimental data. Expressions (20) are valid only for $\beta \ll 1$ (typically $\beta < 0.2$) and $2 \mid x_3 - 0.5 \mid > \beta$. For the pseudo-binary system and in its neighborhood another approximation is needed.

3.2 PSEUDO-BINARY SYSTEM. — On the pseudo-binary line we put $x_1 = x/2$ and $x_2 = (1 - x)/2$. x_{AC} and x_{BC} are given by the eq. (15) with $d_1 = \beta_1$ and $d_2 = \beta_2$. An exact solution is possible. An expression which is particularly interesting is obtained in the practical case β_1, $\beta_2 \ll 1$, because in eq. (15) only terms of the form $1 - \beta$ are used ; then, $1 - \beta_1 \simeq 1 - \beta_2 \simeq 1 - \beta$ and :

$$x_{AC} = \frac{x(1 - \beta)}{1 + \beta}$$
$$x_{BC} = (1 - x)\frac{1 - \beta}{1 + \beta}. \tag{21}$$

Combining (21) and (18) we obtain the equations of pseudo-binary solidus and liquidus :

$$y \exp \frac{W}{RT}(1 - y)^2 = x \exp \frac{\Delta S_1}{R}\left(\frac{T_1}{T} - 1\right)$$
$$(1 - y) \exp \frac{W}{RT} y^2 = (1 - x) \exp \frac{\Delta S_2}{R}\left(\frac{T_2}{T} - 1\right). \tag{22}$$

It is interesting to remark that these equations do not involve β, so that they are general, as discussed later.

Moreover, with β_1, $\beta_2 \simeq 0$, eq. (20) becomes identical to (22) in the pseudo-binary case. In this case the complete ternary phase diagram can be calculated by solving the system (20) only. Due to the complexity of these equations, calculations are to be made on a computer.

4. **Comparison with experiment.** — 4.1 BINARY LIQUIDUS. — For each considered subsystem the eq. (20) is used to obtain the value of the parameters α and β presented in table I. The thermodynamic data needed (ΔS_i and T_i) were recently selected by Steininger [17] and are given in table II. We have used a least square method to obtain the best fit between the experimental data and the theory. The agreement is generally very good as seen on figures 1 and 2. The twelve sub-systems of table I were selected according to three criteria :

TABLE II

Values of the entropy and melting temperature for II-VI *and* IV-VI *compounds used in the calculation of the ternary phase diagrams. (The data come from ref.* [17].) *Computed values of the regular interaction parameter W of the pseudo-binary solid solutions of these compounds.*

System	ΔS_i (e. u.)	T_i (K)	W (kcal/mole)
ZnTe-CdTe	10-8.8	1 560-1 365	1.34
ZnTe-HgTe	10-9.2	1 560-943	3.0
ZnSe-ZnTe	6.9-10	1 803-1 560	1.55
CdTe-HgTe	8.8-9.2	1 365-943	1.40
CdSe-CdTe	6.85-8.8	1 528-1 365	1.50
HgSe-HgTe	6.8-9.2	1 073-943	0.70
PbSe-PbTe	8-7.8	1 353-1 200	1.50
PbTe-SnTe	7.8-7.2	1 200-1 080	0.18
MnTe-GeTe	10-14.6	1 430-1 013	0.8

i) Sufficiently accurate and concordant data are available. For the sub-systems CdTe-Te and ZnTe-Te serious discrepancies among previous published data exist [18]-[20]. We use the more recent work of Steininger, Strauss and Brebrick [15] because it is supposed to be the most reliable and because it includes the study of the complete ternary system. The previously indicated works are in agreement for the metal-rich part of the liquidus of ZnTe and CdTe. We take the values of α and β determined by Jordan [11]. The experimental phase diagrams of Reisman, Berkenblit and Witzen [21] and Burmeister and Stevenson [22] are used for the system cadmium-selenium. The Te side of the liquidus of HgTe is taken from a compilation of data by Hansen [9], and from references [23] and [24]. For PbTe and PbSe we use the data of Miller and Komarek [25]. These authors have found the chalcogen-rich side of the liquidus of Pb-Te and Pb-Se in agreement with Hansen [9]. This agreement is confirmed by recent measurements [26] for PbSe. For Sn-Te the values of Hansen were used. This is supported by the work of Linden and Kennedy about the Pb-Sn-Te system [27].

ii) $\beta \ll 1$. The selected compounds are those for which very strong association is assumed. Indeed, the aim of this paper is to show that the hypothesis of *association* in the liquid is a good model to account for the thermodynamic properties of the ternary systems involved.

iii) The values of α are temperature-independent and not excessively high. The interactions can be very strong (in the metal-rich part generally, and for the sulfides and selenides) so that the regular approximation can fail to take them into account without excessive complication.

