HIGH TEMPERATURE HEAT CONTENTS OF III-V SEMICONDUCTOR SYSTEMS

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SUMMARY
    As part of calorimetric studies on metals and alloys at high temperature,
heat contents of the III-V compounds of AlN, GaN, AlP, GaP, InP, AlAs, GaAs,
InAs, AlSb, GaSb and InSb were measured over the temperature range 650 to 1550K
using a drop calorimeter. The heat content and the heat capacity equations for
the solid compounds were derived by the use of the Shomate function. Heat
contents of the Ga-As, In-As, Ga-P and In-P binary alloys were also measured to
derive the thermodynamic quantities of these liquid alloys by the use of a
thermodynamic analysis method, and the vapour pressure-temperature-composition
diagrams were constructed.

INTRODUCTION

    High temperature data for thermal and thermodynamic properties of metals,
alloys or metallic compounds, and for the reaction between these materials are
of significant importance in the field of metallurgy. The advancement in
calorimeters used for enthalpy of reaction, solution and mixing studies at high
temperature are reviewed in a separate paper (ref.1). Reliable reaction
calorimeters of the isoperibol, heat flow and adiabatic types for use at high
temperature above 1300K are still not easy to construct, though usability of a
very high temperature calorimeter (up to 1800K) of the Eyraud-Petit type was
claimed by Bros et al. (ref.2). A high temperature microcalorimeter of the
Tian-Calvet type has been often used for the investigation of the enthalpies of
formation of alloys, but its upper temperature limit is 1200K. Although the use
of a calorimeter of the jumping type is restricted to the measurement of heat
contents, this type of calorimeter has an advantage that it can be utilized at
higher temperature compared with the reaction calorimeters if the calorimeter
assembly is kept at room temperature, as in the case of a drop calorimeter.
Heat contents up to 3000K were measured for some refractory metals using drop
calorimeters (ref.3).
    A knowledge of the high temperature thermochemical properties of the III-V
alloy systems provides an important basis for processing semiconducting
materials. However, only few data exist for the heat contents and heat
capacities at high temperature above 1000K, which are reported by Cox et al.
(ref.4), Lichter et al. (ref.5) and Pankratz (ref.6). In this study, the heat

contents of the eleven III-V (III: Al, Ga, In V: N, P, As, Sb) compounds and four binary alloys of Ga-As, In-As, Ga-P and In-P were determined over the temperature range 650 to 1550K using a drop calorimeter whose construction is given in a separate paper (ref.7). A thermodynamic analysis method, which enables derivation of the thermodynamic quantities of liquid mixtures on the basis of heat content-temperature-composition plots, was applied to these binary alloy systems to construct vapour pressure-temperature-composition diagrams.

HEAT CONTENTS OF THE III-V COMPOUNDS
Effect of evaporation of sample

As shown in Table 1, the III-V compounds generally represent very high dissociation pressures at elevated temperature, and use of a vacuum-sealed quartz container is indispensable to avoid the evaporation of sample. When the sealed container saturated with the evaporating gas is taken out of the heating furnace and dropped into the water calorimeter, the gas is condensed with evolution of heat, that may afford an error in a determination of the heat content. In the case that the gas evaporated in the container at TK is condensed completely at 298K, the ratio of the heat evolved by its condensation, ΔH_v, to the heat content, $H_T - H_{298}$, is given by eqn.(1).

$$\Delta H_v \;/\; (H_T - H_{298}) = (V_g/V_c)(p\,M_c\,L_c) \;/\; (R\,T\,d\,\int_{298}^{T} C_p\,dT) \tag{1}$$

Where V_g and V_c are volumes of the gas and condensed phases, p is vapour pressure, L_c is enthalpy of condensation, and d and M_c are density and molecular weight of the condensed phase. (V_g/V_c) is the only factor in eqn.(1) that can be controlled in the experiments in order to reduce the error arising from the condensation of vapour, and it should be kept as small as possible. The ratio of $\Delta H_v/(H_T - H_{298})$ in percentage was calculated for the GaAs compound for two cases of $(V_g/V_c) = 1$ and (1/4) and the results are shown in Fig. 1, in relation to temperature. A construction of the sample assembly with (V_g/V_c) of approximately (1/3) can be easily made in the present experiments, where about 8g of sample is enclosed into a fused quartz container with an inner diameter of 20mm and a height of 20mm. It can be considered from Fig. 1 that the error in the present experiments due to the evaporation of sample is very small at less than 0.3% even at high temperature up to 1600K.

