J. Phys. Chem. Solids Pergamon Press 1965. Vol. 26, pp. 785–802. Printed in Great Britain.

PHASE EQUILIBRIA IN THE GaAs AND THE GaP SYSTEMS

C. D. THURMOND

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(*Received* 5 *October* 1964; *in revised form* 1 *December* 1964)

Abstract—A thermodynamically consistent treatment of the available solubility and vapor pressure measurements for the two binary systems Ga–As and Ga–P has been made leading to reasonable estimates of the complete composition-temperature and vapor pressure–temperature curves. It has been found that (a) the decomposition pressure of GaP is essentially the same as that of GaAs in the temperature region where the equilibrium liquid phases are nearly pure gallium; (b) that GaAs should evaporate congruently at temperatures up to about 660 ± 100°C and GaP up to temperatures of about 680 ± 100°C; (c) that both positive and negative departures from ideality occur along the liquidus curves; (d) that the negative departures from ideality that occur in dilute solutions at low temperatures along the liquidus curves arise, principally, from an entropy effect which is inconsistent with the formation of associated complexes previously postulated; (e) that the value of the heat of formation at 298°K of GaAs is $-17{\cdot}7 \pm 1$ kcal and of GaP is $-24{\cdot}4 \pm 1{\cdot}25$ kcal.

INTRODUCTION

RICHMAN(1) has measured the pressure of arsenic over a Ga-rich Ga–As liquid phase saturated with GaAs in the temperature range from 1050°C to the melting point, 1238°C. Measurements were also made of the phosphorus pressures over a Ga-rich Ga–P liquid phase saturated with GaP. Richman pointed out that his measurements in both systems showed the expected curvature for a log P vs. $1/T$ plot and for the Ga–As system a smooth curve could be drawn connecting his higher temperature measurements with those of DROWART and GOLDFINGER(2) obtained at lower temperatures by the Knudsen effusion method using a mass spectrometer to measure effusion rates. The phosphorus pressure measurements for the Ga–P system extrapolated to give a total pressure at the melting point of 35 atm, some 22 atm higher than previously reported by MARINA *et al.*(3) whose melting point for GaP was some 60 deg higher than found by Richman. Richman suggested an extrapolation curve to lower temperatures for the phosphorus decomposition pressures.

Richman also calculated the activity coefficients of arsenic and phosphorus over the saturated liquid phases in the range of temperatures studied by him and found similarities in the two curves. He concluded from these curves that significant association probably occurs between the two different atomic species making up the saturated liquid phases.

The results obtained by Richman for the Ga–As system differed significantly from the measurements of VAN DEN BOOMGAARD and SCHOL(4) and LYONS and SILVESTRI.(5) The results obtained for the Ga–P system differed greatly from those of MARINA *et al.*(3) who found much higher pressures of phosphorus than did Richman over the temperature range studied by him. JOHNSTON(6) has made Knudsen effusion measurements of the phosphorus decomposition pressure over GaP at much lower temperatures and pressures studied by Richman. The extrapolation proposed by Richman does not fit the Johnston measurements, but a smooth curve can be drawn which does fit both sets of measurements satisfactorily.

Sufficient additional information is now available to permit the pressure measurements made on these two systems to be evaluated by the 'Third

---

* Abstract presented at the International Conference on the Physics of Semiconductors, Paris, July, 1964.

Law' method. The heat capacity measurements of PIESBERGEN(7) on a number of III–V compounds, including GaAs, have permitted him to calculate the entropy of these compounds at 298°K. A knowledge of the entropy of GaAs at 298°K places an important restriction upon the decomposition pressure curve in the low temperature region where the liquid phase is essentially pure gallium. In addition, once the lower temperature curve is established, a knowledge of the entropy at 298°K leads to a lower limit to the decomposition pressure curves at all higher temperatures. Such restrictions lead to the conclusion that the DROWART GOLDFINGER(2) decomposition pressure measurements of GaAs are not consistent with the higher temperature measurements of Richman although the discrepancy is probably within the uncertainty of the Drowart and Goldfinger pressure measurements. Measurements of GUTBIER(8) of the heat of decomposition of GaAs, however, can be shown with the aid of the known entropy of GaAs at 298°K to lead to a pressure curve in agreement with Richman's higher temperature measurements.

The entropy of GaP at 298°K has not as yet been measured, but from the regularities which can be shown in the entropies of other III–V compounds measured by PIESBERGEN(7) a good estimate can be made. It can then be shown that the measurements of Richman at high temperatures and Johnston at low, are in very good agreement.

The objective of the present paper is to show in some detail how the Third Law method can be used to decide which decomposition pressure measurements are consistent. From this the most probable values of the heats of formation of GaAs and GaP can be obtained. In addition, it will be shown that it is possible to use the consistent vapor pressure measurements, which have been obtained over certain relatively narrow ranges of temperature and composition, to obtain thermodynamically consistent complete P–T curves. That is, thermodynamic restrictions on the systems lead to interpolation and extrapolation methods from which best estimates of the complete P–T curves can be obtained. The implications of these full curves will be discussed.

2. LIQUIDIUS CURVES

The starting point for the evaluation of the equilibrium pressure measurements is the liquidus curves. The solubility of GaAs in liquid Ga has been measured over a wide temperature range by HALL.(9) KÖSTER and THOMA(10) have made measurements of the solubility of GaAs at higher temperatures in both gallium-rich and arsenic-rich liquid phases. HALL(9) and RUBENSTEIN(11) have measured the solubility of GaP in gallium-rich liquids.

VIELAND(12) has used a regular solution treatment of the P–T and T–X diagrams of a number of III–V compounds. He has shown that the liquidus curve for a pure compound in equilibrium with a regular solution is given by the following equation:

$$\alpha = -\frac{RT}{2(0\cdot5-x)^2}\left[\ln 4x(1-x)+\frac{\Delta S^F}{R}\left(\frac{T_M}{T}-1\right)\right]. \tag{1}$$

When the available experimental points on the GaAs and GaP liquidus curves are used to calculate values of α, it is found that α is not constant. Therefore, the liquid phases of these systems are not regular solutions. (Here, regular solutions are those solutions for which the heat of mixing is proportional to the atom fractions of the two components and the excess entropy of mixing is ideal.) Nevertheless, equation (1) provides an empirical method of interpolating and extrapolating liquidus curves that is consistent with the entropy of fusion and melting point of the saturating phase when the solubility of the other components in this phase is negligibly small. In addition, it is to be expected that α will be a linear function of temperature when the saturated liquid phase is dilute, far from the melting point, since the partial molar heat of mixing and excess entropy of mixing of the dilute component are in general insensitive to temperature changes, and in dilute solutions, are independent of composition changes. It has been found that α is a linear function of temperature to a good degree of approximation for the GaAs and GaP liquidus curves even for saturated liquid phases that are not dilute, as was found for a number of the Ge and Si liquidus curves.(13) In this equation, x is the atom fraction of arsenic or phosphorus in the saturated liquid phase, ΔS^F is the entropy of fusion per mole of compound, assumed to be independent of temperature, and T_M is the melting point. For a regular solution, α is independent of temperature and composition.

2.1 *The* GaAs *liquidus curve*

The entropy of fusion of GaAs has not been measured. An estimate of the entropy of fusion of GaAs can be obtained by a comparison with the entropy of fusion of Ge. The entropy of fusion of GaAs would be expected to be approximately twice the entropy of fusion of Ge (6·7 e.u.) plus a mixing entropy term of $R \ln 4$; about 16·2 e.u. A test of this method of estimating the entropy of fusion can be made using the measured heat of fusion of GaSb obtained by SCHOTTKY and BEVER.(14) The estimate of the entropy of fusion of GaSb is made by taking the sum of the entropy of fusion of grey tin (5·2 e.u.), plus the entropy of fusion of Ge, and the mixing term, giving 14·7 e.u., compared to the measured value of 13 e.u. This suggests that the estimated entropy of fusion of GaAs may be high by about 2 e.u. and therefore a value of 14·0 e.u. has been adopted. If a value of 16 e.u. were used in the following treatment, essentially identical conclusions would be drawn about the Ga–As system. The melting point of GaAs is 1238°C.(10)

The value of the parameter α has been calculated from equation (1) using the experimental measurements of HALL(9) and of KÖSTER and THOMA(10) given in Table 1. The data points have been scaled from published figures. A plot of α as a function of temperature is given in Fig. 1. It can be seen that the points can be fitted satisfactorily to a straight line. The two points on the Ga rich side of the liquidus curve that lie farthest from the line drawn through the points are clearly in error, since it is to be expected that α would be a smoothly varying function in this temperature region.

The straight line of Fig. 1 is given by the equation

$$\alpha = 9960 - 11{\cdot}15T. \tag{2}$$

The full liquidus curve corresponding to α given by equation (2) has been plotted, with the experimental points, in Figs. 2 and 3. Figure 2 is a $\log x_{As} - (1/T)$ plot; all of the experimental points are plotted. Figure 3 is a portion of the $T-x$ diagram in the region of the melting point.