As seen on figure 1, the eq. (20) cannot be applied to the metal-rich part of the Pb-Sn-Te and Cd-Se systems, for mole fractions of chalcogen higher than 0.4, due to the relatively large value of β.

The Te or Se-rich part of the sub-systems of table I satisfies well the last two criteria. Hence particular attention will be paid to the chalcogen-rich region of ternary phase diagrams which is precisely the region of particular interest for crystal growth from non-stoichiometric liquid [28].

4.2 Pseudo-binary systems. — Valid for a regular pseudo-binary solid solution, the system of eq. (22) can be solved. By fitting the computed values to the experimental data, the values of the interaction parameter W (Table II) are obtained for the nine pseudo-binary systems where experimental data are available and exhibiting complete miscibility in the two phases. These systems are characterized by a monotonic variation in liquidus and solidus temperatures with composition.

We use as a reference the work of Steininger [17] which has recently reviewed and discussed this type of pseudo-binary system and used the ideal form of the general liquidus-solidus equation to calculate one of the boundaries of the two-phase liquid-solid field when the other one and the enthalpies of fusion of the pure components are already known. Consequently each system considered here is not discussed in detail and only the particular features of interest for the calculation of the ternary system are noted. References for the experimental liquidus and solidus data are given in the text below or on the corresponding figure caption.

ZnTe-CdTe (Fig. 3). — The compounds ZnTe and CdTe form a complete series of solid solutions with zinc-blende structure and the lattice parameter follows Vegard's law. The pseudo-binary phase diagram was thoroughly studied by differential thermal analysis of cooling and heating curves [15]. The calculated curves with $W = 1\,340$ cal/mole shows excellent agreement with the solidus and liquidus data over the whole composition range.

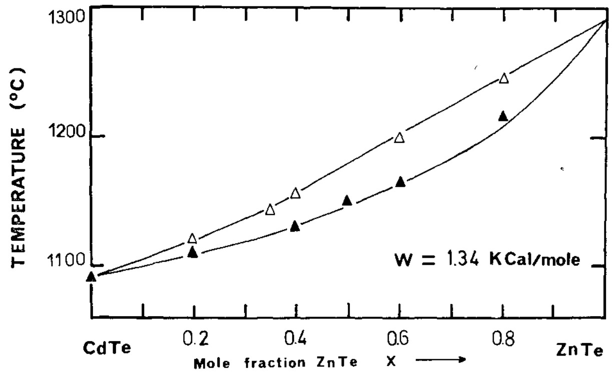

Fig. 3. — ZnTe-CdTe pseudo-binary phase diagram : △, ▲, experimental data of the liquidus and solidus respectively, from Steininger, Strauss and Brebrick (ref. [15]). Solid lines : calculated with eq. (22).

ZnTe-HgTe (Fig. 4.) — A complete series of solid solutions with zinc-blende structure exists with no evidence of miscibility gap down to 500 °C. The solidus curve has been determined by the X-ray method [29]. However, the high pressure over HgTe has prevented an experimental investigation of the liquidus. Only the value $W = 3\,000$ cal/mole was found to give a good fit with the experimental solidus, allowing a reasonably exact evaluation of the liquidus. It is interesting to remark that our computed liquidus is at higher temperature (up to 125°) than the liquidus calculated by Steininger. This is quite normal since the large value of W indicates that the calculation based on the ideal equation fails in this case.

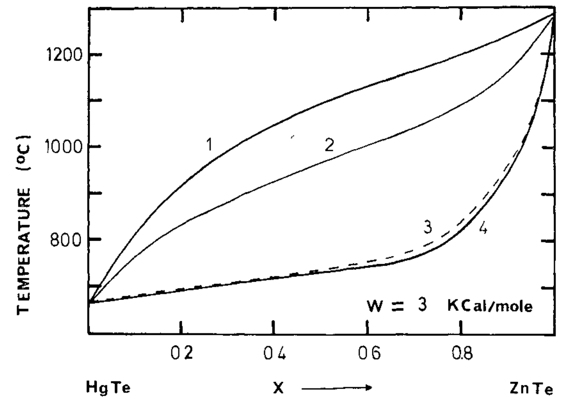

Fig. 4. — ZnTe-HgTe pseudo-binary phase diagram. 1 and 4 calculated liquidus and solidus, 2 liquidus calculated by Steininger (ref. [17]) with the ideal approximation, 3 (dashed curve) experimental solidus of Woolley and Ray (ref. [29]).