TABLE 1
Dissociation pressures of some III-V compounds

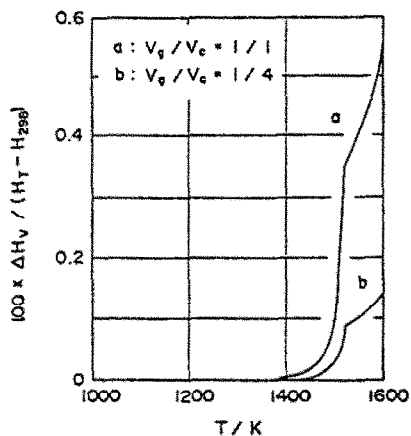| Substance	Melting Point(K)	Dissociation Pressure(kPa)
GaAs	1514	116.4
InAs	1221	15.4
InP	1340	390.0

Fig. 1 Effect of the heat of con-
densation on the measurement of
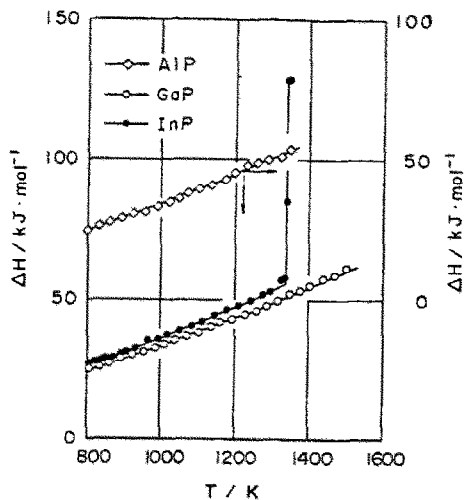heat content.

Fig. 2 Heat contents of the III-P
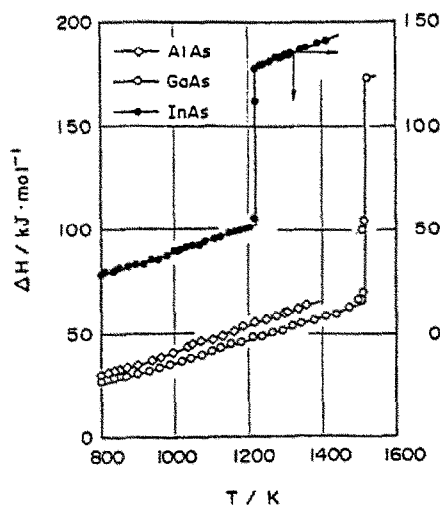compounds ($\Delta H_T = H_T - H_{298}$).

Fig. 3 Heat contents of the III-As
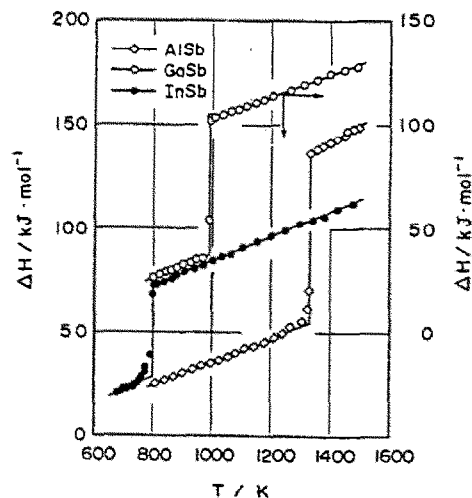compounds ($\Delta H_T = H_T - H_{298}$).

Fig. 4 Heat contents of the III-Sb
compounds ($\Delta H_T = H_T - H_{298}$).

