Quantitative Fits to the Liquidus Line and High Temperature Thermodynamic Data for InSb, GaSb, InAs, and GaAs

R. F. BREBRICK

Quantitatively satisfactory fits are obtained for the liquidus lines of the congruently-melting, "line-compounds", InSb, GaSb, InAs, and GaAs using a recently derived basic liquidus equation. In addition the fits are consistent with 1) the relations imposed by a zero Gibbs free energy change on congruent melting and 2), except for GaAs, the experimental, compound-V element, eutectic temperature. The successful liquid phase model is a simple one in which the enthalpy and excess entropy of mixing are cubic functions of the atomic fraction. With all parameters fixed by these fits, other high temperature properties are calculated and agree satisfactorily with experiment. All fits are shown in tabular form. They appear so good that it seems likely the model will prove adequate for all the III-V systems. A small temperature dependence, consistent with the presently incomplete data, can be incorporated into the enthalpy and excess entropy without adversely affecting the fits obtained. On the other hand, extensive calculation and comparison with experiment conclusively shows that the two-parameter, quasiregular, or simple solution model does not give a satisfactory overall fit.

I. INTRODUCTION

IN this paper we seek simultaneous fits to the liquidus lines and other high temperature thermodynamic data for the congruently melting, narrow homogeneity-range compounds InSb, GaSb, InAs, and GaAs. The basic liquidus equation,[1] in contrast to that commonly used, is general as far as the liquid phase is concerned and takes account of the temperature dependence of the enthalpy and entropy of compound formation. Because the Gibbs free energy of formation of the compounds from their pure elemental liquids can be very accurately represented as a linear function of temperature, it is possible to justify the use of an approximate form of this equation which is more convenient for computation. The liquid model is one in which the enthalpy and excess entropy of mixing are cubic functions of the atom fraction and depend upon temperature. Our prime results are: 1) the quasiregular or simple solution model, which is contained within our model, is grossly inadequate, even though it can reproduce the liquidus line alone and has been successfully used to reproduce the liquidus surface in ternary systems[2] based on the III-V's; and 2) the cubic model can fit all the data with what seems to be reasonable precision. In fact it can do so with a temperature-independent enthalpy and entropy of mixing, and the fits are not significantly changed by allowing a small, temperature dependence consistent with the scanty information presently available.

The analysis presented here differs from that commonly used in a number of respects. 1) A quantitative measure of fit is defined and calculated and, where seems appropriate, the sensitivity of the fit

to the values of the liquid model parameters is established. 2) Use is made of auxiliary relations between the liquid phase properties and those of the compound at the congruent melting point which arise because the Gibbs free energy of melting is zero.[1,3] With our formulation of a liquid model these can serve to fix two of the parameters. 3) The constraints imposed upon the parameters of the liquid model by requiring that the calculated compound-V element eutectic temperature agree with experiment are formulated and applied. Similar constraints for the eutectic with the III element prove not to be useful since these eutectics are almost degenerate with the melting point of the pure element. With a "heat-of-fusion" liquidus equation, used commonly and here, the liquidus point representing the melting point of the compound is always fit exactly. Eutectic temperatures are similar in providing thermal arrests and can be duplicated for a number of compositions. Therefore they potentially are more accurately determined than an arbitrary liquidus point and ought to be handled differently when they have been carefully determined. Since good fit to the liquidus line does not always imply the eutectic temperatures can be fit to within their experimental error, this more complete use of the phase diagram data is generally significant. Recently ternary liquidus surfaces for a number of reciprocal-salt systems have been reproduced well using the simple solution model with only the melting points of the pure salts and the binary eutectic temperatures as experimental input.[4] 4) Having fixed all of the liquid model parameters at this stage, for the case of a temperature independent enthalpy of mixing, values for other properties already measured are calculated and found to agree well with experiment. These include the enthalpy of mixing in the liquid phase for GaSb and InSb, the chemical potential on In in liquid In-Sb, and the partial pressures of As_2 over metal-saturated InAs and GaAs. Because the fits appear to be so good and to be so extensive we have presented the comparison between calcu-

lated and experimental values in tabular form rather than graphical form.

We have previously analyzed[3,5] the liquidus lines for these same four compounds using the features mentioned in (1) and (2) above. However, here we have not made the approximation that the enthalpy and entropy of formation of the compound are independent of temperature and have used the values for these quantities at the melting point in applying the auxiliary relations (2), as should be done. Here we have also used values for the thermodynamic properties of the compounds which are slightly different than those used previously, have included low temperature liquidus points omitted previously, and extended the analysis to more thermodynamic properties as indicated in (3) and (4) above. As a result the conclusion that the quasiregular model is inadequate is based on broader grounds here and the arguments are presented in such a way that the effect on this conclusion of errors in the thermodynamic data can be assessed. This is important since an opposite conclusion has been reached elsewhere[6] for GaAs.

The necessary thermodynamic data for the compounds are presented in the next section. Those for InSb and GaSb are taken or calculated from the critical compilation of Hultgren et al[7] and the sources of data for InAs and GaAs are identified. In particular, recent measurements necessitate some revision for the thermodynamics of As-vapor, which is discussed first.

II. EXPERIMENTAL DATA INPUT

The melting points and heats of fusion for the pure elements were taken from the critical compilation by Hultgren et al.[8] The thermodynamic properties of As(c) and $As_2(g)$ tabulated in Hultgren were used, but those for $As_4(g)$ were taken from Herrick and Feber,[9] who measured a vapor pressure of As(c) some 2 to 3 times lower than that selected in Hultgren. More recent measurements confirm these lower values.[10,11] The pertinent quantities are listed in Table I. Row 1 is from Herrick and Feber. Row 2 for the dissociation of $As_4(g)$ is based on a recent Knudsen-cell mass-spectrographic study[12] in which special

care was taken to minimize spuriously high As_4 signals that apparently affected previous investigations. A least-squares analysis gives a best-fit line in the $\Delta H_{298}-\Delta S_{298}$ plane.[13] The value of ΔH_{298} shown in Row 2 is the value on the best-fit line corresponding to the ΔS_{298} calculated from the entropy of As_4 given in Row 1 and a value of 8.534 eu for As(c) (Ref. 8). The value for ΔH_{298} is 3.8 kcal smaller than that selected by Hultgren. The enthalpy and entropy of dissociation at 900 K are given in Row 3, while ΔC_p which is accurately given as a linear function of T between 800 and 1200 K, is given in Row 4. Since the heat capacity of $As_2(g)$ is essentially constant with T between 700 and 1200 K while that for As_4 is increasing slowly with T between 800 and 1300 K we assume the expression for ΔC_p can be safely extrapolated to the 1513 K melting point of GaAs. The equations derived for the enthalpy and entropy of $As_4(g)$ dissociation above 800 K are given in Row 5. These are used to obtain p_2 for a given total arsenic pressure and T. The partial pressure of As_2 over As(c), p_2^0, calculated using Herrick and Feber's vapor pressure is given in Row 6. It is also desired to know the partial pressure of As_2 over metastable, supercooled As(l) for $T < 1090$ K in order to calculate partial pressures. The thermodynamic properties of the pure supercooled liquid elements must also be defined for our analysis of the liquidus lines. In every case we define these properties following Hultgren et al[7] by assuming the ΔC_p between the stable solid and metastable liquid is zero. Thus in the particular case of As with a heat-of-fusion of 5620 cal/gm-atom and a melting point of 1090 K we have

$$\mu_{As(l)} = \mu_{As(c)} + 5620\ (1 - T/1090)\quad T \leq 1090\ \text{K.}\ [1]$$

With this definition the partial pressure of As_2 in equilibrium with supercooled As(l), p_2', is given in Row 7 of Table I.

The vapor pressure over As(l) has been determined only once and over a short temperature interval. We obtain an approximation up to 1513 K in the following manner. The heat capacity of $As_4(g)$ varies linearly between 1000 and 1300 K as given by the equation in Row 8. It is assumed this equation is valid to 1513 K. That for As(c) is given in Row 9. The free energy function for As(l) is approximated by assuming that its heat capacity to 1513 K is equal to that of As(c) given in Row 9. The values for the vapor pressure of As(l) obtained are given in Row 10. Finally the partial pressure of As_2 over As(l), obtained is given in Row 11.