ZnSe-ZnTe (Fig. 5). — No solidus data exist for this system which forms a continuous series of solid solutions with zinc-blende structure [30]. Very good agreement is obtained for the liquidus between experimental data and the calculated curve with $W = 1\,550$ cal/mole. The calculated solidus indicates a relatively narrow two-phase field of about 0.2 mole fractions. The solidus calculated by Steininger is significantly higher giving a solidus-liquidus gap of less than 0.11 mole fraction. The same argument as for the ZnTe-HgTe system can be used to explain this difference. In both cases we think that our calculation, taking account of the large departure from ideality in the solid, is more correct.

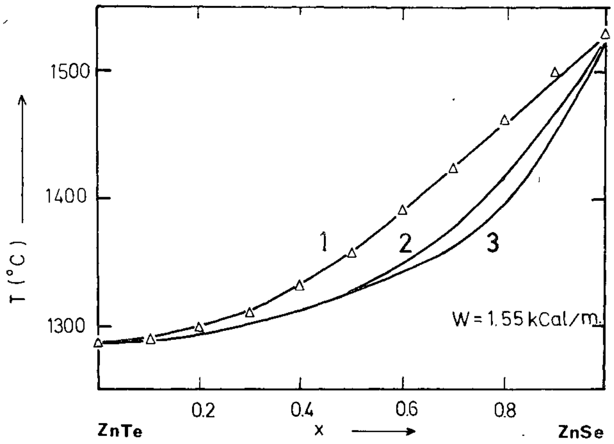

FIG. 5. — ZnTe-ZnSe pseudo-binary phase diagram. 1 and 3, calculated liquidus and solidus, 2, solidus calculated by Steininger (ref. [17]), △ liquidus data (cooling curve arrest) of Fischer and Fonger (ref. [30]).

CdTe-HgTe (Fig. 6). — Significant discrepancies have been observed in the data reported for this system [31]-[34]. Schmit and Speerschneider [31] have suggested that these may be due to the large pressure dependence of the liquidus. The data of Ray and Spencer [32] would correspond to a low Hg partial pressure while the data of Harman and Strauss [33] would correspond to a high partial pressure. The present work can help to explain these discrepancies. It is not possible to find a value of *W* giving agreement between the calculation and the data of Ray and Spencer for the liquidus and the solidus simultaneously, nor even for each curve alone. In contrast, the experimental liquidus of Blair and Newnham [34], and Schmit and Speerschneider [31] agrees very well with the calculated curves ($W = 1\,400$ cal/mole). It is normal to find that the measurements made with too low pressures are erroneous.

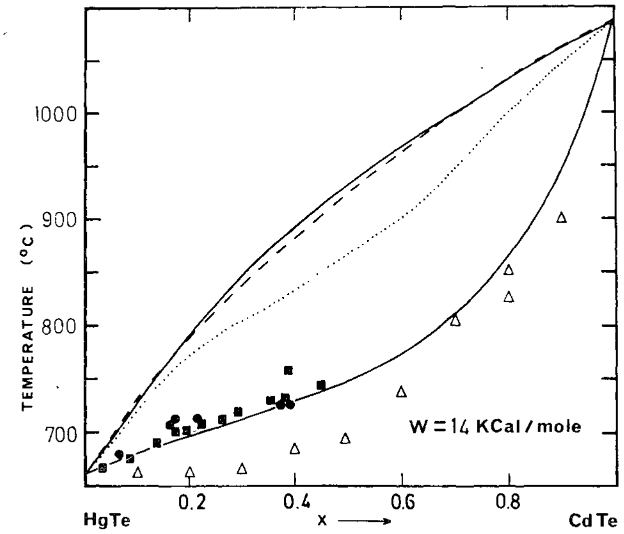

FIG. 6. — CdTe-HgTe pseudo-binary phase diagram. Solid lines : calculated liquidus and solidus. Dashed line : experimental liquidus of Blair and Newnham (ref. [34]). Dotted line : experimental liquidus of Ray and Spencer (ref. [32]). △ solidus from thermal analysis (Ray and Spencer). Solidus from segregation coefficients : ■ (Strauss and Harman : ref. [33]). ● (Schmit and Speerschneider : ref. [31]).