Shomate function

The heat contents of the III-P, III-As and III-Sb compounds measured in this study are shown in Figs. 2, 3 and 4, respectively. These are formulated in functions of temperature as follows.

$$H_T - H_{298} = a\,T + b\,T^2 + c\,T^{-1} + I \tag{2}$$

The coefficients a, b and c as well as the constant I in eqn.(2) can be determined using the Shomate function (ref.8).

$$\text{Shomate function} = T[(H_T - H_{298}) - C_{p,298}(T - 298)] / (T - 298)^2 \tag{3}$$

Here $C_{p,298}$ is heat capacity at 298K. In the case that the heat contents are given by eqn.(2), the Shomate function can be expressed as

$$\text{Shomate function} = b\,T + c / (298)^2 \tag{4}$$

On the basis of eqn.(4), the coefficients b and c can be derived from the Shomate function-temperature plots, and a and I can be determined using two boundary conditions of $H_T - H_{298} = 0$ at 298K and $C_p = C_{p,298}$ at 298K. By the use of literature values for $C_{p,298}$ (ref.9), the heat contents of the III-V compounds were formulated, as shown in Table 2.

TABLE 2
Heat contents of the III-V compounds.

$$\Delta H_T = aT + bT^2 + cT^{-1} + I$$

Substance	ΔH_T in J/mol					Temp. range (K)
	a	$b \times 10^3$	$c \times 10^{-5}$	$I \times 10^{-4}$	probable error	
AlN(s)	42.7	4.27	13.41	−1.76	±60	800–1400
GaN(s)	43.6	4.31	4.84	−1.50	±90	800–1050
AlP(s)	48.4	2.35	6.90	−1.70	±130	800–1400
GaP(s)	49.4	0.67	5.26	−1.65	±120	800–1510
InP(s)	50.1	2.53	5.01	−1.68	±210	800– 910
InP(s)	53.0	0.91	6.76	−4.97	±90	910–1340
AlAs(s)	62.4	1.00	15.28	−2.38	±100	800–1370
GaAs(s)	47.3	3.99	2.40	−1.53	±100	800–1514
InAs(s)	54.2	3.38	7.45	−1.90	±110	800–1221
InAs(l)	65.1	—	—	4.93	±170	1221–1450
AlSb(s)	43.4	5.43	0.17	−1.35	±160	800–1327
AlSb(l)	75.0	—	—	3.66	±150	1327–1500
GaSb(s)	48.4	4.99	1.80	−1.55	±90	800– 991
GaSb(l)	52.0	—	—	5.09	±70	991–1500
InSb(s)	58.3	0.91	8.86	−2.04	±260	650– 800
InSb(l)	57.7	—	—	2.68	±90	800–1500

Heat capacities

The heat capacities can be obtained by differentiating eqn.(2) and are given by

$$C_p = a + 2 b T - c T^{-2} \tag{5}$$

The heat capacities of the III-V compounds are listed in Table 3, and those of the AlAs, GaAs and InAs compounds are shown in Fig. 5.

TABLE 3
Heat capacities of the III-V compounds.

$$C_p = A + B T + C T^{-2}$$

Substance	C_p in J/K·mol			Temp. range (K)
	A	$Bx10^3$	$Cx10^{-5}$	
AlN(s)	42.7	8.55	−13.41	800-1400
GaN(s)	43.6	8.62	−4.84	800-1050
AlP(s)	48.4	4.70	−6.90	800-1400
GaP(s)	49.4	1.34	−5.26	800-1510
InP(s)	50.1	5.07	−5.01	800- 910
InP(s)	53.0	1.82	−6.76	910-1340
AlAs(s)	62.4	2.01	−15.28	800-1370
GaAs(s)	47.3	7.98	−2.40	800-1514
GaAs(l)	67.2	—	—	1514-1550
InAs(s)	54.2	6.75	−7.45	800-1221
InAs(l)	65.1	—	—	1221-1450
AlSb(s)	43.4	10.85	−0.17	800-1327
AlSb(l)	75.0	—	—	1327-1500
GaSb(s)	48.4	9.98	−1.80	800- 991
GaSb(l)	52.0	—	—	991-1500
InSb(s)	58.3	1.81	−8.86	650- 800
InSb(l)	57.7	—	—	800-1500