After completing the calculations to be described in this paper we became aware of recent vapor density measurements by Rau,[42] who determined the vapor pressure of As from 540 to 1123°C, obtained ΔH_{298} for the dissociation of As_4, and obtained values for the van der Waals constants of the vapor. There is some disagreement between Rau's results on the one hand, and the entries of Table I and the results of Herrick and Feber[9] on the other. As an aid to concisely discussing these, we first point out those entries in Table I that enter as direct input to our phase diagram calculations. The equations in Rows 7 and 11 giving the partial pressure of As_2 in the saturated vapor over As(l), p_2', are used in the calculations of p_2 over InAs

Table I. Pertinent Thermodynamic Properties of Arsenic

1) $As(c) \rightarrow \frac{1}{4}As_4(g)$ $\Delta H_{298} = 9.635$ kcal; $\Delta S_{298} = 11.174$ eu; $S_{298}(As_4(g)) = 78.834$ eu

2) $\frac{1}{4}As_4(g) \rightarrow \frac{1}{2}As_2(g)$ $\Delta H_{298} = 13.367$ kcal; $\Delta S_{298} = 9.06$ eu

3) $\Delta H_{900} = 13.057$ kcal; $\Delta S_{900} = 8.53$ eu

4) $\Delta C_p = -0.4947 - 3.875(10^{-6})(T-900)\ 800 \leqslant T \leqslant 1200\ \text{K}$

5) $T \geqslant 800\ \text{K}$ $\Delta H_T\text{(cal)} = 52,229 - (1.9787)(T-900) - 0.775(10^{-5})(T-900)^2$

         $\Delta S_T\text{(eu)} = 34.12 - 1.96475\ \ln\ T/900 - 1.55(10^{-5})(T-900)$

6) Saturated vapor, $T \leqslant 1090$ K, $\log_{10} p_2^0 (\text{atm}) = (9487.7/T + 7.8596$

7) Equilibrium with As(l), $T \leqslant 1090$ K, $\log_{10} p_2' (\text{atm}) = -7031.7/T + 5.6066$

8) $C_p(As_4(g)) = 19.744 + 1.73(10^{-4})(T-1000)$

9) $C_p(As(c)) = 5.536 + 1.328(10^{-3})T\ \ 300 \leqslant T \leqslant 1000$ K

10) Estimated vapor pressure of As(l)

T K	1090	1100	1200	1300	1400	1500	1513
P (atm)	22.18	23.22	34.66	47.39	60.24	69.89	73.82

11) Saturated vapor, $T \geqslant 1090$ K, $\log_{10} p_2' (\text{atm}) = -6557.4/T + 5.1836$

and GaAs. The equations in Row 5 are needed to convert some total arsenic pressure measurements for GaAs to p_2-values. The values in Rows 1 and 2 are needed to obtain the standard enthalpy and entropy of formation of GaAs discussed below. The vapor pressure of As(l) obtained by Rau is 2 to 1.3 times as high as the estimated values in Row 10 and the fugacity coefficient, f_g, is about 0.80. Remarkably, however, the values for $f'_g p'_2$ agree with the values of p'_2 calculated from the equation in Row 11. The vapor pressure of As(c) obtained by Rau is about 1.6 times higher than that from Herrick and Feber. However the values for $f_g p_2^0$ are in agreement with the values calculated for p_2^0 from Row 6 at 527 and 817°C and are within 10 pct of these values at intermediate temperatures. The values of ΔH_{298} in Rows 1 and 2 are within respectively 300 and 100 cal of those obtained by Rau. Therefore the direct input data from Rows 1, 2, 5, 7, and 11 are consistent with Rau's results if p'_2 in the equations of Rows 7 and 11 are replaced by $f'_g p'_2$.
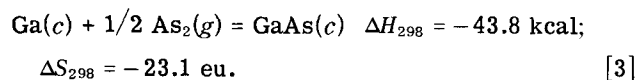
The thermodynamic properties of the compounds used in the calculations are given in Table II. The heats-of-fusion, H_{mn}, are from Lichter and Sommelet.[14] The standard enthalpy and entropy of formation at 298, $\Delta H_f^0(298)$ and $\Delta S_f^0(298)$ respectively, and the heat capacity of the compound above 298 K, C_p, were taken from Hultgren for InSb and GaSb. The values for GaSb were adjusted slightly, $\Delta H_f^0(298)$ being made 56 cal per mole less negative and $\Delta S_f^0(298)$ being made 0.3 eu per mole more negative. The enthalpy, entropy, and Gibbs free energy of formation of AB(c) from the pure *liquid* elements was then calculated at 100 K intervals taking into account the difference in heat capacity between the compound and the pure elements. The enthalpy and entropy at the melting point, T_{mn}, are given under $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ respectively. For temperatures below the melting point of one or both the pure elements, the metastable, supercooled, elemental liquid was defined by assuming a zero difference between the heat capacity of this phase and that of the stable solid element. For each compound the Gibbs free energy of formation from the liquid elements was found to be given to within 0 to 40 cal/mole by a linear function of temperature between 298 K and the melting point, *i.e.*

$$\Delta G_f = \Delta \overline{H}_f - T \Delta \overline{S}_f + \delta(T) \qquad [2]$$

where $\delta(T)$ is less than 40 cal per mole. The average enthalpy and entropy of formation, $\Delta \overline{H}_f$ and $\Delta \overline{S}_f$ respectively were chosen to make $\delta(T_{mn})$ equal to zero, in addition to making $\delta(T)$ small. Their values are given in the last two columns of Table II.

A similar procedure was followed for InAs and GaAs using the heat capacities for these compounds

from Lichter and Sommelet.[15] In the latter case it was necessary to approximate the enthalpy and entropy of As(l) above 1090 K as discussed above. For both InAs and GaAs, ΔG_f was again found to vary linearly with temperature from 298 K to the melting point, the value of $\delta(T)$ being less than 15 cal per mole. The values for $\Delta S_f^0(298)$ are close to those derived from Piesbergen's[16] low temperature heat capacity measurements on the compounds. However, since it has only recently been well established, some discussion is required concerning $\Delta H_f^0(298)$ for GaAs. Panish[6] has analyzed three sets of Knudsen-cell, mass-spectrographic measurements[17-19] of the partial pressure of As$_2$ over coexisting Ga-saturated GaAs(c) and a Ga-rich liquidus corresponding to liquidus compositions less than 0.07 in atomic-fraction As. Making the assumption, confirmed by theoretical analysis here, that the activity coefficient of Ga is unity gives

$$\text{Ga}(c) + 1/2 \text{ As}_2(g) = \text{GaAs}(c) \quad \Delta H_{298} = -43.8 \text{ kcal};$$

$$\Delta S_{298} = -23.1 \text{ eu}. \qquad [3]$$

Combining these quantities with those selected for arsenic by us and given in Rows 1 and 2 of Table I gives the standard enthalpy and entropy of formation of GaAs at 298 K listed in Table II. A more recent[20] mass-spectrographic study yielded an enthalpy *one* kcal more negative than that in Eq. [3]. Earlier[5] we had obtained values of -19.8 and -21.8 kcal per mole for $\Delta H_f^0(298)$ from the analysis of two vapor transport studies. In view of these results, and the fact that the low enthalpy given in Table I for the dissociation of As$_4$ has been confirmed, we believe the values given in Table II for $\Delta H_f^0(298)$ and $\Delta S_f^0(298)$ of GaAs are accurate to ±1.5 kcal and ±0.5 eu respectively. The value of $\Delta H_f^0(298)$ for InAs in Table II is from a determination by solution calorimetry.[21] A recent[20] mass-spectrographic measurement of p_2 over In-saturated InAs coupled with, a) the assumption that the activity of In in the coexisting liquid is unity and, b) the entries in Rows 1 and 2 of Table I, gives a value for $\Delta H_f^0(298)$ that is 0.8 kcal per mole more negative than that shown in Table II. We have chosen the direct calorimetric determination. We believe the values of $\Delta H_f^0(298)$ and $\Delta S_f^0(298)$ in Table II for InAs are also accurate to ±1.0 kcal and ±0.5 eu respectively.

The experimental liquidus points used are given in tables in which the atom fraction of the Group V element is given in the first column and the liquidus temperature in degrees centigrade in the second. The other columns are calculated quantities discussed later. In Table V for InSb all except the first five points are from tabulated results[22] of thermal analysis

Table II. Thermodynamic Properties of the Compounds, $AB(c)$ Enthalpies in kcal/mole, Entropies in eu/mole

| | T_{mn}, °C | H_{mn} | $-\Delta H_f^0(298)$ | $-\Delta S_f^0(298)$ | $C_p = a + (10^{-3})bT$ | | $-\Delta H_f(T_{mn})$ | $-\Delta S_f(T_{mn})$ | $-\Delta \overline{H}_f$ | $-\Delta \overline{S}_f$ |
					a	b				
InSb	525	11.41	7.40	3.82	11.340	2.60	13.27	11.53	13.020	11.22
GaSb	709.2	15.80	9.884	2.558	11.340	2.60	16.300	13.10	16.231	13.03
InAs	942	18.40	14.8	4.25	11.722	2.514	21.298	11.668	21.458	11.79
GaAs	1240	25.18	21.17	2.86	10.450	2.834	28.253	13.05	28.386	13.14

and are rounded off to the nearest degree, the first five are from dissolution experiments and were scaled from a graph.[24] Twelve Sb-liquidus points are also shown. In Table VII for GaSb the first six points were scaled from a graph representing dissolution experiments.[23,24] The remaining points are tabulated results obtained from differential thermal analysis.[26] Since these data appear to be very precise, two older data sets[27,28] covering the same composition range and somewhat in disagreement were ignored. This table also includes Sb-liquidus points.[26] In Table VIII for InAs the first 4 points are from dissolution experiments by Hall[23] as scaled from a graph by Shunk.[24] Two points were eliminated from this set because they appeared inconsistent with the others. The remaining points are from a tabulated set[25] (from which two points were eliminated) determined by thermal analysis and rounded to the nearest degree here. There are only two As-liquidus points. The first nine points in Table X for GaAs are from surface reflectivity measurements[29] summarized by an equation duplicating the individual results to better than 2°C. The next seven points are from dissolution experiments[23] and are scaled from a graph.[24] Because these two low temperature results agree so well and

differ from a third set[30] based on dissolution experiments, the latter was ignored. The remaining points were scaled from a graph representing the results of thermal analysis.[27]