Table 1

Source	GaAs (T°C)	Solubilities (x_{As}, atom fraction As)
HALL(9)	458	$4{\cdot}10 \times 10^{-5}$
	494	$2{\cdot}25 \times 10^{-4}$
	554	$5{\cdot}31 \times 10^{-4}$
	593	$1{\cdot}14 \times 10^{-3}$
	653	$3{\cdot}40 \times 10^{-3}$
	691	$5{\cdot}60 \times 10^{-3}$
	711	$7{\cdot}00 \times 10^{-3}$
	745	$1{\cdot}15 \times 10^{-2}$
	791	$2{\cdot}07 \times 10^{-2}$
	853	$3{\cdot}83 \times 10^{-2}$
	889	$5{\cdot}20 \times 10^{-2}$
	953	$8{\cdot}86 \times 10^{-2}$
	989	$1{\cdot}12 \times 10^{-1}$
	1004	$1{\cdot}22 \times 10^{-1}$
KÖSTER and THOMA(10)	1073	$1{\cdot}90 \times 10^{-1}$
	1175	$3{\cdot}10 \times 10^{-1}$
	1200	$3{\cdot}50 \times 10^{-1}$
	1215	$3{\cdot}82 \times 10^{-1}$
	1238	$5{\cdot}00 \times 10^{-1}$
	1180	$6{\cdot}82 \times 10^{-1}$
	1145	$7{\cdot}32 \times 10^{-1}$
	1065	$7{\cdot}84 \times 10^{-1}$
	1015	$8{\cdot}50 \times 10^{-1}$

Additional experimental support for the proposed GaAs liquidus curve in the arsenic-rich region can be obtained from the measurements of KÖSTER and THOMA,(10) who found that the eutectic temperature on the arsenic-rich side of the phase diagram was 810°C. They apparently believed 810°C to be very near the melting point of arsenic and drew the arsenic-rich portion of

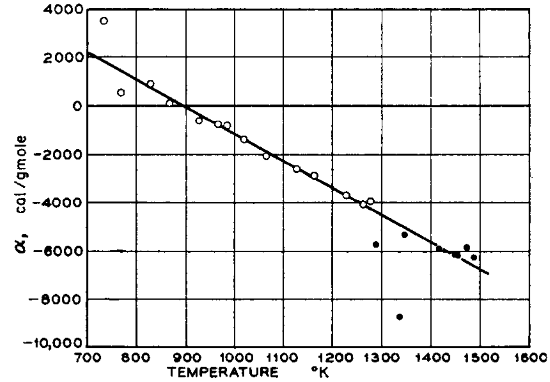

FIG. 1. GaAs. The parameter α [defined by equation (1)] as a function of temperature. ● KÖSTER and THOMA.(10) ○ HALL.(9)

the liquidus curve to show this. They did not measure the melting point of arsenic. Stuhl and Sinke(15) give 817°C as the melting point of arsenic. The measurements of Köster and Thoma suggest that the melting point of arsenic has been depressed 7 deg by the presence of gallium. The composition of the eutectic can be estimated from this temperature depression with the assumption that a negligible amount of gallium dissolves in solid arsenic. Using a heat of fusion for arsenic of 5·6 kcal from Horiba's vapor pressure measurements,(16) the composition of the eutectic is calculated to be 1·6 at. % gallium. The extrapolation of the liquidus curve given by equations (1) and (2) to the eutectic temperature gives 2·4 at. % gallium.

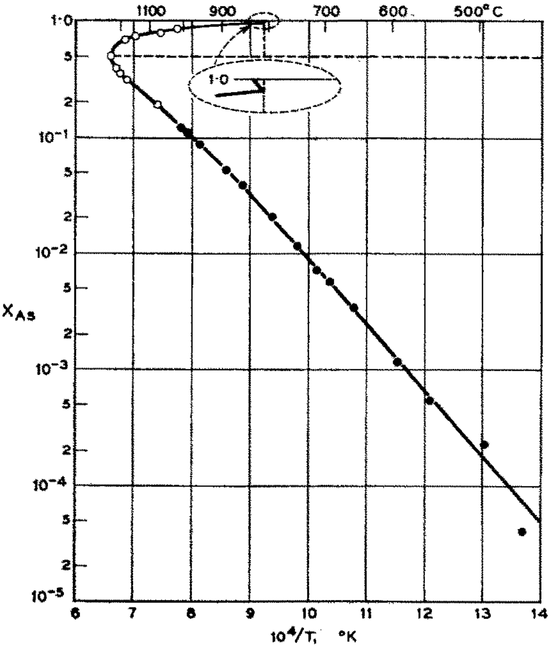

Fig. 2. The GaAs liquidus curve; x_{As} is atom fraction of arsenic. The eutectic on the arsenic-rich side is shown in the inset. The calculated eutectic composition is 2·4 at. % Ga. ○ Köster and Thoma.(10) ● Hall.(9)

2.2 *The* GaP *liquidus curve*

The entropy of fusion of GaP which has not been measured has been assumed to be 15 e.u. for reasons similar to those used to estimate the GaAs entropy of fusion. A melting point of 1465°C has been used.(1,11)

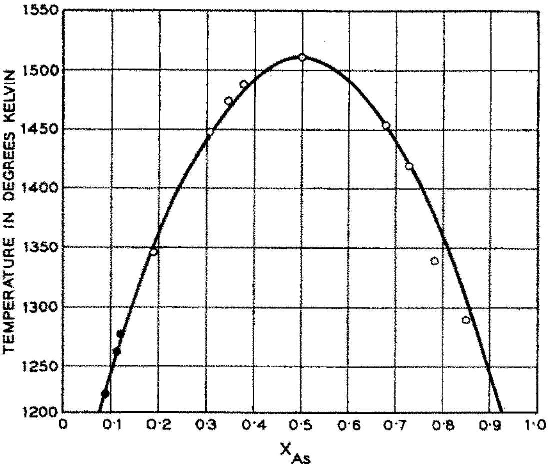

Fig. 3. The GaAs liquidus curve in the region of the melting point; x_{As} is atom fraction of arsenic. ○ Köster and Thoma.(10) ● Hall.(9)

Figure 4 shows a plot of the parameter α as a function of T calculated from the available experimental data given in Table 2 scaled from published figures.(9,11) The scale used for the GaP plot is the same as for GaAs. The experimental scatter is considerably larger than for the Ga–As system (Fig. 1). However, the regularity seen for GaAs is suggested for GaP and a straight line appears to be a satisfactory fit to the available data. The straight line of Fig. 4 is given by the following equation:

$$\alpha = 7900 - 7{\cdot}00T. \qquad (3)$$

The corresponding liquidus curve calculated from equations (1) and (3) is given in Fig. 5 on a log x

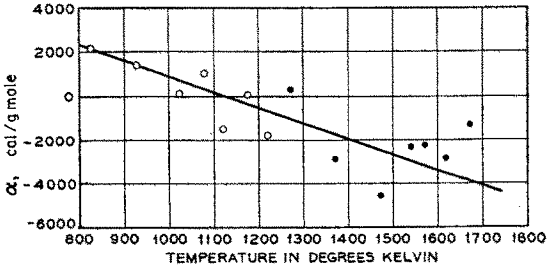

Fig. 4. GaP. The parameter α [defined by equation (1)] as a function of temperature. ● Rubenstein.(11) ○ Hall.(9)

Table 2

Source	GaP (T°C)	Solubilities (x_P, atom fraction P)
Hall[(9)]	551	$3{\cdot}00 \times 10^{-5}$
	653	$2{\cdot}30 \times 10^{-4}$
	750	$1{\cdot}24 \times 10^{-3}$
	804	$1{\cdot}91 \times 10^{-3}$
	846	$4{\cdot}89 \times 10^{-3}$
	901	$6{\cdot}90 \times 10^{-3}$
	945	$1{\cdot}44 \times 10^{-2}$
Rubenstein[(11)]	1000	$1{\cdot}50 \times 10^{-2}$
	1100	$5{\cdot}40 \times 10^{-2}$
	1200	$1{\cdot}15 \times 10^{-1}$
	1268	$1{\cdot}46 \times 10^{-1}$
	1298	$1{\cdot}70 \times 10^{-1}$
	1346	$2{\cdot}20 \times 10^{-1}$
	1400	$2{\cdot}80 \times 10^{-1}$

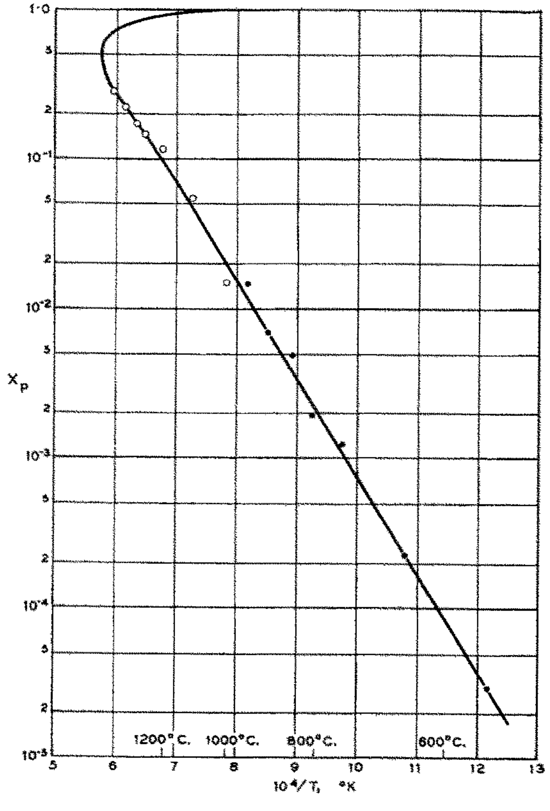

Fig. 5. The GaP liquidus curve; x_P is atom fraction of phosphorus. ○ Rubenstein.(11) ● Hall.(9)

vs. $1/T$ plot with the experimental points. The calculated T–x curve in the region of the melting point is given in Fig. 6. The experimental points are quite satisfactorily represented by the calculated curve and a reasonable extrapolation can be made to the phosphorus-rich side. Equations (1) and (3) lead to a symmetrical liquidus curve on a T–x diagram.