Standard Gibbs free energy of formation

The standard Gibbs free energies of formation of the equi-atomic III-V compounds for the following reaction,

$$A \text{ (III: s, l)} + B \text{ (V: s, l, g)} = AB \text{ (s, l)} \tag{6}$$
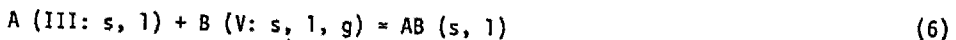
are given by eqn.(7).

$$\Delta G^{\circ}_{f,T} = \Delta H^{\circ}_{f,T} + \int_{298}^{T} \Delta C_p \ dT - T \ \Delta S^{\circ}_{f,298} - T \int_{298}^{T} (\Delta C_p/T) \ dT \tag{7}$$
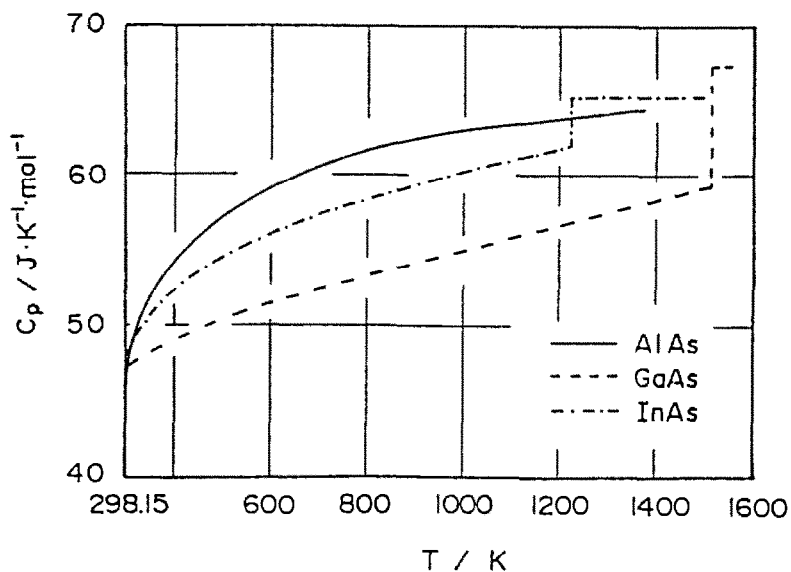
Fig. 5 Heat capacities of the III-As compounds.

From a combination of the Cp values obtained in this study with the literature values for the standard enthalpies and entropies of formation at 298K, as given in Table 4, $\Delta G^{\circ}_{f,T}$ for the II-V compounds were calculated, and are shown in Table 5.

TABLE 4
Heats and entropies of formation at 298K.

Substance	ΔH°_{298} (kJ/mol)	Ref.	ΔS°_{298} (J/K·mol)	Ref.
AlN	−318.0	9	20.2	9
GaN	−109.6	9	29.7	9
AlP	−163.1	13	47.3	14
GaP	−122.2	9	45.9	12
InP	−87.9	15	59.8	16
AlAs	−120.8	13	60.3	14
GaAs	−90.8	17	64.2	16
InAs	−62.0	18	74.7	14
AlSb	−50.0	13	64.3	16
GaSb	−41.6	19	77.3	14
InSb	−29.0	19	87.7	14

TABLE 5
$\Delta G^o_{f,T}$ for the III-V compounds.

