CALCULATING ACTIVITIES USING $\Delta_{fus}H_{A_\eta B_\xi}$ AND CALCULATION OF ACTIVITIES IN Ga-As, Ga-Sb AND In-Sb SYSTEMS[①]

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ABSTRACT Based on the principle of thermodynamics a formula for calculating activities by intermediate compounds enthalpy of fusion has been derived from binary phase diagram. The feasibility of calculation method has been tested for In-Sb system using the activities obtained from experiments and used in many literatures, and the results of calculation are in good harmony with that of experiment. The activities of Ga-As, Ga-Sb and In-As semiconductor binary systems have been calculated using the new formula.
Key words binary phase diagram enthalpy of fusion activity calculation semiconductor

1 INTRODUCTION

Wagner had pointed out that, since the measurement of phase diagram is easier than that of thermodynamical parameters, thermodynamical parameters should be obtained from the phase diagram[1].

Every complicated binary phase diagram can be regarded as the system involving one or several following phase equilibria: (i) solution (including solid solution) with pure solid, such as eutectic and eutectoid phase diagram; (ii) solution with solid solution, such as continuous solid solution and limited solid solution phase diagram; (iii) solution with compound, such as the two-component system involving intermediate compounds; (iv) delamination systems, such as monotectic binary system. Therefore, the methods of calculating activities from binary phase diagram reported before can be classified as shown in Table 1.

Table 1 Methods for calculating activities from phase diagram[2-5]

Nr	$L \Leftrightarrow A$	$L \Leftrightarrow S.S$	$L \Leftrightarrow A_\eta B_\xi$	Delamination system
1	freezing point lowering	freezing point lowering	the method of standard free energy	Gokcen-Austing's calculation method of activities at the liquidus
2	free energy of fusion	entropy of fusion	the θ-function method	simplification method
3	enthalpy of fusion	free energy of fusion	standard entropy of formation	
4	entropy of fusion		entropy of fusion	

In this paper, we will discuss a new method of achieving activities from phase diagram by the enthalpy of fusion of an intermediate compound and calculate the activities of three binary systems.

2　FORMULAS DERIVATION

　　Fig. 1 shows a simple compound eutectic diagram which can be divided into two eutectic binary diagrams. Taking the left side eutectic binary diagram as an example the formula of calculation activities will be derived from the enthalpy of fusion of a compound.

　　In the A-$A_\eta B\xi$ system, the composition and the activity of $A_\eta B\xi$ along a liquidus are represented with $X_{A_\eta B_\xi}$, and $a_{A_\eta B_\xi}(T)$, respectively. From the formulas of freezing point lowering, we obtain

$$\mathrm{d}\ln a_{A_\eta B_\xi}(T) = \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T \tag{1}$$

Integrating eqn. (1) gives

$$\ln a_{A_\eta B_\xi}(T) = \int_{T_m}^{T} \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T \tag{2}$$

Fig. 1　Binary phase diagram involving intermediate compounds

Based on the equilibrium of a liquid phase with a compound at T temperature, we have following relations:

　　In the A-$A_\eta B\xi$ system　　　$RT\ln a_{A_\eta B_\xi}(T) = G_{A_\eta B_\xi(s)} - G_{A_\eta B_\xi(l)}$ (3)

　　In the A-B system　　$RT(\eta \ln a_A(T) + \xi \ln a_B(T)) = G_{A_\eta B_\xi(s)} - \eta G_A^{\ominus}(1) - \xi G_B^{\ominus}(1)$ (4)

where　$a_A(T)$, $a_B(T)$ represent the activities of A and B at liquidus in A-B binary system, respectively. Combining eqns. (3) and (4), and considering

$$G_{A_\eta B_\xi(l)} = \eta G_A^{\ominus}(1) + \xi G_B^{\ominus}(1) + RT[\eta \ln a_A(T) + \xi \ln a_B(T)]_{X_B = \frac{\xi}{\eta + \xi}} \tag{5}$$