CdTe-CdSe (Fig. 7). — In this system, studied by Steininger and Strauss [35], the structure changes from cubic for CdTe to wurtzite for CdSe. Since the liquidus and solidus curves are almost flat over the narrow cubic phase region, these curves are calculated over the hexagonal region using the same approximation as Steininger. The agreement with experiment is excellent.

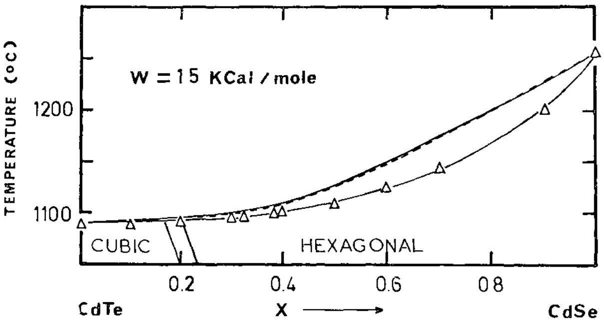

FIG. 7. — CdSe-CdTe pseudo-binary phase diagram. The calculated (solid line) and experimental (dashed line) liquidus curves are nearly the same. For the solidus the agreement is also excellent between the experimental data (△) and the calculated curve (solid line). Experimental data come from Steininger and Strauss (ref. [35]).

HgTe-HgSe. — With $W = 0.7$ kcal/mole our calculated liquidus and solidus curves are nearly the same as the experimental liquidus of Harman and Strauss [33] and the solidus calculated by Steininger (see Fig. 16 of ref. [17]) respectively. This fact confirms the argument that the reported segregation coefficient values do not correspond to equilibrium initial freezing.

PbSe-PbTe (Fig. 8). — The data of Grimes [36] and Steininger [17], which are the more recent and probably the most reliable are used for comparison with our calculated liquidus ($W = 1.5$ kcal/mole). The agreement is excellent with both experimental liquidus curves. Our corresponding calculated solidus agrees well with the data of Steininger and is above the solidus previously reported [36]. This supports the suggestion that the previous results were due to incompletely homogenized alloy samples.

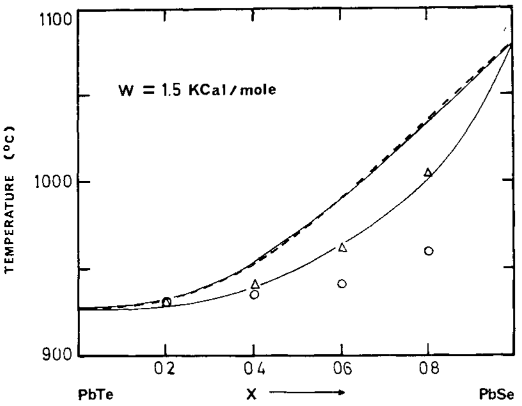

FIG. 8. — PbSe-PbTe pseudo-binary phase diagram. The experimental liquidus curves (dashed) of Grimes (ref. [36]) and Steininger (ref. [17]) are in good agreement with the calculated curve (solid line). The theoretical solidus (solid line) agrees with the data of Steininger (△) but not with the data of Grimes (○).

PbTe-SnTe (Fig. 9). — Excellent agreement is observed between the calculated and experimental liquidus and also between the calculated solidus and the data obtained from segregation coefficient [37]-[39], supporting the suggestion that the slightly lower data obtained by the X-ray method [40] are probably due to changes in the composition of the solid phase during quenching. For this system Reti, Jena and Bever [41] have found that the solid solutions have small exothermic heats of formation, that the Sn and Pb atoms are randomly distributed on the sublattice occupied by them and do not undergo an ordering transition during a thermal treatment designed to promote such a transition. The Vegard's law is obeyed. These results suggest that the solid solutions of SnTe and PbTe approach ideal behaviour. This is confirmed by the present calculation since a particularly small value for W (0.18 kcal/mole) is obtained.

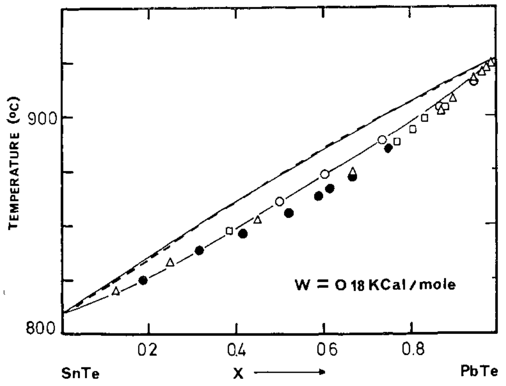

FIG. 9. — PbTe-SnTe pseudo-binary phase diagram. Solid lines : calculated diagram. Dashed line : experimental liquidus (Wagner and Willardson, ref. [37], Linden and Kennedy, ref. [27]). ● Solidus from X-rays (Wagner and Wooley ref. [40]). Solidus from segregation coefficients : △ (Wagner and Willardson, ref. [37]), □ (Calawa *et al.* ref. [38]), ○ (Hiscoks and West, ref. [39]).