$$\Delta G^* = a + bT \ln T + cT + dT^2 + eT^{-1} + fT^3$$

Reaction		ΔG^* in J						Temp. range (K)
		a	b	c	$d \times 10^3$	$e \times 10^{-5}$	$f \times 10^6$	
Al(s) + 1/2N$_2$(g)	= AlN(s)	−321300	2.64	97.66	−11.40	4.90	3.46	298- 933
Al(l) + 1/2N$_2$(g)	= AlN(s)	−330500	3.01	100.17	−3.21	6.70	—	933-1400
Ga(s) + 1/2N$_2$(g)	= GaN(g)	−124200	−81.35	578.55	127.22	2.42	—	298- 303
Ga(l) + 1/2N$_2$(g)	= GaN(s)	−119600	−5.31	166.57	−2.10	3.97	—	303- 700
Ga(l) + 1/2N$_2$(g)	= GaN(s)	−118200	−3.13	151.40	−3.24	2.42	—	700-1050
Al(s) + 1/2P$_2$(g)	= AlP(s)	−235800	1.13	88.40	−10.35	0.60	3.46	298- 933
Al(l) + 1/2P$_2$(g)	= AlP(s)	−245000	1.50	90.91	−2.15	2.41	—	933-1400
Ga(s) + 1/2P$_2$(g)	= GaP(s)	−208200	−82.85	583.13	130.00	1.59	—	298- 303
Ga(l) + 1/2P$_2$(g)	= GaP(s)	−203700	−6.82	171.16	0.68	3.14	—	303- 700
Ga(l) + 1/2P$_2$(g)	= GaP(s)	−202300	−4.64	155.98	−0.47	1.59	—	700-1510
In(s) + 1/2P$_2$(g)	= InP(s)	−173400	−40.95	367.64	36.33	7.10	—	298- 430
In(l) + 1/2P$_2$(g)	= InP(s)	−164600	−2.09	131.31	−2.77	1.46	—	430- 900
In(l) + 1/2P$_2$(g)	= InP(s)	−165000	−2.87	136.60	−2.33	1.46	—	900- 910
In(l) + 1/2P$_2$(g)	= InP(s)	−166100	−5.80	156.25	−0.71	2.34	—	910-1340
In(l) + 1/2P$_2$(g)	= InP(l)	−83200	−11.35	133.35	0.20	−1.04	—	1340-1400
Al(s) + 1/2As$_2$(g)	= AlAs(s)	−224100	−12.42	181.45	−9.16	5.33	3.46	298- 933
Al(l) + 1/2As$_2$(g)	= AlAs(s)	−233300	−12.05	183.96	−0.97	7.14	—	933-1370
Ga(s) + 1/2As$_2$(g)	= GaAs(s)	−199400	−80.36	559.86	126.52	0.69	—	298- 303
Ga(l) + 1/2As$_2$(g)	= GaAs(s)	−194800	−4.33	147.88	−2.81	2.25	—	303- 700
Ga(l) + 1/2As$_2$(g)	= GaAs(s)	−206900	−21.45	278.45	−3.95	0.69	—	700-1514
Ga(l) + 1/2As$_2$(g)	= GaAs(l)	−91800	−22.07	201.02	0.04	−0.51	—	1415-1550
In(s) + 1/2As$_2$(g)	= InAs(s)	−173500	−44.62	390.46	35.33	8.85	—	298- 430
In(l) + 1/2As$_2$(g)	= InAs(s)	−164700	−5.76	154.13	−3.77	3.22	—	430- 900
In(l) + 1/2As$_2$(g)	= InAs(s)	−165000	−6.54	159.42	−3.34	3.22	—	900-1221
In(l) + 1/2As$_2$(g)	= InAs(l)	−96800	−17.40	176.87	0.04	−0.51	—	1221-1450
Al(s) + Sb(s)	= AlSb(s)	−44200	18.48	−106.27	−21.32	−2.72	6.45	298- 904
Al(s) + Sb(l)	= AlSb(s)	−61600	19.39	−97.83	−13.62	−1.72	3.46	904- 933
Al(l) + Sb(l)	= AlSb(s)	−70800	19.76	−95.32	−5.43	0.08	—	933-1327
Al(l) + Sb(l)	= AlSb(l)	−20700	−11.85	87.02	—	—	—	1327-1500
Ga(s) + Sb(s)	= GaSb(s)	−51600	−69.58	403.87	117.79	−0.10	2.99	298- 303
Ga(l) + Sb(s)	= GaSb(s)	−47100	6.46	−8.10	−11.54	1.45	2.99	303- 700
Ga(l) + Sb(s)	= GaSb(s)	−45700	8.64	−23.27	−12.68	−0.10	2.99	700- 904
Ga(l) + Sb(l)	= GaSb(s)	−63100	9.55	−14.83	−4.99	0.90	—	904- 991
Ga(l) + Sb(l)	= GaSb(l)	3300	5.94	−61.79	—	—	—	991-1500
In(s) + Sb(s)	= InSb(s)	−43300	−36.80	253.62	30.07	9.06	2.99	298- 430
In(l) + Sb(s)	= InSb(s)	−34400	2.06	17.29	−9.03	3.43	2.99	430- 800
In(l) + Sb(s)	= InSb(s)	12800	2.64	−45.64	−8.13	−1.00	2.99	800- 900
In(l) + Sb(s)	= InSb(l)	12400	1.87	−40.35	−7.69	−1.00	2.99	900- 904
In(l) + Sb(l)	= InSb(l)	−5000	2.77	−31.91	—	—	—	904-1500