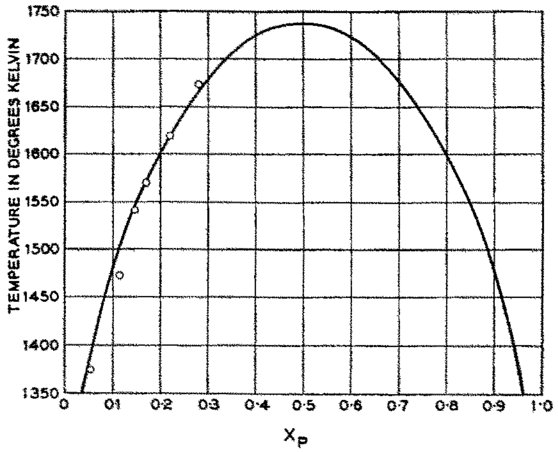

Fig. 6. The GaP liquidus curve in the region of the melting point; x_P is atom fraction of phosphorus. ○ Rubenstein.(11)

3. THE PRESSURE-TEMPERATURE CURVES

3.1 GaAs, *low temperatures*

Drowart and Goldfinger(2) and Gutbier(8) have used mass spectrometers with effusion cells to obtain vapor pressure information in the temperature range where GaAs is in equilibrium with a liquid of nearly pure gallium. The liquid phase forms by decomposition of GaAs since the pressures of As_2 and As_4 are considerably higher than the pressure of gallium. The highest temperature of about 900°C was reached by Gutbier, where the composition of the liquid phase saturated with GaAs is 5·6 at. % in arsenic (Fig. 2).

The results of the measurements of the temperature coefficient of the decomposition pressures reported by Drowart and Goldfinger(2) and by Gutbier(8) are given in Table 3 in terms of the heat content change at 298°K for the designated reactions. Drowart and Goldfinger reported 22·1 kcal for the heat of decomposition of GaAs to Ga(l) and $\frac{1}{4}$ As_4(g) at 1080°K. When this is

Table 3. ΔH°_{298}, kcal

Reaction	Literature	Adopted
$GaAs(s) = Ga(s)+\frac{1}{4}As_4(g)$	$20{\cdot}4^{(2)*}$, $(25{\cdot}2)^{(2)\dagger}$ $26{\cdot}3^{(8)}$	$26{\cdot}3\pm0{\cdot}75$
$GaAs(s) = Ga(s)+\frac{1}{2}As_2(g)$	$39{\cdot}3^{(2)*}$, $(43{\cdot}2)^{(2)\dagger}$ $44{\cdot}6^{(8)}$	$44{\cdot}4\pm1{\cdot}5$
$2As_2(g) = As_4(g)$	$-71{\cdot}8^{(2)}$, $-73{\cdot}2^{(8)}$ $-69{\cdot}6^{(31)}$, $-61{\cdot}5^{(15)}$	$-72{\cdot}5\pm3$
$4As(s) = As_4(g)$	$34{\cdot}5^{(15)}$	$34{\cdot}5\pm1$
$2As(s) = As_2(g)$	$48{\cdot}0^{(15)}$	$53{\cdot}5\pm2$
$As(s) = As(g)$	$69{\cdot}0^{(15)}$	$71{\cdot}75\pm1{\cdot}5$
$\frac{1}{2}As_2(g) = As(g)$	$45{\cdot}0^{(15)}$	$45{\cdot}0\pm0{\cdot}5$
$Ga(s) = Ga(g)$	$65{\cdot}0^{(15)}$, $68{\cdot}96^{(24)}$ $65{\cdot}4^{(23)}$	$65{\cdot}4\pm1$
$GaAs(s) = Ga(g)+As(g)$	$149{\cdot}8^{(12)}$	155 ± 3
$Ga(s)+As(s) = GaAs(s)$	$-17{\cdot}7^{(8)}$	$-17{\cdot}7\pm1$

* Second Law.
† Third Law.

corrected to 298°K the value of 20·4 kcal given in Table 3 is obtained. The measured value of 39·7 kcal for the decomposition to Ga(l) and $\frac{1}{2}$ As_2 at 1080°K gives 39·3 kcal when corrected to 298°K. These are 'Second Law' values, obtained from the temperature dependence of the pressures. Gutbier obtained values of 27·0 kcal and 45·0 kcal respectively for these two reactions, which, when corrected to 298°K, give the values 26·3 kcals and 44·6 kcals listed in Table 3. It can be seen that there is considerable disagreement between these two sets of measurements.

An examination of the experimental measurement reported by Drowart and Goldfinger and by Gutbier shows that Gutbier's measurements have considerably less scatter than those of Drowart and Goldfinger. Furthermore, the recent heat capacity measurements of PIESBERGEN,(7) giving the entropy of GaAs at 298°K, permit a Third Law treatment of the pressure measurements of Drowart and Goldfinger which gives heats of decomposition in much better agreement with Gutbier's heats. A free energy function for GaAs based upon Piesbergen's entropy for GaAs of 15·34 ± 0·10 cals deg^{-1} mole^{-1} is given in Table 4. It has been necessary to estimate the high temperature heat capacity of GaAs in order to calculate the free energy function since there are at present no available experimental measurements. A satisfactory estimate can be expected by assuming the heat capacity of GaAs to be twice that of Ge.(17)

Table 4. GaAs *free energy function*

T(°K)	$-(F^{\circ}_T-H^{\circ}_{298})/T$ cal deg^{-1}	ΔH°_f, kcal.
298	15·34	$-26{\cdot}3$ (As_4)
700	18·72	
800	19·68	
900	20·61	
1000	21·50	
1100	22·36	
1200	23·19	
1300	23·98	
1400	24·74	
1500	25·47	

$Cp = 11{\cdot}96+1{\cdot}64\times10^{-3}\,T-(1{\cdot}12\times10^5)/T^2$

$$Cp = 11{\cdot}96+1{\cdot}64\times10^{-3}\,T-\frac{1{\cdot}12\times10^5}{T^2}. \quad (4)$$

The pressure measurements of Drowart and Goldfinger may now be used with the free energy function of GaAs given in Table 4 and the free energy functions of Ga, As_4 and As_2 given by STUHL and SINKE,(15) to calculate the heat of decomposition of GaAs at 298°K. The results of such a calculation are given in parentheses in

Table 3. Much better agreement with the measurements of Gutbier has been obtained.

It is now possible, however, to go one step further and show that the high temperature measurements of Richman of the GaAs decomposition pressure are not consistent with the lower temperature measurements of Drowart and Goldfinger. The inconsistency arises when the Third Law fit to their measurements is extrapolated into the temperature range studied by Richman. It is found that many of Richman's pressures lie below the extrapolated line, as is shown in Fig. 7, where the pressure of As_4 has been plotted as a function of T on a log P–$1/T$ graph. The dashed line is the Third Law fit to the low temperature Drowart and Goldfinger pressures and corresponds to equilibrium pressures of As_4 over solid GaAs in equilibrium with pure liquid gallium. It is not possible to have a pressure of As_4 lower than the dashed curve since this implies that the pressure of gallium is greater than that of pure liquid gallium.*

A low temperature decomposition pressure curve which is consistent with Richman's high temperature measurements can be obtained from Gutbier's heat of decomposition, Table 4, and the free energy function of Table 4. The solid line between the crosses of Fig. 7 represents the decomposition pressures of As_4 calculated in this way over the temperature range studied by Gutbier. An extrapolation to higher temperatures leads to a line consistent with Richman's pressures.

The pressures of As_4 plotted in Fig. 7 measured by RICHMAN(1) were obtained from his total pressure measurements. The equilibrium constant for the formation of As_4 from As_2 was obtained from a heat of reaction at 298°K of $-72{\cdot}5$ kcal/mole, and the free energy functions given by STUHL and SINKE.(15) The measurements of Drowart and Goldfinger and of Gutbier are in good agreement for this heat (see Table 3), but differ from the number used by Stuhl and Sinke. Gutbier has another measurement of the heat of this reaction, obtained from decomposition pressure measurements on InAs. His value of -71 kcal is in good agreement with the GaAs measurement. An average of the GaAs data of Drowart and Goldfinger and of Gutbier was used.

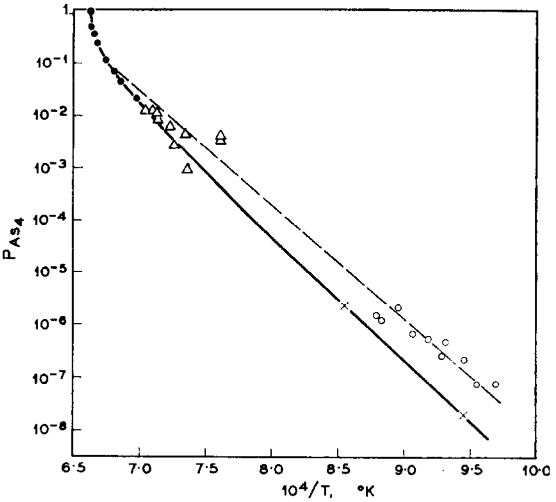

FIG. 7. GaAs. The pressure of As_4 in atmospheres as a function of $1/T$. ● RICHMAN(1)—(scaled from smoothed curve). △ RICHMAN(1)—(individual points). ○ DROWART and GOLDFINGER.(2) — — Third Law fit. —— Calculated (see text).