we obtain　　　$\ln a_{A_\eta B_\xi}(T) = \ln a_A^{\eta}(T)a_B^{\xi}(T) - [\ln a_A^{\eta}(T)a_B^{\xi}(T)]_{X_B = \frac{\xi}{\eta + \xi}}$ (6)

where　$[\ln a_A^{\eta}(T)a_B^{\xi}(T)]_{X_B = \frac{\xi}{\eta + \xi}}$ is the activity product of $X_B = \frac{\xi}{\eta + \xi}$ at temperature T. Substituting eqn. (6) into eqn. (2) gives

$$\ln a_A^{\eta}(T)a_B^{\xi}(T) - (\ln a_A^{\eta}(T)a_B^{\xi}(T))_{X_B = \frac{\xi}{\eta + \xi}} = \int_{T_m}^{T} \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T \tag{7}$$

$$\ln \gamma_A^{\eta}(T)\gamma_B^{\xi}(T) - (\ln \gamma_A^{\eta}(T)\gamma_B^{\xi}(T))_{X_B = \frac{\xi}{\eta + \xi}} = \int_{T_m}^{T} \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T + (\eta\ln\frac{\eta}{\eta + \xi} + \xi\ln\frac{\xi}{\eta + \xi}) -$$
$$(\eta\ln X_A + \xi\ln X_B) \tag{8}$$

　　Multiplying throughout by T and taking into account $T\ln \gamma_i(T) = T_0\ln \gamma_i$ (i. e. the relationship between activities coefficient and temperature obey the law of regular solution), we have

$$T_0\ln \gamma_A^{\eta}\gamma_B^{\xi} - T_0(\ln \gamma_A^{\eta}\gamma_B^{\xi}))_{X_B = \frac{\xi}{\eta + \xi}} = T\int_{T_m}^{T} \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T + T(\eta\ln\frac{\eta}{\eta + \xi} +$$
$$\xi\ln\frac{\xi}{\eta + \xi}) - T(\eta\ln X_A + \xi\ln X_B) \tag{9}$$

Differentiating the preceding equation, we obtain

$$T_0\mathrm{d}\ln \gamma_A^{\eta}\gamma_B^{\xi} = \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT}\mathrm{d}T + (\int_{T_m}^{T} \frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T)\mathrm{d}T + (\eta\ln\frac{\eta}{\eta + \xi} + \xi\ln\frac{\xi}{\eta + \xi})\mathrm{d}T -$$
$$(\eta\ln X_A + \xi\ln X_B)\mathrm{d}T - T(\frac{\eta X_B - \xi X_A}{X_A X_B})\mathrm{d}X_A \tag{10}$$

where　γ_A and γ_B are the activity coefficient of component A and B at T_0 temperature, respectively. And from the developed Gibbs-Duhem relation, we have

$$d\ln\gamma_A = \frac{1}{(\eta X_B - \xi X_A)T_0}[\frac{X_B\Delta_{fus}H_{A_\eta B_\xi}}{RT} + X_B\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + X_B(\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi}) -$$
$$\xi(X_A\ln X_A + X_B\ln X_B)]dT - d(\frac{T}{T_0}\ln X_A) \tag{11}$$

$$d\ln\gamma_B = \frac{-1}{(\eta X_B - \xi X_A)T_0}[\frac{X_A\Delta_{fus}H_{A_\eta B_\xi}}{RT}dT + X_B\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + X_A(\eta\ln\frac{\eta}{\eta+\xi} +$$
$$\xi\ln\frac{\xi}{\eta+\xi}) - \eta(X_A\ln X_A + X_B\ln X_B)]dT - d(\frac{T}{T_0}\ln X_B) \tag{12}$$

Integrating eqns. (11) and (12), the activities of A and B can be achieved.

Since the integrand tends to infinity in the compound region for eqns. (11) and (12), θ function is defined in order to avoid calculation error during integration. From eqn. (9) we obtain

$$\theta' = T[\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + (\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi}) - (\eta\ln X_A + \xi\ln X_B)]/$$
$$[T_0(\eta X_B - \xi X_A)^2] \tag{13}$$

then we can calculate the activities coefficient of A and B by eqns. (11) and (12).