VAPOUR PRESSURE OF THE LIQUID III-V ALLOYS

Due to very high vapour pressures of the alloy components, the high temperature determination of the thermodynamic quantities for the liquid III-V alloys is very difficult by means of conventional methods, such as gas equilibration, vapour pressure measurement or electromotive force measurement. For these alloys, a thermodynamic analysis method by means of calorimetry is useful.

Thermodynamic analysis method

The principles of the thermodynamic analysis method are described in a separate paper (ref.10).

$$\Delta G_{X,T}^{mix} = T[\int_{1/\theta}^{1/T} J_T \, d(1/T) - (1 - X)\int_{1/\theta}^{1/T} J_{A,T} \, d(1/T)$$

$$- X\int_{1/\theta}^{1/T} J_{B,T} \, d(1/T)] + \Delta H_{X,\theta}^{mix} - T\Delta S_{X,\theta}^{mix} \tag{8}$$

Here J_T, $J_{A,T}$ and $J_{B,T}$ are heat contents of the binary mixture, and the pure components A and B at TK, which are defined as

$$J = H_T - H_\theta \tag{9}$$

Where H_T and H_θ are enthalpies of specimen at TK and a specified reference temperature of θK, respectively. $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are enthalpy and entropy of mixing at θK. Thus, we can derive $\Delta G_{X,T}^{mix}$ solely from the heat contents of the mixture and its components, provided that the values of $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are known. This method is very useful for the alloy systems which represent the phase diagrams as schematically illustrated in Fig. 6. A simple eutectic having negligibly small primary solid solutions on both sides of the components A and B is shown in Fig. 6(a). When a temperature below the eutectic is taken as the reference of θ, both $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are zero because the components A and B are immiscible at temperature below the eutectic. Consequently, we can derive $\Delta G_{X,T}^{mix}$ at a desired temperature solely from the heat content values, $J_{A,T}$, $J_{B,T}$ and J_T. In the case that a line compound is formed and it makes a simple eutectic with the component A or/and B, as shown in Fig. 6(b), $\Delta H_{X,\theta}^{mix}$ and $\Delta S_{X,\theta}^{mix}$ are strictly proportional to the molar enthalpy and entropy of formation of the compound, $\Delta H_{f,\theta}$ and $\Delta S_{f,\theta}$, when a temperature below the eutectic is taken as the reference. All the III-V alloy systems correspond to the latter case, and we can use the thermodynamic analysis method for the liquid III-V alloys because $\Delta H_{f,\theta}$ and $\Delta S_{f,\theta}$ of the III-V compounds are well established, as shown in Table 4.
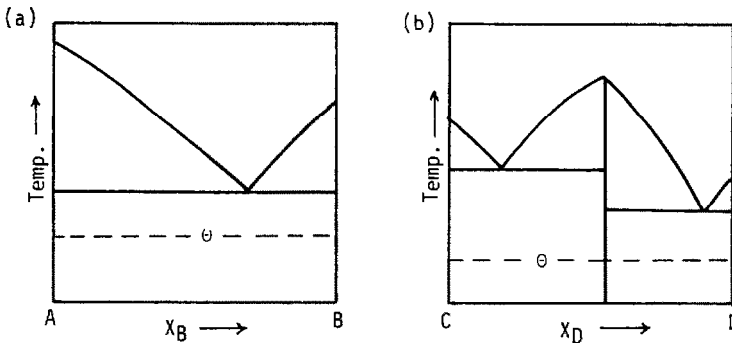