Because it is desired to handle the eutectic temperatures in our analysis in a special way, these and the corresponding compositions are given in Table III. As discussed later, only those between the compound and the Group V element prove useful and are discussed below. The temperatures for the eutectic with the Group V elements are from tabulated results except for GaAs, for which only a small graph was given. Although a 810°C temperature was given[27] for GaAs it appears that this may not be too reliable. The liquidus points for the two most As-rich compositions do not fit smoothly with the other two and the GaSb diagram reported in the same paper is in significant disagreement with more recent and evidently more precise results. Thus although we shall refer to 810°C for the GaAs-As eutectic we do not consider it well established. For InSb and GaSb the results appear quite accurate, the entire range covered by all the determinations falling in each case within an interval 2°C wide.

Although the InAs-As eutectic temperatures cover a 731 to 742°C range those compositions closest to the eutectic composition gave 731 ± 1°C. Other experimental data were used as further checks on the validity of the liquid phase models adopted here and are discussed in the section on results.

III. LIQUID PHASE MODEL

The model used for the liquid phase is defined by specifying the enthalpy and excess entropy of mixing as

Table III. Eutectic Temperatures and Compositions
(Degrees Centigrade and Atom Fraction of Group V Element)

Compound	(III-V) V T	x_V	III (III-V) T	x_V
InSb	494 ± 0.5	0.69	154.8 ± 0.2	$7(10^{-3})$
GaSb	589 ± 0.5	0.88		
InAs	731 ± 1	0.87	155.2 ± 0.2	$2(10^{-4})$
GaAs	810?	–	29.7	–

Table IV. Summary of Fits to Thermodynamic Data ($\sigma(T, V)$ is the Fit to the Group V Liquidus, T(eut) and x(eut) are the Calculated Temperature and Atom Fraction V-Element at this Eutectic, $\Delta H_M^L(\frac{1}{2})$ is the Enthalpy-of-Mixing at $x = \frac{1}{2}$ and the Specified T for the Liquid in cal/gm-atom)

		W, cal	a	V, eu	c	f	$\sigma(T)$, °C	$\sigma(T, V)$, °C	T(eut), °C	x(eut)	$\Delta H_M^L(\frac{1}{2})$ $T = 900$ K	$\sigma(\mu(\text{In}))$ cal/gm-atom
InSb	1a	+3522	0	+11.988	0	0	7.6	27	<470	>0.721	+881	1275
$\sigma(T, \text{crit}) = 5–10$	1b	−3720	0	0.02377	0	0	18.8	–	–	–	–	–
	2a	−3720	0	0.02377	0	−9.057	10.23	15.4	480	0.717	−1161	179
	2b	−3720	0	0.02377	0	−872.9	182.0	–	494	0.729	–	–
	3	−3720	1.559	0.02377	−395.83	0	7.2	6.0	494	0.689	−930	94

											$\Delta H_M^L(\frac{1}{2})$ $T = 1023$ K cal/gm-atom	
GaSb	1a	+7524	0	+10.126	0	0	3.2	0.97	589	0.885	+1881	
$\sigma(T, \text{crit})$ 5–8°C	1b	−1000	0	0.4602	0	0	14.1	1.10	–	–	−250	
	2	−1000	0	0.4602	0	−16.78	4.9	1.1	589	0.889	−421	
	3	−1000	12.350	0.4602	−31.35	0	5.8	1.0	589	0.887	−250	

											$\sigma(p_2)$	
InAs	1a	+2270	0	9.020	0	0	15.6	14.8	733	0.860	0.41	
$\sigma(T, \text{crit}) = 10–20$	1b	−5780	0	1.440	0	0	22.5	–	–	–	0.10	
	2	−5780	0	1.440	0	−11.52	15.5	–	733	0.861	0.09	
	3	−5780	1.98	1.440	−7.80	0	12.9	15.0	731	0.859	0.12	
GaAs	1a	+5432	0	9.66	0	0	5.3	–	806	0.979	1.85	
$\sigma(T, \text{crit}) = 5–10$	1b	−6146	0	1.674	0	0	53.5	–	–	–	–	
	2	−6146	0	1.674	0	−15.98	12.23	–	804.3	0.972	0.35	
	3	−6146	1.806	1.674	−4.430	0	7.4	–	788	0.947	0.36	

$$\Delta H_M^L = x(1 - x)W\{1 + (f/W)(T - T_{mn}) + a(x - 1/2)\} \quad [4]$$

$$\Delta S_{M'}^{L,e} = x(1 - x)V\{1 + (f/V) \ln T/T_{mn} + c(x - 1/2)\} \, [5]$$

where W, V, a, c, and f are constants which can be adjusted to fit the data for a particular system, T_{mn} is the maximum melting point of the compound, and x is the atom fraction of component B in the A-B system. Mathematically these truncated Margules expansions are entirely equivalent to similar expressions in which the factor $x - 1/2$ in the cubic term is replaced by a factor $x - x_0$ where x_0 is some constant.

Table V. Liquidus Lines in the In-Sb System (InSb Liquidus; $W = -3720$, $a = 1.5590$, $V = 0.02377$, $c = -395.83$, $\sigma(T) = 7.2°C$)

x, Sb	T, obs	T, cal	Diff	γ, Sb	γ, In
0.0016	165	152	-13	0.0352	1.000
0.0056	205	192	-13	0.0389	1.000
0.0150	235	231	-4	0.0435	0.999
0.0300	265	265	0	0.0498	0.998
0.1200	350	366	16	0.0991	0.956
0.0470	283	291	8	0.0571	0.994
0.0950	329	344	15	0.0824	0.973
0.191	420	420	0	0.163	0.886
0.239	452	451	-1	0.220	0.827
0.288	479	476	-3	0.289	0.761
0.337	497	497	0	0.367	0.693
0.386	512	511	-1	0.449	0.627
0.442	523	522	1	0.544	0.554
0.500	525	525	0	0.635	0.485
0.5362	524	524	0	0.687	0.444
0.586	518	518	0	0.750	0.393
0.636	510	508	-2	0.805	0.344
0.687	495	492	-3	0.851	0.297
Sb Liquidus; $\sigma(T) = 6.0°C$					
0.713	507	494	-13	0.877	0.278
0.7387	527	512	-15	0.909	0.267
0.7904	547	544	-3	0.955	0.251
0.8165	560	558	-2	0.971	0.246
0.8423	572	570	-2	0.982	0.242
0.8684	583	582	-1	0.990	0.241
0.8945	593	592	-1	0.995	0.240
0.9155	600	601	+1	0.998	0.242
0.9366	610	608	-2	0.999	0.245
0.9577	616	616	0	1.000	0.249
0.9788	624	623	-1	1.000	0.255
0.9884	625.4	626.5	+1	1.000	0.259

Table VI. Chemical Potential of In in In-Sb Melt at 627°C ($(\sigma(\mu(In))) = 94$ cal/gm-atom)

x, Sb	$-\mu(In)$obs	$-\mu(In)$cal	Diff
0.889	6432	6302	130
0.731	4400	4402	-2
0.708	4204	4189	145
0.646	3545	3650	-105
0.563	2920	2983	-63
0.418	1827	1931	-104
0.349	1356	1484	-128
0.303	1095	1208	-113
0.293	1010	1151	-141
0.234	745	832	-87
0.142	337	415	-78
0.085	182	212	-30