As to irregular solution θ is defined as

$\theta = \Delta H_{i,m}/\Delta S_{i,m}$; $\sigma = T/(1- T/\theta)$

Multiplying eqn. (8) by σ gives

$$\sigma\ln\gamma_A^\eta(T)\gamma_B^\xi(T) - \sigma(\ln\gamma_A^\eta(T)\gamma_B^\xi(T))_{X_B=\frac{\xi}{\eta+\xi}} = \sigma[\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + (\eta\ln\frac{\eta}{\eta+\xi} +$$
$$\xi\ln\frac{\xi}{\eta+\xi}) - (\eta\ln X_A + \xi\ln X_B)] \tag{14}$$

and substituting $\sigma\ln\gamma_i(T) = \sigma_0\ln\gamma_i$ into the above equation, we can obtain

$$\sigma_0\ln\gamma_A^\eta\gamma_B^\xi - \sigma_0(\ln\gamma_A^\eta\gamma_B^\xi)_{X_B=\frac{\xi}{\eta+\xi}} = \sigma[\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + (\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\eta}{\eta+\xi}) -$$
$$(\eta\ln X_A + \xi\ln X_B)] \tag{15}$$

Differentiating the equation, the following equation is obtained:

$$\sigma_0 d\ln\gamma_A^\eta\ln\gamma_B^\xi = [\int_{T_m}^T\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT]d\sigma + \sigma\frac{\Delta_{fus}H_{A_\eta B_\xi}}{RT^2}dT + (\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi})d\sigma -$$
$$(\eta\ln X_A + \xi\ln X_B)]d\sigma - \sigma(\frac{\eta}{X_A} - \frac{\xi}{X_B})dX_A \tag{16}$$

Substituting $dT = (1- T/\theta)^2 d\sigma$ into eqn. (16) gives

$$d\ln\gamma_A^\eta\ln\gamma_B^\xi = \frac{1}{\sigma_0}[\int_{\sigma_m}^\sigma\frac{\Delta_{fus}H_{A_\eta B_\xi}}{R\sigma^2}d\sigma + \frac{\Delta_{fus}H_{A_\eta B_\xi}}{R\sigma} + (\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi}) -$$
$$(\eta\ln X_A + \xi\ln X_B)]d\sigma - \sigma(\frac{\eta}{X_A} - \frac{\xi}{X_B})dX_A \tag{17}$$

and substituting this form into Gibbs-Duhem equation, we have

$$d\ln\gamma_A = \frac{1}{(\eta X_B - \xi X_A)\sigma_0}[X_B\frac{\Delta_{fus}H_{A_\eta B_\xi}}{R\sigma} + X_B\int_{\sigma_m}^\sigma\frac{\Delta_{fus}H_{A_\eta B_\xi}}{R\sigma^2}d\sigma + X_B(\eta\ln\frac{\eta}{\eta+\xi} +$$
$$\xi\ln\frac{\xi}{\eta+\xi}) - \xi(X_A\ln X_A + X_B\ln X_B)]d\sigma - d(\frac{\sigma}{\sigma_0}\ln X_A) \tag{18}$$

$$\mathrm{d}\ln Y_B = \frac{1}{(\xi X_A - \eta X_B)\sigma_0}[X_A\frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{R\sigma} + X_A\int_{\sigma_m}^{\sigma}\frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{R\sigma^2}\mathrm{d}\sigma + X_A(\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi}) -$$

$$\eta(X_A\ln X_A + X_B\ln X_B)]\mathrm{d}\sigma - \mathrm{d}(\frac{\sigma}{\sigma_0}\ln X_B) \tag{19}$$

similarly, we can obtain

$$\theta' = \sigma[\int_{T_m}^{T}\frac{\Delta_{\mathrm{fus}}H_{A_\eta B_\xi}}{RT^2}\mathrm{d}T + (\eta\ln\frac{\eta}{\eta+\xi} + \xi\ln\frac{\xi}{\eta+\xi}) - (\eta\ln X_A + \xi\ln X_B)]/$$

$$[\sigma_0(\eta X_B - \xi X_A)^2] \tag{20}$$

The eqns. (18), (19) and (20) are suitable for both regular and irregular solutions, since eqns. (11), (12) and (13) can be respectively derived from them under $\theta \rightarrow \infty$.