In conclusion we have calculated both solidus and liquidus lines of 9 pseudo-binary systems using one parameter W to describe the regular solid solution, and we obtain excellent agreement with experimental data (Fig. 3 to 9). This agreement can be understood because the eq. (22) are independant of β, consequently of a particular model of the liquid, and because the pseudo-binary selected data indicate a small departure from ideality in both phases [42], showing that the regular approximation can be a good description of the solid solution.

4.3 TERNARY SYSTEMS. — Eq. (20) are used to interpret ternary diagrams, the parameters α and β being those of table I, determined in part 4.1. The Te-rich part of the system Zn-Cd-Te is very convenient for testing the validity of the theory because all three criteria previously discussed are obeyed. In contrast, in the metal-rich part the parameters of dissociation are not negligible and the interactions are relatively strong as indicated by the high value of α. The agreement with the experimental data of Steininger, Strauss and Brebrick [15] is excellent, as shown by figure 3 for $x_{\mathrm{Te}} = 0.5$ and figure 2 for the Te-rich ternary liquidus isopleths for constant Zn/Cd ratios and the limiting CdTe-Te and ZnTe-Te binary liquidus. The thermodynamic behaviour in this region is nearly the same as that of an *ideal totally associated solution* ($\alpha = \beta = 0$), as shown by the dashed curves of figures 2 and 11. In addition the calculation gives the composition of the solid for each point of the liquidus surface. The isoconcentration curves are given in figure 10 for the Te-rich region.

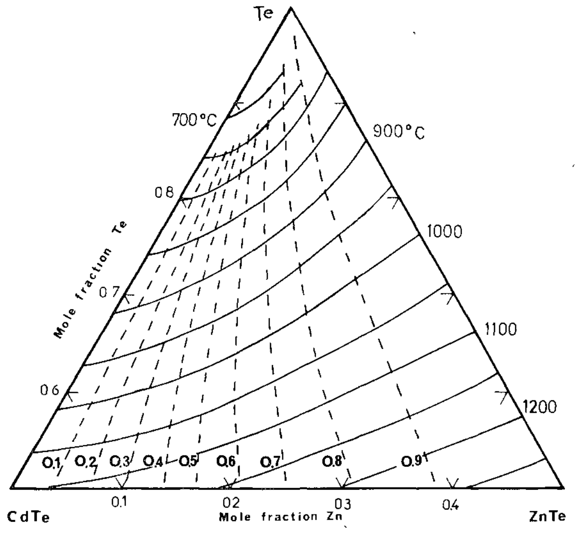

FIG. 10. — Calculated ternary phase diagram of the Zn-Cd-Te system in the Te rich part. Solid lines : liquidus isotherms. Dashed lines iso-concentration curves in the solid solution.

Figure 11 shows some liquidus isotherms of the complete T, x phase diagram. As predicted, the strong interaction in the metal-rich region largely modifies the feature of the liquidus isotherm curves

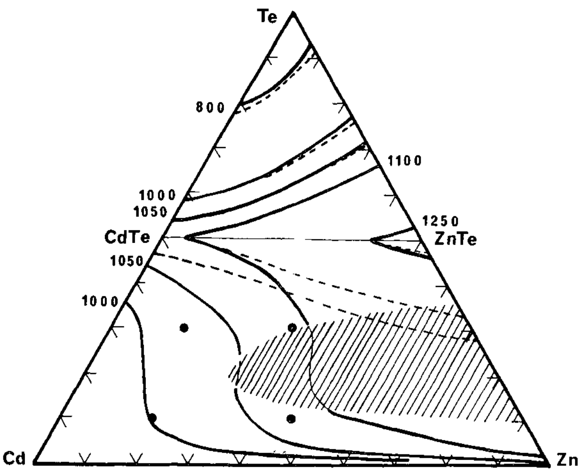

FIG. 11. — Calculated ternary liquidus isotherms of Zn-Cd-Te. Solid line : calculated as explained in the text ; dashed line : calculated in the case of ideal associated solution ($\alpha = \beta = 0$). The dashed aera is the region where demixion in the liquid is possible. The experimental points (●) comes from reference [15] and corresponds to the following data : $x_{\mathrm{Te}} = 0.1$, $T = 970$ and 1 043 °C ; $x_{\mathrm{Te}} = 0.3$, $T = 1\,045$ and 1 112 °C.

from the ideal case. The agreement with the experimental data is not as good as in the Te-rich region but is better than 20°. This small disagreement can be explained by two reasons :

— First, the regular approximation is not sufficient to account for the strong interactions.