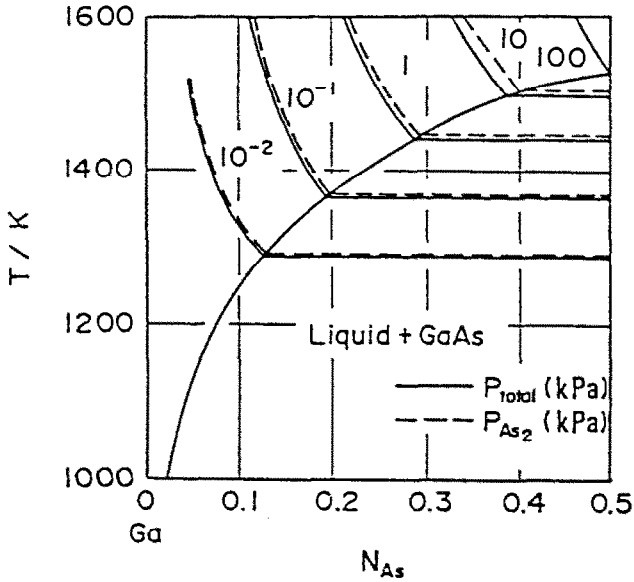Fig. 6 Schematic illustration of phase diagrams.

Fig. 7 Partial or total pressure-temperature-composition
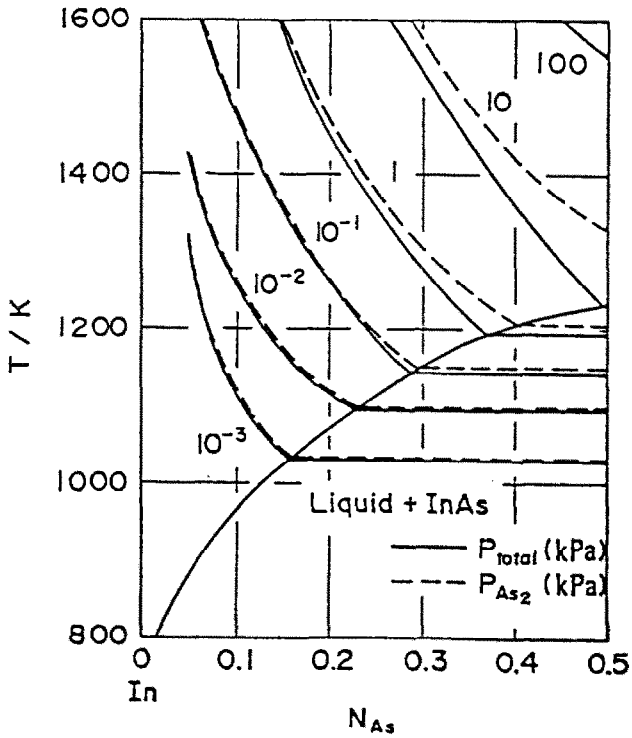diagram of the Ga-As system.