3   VERIFICATION AND COMPARISON OF FORMULAS

Since the experimental data on In-Sb system have been referred in many papers, we take this system to verify the previous equations.

The data on enthalpy of fusion is obtained from the reference [6]. That is

$\Delta_{\mathrm{fus}}H_{\mathrm{InSb}}/\mathrm{J}\cdot\mathrm{mol}^{-1} = 17.573T - 7.531\times10^{-3}T^2 + 40141.296$

$\Delta_{\mathrm{fus}}H_{\mathrm{InSb}}/\mathrm{J}\cdot\mathrm{mol}^{-1} = 0.9079T + 7.692\times10^{-3}T^2 - 2.0\times10^5/T -$
$$5.979\times10^{-6}T^3 + 17405.748$$

For regular and irregular solution, when $X_{\mathrm{Sb}} \geqslant 68.2\%$ (in mole) the activities of the right part from eutectic point can be calculated with following forms, respectively:

$$\ln Y_{\mathrm{Sb}} = \frac{T}{T_0}(\int_{T_{m(\mathrm{Sb})}}^{T}\frac{\Delta_{\mathrm{fus}}H_{\mathrm{Sb}}}{RT^2}\mathrm{d}T - \ln X_{\mathrm{Sb}}) \tag{21}$$

$$\ln Y_{\mathrm{Sb}} = \frac{\sigma}{\sigma_0}(\int_{T_{m(\mathrm{Sb})}}^{T}\frac{\Delta_{\mathrm{fus}}H_{\mathrm{Sb}}}{RT^2}\mathrm{d}T - \ln X_{\mathrm{Sb}}) \tag{22}$$

And the activity of a component of liquidus which is equlibrium with InSb compound can be calculated using eqns. (11) and (18). The results are shown in Fig. 2. From the figures, it is obvious that the results of calculation are coincident with that of experiment under $\theta \rightarrow \infty$ and $\theta = 3000$. In particular, the activities of Sb are more close to that of experiment than inrium's under $\theta = 3000$.

4   CALCULATION OF ACTIVITIES OF SEMICONDUCTOR BINARY SYSTEMS

4. 1   Activities of Ga-As system

The Ga-As system plays an important role in the study of semiconductors. But it is difficult to measure the arsenic's activities, because of some of its characteristics. Moreover, the standard enthalpy of formation, entropy of formation and standard free energy of arsenic are also difficult to obtain, because generally liquid arsenic can't be obtained. This causes the activity calculation methods reported before insuperable, but the method present here has no such limit.

We calculate the activities of this system by the enthalpy of fusion. In order to avoid integral infinity, eqns. (11) and (18) are used to calculate, and θ' function are also given by eqns. (13) and (20), respectively. The calculating results are shown in Fig. 3.

Fig. 4 shows the Ga-As phase diagram including a stable compound. The enthalpy of fusion of GaAs can be achieved from handbooks[6].