Table VII. Liquidus Lines in the Ga-Sb System (GaSb Liquidus; $W = -1000$, $a = 12.35$, $V = 0.46024$, $c = -31.350$) $\sigma(T) = 5.9$

x, Sb	T, obs	T, cal	Diff	γ, Sb	γ, Ga
0.0010	330	348	18	1.380	1.000
0.0040	390	402	12	0.981	1.000
0.0140	460	458	-2	0.721	1.000
0.0700	560	549	-11	0.528	0.998
0.1800	630	627	-3	0.568	0.962
0.3100	685	682	-3	0.727	0.872
0.0804	557	559	2	0.523	0.996
0.1000	576	575	-1	0.521	0.993
0.1201	592	590	-2	0.526	0.987
0.1501	611	610	-1	0.543	0.976
0.1801	629	627	-2	0.568	0.962
0.2040	641	639	-2	0.593	0.948
0.2054	636	640.2	4	0.595	0.947
0.3031	682	680	-2	0.718	0.878
0.3500	694	692	-2	0.780	0.841
0.3998	703	702	-1	0.840	0.803
0.4490	707	707	0	0.892	0.769
0.5000	709.2	709.2	0	0.933	0.739
0.5515	707.5	707.5	0	0.963	0.713
0.6139	701	701	0	0.984	0.689
0.6495	693	695	2	0.990	0.678
0.7004	682	684	2	0.994	0.664
0.7510	660	669	9	0.993	0.649
0.8000	638	648	10	0.992	0.628
0.8247	626	635	9	0.991	0.611
0.8596	606	611	+5	0.990	0.575
0.8701	600	603	+3	0.990	0.559
0.8840	589	589	0	0.990	0.534
Sb Liquidus; σ, $T = 1.0°C$					
0.8840	589	587	-2	0.990	0.532
0.9150	601	600	-1	0.995	0.528
0.9199	600	601.6	1.6	0.996	0.528
0.9270	604.5	604.4	-0.1	0.997	0.528
0.9389	609	609	0	0.998	0.529
0.9668	619	619	0	0.999	0.535
0.9599	617	616.5	-0.5	0.999	0.533
0.9800	623.5	623.6	0.1	1.000	0.540

Table VIII. Liquidus Lines in the In-As System (InAs Liquidus; $W = -5780$, $a = 1.98$, $V = 1.440$, $c = -7.80$) $\sigma(T) = 12.9°C$

x, As	T, obs	T, cal	Diff	γ, As	γ, In
0.019	530	531	11	0.0299	0.999
0.038	580	581	1	0.0335	0.996
0.120	700	703	3	0.0597	0.952
0.170	750	760	10	0.0863	0.900
0.144	721	732	11	0.0712	0.929
0.210	793	800	7	0.115	0.848
0.274	851	855	4	0.177	0.750
0.334	889	895	6	0.253	0.653
0.458	928	939	11	0.446	0.465
0.500	942	942	0	0.514	0.409
0.547	941	938.5	-2.5	0.588	0.352
0.697	892	882	-10	0.784	0.200
0.781	857	817	-34	0.866	0.128
0.80	-	798	-	0.882	0.112
0.82	-	775	-	0.898	0.096
0.85	-	737	-	0.921	0.073
As Liquidus; σ, $T = 16.1°C$					
0.897	747	759	12	0.964	0.0589
0.932	765	783	18	0.985	0.0516

However, as shown in the next section, the form given is more convenient in describing the liquidus line of a compound AB, whereas the form with $x - 1/2$ replaced by $x - n/(n + m)$ would be more convenient in dealing with $A_m B_n$. For the same reason the temperature dependence of ΔH_M^L is written in terms of $T - T_{mn}$. From the fundamental thermodynamic relations for the temperature dependence of ΔH_M^L and $\Delta S_M^{L,e}$ it can be seen that the temperature dependence of $\Delta S_M^{L,e}$ is consistent with that of ΔH_M^L and implies a difference in constant-pressure heat capacity between the liquid of composition x and $1 - x$ gm-atoms of pure liquid A and x gm-atoms of pure liquid B given by

$$\Delta C_p(l - e) = x(1 - x)f. \qquad [6]$$

In view of the above, the relative partial enthalpies and excess entropies (by definition) are given by

Table IX. Partial Pressure of As$_2$ in Atm Over In-Saturated InAs(c) $\sigma(p_2) = 0.12$

$T^\circ C$	x, As	p_2(obs) $\times 10^5$	p_2(cal) $\times 10^5$	100 $\times$ Diff/obs
810.9	0.221	7.75	10.12	31
795.3	0.205	4.45	5.51	24
787.7	0.197	3.67	4.10	11
779.6	0.189	2.62	2.9	1
762.8	0.173	1.52	1.52	0.3
746.2	0.157	0.781	0.779	-0.2
729.6	0.142	0.418	0.393	-6
712.8	0.128	0.207	0.194	-6
696.9	0.115	0.101	0.0982	-3
679.2	0.101	0.0447	0.0451	1
661.3	0.087	0.0212	0.0201	-5
653.0	0.081	0.0139	0.0137	-1
645.5	0.076	0.0094	0.0097	3

Table X. Liquidus Line for GaAs
($W = -5186, a = 1.830, V = 1.6735, c = -4.0520, \sigma(T) = 5.7^\circ C$)

x, As	T, obs	T, cal	Diff	γ, As	γ, Ga
0.00559	685	691	6	0.063	1.000
0.0119	744	746	2	0.065	1.000
0.0196	787	786	-1	0.068	1.000
0.0208	793	792	-1	0.068	0.999
0.0236	805	803	-2	0.069	0.999
0.0248	809	807	-2	0.0695	0.998
0.0277	820	817	-3	0.070	0.998
0.0392	854	851	-3	0.074	0.997
0.0628	905	904	-1	0.084	0.991
0.00004	445	444	-1	0.057	1.000
0.00020	510	509	-1	0.059	1.00
0.0010	585	587	+2	0.061	1.00
0.005	680	683	+3	0.062	1.00
0.020	790	788	-2	0.068	0.999
0.050	880	878	-2	0.079	0.995
0.10	965	967	+2	0.102	0.976
0.19	1071	1079	+8	0.164	0.909
0.32	1174	1186	+12	0.299	0.755
0.343	1200	1199	-1	0.328	0.723
0.392	1208	1221	+13	0.393	0.656
0.500	1240	1240	0	0.543	0.510
0.68	1169	1187	18	0.773	0.294
0.74	1144	1144	0	0.836	0.230
0.856	1015	1013	-2	0.935	0.116
0.90	–	936	–	0.964	0.077
0.92	–	892	–	0.975	0.060
0.94	–	840	–	0.984	0.045

$$h_A = x^2 W\{1 + (f/W)(T - T_{mn}) + a(2x - 3/2)\} \qquad [7]$$

$$h_B = (1 - x)^2 W\{1 + (f/W)(T - T_{mn}) + a(2x - 1/2)\} \qquad [8]$$

$$s_A^e = x^2 V\{1 + (f/V)\ln T/T_{mn} + c(2x - 3/2)\} \qquad [9]$$

$$s_B^e = (1 - x^2)V\{1 + (f/V)\ln T/T_{mn} + c(2x - 1/2)\}. \qquad [10]$$

This model contains a number of other important models as special cases. When W, a, V, and c are all zero we have the ideal solution model. When $a = c = f = 0$ we have the quasiregular or so-called simple solution model with a linearly temperature-dependent interaction-constant. This latter model has been widely used in fitting the liquidus lines in the Ge, Si,[31] and III-V systems.[2] Since the simple solution model appears to give an almost correct description of these systems we sought the simplest (possible) extension in arriving at the model used here. Previously[3] we had employed another generalization of the quasiregular model which has proved to be no better than that used here. For comparison the solution model recently[32] used in extensive computer analysis of binary metallic systems is characterized by an excess Gibbs free energy of mixing given by

$$\Delta G_M^{L,e} = x(1 - x)\{(1 - x)g(T) + xh(T)\} \qquad [11]$$

where $g(T)$ and $h(T)$ are temperature dependent functions. It appears that phase diagrams for a number of metallic systems can be reproduced well taking $g(T)$ and $h(T)$ as constants or linear functions of T. In either case the enthalpy and excess entropy of mixing derived from Eq. [11] are independent of temperature and are equivalent to Eqs. [4] and [5] if f is put equal to zero.

IV. BASIC EQUATIONS

A liquidus equation has recently been derived for a congruently melting, narrow homogeneity range compound which takes account of the temperature dependence of the enthalpy and entropy of formation of the compound and which is general as regards the liquid phase.[1] For the compounds considered here, the Gibbs free energy of formation from the pure elemental liquids is accurately, though not precisely, a linear function of temperature. Therefore, as discussed below, it proves valid to use an approximate form of Eq. [10] of Ref. 1. This proves convenient since the approximate equation is an explicit equation for T when the partial molar quantities for the liquid phase are independent of T. In contrast the exact equation is implicit in T and its use in our calculations to minimize $\sigma(T)$ of Eq. [15] below would require considerably more computer time. The approximate equation contains the heat of fusion per mole of $A_m B_n(c)$ H_{mn}; the congruent melting point, T_{mn}, and the relative partial enthalpies, h_A and h_B, and excess entropies, s_A^e and s_B^e, for the liquid phase. For $m = n = 1$ the equation is:

$$T = \frac{H_{mn} - \Delta + (h_A - h_A^*) + (h_B - h_B^*)}{\dfrac{H_{mn} - \Delta}{T_{mn}} + (s_A^e - s_A^{*,e}) + (s_B^e - s_B^{*,e}) - R\ln 4x(1-x)} \qquad [12]$$

where $\Delta = \Delta \bar{H}_f - \Delta H_f(T_{mn})$ and where the asterisk

superscript means the partial quantities are evaluated at $x = 1/2$ and $T = T_{mn}$.