Fig. 8 Partial or total pressure-temperature-composition
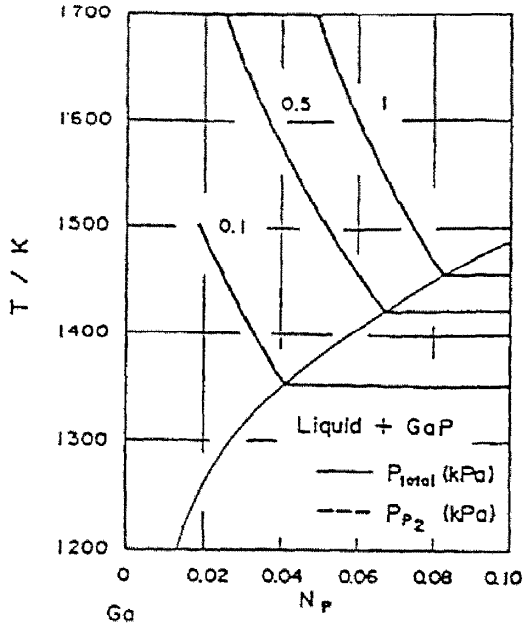diagram of the In-As system.

Fig. 9 Partial or total pressure-temperature-composition diagram for the Ga-P system.
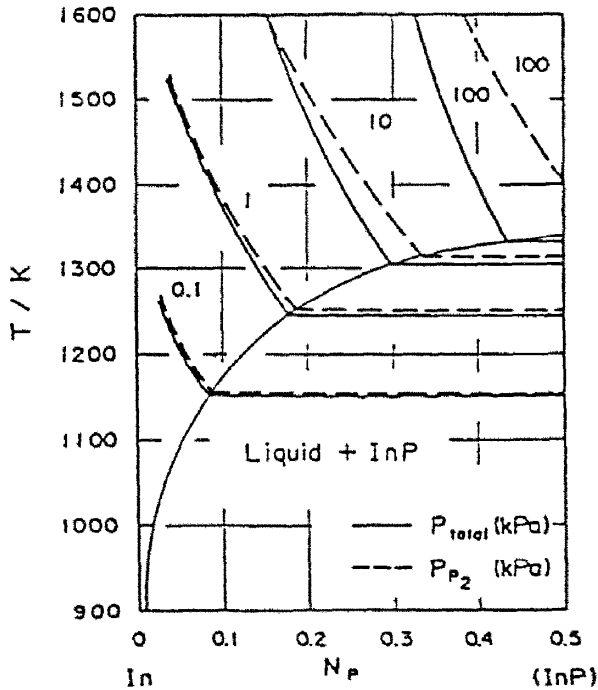

Fig. 10 Partial or total pressure-temperature-composition diagram of the In-P system.

The activities (vapour pressures) of alloy components can be derived from ΔG_T^{mix}- X plots using a tangent-intercept method. The utility of the thermodynamic analysis method to obtain vapour pressure values by means of calorimetry was discussed for the Fe-S system (ref.11).

Heat contents of some III-V alloy systems

The heat content-temperature-composition diagrams were constructed for the Ga-As, In-As, Ga-P and In-P systems, and are shown in a separate paper (ref.10).

Vapour pressure-temperature-composition diagrams

On the basis of eqn.(8) and using the heat content data obtained, vapour pressures of the arsenic and phosphorus gas species were calculated for the liquid Ga-As, In-As, Ga-P and In-P systems. The vapour pressure-temperature composition diagrams of these liquid alloy systems are shown in Figs. 7, 8, 9 and 10, respectively. The total pressure of $P_t = P_{As} + P_{As_2} + P_{As_3} + P_{As_4}$ or $P_t = P_P + P_{P_2} + P_{P_4}$ and the partial pressure of the predominant diatomic gas of As_2 or P_2 are given in these figures by solid and broken lines, respectively.

CONCLUSIONS

High temperature thermochemical data for the III-V compounds and the III-V alloy systems are lacking in spite of their importance in researches of semiconducting materials. Hence, the heat contents, heat capacities and standard Gibbs free energy of formation of the III-V compounds were determined in the present study, using a drop calorimeter. The vapour pressure-temperature composition diagrams for the liquid Ga-As, In-As, Ga-P and In-P binary alloys, which were constructed by means of a thermodynamic analysis method, may be useful in the production of the semiconductors.

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