4. 2   Activities of Ga-Sb binary system

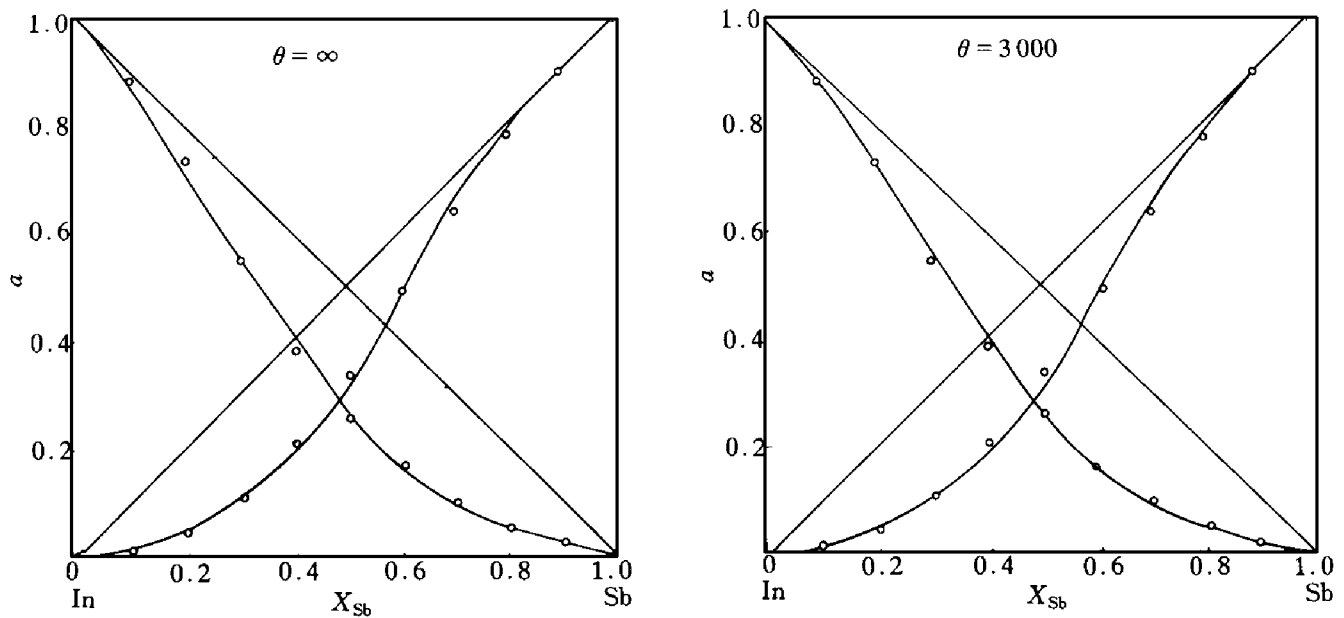Fig. 5 shows Ga-Sb phase diagram involving an intermediate phase β-GaSb. The activities for this

Fig. 2   Calculation of activities using $\Delta_{fus}H_{A_\eta B_\xi}$ **in In-Sb system at** 900 K

Solid line —calculating;   ◯—experimental

system at 1 000 K can be calculated by eqns. (12) , (19) , (21) and (22) .

The thermodynamic data needed are obtained from handbooks[6] as

$$\Delta_{fus}H_{Sb}/J \cdot mol^{-1} = 0.\,907\,9T + 7.\,692 \times 10^{-3}T^2 - 2.\,0 \times 10^5 T^{-1} - 5.\,979 \times 10^{-6}T^3 + 17\,405.\,748$$

$$\Delta_{fus}H_{GaSb}/J \cdot mol^{-1} = -10.\,162\,9T + 5.\,131\,7 \times 10^{-3}T^2 + 3.\,104\,5 \times 10^5 T^{-1} - 63\,419.\,816\,8$$

$$\Delta_{fus}H_{GaSb}/J \cdot mol^{-1} = -12.\,342\,8T + 6.\,276 \times 10^{-3}T^2 - 62\,011.\,064 \qquad (700 \sim 982.\,6K)$$

The results of calculation are exhibited in Fig. 6.