— Second, the tendency to liquid immiscibility can give somewhat erroneous experimental data.

In the metal-rich part of the system, indeed, it is interesting to remark that the calculated activity of the complexes (eq. (17)) versus x_{Te} at constant temperature and Zn/Cd ratio can exhibit a maximum and a minimum. This could be related, by using the Gibbs-Duhem relation, to a maximum and a minimum in a_{Zn} and a_{Cd} also. As discussed by Jordan [11] for ZnTe-Zn and CdTe-Cd, $\partial^2 G/\partial x_{\mathrm{Zn}}^2$ and $\partial^2 G/\partial x_{\mathrm{Cd}}^2$ can be negative. So, the liquid is unstable and the separation of this metastable liquid into two immiscible liquids is thermodynamically favored. The dashed zone of figure 11 is the estimated two-liquid region. However no *experimental* evidence of liquid immiscibility in the Zn-Te system has been found despite thorough re-investigations [15].

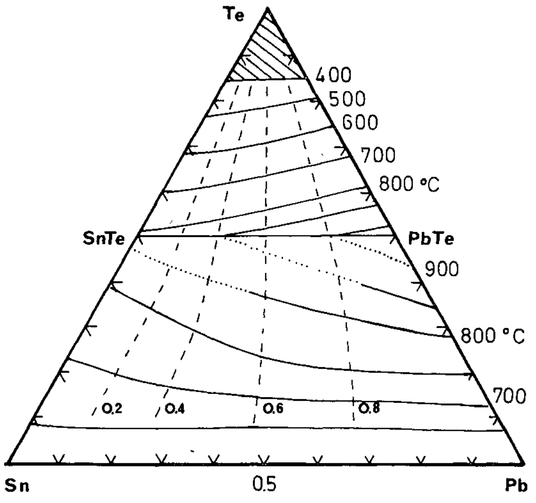

FIG. 12. — Calculated Pb-Sn-Te ternary diagram. Solid lines : liquidus isotherms. Dashed lines : solid-iso concentration curves. Dotted line : interpolated isotherms. The dashed aera corresponds to the monotectics.

The figures 1 and 12 show the calculated Pb-Sn-Te system. The experimental data (+) [27] agree with the theoretical isopleths A and B (Fig. 1) within experimental errors. For $0.4 < x_{\mathrm{Te}} < 0.5$ these curves and the liquidus isotherms are interpolated, due to the large values of β.

5. **Discussion.** — 5.1 BINARY SYSTEMS. — According to Jordan [11] for a binary system AC in the RAS model, the activity coefficients of species A and C in the liquid are [11] :

$$\gamma_{\mathrm{A}} = \exp \frac{\alpha x_3^2}{RT}$$

$$\gamma_{\mathrm{C}} = \exp \frac{\alpha x_1^2}{RT} .$$

The expression of $\gamma_{\mathrm{AC}}^{\mathrm{L}}$ is obtained by integration of the Gibbs-Duhem equation :

$$\gamma_{\mathrm{AC}}^{\mathrm{L}} = B(T) \exp \frac{2\, x_1\, x_3\, \alpha}{RT} \tag{23}$$

where $B(T)$ is only temperature dependent. This expression is more general that the eq. (17). Then one can obtain [43] :

$$\begin{aligned} a_1 &= x_{\mathrm{A}}\, \gamma_{\mathrm{A}} = \frac{x_1 - x_3 + d_1}{1 + d_1} \exp \frac{\alpha x_3^2}{RT} \\ a_3 &= x_{\mathrm{C}}\, \gamma_{\mathrm{C}} = \frac{x_3 - x_1 + d_1}{1 + d_1} \exp \frac{\alpha x_1^2}{RT} \end{aligned} \tag{24}$$

where

$$d_1^2 = \frac{\beta^2 + (1 - \beta^2)(x_1 - x_3)^2 \exp[\alpha(x_1 - x_3)^2/RT]}{\beta^2 + (1 - \beta^2) \exp[\alpha(x_1 - x_3)^2/RT]}$$

with $d_1 = \beta$ for $x_1 = x_3 = 0.5$.