The average quantities, $\Delta \bar{H}_f$ and $\Delta \bar{S}_f$, have been chosen here so that $\delta(T)$ of Eq. [2] is small and $\delta(T_{mn})$ is zero for each compound. Eq. [12] is then approximate only in the omission of the term, $-\delta(T)$, in the numerator of its right hand member. This numerator was obtained for all the calculations presented here and is approximately equal to the heat of fusion for each compound. Except for InSb the value of $\delta(T)$ is 15 cal per mole or less and the error incurred by using Eq. [12] is less than 1°C over the temperature ranges involved here and about the same for all fits. This error is negligible for our purposes. For InSb $\delta(T)$ is respectively -45 and -32 cal per mole at 600 and 500 K and the temperatures calculated using Eq. [12] are high by 2.5 and 1.5 K. Rather than use the exact equation for InSb we make a new selection for the experimental $\Delta G_f(T)$ for InSb which differs from the original only in that $\delta(T)$ in the 500 to 600 K is now in the ± 15 cal per mole range. This shift is of course well within the experimental error for $\Delta G_f(T)$ and Eq. [12] now gives liquidus temperatures accurate to better than 1 K, sufficient for our purposes.

The effect of experimental uncertainty in $\Delta G_f(T)$ and $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ on our calculations is considered as a separate question and discussed in Section VI.

Because the Gibbs free energy of melting is zero at the congruent melting point two auxiliary equations must be considered with the liquidus equation. These are given by:[1]

Auxiliary Relations

$$\Delta H_f(T_{mn}) + H_{mn} = (h_A^* + h_B^*) = W/2 \qquad [13]$$

$$\Delta S_f(T_{mn}) + H_{mn}/T_{mn} - 2.7546$$
$$= (s_A^{*,e} + s_B^{*,e}) = V/2. \qquad [14]$$

The fact the auxiliary relations conveniently involve only the liquid phase parameters W and V is attributable to the choice of the factor $(x - 1/2)$ in the cubic term for ΔH_M^L and $\Delta S_M^{L,e}$ and the use of T_{mn} as a reference temperature in the temperature dependence of these quantities.

As before[3,33] we define a quantitative measure of fit to a set of experimental liquidus points, T_j, $x_j (j = 1, N)$, as

$$\sigma^2(T) = \sum_{j=1}^{N} (T_j - T_{j,\text{cal}})^2/N \qquad [15]$$

where $T_{j,\text{cal}}$ is calculated by inserting x_j for x in Eq. [12]. An initial set of values for the five, liquid-model parameters, some or all of which may be zero, are chosen. Then a computer program systematically varies these in a trial and error search based on the simplex technique of Nelder and Mead[34] until a minimum value is found for $\sigma(T)$. As an option some or all of the variables may be held fixed at their initial values. If the parameter f in Eqs. [7] to [10] for the partial molar quantities is not zero, then the right side of the liquidus equation contains T and the equation is not an explicit solution for the calculated liquidus temperature. In this case a second simplex

subroutine is used to solve Eq. [12] for T, the solution being judged acceptable when the left and right sides of the equation differ by 0.005°C or less.

After each calculation of $\sigma(T)$, the activities of both components were calculated for the experimental compositions and a message printed if any of these were greater than unity. For the calculated liquidus points tabulated here the activities are all unity or less.

If the terminal solid solutions are the essentially pure elements, the equations for the associated liquidus can be demonstrated by writing that for component B.

$$T = \frac{H_B + h_B}{H_B/T_B + s_B^e - R \ln x} \qquad [16]$$

where H_B and T_B are the heat-of-fusion and melting point of B. The equation for the liquidus of $A(c)$ is obtained by changing all the B subscripts in Eq. [16] to A and replacing x by $1 - x$. The form of Eq. [16] is dependent upon the definition given in the Section I for the chemical potentials of the supercooled, pure liquid A and B and illustrated for arsenic by Eq. [1].

The eutectic temperature and composition involving $AB(c)$ and say pure $B(c)$ is given by the simultaneous solution of the corresponding liquidus equations, Eqs. [12] and [16]. We first consider the special case when $a = c = f = 0$. If T_e and x_e are respectively the eutectic temperature and composition (in atom fraction B) for the AB-B eutectic, Eqs. [13] and [16] can be rearranged to give

$$W - V T_e = \frac{(H_{mn} - \Delta)(T_e/T_{mn} - 1) - RT_e \ln 4x_e(1 - x_e)}{x_e^2 + (1 - x_e)^2 - 1/2} \qquad [17]$$

$$W - V T_e = \frac{H_B(T_e/T_B - 1) - RT_e \ln x_e}{(1 - x_e)^2}. \qquad [18]$$

Upon specification of the eutectic temperature the simultaneous solution of Eqs. [17] and [18] was accomplished by a trial and error search to obtain x_e and the quantity, $W - V T_e = k$, where k is a constant. Thus the values of W and V that are consistent with the eutectic temperature must fall along a straight line in the W-V plane, $W - V T_e = k$.

In the second case considered, $a = c = 0$ and W and V are fixed by the auxiliary relations. The simultaneous solution of Eqs. [12] and [16] for a specified eutectic temperature gives the eutectic composition and a value for the liquid phase parameter f.

In the final case considered W and V are fixed by the auxiliary relations. For a specified value of f, which can include zero, and a specified eutectic temperature Eqs. [12] and [16] can be solved simultaneously for the eutectic composition and the quantity, $Wa - VcT$. The latter quantity equal to a constant defines a straight line in the a-c plane passing through those values consistent with the specified eutectic temperature and value of f. Entirely analogous equations hold for the $A(c) - AB(c)$ eutectic provided the terminal solid solution is essentially pure $A(c)$.

The partial pressure data are in the form p_2, T. First a liquidus composition was calculated for the experimental temperature using a trial and error computer technique. Then a calculated value for p_2 was obtained using Eqs. [7] to [10] defining the liquid

phase model. Thus if p_2' is the partial pressure of As_2 in the saturated vapor over the *liquid* phase, the partial pressure of As_2 along the liquidus at T and $x = x_B = x_{As}$ is given by

$$1/2 \ln (f_g p_2 / f_g' p_2') = \ln x + \{h_B - Ts_B^e\}/RT \qquad [19]$$

where f_g is the fugacity coefficient. The experimental partial pressures for InAs and GaAs are low enough that the values of f_g from Rau[42] are essentially unity. The values for $f_g' p_2'$ are taken from Rows 7 and 11 of Table I with the proviso that f_g' may either be assumed to be unity, in which case the values of p_2' are consistent with Herrick and Feber's vapor pressure measurements, or p_2' in Row 7 and 11 is to be interpreted as $f_g' p_2'$, in which case the values of $f_g' p_2'$ are consistent with Rau's measurements. The measure of fit to the observed partial pressures was defined as

$$\sigma^2(p_2) = \sum_{j=1}^{M} \left[\frac{p_{2,j,\text{obs}} - p_{2,j,\text{cal}}}{p_{2,j,\text{obs}}} \right]^2 /M \qquad [20]$$

so that $\sigma(p_2)$ can be described as the standard deviation of the fractional difference between observed and calculated pressures. Such a definition is more appropriate than an analogue of Eq. [15] for $\sigma(T)$ since the experimental partial pressures cover many orders of magnitude and the measurements are more accurately characterized as possessing a nearly constant fractional error than a nearly constant absolute error.

V. RESULTS

Three special cases of the liquid model were investigated: 1) $a = c = f = 0$ with W and V free, 2) $a = c = 0$, W and V fixed by the auxiliary relations, 3) $f = 0$, W and V fixed by the auxiliary relations. The results are summarized in Table IV and those for each case are discussed in turn.