3.2 GaAs *high temperatures*

The solid line of Fig. 7 drawn through the P_{As_4} pressures obtained from Richman's total pressure measurements and interpolated to the pressure range studied by Gutbier, is a calculated curve. The interpolation has been made on a logarithmic plot of the activity coefficient of arsenic in the saturated liquid phases as a function of the atom fraction of arsenic in the liquid phase. Such a plot also permits a reasonable extrapolation to be made to the melting point of GaAs and beyond, to the eutectic on the arsenic-rich side of the melting point.

Richman has calculated γ–x curves (γ, activity coefficient) for GaAs and GaP. He concluded that the liquid phases were not regular solutions; rather, the minimum in each γ–x curve, he suggested, was caused by liquid phase interactions producing association. A recalculation of these curves using the liquidus curves described in

---

* $$AB(s) = A(l)+B(g)$$
$$a_A^L P_B = K(T)$$

When a_A^L, the activity of A, is equal to unity, P_B equals $K(T)$. But a_A^L must always be less than or equal to unity, therefore P_B must always be greater than or equal to $K(T)$.

Section 2, and revised pressure–temperature curves for the pure Group V components, produce γ–x curves differing in detail from those obtained by Richman. In the present paper, however, emphasis will be placed on the usefulness of the γ–x curves as a means of interpolating and extrapolating vapor pressure measurements obtained over limited sections of the P–T curve.

In order to calculate the activity coefficients, the pressure of arsenic over pure liquid arsenic must be known. A review of the literature has been made by NESMEYANOV.(18) The only vapor pressure measurements that have been made for liquid arsenic are those by HORIBA,(16) who obtained a vapor pressure of arsenic at its melting point of about 36 atm. The equation recommended by Nesmeyanov for the pressure over solid arsenic as a function of temperature extrapolates to the melting point of arsenic to give 22·8 atm. Stuhl and Sinke say that the data they have used in their tables lead to a pressure of 28 atm at the melting point.(19) This appears to have been obtained by a linear extrapolation from the sublimation point to the melting point using the heat of sublimation at the sublimation temperature. An extrapolation from the sublimation temperature using the heat capacities recommended by KELLEY(17) (these were used up to the sublimation temperature by Stuhl and Sinke) lead to a pressure at the melting point of 23·3 atm. Figure 8 is a plot of the data recommended as most reliable by Nesmeyanov. The line up to the melting point is calculated from the free energy functions of As (solid) and As_4 (gas) as given by Stuhl and Sinke extended to temperatures above the sublimation point. This curve is essentially identical to the curve recommended by Nesmeyanov.

The pressure curve for pure liquid arsenic, shown in Fig. 8, has been made consistent with a value of the vapor pressure at the melting point of 23·3 atm. The slope of the line was obtained from the difference in slope between the solid and liquid portions of the curve at the melting point, found by HORIBA,(16) giving a heat of fusion of 5·62 kcal/g atom. STUHL and SINKE(15) accept the estimate, made by Kelley from a freezing point depression curve, of 6·62 kcal/g atom, but the entropy of fusion obtained from this value of the heat of fusion appears to be too large when compared with the entropies of fusion of the other Group V elements (see Table 5). The entropy of fusion obtained from a heat of fusion of 5·62 kcal is in better agreement with the number to be expected from the other Group V elements. Using a heat of fusion of 5·62 kcal/g atom from Horiba's measurements, a heat of vaporization at the melting point of 5·88 kcal/g atom is obtained and the following equation gives the pressure of As_4 over liquid arsenic as a function of temperature (As_4 is

Table 5. Entropy of fusion

Element	ΔS^F, cal deg^{-1} g atom^{-1}	Reference
P	5·17	JANAF(28)
As	5·15	HORIBA(16)
	6·06	KELLEY(29)
Sb	5·25	STUHL and SINKE(15)
Bi	4·78	STUHL and SINKE(15)

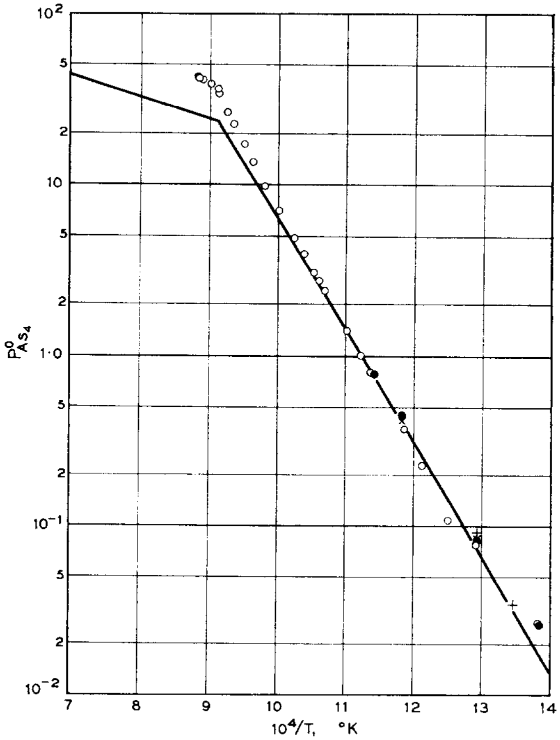

FIG. 8. Arsenic. The pressure of As_4, in atmospheres, over pure solid and liquid arsenic as a function of $1/T$. ○ HORIBA.(16) ● PREUNER and BROCKMÖLLER(20) + GIBSON.(21) × WIECHMANN and HEIMBURG.(22)

the major species in this pressure and temperature range).

$$\log P^{\circ}_{As_4} = -\frac{1286\cdot5}{T} + 2\cdot547. \tag{5}$$

The activity coefficient of arsenic, γ_{As}, is related to the partial pressure of As_4 over pure arsenic, P_{As_4} and the atom fraction of arsenic in the saturated liquid phase, x_{As} by the equation:

$$\gamma_{As} = \frac{1}{x_{As}}\left(\frac{P_{As_4}}{P^{\circ}_{As_4}}\right)^{1/4}. \tag{6}$$

The experimental points obtained from Richman's measurements are shown in Fig. 9. Total pressures were read from Richman's plot; at higher temperatures, points were read at intervals from a smooth curve through the numerous data points; the ten experimental points obtained at the lowest temperatures (solid circles) were read from the plot individually. The As_4 partial pressure was calculated using a ΔH°_{298} of $-72\cdot5$ kcal for the formation of As_4 from As_2 (Table 3) and the free energy functions given by STUHL and SINKE.(15) The pressure of monatomic arsenic is completely negligible.

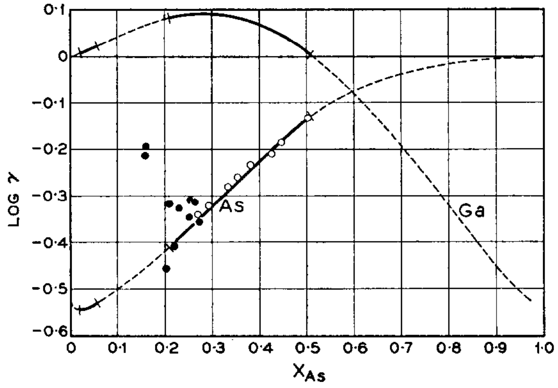

FIG. 9. The activity coefficients of arsenic and gallium as a function of x_{As}, the atom fraction of arsenic along the liquidus curve. ○ RICHMAN(1)—(scaled from smoothed curve). ● RICHMAN(1)—(individual points). —— γ_{As} at low x_{As} from GUTBIER.(8)

The activity coefficients of arsenic along the liquidus curve calculated from Richman's measurements suggest that at lower arsenic concentrations the activity coefficient curve rises after passing through a minimum. There is considerable scatter of the data at lower arsenic concentrations, and an extrapolation of the data would be quite uncertain. Such an extrapolation is not necessary, however. The low temperature portions of the P–T curve are quite well defined by the measurements of Gutbier of the temperature coefficient of the decomposition pressure and the entropy of GaAs calculated by Piesbergen. From the pressures plotted in Fig. 7 in the temperature range studied by Gutbier, activity coefficients can be calculated. These have been plotted in Fig. 9 as a short solid line in the composition range of 1·9 to 5·5 atom fraction arsenic. It is now possible to interpolate the $\log \gamma_{As}$–x_{As} curve between the low temperature and high temperature measurements in a reasonable way, as shown in Fig. 9. It is quite improbable that the $\log \gamma_{As}$–x_{As} curve corresponding to activities of arsenic along the liquidus would exhibit any characteristic other than that of a smoothly varying curve in this region of temperature and composition; consequently, the existence of a minimum in the $\log \gamma_{As}$–x_{As} curve, suggested by Richman's measurements, is very unlikely. The significance of the minimum in the $\log \gamma_{As}$–x_{As} curve at much lower compositions will be discussed in a following section.

The extrapolation of the $\log \gamma_{As}$–x_{As} curve to larger values of x_{As} is influenced by the knowledge that γ_{As} must approach unity as the atom fraction of arsenic in the saturated liquid phase approaches unity. Again, a smoothly varying curve is to be expected, as shown by the dashed line of Fig. 9. This line terminates at the eutectic composition, 2·4 at. % gallium.