4. 3   Activities of In-As binary system
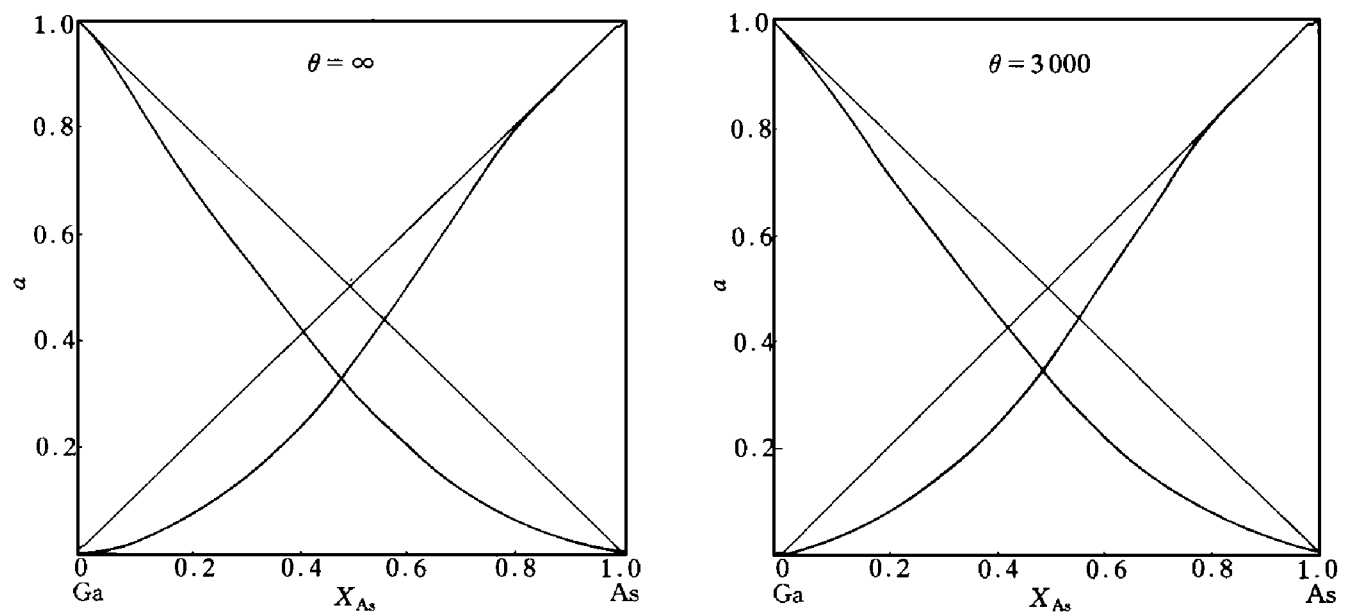

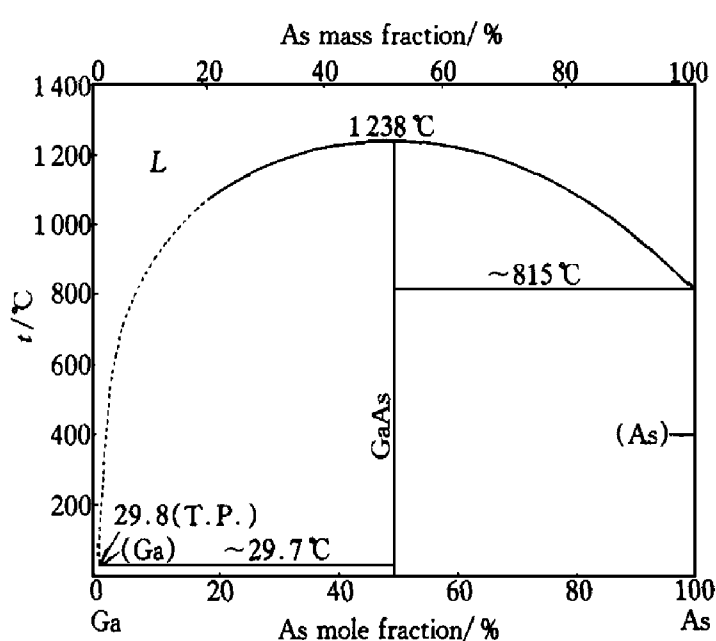**Fig. 3   Calculation of activities in Ga-As system at** 1 573 K
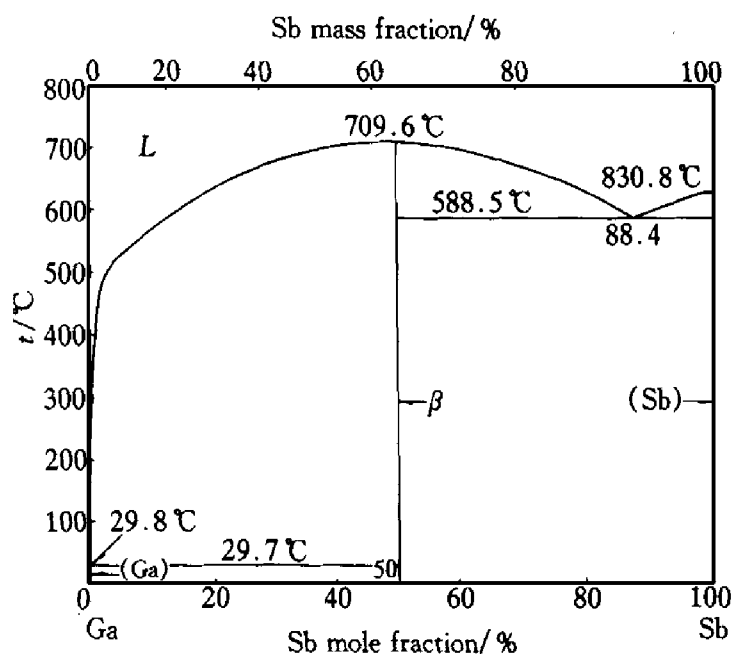
Fig. 4   Ga-As phase diagram