1) $a = c = f = 0$

The best-fit for case (1) is shown in Row 1a for each compound. In each case a satisfactorily low value is obtained for $\sigma(T)$ compared to our range for the critical value, $\sigma(T,\text{crit})$, characterizing the accuracy of the liquidus points. The corresponding values for W range from 2.2 to 7.5 kcal, for V from 9 to 12 eu, and except for GaSb are in close agreement with earlier analyses.[2,3,5] The difference for GaSb is due to our elimination of the older liquidus points in favor of the more recent and more precise results. In contrast, Row 1b shows the results when W and V are fixed by the auxiliary relations. In no case, except possibly InAs, is the value of $\sigma(T)$ small enough to be considered consistent with the accuracy of the liquidus points. Moreover the values for W are all negative and the values V are all small, between 0 and 1.7 eu. Significant details of the calculations are shown for each compound in a set of similar plots in Figs. 1 to 4. Fig. 1 for InSb shows contours for $\sigma(T)$ of 10, 15 and 30 deg in the W-V plane. These are narrow, elongated ellipses whose major axes fall along the heavy line (best-fit line) running from lower left to upper right. The best-fit point for which $\sigma(T) = 7.6°C$ is indicated by the square, the cross at the lower left indicates the value of W and V given by

the auxiliary relations, Eqs. [13] and [14]. The three dashed lines are the eutectic constraint lines obtained from the simultaneous solution of Eqs. [17] and [18]. From upper to lower they correspond to InSb-Sb eutectic temperatures of 494, 480, and 470°C. The experimental value of 494°C corresponds to values of $\sigma(T)$ that are greater than 30°C for positive W. Values less than 10°C for $\sigma(T)$ can be obtained only with eutectic temperatures of 470°C or slightly lower. We note that best-fit lines also occur in the analysis of
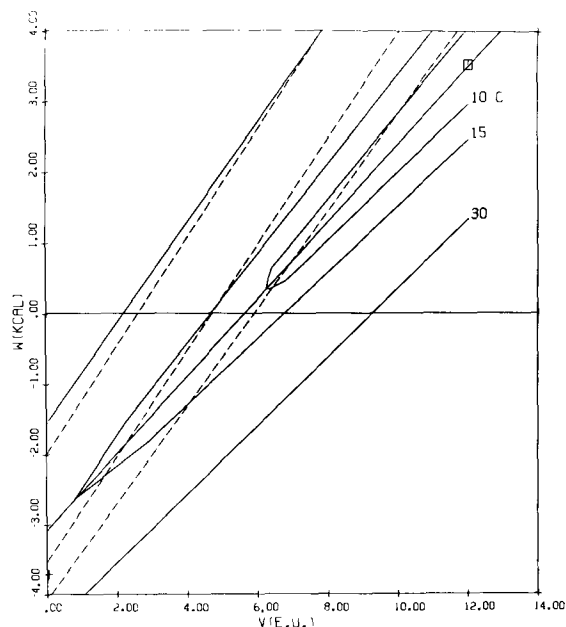

Fig. 1—Sensitivity of fit to InSb liquidus with only W and V nonzero. Lower half of contours of constant $\sigma(T)$ shown for 10, 15, and 30°C. The line through the middle of these contours is the best-fit line with the best-fit point of 7.6 deg indicated by a square. The cross at lower left marks the value for W and V given by the auxiliary relations, Eqs. [13] and [14]. The dashed lines define those values of W and V consistent with InSb-Sb eutectic temperatures of 494 (upper), 480 (middle), and 470°C.
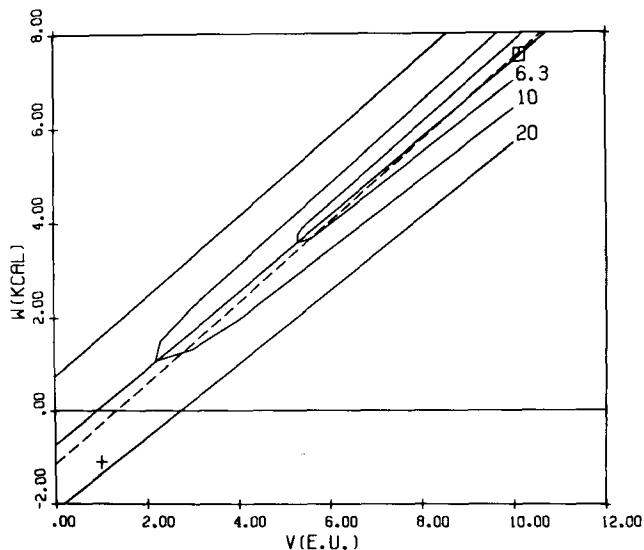

Fig. 2—Sensitivity of fit to GaSb liquidus with only W and V nonzero. Symbolism is the same as in Fig. 1. Dashed line is for a GaSb-Sb eutectic temperature of 589°C.
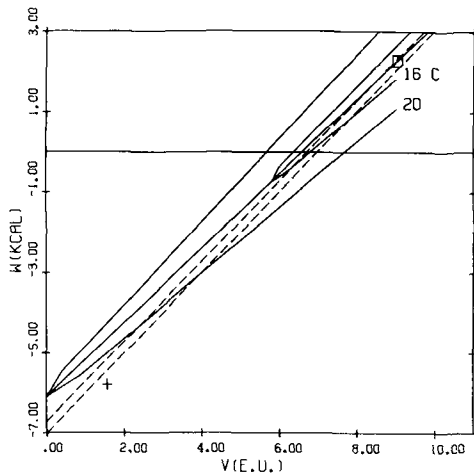
Fig. 3—Sensitivity of fit to InAs liquidus with only W and V nonzero. Symbolism is the same as in Fig. 1. Upper and lower dashed lines are for InAs-As eutectic temperatures of respectively 733 and 731°C.
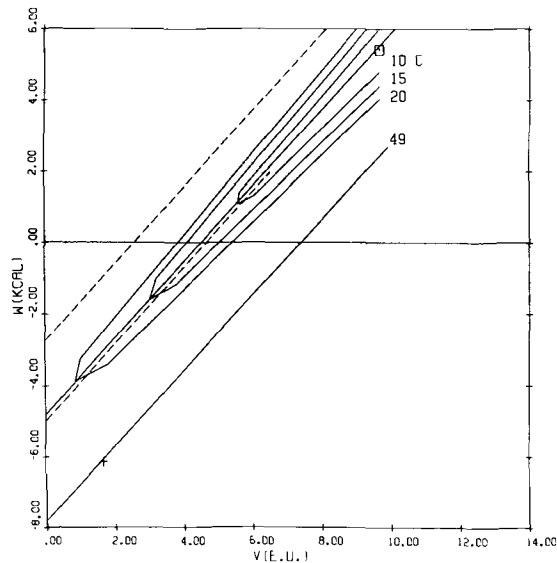

Fig. 4—Sensitivity of fit to GaAs liquidus with only W and V nonzero, symbolism as in Fig. 1. Upper dashed line for GaAs-As eutectic temperature of 810°C. Lower dashed line, close to best-fit line and through best-fit point, is for 806°C.

III-V pseudobinaries[33] and in the determination of second law enthalpies and entropies.[13]

In Figs. 1 to 4 the best-fit point and the point obtained from the auxiliary relations (indicated by a cross) differ by more than any reasonable errors in the quantities, $\Delta H_f(T_{mn}) + H_{mn}$ and $\Delta S_f(T_{mn}) + H_{mn}/T_{mn}$, defining the latter. The errors would have to be respectively -5 kcal and -5.6 eu for GaAs. Moreover, it also seems unlikely that the errors in these quantities are large enough to move the point fixed by the auxiliary relations close enough to the best-fit point to obtain a sufficiently good fit to the liquidus points. Simultaneous negative errors would have to be assumed for both quantities and for each compound. Except for InAs, they would have to be larger in magnitude than -1 eu per mole in the entropy quantity to reduce $\sigma(T)$ to within or the range of critical values. Such errors seem unlikely to us and rule out the quasiregular model as inadequate. Further compari-

son with the experimental data immediately below supports this conclusion.

The best-fit point in Row 1a for GaSb predicts an enthalpy-of-mixing at $x = 1/2$ in the liquid phase of 1881 cal per gm-atom, too large and of the wrong sign compared to the experimental values[35,36] at 982 and 1023 K of respectively -250 and -200 cal per gm-atom.

The best-fit point in Row 1a for InSb fits the 12 Sb liquidus points poorly with $\sigma(T, V) = 27$°C, predicts an InSb-Sb eutectic temperature of less than 470°C compared to the experimental value of 494°C, predicts a positive enthalpy-of-mixing in the liquid at $x = 1/2$ of 881 cal per gm-atom compared to negative experimental values near 900 K ranging from -600 to -1100 cal per gm-atom,[37-39] and fits the measured chemical potential of In at 900 K with a standard deviation of 1275 cal, which is comparable to the experimental value at $x = 1/2$ and is too large to be considered satisfactory. An InSb-Sb eutectic temperature of 494°C can only be obtained with values of W and V lying along the upper dashed line in Fig. 1 which lies outside the contour for $\sigma(T) = 15$°C and crosses that for $\sigma(T) = 30$°C, both too large to be satisfactory.

The best-fit point to the InAs liquidus fits the As-liquidus well and as seen in Fig. 3 and Row 1a is consistent with the experimental InAs-As eutectic temperature of 731°C. The fit to the partial pressure of As$_2$, $\sigma(p_2)$, is not as good as with the other cases of the model considered and probably should be considered inadequate.

For GaAs the best-fit point is consistent with an 806°C GaAs-As eutectic temperature but not with the 810°C value (which we consider uncertain). The partial pressure of As$_2$ is not fit well, the standard deviation in the fractional difference between calculated and observed values being 1.85.