Also shown in Fig. 9 is a curve for the activity coefficient of gallium. This curve follows directly from the arsenic curve since the range of nonstoichiometry of GaAs must be quite narrow. Thus, the composition and activity coefficients of the liquid phase along the liquidus curve meet the condition that the product of the atom fractions and activity coefficients equals a constant which is a function of temperature only.

$$\text{GaAs(solid)} = \text{Ga(liq.solu.)} + \text{As(liq.solu.)} \tag{7}$$

$$x_{As}\gamma_{As}x_{Ga}\gamma_{Ga} = K(T). \tag{8}$$

The value of the constant $K(T)$ is known. It can be calculated from the free energy of decomposition of GaAs to Ga(liq.) and As_4(g) and the free energy of vaporization of pure liquid arsenic. The log γ_{Ga}–x_{As} curve of Fig. 9 has been calculated from the log γ_{As}–x_{As} curve and the known liquidus curve, with the aid of equation (8).

It is now possible to calculate the complete P_{As_4}, P_{As_2}, P_{As} and P_{Ga} curves over the GaAs liquidus curve. These curves are shown in Fig. 10. The free energy functions given by STUHL and SINKE(15) were used in the calculations of P_{As}. Revised heats of reaction were used, however, as a result of the newly adopted As_2–As_4 heat. Table 3 summarizes a consistent set of relevant heats of reaction.

The gallium pressure curve of Fig. 10 is based upon a value of the heat of sublimation at 298 of 65·4 kcal obtained recently by MUNIR and SEARCY(23) from torsion-effusion measurements. This value conflicts with a value of 68·96 kcal reported by COCHRAN and FOSTER(24) from effusion measurements. The value given by Munir and Searcy has been accepted for the following reasons: (1) the data cover a very long temperature range with good precision meeting a Third Law test satisfactorily; (2) the torsion-effusion technique is superior to the effusion method; (3) recent measurements by MOORE and THURMOND(25) using an effusion technique with mass spectrometer are in agreement with the Munir and Searcy results —the Cochran and Foster results lie outside experimental uncertainty.

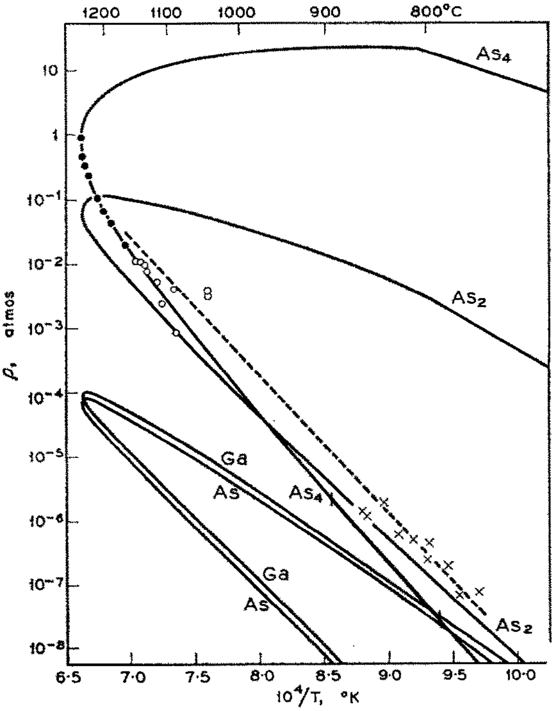

FIG. 10. The equilibrium pressures of various vapor species along the GaAs liquidus curve as a function of $1/T$. The experimental points of RICHMAN(1) and of DROWART and GOLDFINGER(2) for P_{As_4} are shown. The dashed curve is the Third Law fit to P_{As_4} measured by DROWART and GOLDFINGER.(2)

3.3 GaP

3.31. *Low temperatures*: JOHNSTON(6) has measured GaP decomposition pressures by the effusion–weight loss method. THURMOND and FROSCH(26) calculated a heat of reaction to form GaP at 298°K from Ga(s) and P_2(g) and an entropy at 298°K from Johnston's measurements. The heat of reaction and entropy were found to be in agreement within experimental uncertainties with equilibrium constant measurements made on the reaction of H_2O with GaP in H_2.(26)

The entropy of GaP at 298°K obtained from Johnston's measurements was 14·39 cal deg^{-1}, a value somewhat larger than was expected by a comparison with the sum of the entropies of Si and Ge, 11·96 cal deg^{-1}. The recent measurements by PIESBERGEN(7) of the low temperature heat capacities of a number of III–V compounds, from which entropies at 298°K were calculated, show that there is rather good agreement between experimental entropies and entropies calculated from appropriate combinations of Group IV elements. This comparison is shown in Table 6 for 6 compounds of the Group III–V elements. In every case the agreement between the measured and estimated entropy is within 0·6 cal deg^{-1}. The entropy of GaP obtained from Johnston's measurements by Thurmond and Frosch is 2·43 cal deg^{-1} larger than the entropy estimated from the sum of the entropies of Si and Ge. As a result of this comparison, it is concluded that the entropy of GaP at 298°K is probably closer to 11·96 than to 14·39 and the former value will be adopted.

The free energy function calculated by THURMOND and FROSCH(26) was obtained from an estimated heat capacity for GaP. It was assumed that the heat capacity of GaP was equal to the sum of the heat capacities of Si and Ge. Recently

Table 6. Entropies at 298°K

Element or compound	S°_{298} (meas) cal deg^{-1}	S°_{298} (est) cal deg^{-1}	Assumed	Δ
AlSb	15·36(7)	14·86	$2S^\circ_{Ge}$	+0·50
GaP	14·39(6,25)*	11·96	$S^\circ_{Si}+S^\circ_{Ge}$	+2·43
GaAs	15·34(7)	14·86	$2S^\circ_{Ge}$	+0·48
GaSb	18·18(7)	17·89	$S^\circ_{Ge}+S^\circ_{Sn}$	+0·29
InP	14·28(7)	14·86	$2S^\circ_{Ge}$	−0·58
InAs	18·10(7)	17·89	$S^\circ_{Ge}+S^\circ_{Sn}$	+0·21
InSb	20·60(7)	20·92	$2S^\circ_{Sn}$	−0·32
Si	4·53(15)			
Ge	7·43(15)			
Sn (grey)	10·46(15)			

* Second Law.

PANKRATZ(27) has measured the heat content of GaP up to 1100°K. His results are shown in Fig. 11, where the function $(H_T-H_{298})/(T-298)$ is plotted as a function of T. The line through the experimental points is obtained from the following heat capacity equation:

$$Cp = 11{\cdot}97+4{\cdot}82\times10^{-4}\,T-\frac{1{\cdot}51\times10^5}{T^2}. \qquad (9)$$

Shown in Fig. 11 for comparison is the curve calculated from the sum of the heat capacities of Si and Ge, which agrees quite well with the measured heat content function.

A recalculated free energy function for GaP is given in Table 7 which uses the heat capacity given by equation (9) and an entropy at 298°K obtained from the sum of the entropies of Si and Ge (11·96 cal deg^{-1}). Included in the table is the new value of the heat of reaction to form GaP(s) from Ga(s) and P_2(g) at 298°K, obtained from Johnston's measurements and the new free energy function. The heat of reaction of −45·7 kcal is to be compared with the earlier value of −42·75 kcal.(23) The solubility of GaP in liquid Ga at the highest temperature used by Johnston is 2 at. % P. A recalculation of the heat of formation at 298°K from Johnston's measurements, correcting for the solubility of GaP, leads to a correction of less than 0·1 kcal, and can be ignored.

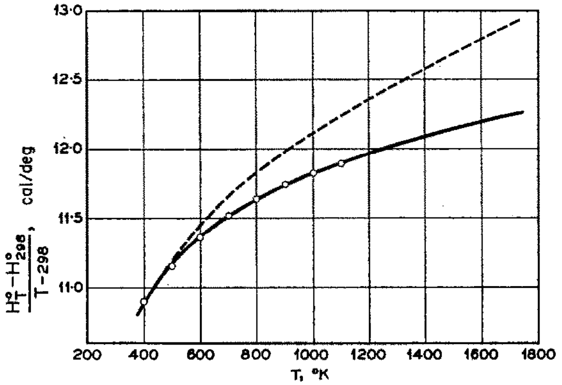

FIG. 11. The heat content function of GaP vs. temperature. ○ PANKRATZ.(27) —— Calculated curve from equation (9). - - - - Calculated curve from the sum of the heat capacities of Ge and Si.

Table 7. GaP *free energy function*

T	$-(F^\circ_T-H^\circ_{298}/T)$, cal deg^{-1}	ΔH°_f, kcal
298	11·96	−45·7
800	16·01	
900	16·90	
1000	17·74	
1100	18·55	
1200	19·32	
1300	20·05	
1400	20·74	
1500	21·40	
1600	22·02	
1700	22·60	

$Cp = 11{\cdot}97+4{\cdot}82\times10^{-4}T-(1{\cdot}51\times10^5/T^2)$

It will now be shown that the low temperature pressure measurements by Johnston when fit by a curve consistent with a reasonable entropy of GaP at 298°K, leads to a curve in very good agreement with the high temperature measurements by Richman.

3.32. *High temperatures*: The high temperature measurements by RICHMAN(1) of the decomposition pressure of GaP can be used to obtain the partial pressures of P_2 and P_4 by using the free energy functions and heats of reaction given in the JANAF Tables.(28) The pressures of P_2 over liquid phosphorus are also available in the JANAF Tables.

The activity coefficient of P in liquid solutions has been calculated from Richman's measurements, the JANAF Tables and the liquidus curve. Figure 12 shows the results, where log γ_P has been plotted as a function of x_P, the atom fraction of P in the saturated liquid phase.