The use of (23) and (24) for the ternary systems would lead to great mathematical complications. Our method allows to avoid it. As Jordan, we take $B(T)$ to have the boundary condition $\gamma_{\mathrm{AC}}^{\mathrm{L}} = 1$ for $x_3 = 0.5$.

Moreover eq. (20) is not valid near the melting point. However, this equation generally describes well the liquidus of the sub systems indicated on table I and shown in figures 1 and 2. As predicted a bad fit is obtained near $x_3 = 0.5$ for those systems which present a relatively large value of β. The corresponding calculated liquidus curves are the dashed lines of figure 1. For each system considered here the values of β are different for the chalcogen and metal rich sides. This fact is a consequence of our approximations :

— First, in eq. (20) β is determined through quantities of the form $(1 + \beta)/(1 - \beta)$. With $\beta \ll 1$ a bad accuracy is expected for β. Moreover, β has an important influence on the liquidus shape, especially near the melting point : unfortunately eq. (20) is not valid for this region (except if $\beta = 0$). Consequently, small uncertainties on experimental data can give an important variation on the value of β.

— Second, we have assumed α and β temperature independent. Actually, these parameters are slowly temperature dependent. For instance, the system Pb-PbSe cannot be described with constant α and β as shown by the recent work of Schneider and Guillaume [43] from electrochemical measurements. The thorough study of these authors shows that α and β are not independent. So, the relatively large value of β in the metal-rich side is connected to the large positive value of α in this region. For PbSe, α and β are approximately constant near the melting point and variable at lower temperatures. The values of β (and α) given in this work are only best fit values for each side of the liquidus. The different values of β result from the asymmetry of the temperature dependence and the asymmetry of α.

5.2 PSEUDO-BINARY SYSTEMS. — The eq. (22) are independent of the model of liquid since β is eliminated. It is important to remark that these equations are the same as the equations obtained for non-associated solution by using the Vieland relations (eq. (11)) in the pseudo-binary case, assuming an ideal liquid solution and a regular solid. This model can be correct since it is expected that the departure from ideality in the solid, due to strain, is larger than in the liquid. If the liquid is taken to be non-ideal, one more parameter is needed, ω_{12}. This is not taken into account by our model. In the III-V semiconducting systems also, this parameter may often be neglected. For instance, we have applied eq. (22) to the systems Ga-In-As and Ga-In-Sb. For GaAs-InAs a good fit is obtained with $W = 2.2$ kcal/mole, with the experimental data of Van Hook and Lenker [44] for the liquidus and Woolley and Smith [45] for the solidus. For GaSb-InSb the value $W = 1.7$ kcal/mole gives an excellent fit with the data of Lichter and Sommelet [46] and of Woolley and Lees [47]. These systems were selected because the recent thermodynamic analysis of Foster and Woods [48] shows that the departure from ideality in the liquid is very small. In contrast, for InP-GaP where a non-ideal behaviour is expected [48] we obtain a good fit only with the solidus data of Foster and Scardfield [49], using $W = 3.2$ kcal/mole. The calculated liquidus is at 20° below the extrapolated data of Panish [50]. Our values of W are slightly lower than the value used in the quasi-chemical equilibrium treatment for Ga-In-As (2.8 kcal/mole) (7) and Ga-In-P (4.0 kcal/mole) (8).

5.3 TERNARY SYSTEMS. — The present treatment gives good agreement with experiment for known systems where $\beta \simeq 0$ and α is small. We can apply it to obtain unknown ternary phase diagrams when these criteria are obeyed. The Te-rich part of the alloys of HgTe and CdTe is particularly convenient. We have computed the ternary phase diagram of the Te-rich part of Cd-Hg-Te, because of the importance of this system for the study of semimetal-semiconductor transitions. The result is given in figure 13. In order to also apply the theory to a system where two chalcogens are involved we have computed the chalcogen rich part of Cd-Se-Te, shown in figure 14. For this system the change of crystalline structure is given in reference [35] and on figure 8.