On the basis of the above considerations it is concluded that this special case of the liquid model is inadequate.

2) $a = c = 0$

In this special case W and V are fixed by the auxiliary relations and f is the only adjustable parameter. Thus the enthalpy and excess entropy of mixing in the liquid phase are quadratic in atom fraction as in case (1) but, in contrast to case (1), depend upon temperature. Thus this is possibly the simplest extension of the quasiregular model of case (1) and it is of interest to see whether it is adequate. We do not elaborate in detail on the results which are summarized in Row 2 of Table IV for each compound. The fits are greatly improved over those shown in 1a but are not good enough to be satisfactory. The values of f required range from -9 to -16 and seem large. Experimental values[14] for the 50 at. pct melts of InSb and GaSb at 1300 K, subject to a 100 pct probable error, correspond to positive values of f of respectively 7.0 and 3.4.

3) $f = 0$

In this version of the liquid model the enthalpy and excess entropy of mixing are independent of temperature and are cubic functions of the atom fraction.

Since W and V are fixed by the auxiliary relations only a and c are adjustable to fit the liquidus data. The results are shown in Row 3 for each compound in Table IV. A fit to the liquidus points of the compound serves to define a best-fit line in the a-c plane along which $\sigma(T)$ varies relatively slowly and perpendicular to which $\sigma(T)$ varies relatively rapidly. Thus a range of values for a and c give values of $\sigma(T)$ less than the critical value. However, except for GaAs, the values of a and c consistent with the Group V element eutectic temperature fall along another, "eutectic constraint" line which intersects the best-fit line at a point where $\sigma(T)$ is still less than the critical value. The acceptable range for a and c is therefore narrowed enough to be ignored. With the liquid parameters thus fixed, the other thermodynamic quantities are calculated for comparison with experiment.

The data for InSb can be fit quite well with values of a and c consistent with the 494°C InSb-Sb eutectic temperature. The fits to the InSb and Sb liquidus points are shown in Table V. The experimental atom-fraction of Sb and liquidus temperature in degrees centigrade are given in the first two columns. The calculated liquidus temperature, the difference between observed and calculated temperatures, and the calculated activity coefficients of Sb and In are shown in successive columns. The bottom portion of the table shows the fit to the Sb-liquidus. Tables for the liquidus lines of the other compounds are similarly constructed and discussed below. In each case the source of the data was identified in Section II. It is seen that the fit appears slightly biased in that the calculated temperature near pure In is consistently 3 to 13°C low. Having determined all the liquid model parameters, the values for the chemical potentials for In in the liquid can be calculated. These are compared with experimental values[37] at 627°C in Table VI. Although the calculated values are almost everywhere more negative, the standard deviation of 94 cal is satisfactorily small. The enthalpy of mixing at $x = 1/2$ in the liquid phase is -930 cal per gm-atom and within the -600 to -1100 range for the experimental results.[37-39]

The fit to the GaSb and Sb liquid are satisfactory and are shown in Table VII. The enthalpy-of-mixing at $x = 1/2$ agrees with the experimental value[35,36] measured at 1023 K.

The overall fit for InAs is satisfactory as can be seen from Row 3 of Table IV. The experimental and calculated liquidus temperatures and calculated activity coefficients are shown in Table VIII. The calculated values for the liquidus temperature are consistently low near the As-rich eutectic. The experimental point at $x = 0.458$ appears to be out of line with the others. A few calculated liquidus points with no experimental counterpart are included to better define the calculated liquidus lines for As-rich compositions. With the liquid phase parameters fixed by the fit to the auxiliary relations, InAs(c) liquidus points, and the InAs-As eutectic temperature, the partial pressure of As_2 over the coexisting In-rich liquid and In-saturated InAs(c) can be calculated. The results are shown in Table IX. The experimental[20] temperature and partial pressure are given in respectively the first and the third columns. The second column gives the calculated atom fraction

of As in the liquid phase. Both experimental and calculated partial pressures fall along straight lines in a log pressure-$1/T$ plot, the calculated pressures tending to be low at the lowest temperatures. The average fit is 12 pct over 3 orders of magnitude in pressure and is considered satisfactory.

Row 3 for GaAs in Table IV shows the liquidus data can be fit well but the calculated GaAs-As eutectic temperature of 788°C is significantly below the doubtful experimental value of 810°C. The fit to the partial pressures is also good enough to be considered satisfactory. Because a comparable fit to the liquidus points and an even better fit of 15 pct to the partial pressures can be obtained by correcting the selected value for $\Delta H_f(T_{mn})$ by 500 cal per mole (see Section VI and Table XII) the calculated liquidus points and partial pressures are shown only for this latter case. In both case the calculated activity coefficient for Ga is greater than 0.988 for atomic fractions of As as high as 0.063, supporting the assumption made in connection with Eq. [3] and used to establish the standard enthalpy and entropy of formation of GaAs. The calculated liquidus temperatures are shown in Table X and the calculated GaAs-As eutectic temperature is 794°C. The fit to the partial pressure of As_2, p_2, over Ga-saturated GaAs and its coexisting Ga-rich liquid is shown in Table XI. The second column gives the calculated atom fraction of As on the liquidus. The experimental pressures cover 11 orders of magnitude and on a log p_2 vs $1/T$ plot are well represented by a straight line up to about 1080 K. Above 1080 K the experimental points rise increasing from the extrapolation of this line and approach the infinite

Table XI. Partial Pressure of As_2 in Atm Over Ga-Saturated GaAs(c)
($\sigma(p_2) = 0.15$)

$T°, C$	x, As	$p_2 \times 10^5$ obs	$p_2 \times 10^5$ cal	$100 \times$ Diff/obs
627	0.0020	7.1 (10^{-6})	9.7 (10^{-6})	36
727	0.0093	0.0010	0.00134	35
827	0.0307	0.0750	0.0804	7
927	0.0751	3.16	2.38	−25
1018	0.137	4.3	3.7	−14
1055	0.168	100	106.6	7
1085	0.196	230	248	8
1094	0.205	300	319	6
1103	0.214	480	410	−15
1109	0.220	480	485	1
1158	0.279	2000	1946	−3
1162	0.284	2400	2186	−9
1184.6	0.318	4690	4303	−8
1204	0.353	8890	8036	−10
1226.1	0.409	19900	18570	−7
1237.5	0.461	35200	35370	5
1239.8	0.489	58400	47130	−19
746.5	0.012	0.0038	0.0032	−17
762	0.0147	0.0064	0.0061	−5
779.8	0.0182	0.017	0.0126	−26
795.6	0.0218	0.027	0.024	−12
812.5	0.0263	0.050	0.046	−9
842.7	0.0360	0.16	0.142	−12
859	0.0421	0.29	0.25	−14
875.7	0.0491	0.50	0.445	−11
889	0.0552	0.82	0.69	−15
906	0.0637	1.4	1.21	−13
919.5	0.0709	2.1	1.87	−11
950	0.0889	5.2	4.88	−6
965.3	0.0988	7.7	7.79	1

Table XII. Fits to the Phase Diagram and Thermodynamic Data for Various Corrections, c_H and c_S to the Selected Values of $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ Respectively

	c_H, cal/mole	c_S, eu/mole	W, cal	a	V, eu	c	$\sigma(T)$, °C	$\sigma(T, V)$, °C	T(eut), °C	x(eut)	$\Delta H_M^L(\frac{1}{2})$ cal/gm-atom	$\sigma(\mu_{In})$ cal/gm-atom
InSb	−300	0	−4320	2.878	0.02377	−867.0	5.6	8.8	494	0.684	−1080	464
	300	0	−3120	1.334	0.02377	−318.0	9.1	2.0	494	0.693	−780	227
	0	0.5	−3720	3.439	1.02377	−20.90	6.4	9.3	494	0.683	−930	546
	−500	−0.5	−4720	2.267	−0.9762	+18.099	4.3	6.9	494	0.687	−1180	332
GaSb	−250	−0.5	−1500	5.064	−0.5398	16.00	5.8	1.0	589	0.888	−375	
	+620	0.5	+160	−38.14	1.360	−5.113	5.5	0.9	589	0.889	+40	
												$\sigma(p_2)$
InAs	−840	−0.5	−7460	3.287	0.4404	−58.0	11.5	−	731	0.857		0.76
	+160	0.5	−5460	4.041	2.4404	−9.459	12.4	−	731			0.20
GaAs	−1000	−1.1	−8146	1.534	−0.5265	+17.095	6.2	−	789	0.948		0.22
	+500	0	−5186	1.830	1.6735	−4.052	5.7	−	794	0.955		0.15
	+1000	0.5	−4146	2.083	2.674	−2.232	5.6	−	794	0.955		0.19

slope at the 1513 K melting point where the three phase curve would reverse slope. The calculated pressures fit the experimental ones to within 15 pct on the average, which is considered satisfactory. The first four experimental values are from a mass-spectrographic measurement of p_2 by Arthur.[17] The next eight points between 1018 and 1162°C are values calculated by Panish[6] from his experiments using values for the enthalpy and entropy of dissociation of $As_4(g)$ essentially the same as those given in Table I. The next five points between 1184.6 and 1239.8°C were calculated by us using selected points on a smoothed curve through the total arsenic pressure points of Richman.[40] The last thirteen points are from a recent mass-spectrographic measurement by Pupp et al.[20] Similar measurements by Foxton et al[19] and by De-Maria et al[18] were not included in the analysis. However, the former are in excellent agreement with those of Pupp et al, the latter are somewhat lower. A number of other experimental determinations are in poor agreement with those cited and, following Panish,[6] are ignored.