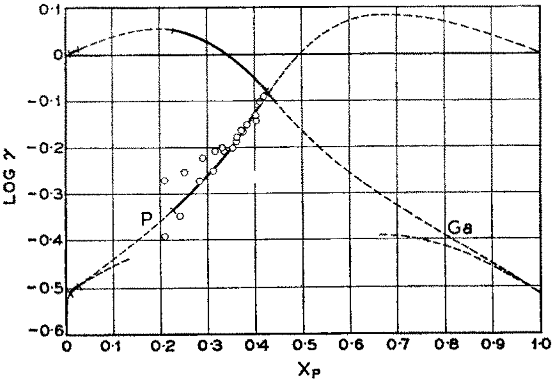

FIG. 12. The activity coefficient of phosphorus and gallium as a function of x_P, the atom fraction of phosphorus along the GaP liquidus curve. ○ RICHMAN.(1) —— γ_P at low x_P, from JOHNSTON.(6)

In order to draw a reasonable curve through the points obtained from Richman's measurements, the activity coefficients of P at low temperatures, coming from the Third Law fit to Johnston's measurements, have also been plotted. The solid line in the atom fraction range of 0·006 to 0·026 has been obtained in this way. The short dashed curve in the low composition region has been calculated from the pressure of P_2 over liquid solutions for which the gallium activity has been assumed to be unity. The phosphorus activity coefficient curve must lie on or above the dashed line. A γ_P curve below the line would imply a metastable liquid phase. Thus, a reasonable interpolation can be made between Richman's measurements and the low temperature measurements of Johnston, in a manner analogous to that used for the GaAs system.

The extrapolation of the phosphorus activity coefficient to larger values of the atom fraction presents certain problems. It is clear that γ_P must approach unity as γ_P approaches unity, but with the knowledge that the log γ_P–x_P curve must be a smooth curve, it appears that the values of γ_P must rise above unity, pass through a maximum and then approach unity at higher phosphorus concentrations. If the γ_P curve did not pass through a maximum, a point would be reached where the activity coefficient would be sufficiently large to make the pressure of phosphorus over the liquid solution equal to the pressure of pure liquid phosphorus, at which temperature and composition phase separation would occur.

It is difficult to say from the log γ_P–x_P curve itself just how the extrapolation to higher phosphorus concentrations is to be made. However, the extrapolation can be made in a reasonable way in terms of the gallium activity coefficient curve. This curve can be calculated in the region of lower phosphorus concentrations from the γ_P curve as was done for the Ga–As system. In the case of GaP, however, the vapor species P_2 has been used.

From the free energy of decomposition of GaP to form Ga(liq.) and P_2(g) and the free energy of vaporization of pure liquid phosphorus, γ_{Ga} can be calculated from the liquidus curve and the γ_P curve in the phosphorus atom fraction range up to about 0·42. The logarithm of γ_{Ga} in this range has been plotted as a function of x_P in Fig. 12. The extrapolation of this curve to larger values of x_P is aided by the fact that the activity coefficient of gallium in solutions rich in phosphorus can be calculated from the pressure of gallium over these solutions which is known from the free energy of formation of GaP. The major uncertainty in such a calculation comes from the uncertainty in the position of the liquidus curve in the phosphorus rich region. For the liquidus curve recommended here for the Ga–P system, the activity coefficient of gallium in phosphorus rich liquids must lie above the dashed curve segment plotted in Fig. 12 at large phosphorus atom fractions, but it must approach this curve and join it in the range where gallium forms an ideal dilute solution with phosphorus. The extrapolation of the γ_{Ga} curve from about 0·42 atom fraction P to pure P can be done in a reasonable manner as shown in Fig. 12. The log γ_P curve follows.

The log γ_P curve of Fig. 12 provides the basis for the estimation of the pressures of P_2, P_4, P and P_{Ga} over an extended temperature and composition range. The JANAF Tables(28) have been used for P_4 and P_2. The heat of sublimation of Ga obtained by MUNIR and SEARCY(23) has been used for the P_{Ga} curve. The full curves are shown in Fig. 13. The pressures of P_2 calculated from Richman's total pressures and pressures measured by Johnston have also been plotted. The pressures of P_2 and P_4 at higher temperatures have been plotted in Figure 14 on an expanded scale along with the pressure of P_2 calculated from Richman's measurements.

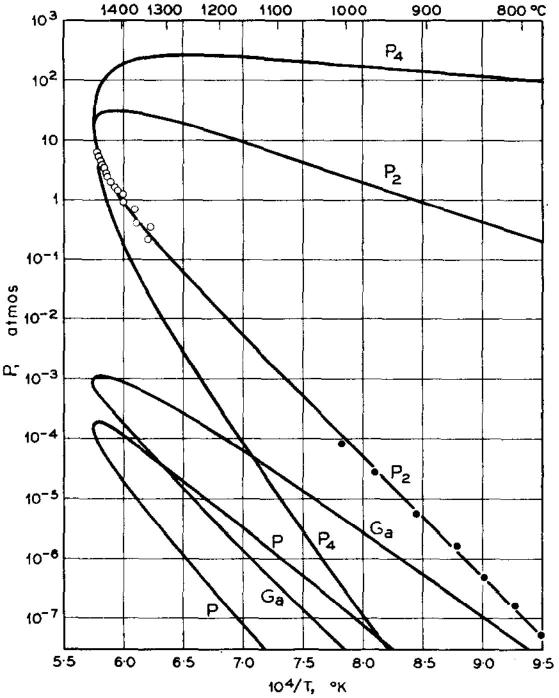

FIG. 13. The equilibrium pressures of various vapor species along the GaP liquidus curve as a function of $1/T$. ○ RICHMAN.(1) ● JOHNSTON.(6)

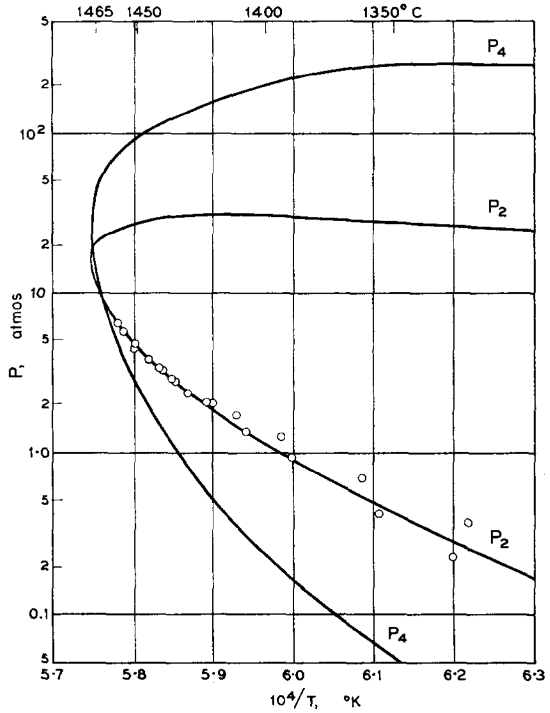

FIG. 14. The equilibrium pressure of P_2 and P_4 along the GaP liquidus curve as a function of $1/T$. ○ RICHMAN.(1)

4. DISCUSSION

4.1 *Melting point pressures*

The log γ_{As}–x_{As} curve of Figure 9, for GaAs, was made to pass through the melting point pressure measured by Richman. At the melting point, $P_{As_4} = 0{\cdot}902$ atm and $P_{As_2} = 0{\cdot}074$ atm, for a total pressure of 0·976 atm. The pressures of As and Ga are less than 10^{-4} atmospheres (see Fig. 10).

The log γ_P–x_P curve of Fig. 12 leads to a pressure of 24 atm. for P_4 and 15 atm for P_2, giving a total pressure of 39 ± 7 atm at the melting point of GaP. RICHMAN(1) obtained 35 ± 10 atm by a different extrapolation method. The uncertainty of 7 atm arises from a 3 deg uncertainty in the melting point of GaP.

4.2 *Congruent evaporation*

Along the low temperature portion of the gallium-rich liquidus curve, the pressures of As_2 and As_4 are larger than the pressure of Ga (Fig. 10). As a result, GaAs decomposes when heated to give a gallium-rich liquid phase and As_2 and As_4 in the vapor phase. It can be seen from Fig. 10, however, that at lower temperatures the P_{As_2} line will cross the P_{Ga} line. This means that at some lower temperature it will be possible for the vapor phase to have the same composition as the solid phase. This will occur at temperatures below the temperature, defined as the decomposition temperature, where $P_{Ga} = 2P_{As_2}$ (P_{As_4} is negligible at the lower temperatures). Above the decomposition temperature, GaAs decomposes; below the decomposition temperature, GaAs will evaporate congruently. A similar condition applies to the GaP system (Fig. 13). The decomposition temperatures and the pressures at the decomposition temperatures for GaAs and GaP are given in Table 8.

Table 8

	Decomposition temp (°C)	P_{Ga}, Atm
GaAs	660 ± 100	$5 \times 10^{-10}(10^{-7} - 10^{-11})$
GaP	680 ± 100	$1 \times 10^{-9}(10^{-7} - 10^{-11})$

4.3 *Vacancy concentration range*

The equilibrium concentration of neutral gallium vacancies in GaAs at a particular temperature is proportional to the pressure of atomic arsenic, P_{As}. The ratio of maximum to minimum pressures of P_{As} at any T gives the ratio of the maximum possible gallium vacancy concentration to the minimum possible concentration at that temperature; that is, the range of vacancy concentration. The range of the gallium vacancy concentration is the same as that of the arsenic vacancy concentration. Similar comments apply to GaP. Figure 15 is a logarithmic plot of the vacancy concentration range as a function of $1/T$ for GaAs and GaP as obtained from the pressure curves of Figs. 10 and 13. At 300 deg below the melting points of GaAs and GaP, the vacancy concentration range is just less than 400 for both compounds.