Fig. 5   Ga-Sb phase diagram

Fig. 7 shows In-As phase diagram involving an intermediate compound.

The thermodynamic characteristics of liquid arsenic is unknown, because arsenic will become gas under normal pressure at 630 ℃, which causes calculating activities of the liquidus in the right side of eutectic point very difficult using present methods. We would calculate the activities of indium in the left side of eutectic point, and calculating activities of arsenic are difficut for lack of initial data. Either eqns. (11), (13) or eqns. (18), (20) are used for calculating. The results of calculation are given in Table 2.

5 CONCLUSIONS

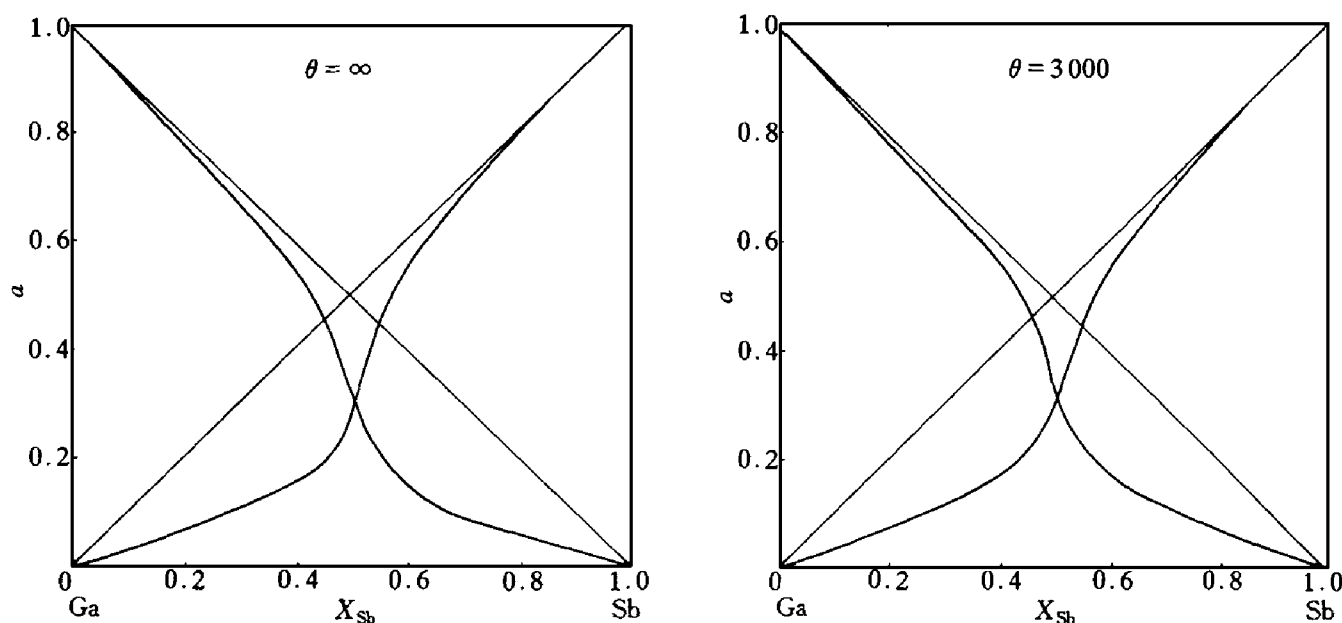(1) The fomulas for calculating activities with enthalpy of fusion of the intermediate compounds