4) In the full version of the liquid model W and V are fixed by the auxiliary relations. The enthalpy and excess entropy of mixing are cubic in composition and temperature dependent. Satisfactory fits have already been obtained with $f = 0$. However in principle one would expect some temperature dependence for the enthalpy and excess entropy of mixing, although this has not been established for the cases considered. Therefore it is of interest to determine whether satisfactory fits can still be obtained with small values for f. Consequently the calculations of the last subsection were repeated for $f = +3$ and $f = -3$. It was found that the fits were only slightly changed from those presented for $f = 0$ and were still satisfactory.

VI. EFFECT OF UNCERTAINTIES IN THE ENTHALPY AND ENTROPY OF COMPOUND FORMATION

We have obtained satisfactory quantitative fits to the liquidus lines and high temperature thermodynamic properties for the InSb, GaSb, InAs, and GaAs systems using a four-parameter solution model. Moreover we have shown the commonly used, two-parame-

ter, quasiregular or simple solution model does not give satisfactory fits to the same data. The situation is least satisfactory for Ga-As since there is no reliable GaAs-As eutectic temperature, the experimental liquidus points for As-rich compositions are few and scattered, and the high temperature thermodynamic properties of As(l) are not well established.

The remaining question concerning the results obtained thus far involves those experimental quantities which enter the auxiliary relations given by Eqs. [13] and [14] and for which selected values were used. These quantities are of course subject to experimental error.

For simplicity, and because they seem the most important, we only consider errors in the enthalpy and entropy of compound formation at the melting point, $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ respectively. The measured values[14,15] of ΔC_p for compound formation from the liquid elements are small and lead to relatively small variations of a few hundred cal per mole in $\Delta H_f(T)$ and variations of 0.7 eu per mole or less in $\Delta S_f(T)$ between room temperature and the melting point. Possible errors in ΔC_p are neglected here so that an error in the enthalpy or entropy of compound formation is the same at all temperatures. The heat-of-fusion enters both the liquidus equation and an auxiliary relation, Eq. [13]. Computation shows that it is in the latter role that variations in the heat of fusion have the greatest effect in whether a good fit is obtained or not. Therefore the most important effects of uncertainties in H_{mn} can be viewed as implicitly included when the effects of uncertainties in $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ are determined.

The solution parameters W and V are directly affected by changes in the values of $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$. The parameters a and c are affected indirectly in that they must generally also be changed to maintain satisfactory fits. There are three points to be made in this connection. First the tabulation here of W, a, V, and c to four or five significant figures is not inconsistent with the above. For the selected experimental values of $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ this precision is required to reproduce the calculated values given here. Secondly, because data for the liquid phase other than the liquidus points themselves have been fit, the errors in W, a, V, and c

are limited and/or correlated. For InSb the uncertainty in W is limited by the error of ± 300 cal per mole in the experimental[37-39] heat-of-mixing in the liquid at $x = 1/2$, that in V is determined only by an estimate of the experimental error in $\Delta S_f(T_{mn})$, but that of $W(1 - a/2) - 1000 V(1 - c/2)$ is limited to about ± 400 cal by the fit to the experimental[37] value for the chemical potential of In at 1000 K (assuming the experimental values are good to ± 100 cal per gm-atom). Therefore it is necessary to list a set of values for the liquid solution parameters for each set of assumed corrections for $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$. Finally, it remains to be established whether or not satisfactory fits can be attained for a reasonable range of uncertainty for $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$.

The values for $\Delta S_f(T_{mn})$ are based upon heat capacity measurements[14-16] over the whole temperature range to the melting point and, as previously stated, are assumed to be equal to the selected values in Table II to within ± 0.5 eu per mole. Based upon the experimental heats-of-mixing in the liquid at $x = 1/2$, the errors in $\Delta H_f(T_{mn})$ are ± 300 cal per mole for InSb[37-39] and ± 50 for GaSb.[35,36] For InAs and GaAs values for $\Delta H_f(298)$ have been averaged and recommended values given[20] that are respectively 1000 and 1200 cal per mole more negative than our selected values. Therefore we choose an uncertainty of ± 1000 cal per mole in $\Delta H_f(T_{mn})$ for these compounds.

Using values of W and V corresponding to various corrections to our selected values for $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$, the values of the parameters a and c were found which gave a best-fit to the liquidus points and which gave a best-fit consistent with the experimental eutectic temperatures. In both cases the best-fits (minimum values for $\sigma(T)$) tend to lie along a line in the W-V plane. Selected results are shown in Table XII in which c_H and c_S are the corrections to our selected values of $\Delta H_f(T_{mn})$ and $\Delta S_f(T_{mn})$ respectively.

For InSb satisfactory fits can be obtained at three of the four correction limits. At $c_H = 0$ cal per mole, $c_S = -0.5$ eu per mole the best-fit consistent with the 494°C eutectic temperature is 23°C and too large. However, as shown in the last entry for InSb, a satisfactory fit is obtained if a simultaneous correction of -500 cal per mole is made for the enthalpy of formation. Because our selected values provide the best-fit to the chemical potential of In they are preferred. The variation in the individual solution parameters is significant but the predicted values for the excess entropy of mixing at $x = 1/2$ lie in a narrow range between ± 0.25 eu per gm-atom.

For GaSb, $c_H = 0$ and $c_S = \pm 0.5$ give values of $\sigma(T)$ of about 13°C, slightly higher than the 5 to 8°C range we judge acceptable. However as shown in Table XII satisfactory fits to the liquidus points and experimental eutectic temperature can be achieved by allowing appropriate corrections in the enthalpy of formation. Presentation of these values of W and V shows the widest excursion in the latter consistent with the ± 0.5 eu per mole range adopted for the uncertainty in $\Delta S_f(T_{mn})$ while maintaining essentially the same measure of fit to the liquidus points and eutectic temperature constraint. Again the selected values giving the results in Row 3 for GaSb in Table

IV give the best agreement with the heat-of-mixing at $x = 1/2$ and are therefore preferred.

For the same reason as above the values of W and V shown for InAs in Table XII are from near the best-fit line for a simultaneous fit to the liquidus points and a 731°C eutectic temperature. Correction values of $c_H = -1000$ and $c_S = 0$ give a too high value of 25°C for $\sigma(T)$. Values of $c_H = -1000$ and $c_S = -0.5$ give a satisfactory value of 13°C for $\sigma(T)$. Again the selected values are preferred since they give the best fit to the partial pressures of $As_2(g)$ along the In-rich liquidus.

As before, only the liquidus points for GaAs were fit, the reported eutectic temperature being considered unreliable. Fits lying between 4.5 and 5.5°C can be achieved along a best-fit line defined by $c_H = -500$, $c_S = -1.0$, and $c_H = +1400$, $c_S = 1.0$. The fits at the correction limits of $c_H = \pm 1000$, $c_S = \pm 0.5$ are all below 13°C except that at $c_H = -1000$, $c_S = 0$ which is 17°C. The entries in Table XII are for values of W and V along the best-fit line. It should be noted that the best fit to the partial pressures of As_2 is obtained with $c_H = +500$, $c_S = 0$. The calculated liquidus points in Table X and partial pressures in Table XI were obtained using the parameters for this case.

VII. CONCLUSION

We have established the solution model used here is capable of providing satisfactory fits over a substantial part of the uncertainty range adopted here for the enthalpy and entropy of compound formation. Moreover the entries of Row 3 for each compound in Table IV coupled with those in Table XII provide a basis for estimating the uncertainty in values for as yet unmeasured thermodynamic properties of the liquid phase in the systems considered. Although this uncertainty is larger than desired for some properties, it can most likely be lessened as the values for the experimental quantities are refined and/or new properties are measured. In any case, simultaneous, satisfactory fits have been obtained to the liquidus lines and thermodynamic properties for the four compound considered for the first time. At the very minimum these should be useful in smoothing and interpolating these data in the most reliable way presently available. Hopefully the solution model used here will prove reliable for all the III-V systems and serve to efficiently systematize the data. Unfortunately this solution model is inadequate[41] to simultaneously provide a satisfactory fit to the liquidus lines and satisfy the auxiliary relations for the more ionic IVb-VI and II-VI systems.

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