4.4 *Liquidus curves*

The parameter α has been defined by equation (1). If the liquid solutions were regular solutions, in the sense that the heat of mixing is proportional to the atom fraction product and the entropy of mixing is ideal, α would be a constant, independent of temperature. If α is viewed as an empirical parameter defined by equation (1) it would be expected that, in general, α vs. T would be a smooth curve having two branches, one for each side of the liquidus. From Fig. 1 it appears that α is rather well represented by a linear function of temperature which is the same function on both sides of the Ga–As liquidus curve. The experimental measurements on the arsenic-rich side of the melting point are sparse, and the two points by Köster and Thoma at the highest arsenic concentrations are undoubtedly in error. (Fig. 3). The extrapolation of the liquidus curve to the arsenic-rich eutectic (2·4 at. % Ga) is in good agreement with a composition expected from the eutectic temperature and heat of fusion of arsenic of 5610 cal/g atm (1·6%).

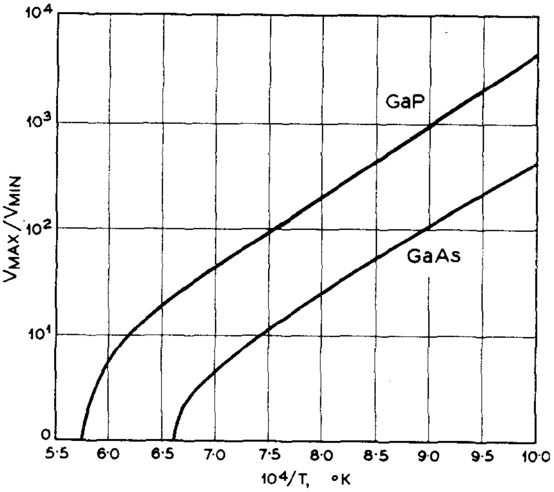

FIG. 15. The ratio of the maximum neutral vacancy concentration to the minimum neutral vacancy concentration as a function of $1/T$ for GaAs and GaP.

The GaP solubility measurements are all on the gallium-rich side of the liquidus curve and show considerably more experimental scatter than the GaAs measurements. The α plot (Fig. 4) can be represented within experimental uncertainty by a straight line. The phosphorus-rich region of the liquidus curve has been estimated by assuming that the α line drawn in Fig. 4 applies to both sides of the liquidus curve as appears to be a good approximation for the GaAs liquidus curve.

The simplest liquid phase thermodynamic properties leading to a liquidus curve for which the parameter α is linear in T are those which have the following properties:

$$\Delta H_m = ax_1x_2 \tag{10}$$

$$\Delta S^e_m = bx_1x_2 \tag{11}$$

$$\alpha = a - bT. \tag{12}$$

ΔH_m is the molar heat of mixing to form solutions from the pure liquid components; ΔS^e_m the excess molar entropy of mixing; a and b are constants. It does not follow, however, that if the parameter α, defined by equation (1) is linear in T that the thermodynamic properties of the liquid phase must be given by equations (10) and (11). In particular, the thermodynamic properties of the GaAs and GaP liquid phase are not those given by equations (10) and (11). If they were given by these equations, the activity coefficient of arsenic along the liquidus curve would be given by the equation:

$$\frac{RT \ln \gamma_{\mathrm{As}}}{(1-x_{\mathrm{As}})^2} = \alpha_{\mathrm{As}} = a - bT. \tag{13}$$

This function can be calculated from the log γ_{As}–x_{As} curve of Fig. 9, and it has been plotted in Fig. 16. It is seen that α_{As} is not a linear function of temperature.

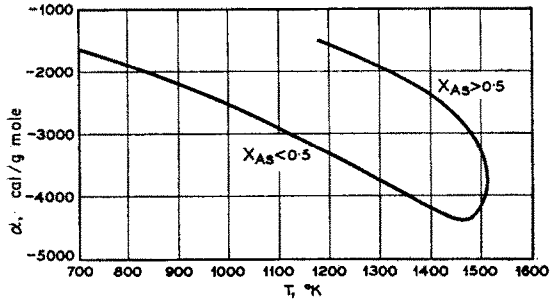

FIG. 16. GaAs. The parameter α, calculated from equation (13), as a function of temperature.

It is not clear why the parameter α as defined by equation (1) is a linear function of temperature for the GaAs system. The binary systems formed by Si and by Ge with a rather large number of other components have liquidus curves that lead to a linear α-T plot,(13) although it is unlikely that the thermodynamic properties of the liquid phases are more than roughly approximated by equations (10), (11) and (12). For the present, it is accepted as an empirical observation in the GaAs system and used to find a best estimate of the complete GaP liquidus curve from the limited experimental points available.

4.5 *The log γ–x curves*

RICHMAN(1) found that when γ was plotted as a function of x calculated from vapor pressure measurements along the liquidus curve, a minimum occurred in the curves for the GaAs, GaP and InP systems. The activity coefficient curves of GaAs and GaP, recalculated in the present work using revised liquidus curves and pressure curves for the pure Group V components, show somewhat different behavior. A minimum is found in the log γ_{As}–x_{As} curve, although altered in shape considerably from that found by Richman. The log γ_{P}–x_{P} curve does not now show a minimum.

The fact that the activity coefficients of both arsenic and phosphorus approach unity as the composition of the liquid phase along the liquidus curve approaches unity is to be expected. The upturn in the activity coefficient of arsenic in gallium-rich solutions is evidence that the partial molar heat of mixing liquid arsenic with liquid gallium to give a dilute solution is a positive number. In particular, from the functions used for the liquidus curve, from the pressure of As_4 over liquid arsenic, and from the decomposition pressure of GaAs, all at low temperatures, the dilute solution partial molar heat of mixing and partial molar excess entropy of mixing can be calculated. The results are shown in Table 9. The uncertainties in these numbers are quite large, and the number of significant figures used is meant to permit calculation of the activity coefficient in dilute solutions consistent with the activity coefficient curves of Figs. 9 and

Table 9

	ΔH^*, cal g-atom^{-1}	ΔS^{e*} cal deg^{-1}
GaAs	$+175 \pm 1{,}500$	$+2{\cdot}59 \pm 1{\cdot}5$
GaP	$-680 \pm 1{,}500$	$+1{\cdot}74 \pm 1{\cdot}5$

12. It is estimated that ΔH^* is uncertain to 1·5 kcal g-atom^{-1} and $\Delta S^{e}.^*$ to 1·5 cal deg^{-1}.

The suggestion offered by the figures in Table 9 is that the departures from ideality of these liquid phases arises from an entropy term rather than a heat term. The positive excess entropy of mixing means that the entropy change is greater than for ideal solutions and can arise if volume expansion occurs upon mixing. RICHMAN(1) has suggested that the minima he found in the γ–x curves arose from association of the two species in the solutions. Such associative interactions could lead to negative departures from ideality if the heat of interaction outweighed the entropy effect, but would not lead to a minimum in γ along the liquidus curve. The presently available experimental data for GaAs and GaP provide evidence that little or no association occurs in the liquid phase, a conclusion reached by WEISER(30) from a less detailed analysis than presented here of the pressure–temperature–solubility relationships for a number of III–V compounds, including GaAs.

4.6 *Heat content change at* 298°K, ΔH°_{298}

The various reactions of significance in the GaAs system are summarized in Table 3 with the values of ΔH°_{298} appearing in the literature and the values adopted here. An attempt has been made to estimate the uncertainties in ΔH°_{298}. Table 10 summarizes similar information for the GaP system.

The heats of atomization of GaAs and GaP are given in the next to the last lines of Tables 3 and 10. GOLDFINGER(31) concluded from a number of III–V compounds that the heat of atomization was 12 to 15% smaller than that of the corresponding Group IV lattice. From the data available to him at the time, he calculated 17·5% for GaAs. The value of 155 kcal in Table 3 is 14% smaller than the value of 180 kcal for 2 moles of Ge, in closer agreement with Goldfinger's generalization. The value of 170 kcal for the heat of atomization of GaP is 13% of 195 kcal, the sum of the heat of sublimation of Ge and Si,(15) again in agreement with Goldfinger's generalization.

The heats of formation of GaAs and GaP are given in the last lines of Tables 3 and 10. GUTBIER(8) has shown that the heat of formation of a number of III–V compounds can be well approximated by an equation suggested by PAULING.(32)

$$Q = 4\times 23\cdot 06(X_{III}-X_{V})^2 \text{ kcal/mole.} \quad (14)$$

In equation (14), X_{III} is the electronegativity of the Group III element and X_{V} of the Group V element. Gutbier showed that the value of the heat of formation for GaAs was in satisfactory agreement with the value predicted from equation (14) using the electronegativities given by GORDY and THOMAS.(33) Equally good agreement is obtained for GaP, where the experimental value of 24·4 kcal in Table 3 is to be compared to 23 kcals calculated from equation (14).

4.7 *The activity coefficients*

The activity coefficients of arsenic and of phosphorus have been calculated using the pressures of As_4 and of P_4 over the respective liquid phases. In the case of arsenic, these pressures are in the 20 to 30 atm range (see Fig. 10), while for phosphorus, the pressures are as high as 300 atm.