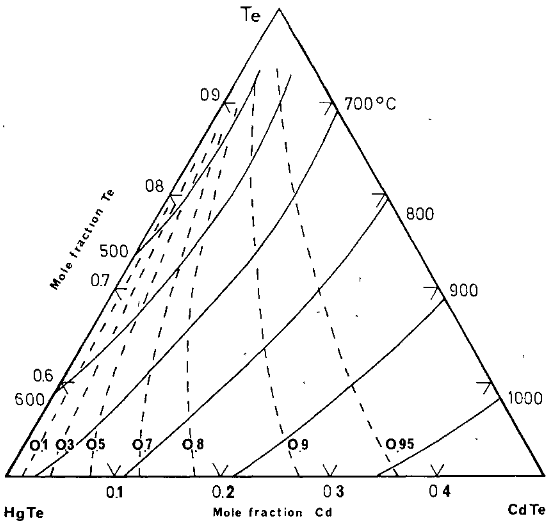

FIG. 13. — Calculated Cd-Hg-Te ternary phase diagram in the Te rich part. Solid lines : liquidus isotherms, dashed lines : solid-iso-concentration curves.

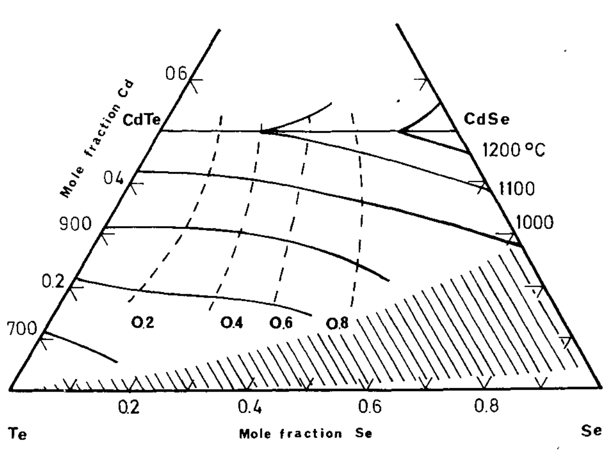

FIG. 14. — Calculated chalcogen-rich part of the Cd-Se-Te system. Solid lines : liquidus isotherms, dashed lines : solid-iso-concentrations curves. The dashed aera corresponds to the monotectics.

6. **Conclusion.** — We have shown that the ternary T-x phase diagrams of some II-VI and IV-VI systems can be well described by the regular associated solution theory. Five parameters are used : α_1, α_2, β_1, β_2, obtained from the binary liquidus and W, given by the pseudo-binary diagrams. One should not infer, however, that this is a complete proof of the assumptions of this theory. A systematic study of various solution model available for these systems was made recently [51]. This study indicates that the RAS model is only one among several others which give reasonably good fit to the experimental data. However, this model is attractive for ternary systems because of its relative simplicity and of the small number of parameters involved. A good approach to the problem seems to be a development of the surrounded atom model (13).

Experiments independent of phase equilibria are needed to prove the existence of species A, C, AC in the binary liquids. Some attempts have previously been made. Regel [52] has considered the relation between the structure of liquids and their physical properties. Melting of Si, Ge, GaSb, InSb, results in a sharp increase of density ρ and electrical conductivity σ which apparently is connected with rearrangement from a diamond structure to a more closely packed one having metallic characteristics. In contrast, melting of HgSe results in a sharp decrease of ρ and σ attributed to the formation of complexes. For ZnTe and CdTe, Glazov and Chizhevskaya [53] have found a maximum of viscosity and an anomaly of σ for the stoichiometric liquid over a large temperature range. The observed behaviour is well accounted for by the hypothesis of strong association. The same experiments were made by Glazov *et al.* [54] on binary systems formed by Te with elements of column IV. In particular, for PbTe and SnTe, the estimated degree of dissociation is again negligible up to 50° above the melting point. The electrochemical data also give some information. The activity of Pb in the Pb-Se was directly determined by e. m. f. measurements [43]. In a large range of concentration and temperature the results are in excellent agreement with eq. (24), the association being quite complete on the liquidus. In this case the RAS model seems confirmed.

All these methods are indirect, as is the phase diagram study. X-ray measurements, or neutron diffraction experiments could give direct information on the structure of these liquids. This is already the case for pure Te as studied through neutron diffraction by Tourand and Breuil [55] but for binary systems the interpretation of experimental data will be delicate because four correlation functions : g_{AA}, g_{BB}, g_{AB}, g_{BA} are to be considered.

As a conclusion, it seems that the association is a very useful and fruitful concept to take into account the properties of liquid solutions of chalcogens with metals of groups II and IV.

Acknowledgment. — The author is greatly indebted to M. Rodot, H. Rodot and M. Schneider for many useful and critical discussions and wishes to acknowledge the assistance of J. C. Guillaume for the computer programming.

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