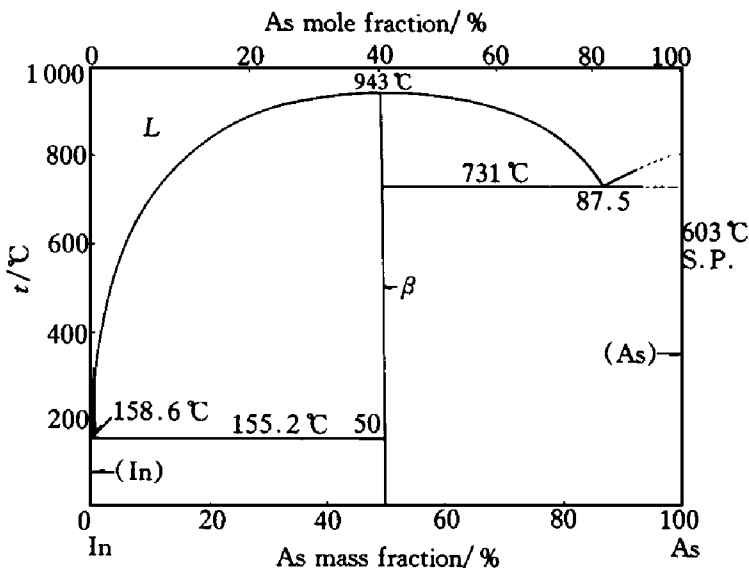**Fig. 6   Calculation of activities in Ga-Sb system at 1 000 K**

As mole fraction/ %

Fig. 7　In-As phase diagram

Table 2　Calculation of activities in In-As system at 1 220 K

X_{In}	$\theta \to \infty$			$\theta = 3\,000$		
	γ_{In}	α_{In}	$\Delta_{fus}H_{A}\,_T{}^B\xi$	γ_{In}	α_{In}	$\Delta_{fus}H_{A}\,_T{}^B\xi$
0. 95	0. 998	0. 948	− 22	0. 999	0. 949	− 12
0. 90	0. 982	0. 883	− 170	0. 988	0. 890	− 107
0. 85	0. 968	0. 823	− 277	0. 981	0. 834	− 165
0. 80	0. 948	0. 754	− 431	0. 963	0. 770	− 309
0. 75	0. 930	0. 697	− 556	0. 951	0. 713	− 388
0. 70	0. 910	0. 639	− 672	0. 943	0. 660	− 417
0. 65	0. 868	0. 564	− 935	0. 898	0. 584	− 707
0. 60	0. 799	0. 479	− 1 369	0. 832	0. 499	− 1 121
0. 55	0. 665	0. 366	− 2 280	0. 701	0. 386	− 1 979
0. 50	0. 572	0. 286	− 2 830	0. 598	0. 299	− 6 126
0. 45	0. 519	0. 234	− 2 991	0. 543	0. 244	− 2 788
0. 40	0. 472	0. 189	− 3 044	0. 498	0. 199	− 2 826
0. 35	0. 444	0. 156	− 2 880	0. 465	0. 163	− 2 722
0. 30	0. 414	0. 124	− 2 686	0. 434	0. 130	− 2 544
0. 25	0. 367	0. 090	− 2 585	0. 381	0. 095	− 2 450
0. 20	0. 303	0. 051	− 2 426	0. 324	0. 065	− 2 288
0. 15	0. 232	0. 035	− 2 220	0. 256	0. 038	− 2 074
0. 125	0. 180	0. 023	− 2 172	0. 207	0. 026	− 1 997

in binary system are derived. The results of calculation are in good harmony with that of experiment.

(2) The activities of Ga-As, Ga-Sb and In-As three semiconductor binary systems have been calculated.

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