Table 10. ΔH°_{298}, *kcal*

Reaction	Literature	Adopted
$GaP(s) = Ga(s)+\frac{1}{2}P_2(g)$	42·75(26)	45·7 ± 1
$GaP(s) = Ga(s)+\frac{1}{4}P_4(g)$	—	32·0 ± 1·5
$2P_2(g) = P_4(g)$	−55·7(31), −54·6(28)	−54·6 ± 1·5
$4P(s) = P_4(g)$	30·8(28)	30·8 ± 0·5
$2P(s) = P_2(g)$	42·7(28)	42·7 ± 0·5
$2P(l) = P_2(g)$	34·0(28)	34·0 ± 0·5
$P(s) = P(g)$	79·8(28)	79·8 ± 0·05
$\frac{1}{2}P_2(g) = P(g)$	58·5(28)	58·5 ± 0·6
$GaP(s) = Ga(g)+P(g)$	—	170 ± 2·6
$Ga(s)+P(s) = GaP(s)$	—	−24·4 ± 1·25

(Figures 13 and 14.) No corrections for departures from perfect gas behavior have been made because it is believed that such corrections will be negligibly small compared to uncertainties in the liquidus curves, measured pressures, and equilibrium constants.

An estimate of the magnitude of the errors introduced by using pressure ratios rather than fugacity ratios to calculate activity coefficients can be made for phosphorus by using the Berthelot equation for P_4,(34) and the critical constants given in the JANAF Tables.(28) If the pressure of P_4 is 300 atm at 1700°K, the ratio of the fugacity to the pressure will be about 0·87, according to the Berthelot equation.(34) Since the activity coefficient comes in as the $\frac{1}{4}$ power of the pressure ratio, a discrepancy in γ_P of less than 4 per cent is expected.

5. SUMMARY

It has been found that the available experimental measurements on the GaAs liquidus curve can be fit to a straight line when plotted as the parameter α vs. T (Fig. 1), where α has been defined by equation (1). A reasonable estimate can then be made of the complete liquidus curve (Figs. 2 and 3). A plot of α vs. T using the available GaP liquidus curve data suggests a linear relationship (Fig. 4) although the experimental uncertainties do not permit as definite a conclusion as for the GaAs system. The complete GaP liquidus curve is estimated from the linear α vs. T line drawn through the experimental points (Figs. 5 and 6). The GaAs and GaP liquidus curves are the starting point for the evaluation of decomposition pressures of GaAs and GaP measured by various workers.

It has been found that the low temperature decomposition pressures over GaAs measured by GUTBIER(8) are consistent with the high temperature pressure measurements of RICHMAN.(1) Gutbier did not, in fact, measure pressures, but obtained what appears to be a good measurement of the heat of decomposition of GaAs from mass spectrometer ion currents. The heat capacity measurements of PIESBERGEN(7) gave him the entropy of GaAs at 298°K, from which it has been possible to calculate a free energy function for GaAs and to use Gutbier's heat of decomposition of GaAs to obtain a decomposition pressure curve. The pressure measurements of DROWART and GOLDFINGER(2) have been found by a Third Law treatment to be inconsistent with the high temperature measurements of Richman.

The high temperature pressure measurements of Richman along the GaAs liquidus curve have been used to calculate activity coefficients for arsenic. An evaluation of the vapor pressure measurements of pure solid and liquid arsenic has led to a proposal for the vapor pressure of pure liquid arsenic [equation (5)]. The low temperature pressure curve obtained from Gutbier's measurement permits one to calculate activity coefficients at low atom fractions of arsenic. When the experimental activity coefficients obtained in the two temperature and composition ranges are plotted as log γ_{As} vs. x_{As}, it is possible to draw a smooth curve through both sets of data (Fig. 9). A simple extrapolation to higher arsenic concentrations can be made utilizing the fact that γ_{As} must approach unity as x_{As} approaches unity along the liquidus curve. The activity coefficient of gallium has been calculated from the arsenic curve, and the complete pressure–temperature curves follow (Fig. 10).

The available decomposition pressure measurements for GaP have been treated in an analogous manner to that used for GaAs. The activity coefficient curves are given in Fig. 12 and the pressure–temperature curves in Figs. 13 and 14.

The decomposition pressures of GaAs and GaP are found to be very nearly identical in the low temperature region. When the temperature is below about 660°C for GaAs and 680°C for GaP, congruent evaporation will occur. The maximum and minimum pressures at each temperature give the ratio of the maximum to minimum vacancy concentration (Fig. 15).

The activity coefficients of gallium in both GaAs and GaP are found to be greater than unity in solutions along the liquidus curve rich in gallium. The activity coefficient of phosphorus is found to be greater than unity in phosphorus-rich liquids. The variation of the arsenic and phosphorus activity coefficients along the liquidus curves in the composition range where the liquids are nearly pure gallium gives the temperature dependence of the activity coefficients. From the temperature dependence it is concluded that the heats of mixing are small and that the excess entropies of mixing are small, but large enough to be the dominant term in the determination of the magnitude of the dilute solution activity coefficients. No evidence is found for association in the GaAs and GaP liquid solutions; the dilute solution temperature dependence of the arsenic and phosphorus activity coefficients suggests that the excess entropy is greater than zero while association would be expected to lead to an excess entropy less than zero. The dilute solution heats of mixing are found to be small, positive for GaAs and negative for GaP. If association occurs, a large negative heat would be expected.

The heat of decomposition of GaAs at 298°K to form Ga(s) and As_4(g) obtained by Gutbier,(8) $+26{\cdot}3 \pm 0{\cdot}75$ kcals, has been adopted. A Third Law evaluation of Johnston's(6) effusion measurements with GaP leads to a heat of decomposition at 298°K to form Ga(s) and P_2(g) of $+45{\cdot}7 \pm 1$ kcal. Free energy functions have been calculated for both GaAs and GaP. A consistent set of values of ΔH°_{298} for relevant reactions has been adopted (Tables 3 and 10).

Acknowledgements—I wish to thank K. K. Kelly and L. B. Pankratz for the GaP heat content data they have recently obtained. Discussions with F. A. Trumbore and M. B. Panish have been very helpful.

REFERENCES

1. Richman D., *J. Phys. Chem. Solids* **24,** 1131 (1963).
2. Drowart J. and Goldfinger P., *J. Chim. Phys.* **55,** 721 (1958).
3. Marina L. I., Nashel'shii A. Ya and Yakolason S. V., *Zh. Fiz. Khem.* **36,** 1086 (1962).
4. van den Boomgaard J. and Schol K., Philips Res. Rept. **12,** 127 (1957).
5. Lyons V. J. and Silvestri V. J., *J. Phys. Chem.* **65,** 1275 (1961).
6. Johnston W. D., *J. Electrochem. Soc.* **110,** 117 (1963).
7. Piesbergen U., *Z. Naturf.* **18a,** 141 (1963).
8. Gutbier H., *Z. Naturf.* **16a,** 268 (1961).
9. Hall R. N., *J. Electrochem. Soc.* **110,** 385 (1963).
10. Köster W. and Thoma B., *Z. Metall.* **46,** 291 (1955).
11. Rubenstein M., *J. Electrochem.* Abstracts **11,** 129 (1962).
12. Vieland L., *Acta Meta.* **11,** 137 (1963).
13. Thurmond C. D. and Kowalchik M., *Bell Syst. Tech. J.* **39,** 169 (1960).
14. Schottky W. F. and Bever M. B., *Acta Meta.* **6,** 320 (1958).
15. Stull D. R. and Sinke G. C., *Thermodynamic Properties of the Elements,* A.C.S. (1956).
16. Horiba S., *Z. Phys. Chem.* **106,** 295 (1923).
17. Kelley K. K., U.S. Bureau of Mines, Bul. 584 (1960).
18. Nesmeyanov An. N., *The Vapor Pressure of the Elements,* p. 297. Academic Press, New York (1963).
19. Ref. 15, p. 11.
20. Preuner G. and Brockmöller J., *Z. Phys. Chem.* **81,** 129 (1912).
21. Gibson G. E., Dissertation, Breslau, 1911, reported in *Landolt-Bornstein Tabellen,* Vol. 2, p. 1332. Springer, Berlin (1923).
22. Wiechmann F. and Heimburg M., *Z. Anorg. Chem.* **240,** 129 (1938).
23. Munir Z. A. and Searcy A. W., *J. Electrochem. Soc.* **111,** 1170 (1964)
24. Cochran C. N. and Foster L. M., *J. Electrochem. Soc.* **109,** 144 (1962).
25. Moore G. E. and Thurmond C. D., unpublished results.
26. Thurmond C. D. and Frosch C. J., *J. Electrochem. Soc.* **111,** 184 (1964).
27. Pankratz L. B., Bureau of Mines, Berkeley, California, to be published.
28. JANAF, Interim Thermochemical Tables, Thermal Laboratories, Dow Chemical Company.
29. Kelly K. K., U.S. Bureau of Mines, *Bulletin,* p. 371 (1934).
30. Weiser K., *Compound Semiconductors,* Vol. 1, edited by R. K. Willardson and H. L. Goering, Chap. 51, p. 471. Reinhold, New York.
31. Goldfinger P., *Compound Semiconductors,* Vol. 1, edited by R. K. Willardson and H. L. Goering, Chap. 52, p. 483. Reinhold, New York.
32. Pauling L., *The Nature of the Chemical Bond,* p. 92. University Press, Third Ed. (1960).
33. Gordy W. and Thomas W. J., *J. Chem. Phys.* **24,** 439 (1956).
34. Lewis G. N. and Randall M., *Thermodynamics,* Second Edn., revised by K. S. Pitzer and Leo Brewer, p. 187 (1961).