

Nonstoichiometry and P – T – x diagrams of binary systems

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Abstract

A P – T – x three-dimensional space diagram forms the complete representation between pressure (P), temperature (T) and composition (x) of coexisting phases—solid (S), liquid (L) and vapor (V). It gives the number of nonstoichiometric compounds that may be formed by the components and the stability limits of phases which are in equilibrium. Definitions of stoichiometry and nonstoichiometry are given. Some features of P – T – x diagrams with nonstoichiometric compounds are considered: maximum (T_m^{\max}) and congruent (T_m^c) melting points, difference between the compositions of solid (x^S), liquid (x^L) and vapor (x^V): $x^L \neq x^S \neq x^V$ at maximum melting point $T = T_m^{\max}$, the width and position of the homogeneity range, and the nonstoichiometry caused by defects are also discussed. A new technique for the investigation of P – T – x diagrams is presented.

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1. Introduction

Although significant progress has been made in understanding nonstoichiometry and phase diagrams, several challenges remain. These challenges include the definition of stoichiometry and nonstoichiometry; the situation under conditions met in practice when a system is heated in a sealed tube and vapor is always present; and also some features of P – T – x phase diagrams of binary systems with a nonstoichiometric compound. The problems of nonstoichiometry and defects, as well as a new technique for the investigation of P – T – x diagrams are also discussed.

2. Stoichiometry and nonstoichiometry

When a large number of gaseous molecules condense to form a liquid (or solid), they are arranged with short-range (or long-range) order to provide the minimum free energy and electroneutrality. The minimum energy depends not only on the energy factors but also on the

arrangement of atoms and charges, i.e. entropy factors. It appears that the minimum free energy of a real crystal formed upon condensation of molecules AB (or the equal amounts of A and B atoms) is not attained at a strictly stoichiometric composition, i.e., obeying the multiple-proportion law. A solid compound dissolves some amount of A and B atoms and exists as a homogeneous stable phase in a certain composition range. This range is called the homogeneity (stability) range of the phase. Its extent is characterized by the deviation from stoichiometry Δ . The deviation from stoichiometry (nonstoichiometry) is determined as the difference between the ratios of the numbers of A and B atoms in a real crystal of composition $A_n B_{m+\delta_B}$ ($\delta_B > 0$ or < 0) and in a stoichiometric crystal $A_n B_m$:

$$\Delta = (m + \delta_B)/n - m/n = \delta_B/n. \quad (1)$$

3. Some features of P – T – x phase diagram of a two-component system with a nonstoichiometric compound

Let us concentrate on some features of a phase diagram for a two-component system with a nonstoichiometric compound AB [1,2]. The notation AB describing the compound is shorthand for a nonstoichiometric phase $A_{1/2-\delta} B_{1/2+\delta}$ with a given crystal structure and deviation from stoichiometry δ .

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3.1. Maximum melting point $T_{m,AB}^{\max}$, nonvariant congruent (T_m^c), sublimation (T_S^c) and evaporation (T_{ev}^c) points

The Gibbs energy G of a phase in a two-component system is given by

$$dG = -SdT + VdP + (\partial G/\partial x)_{P,T}dx, \quad (2)$$

where G , S and V are the molar Gibbs energy, entropy and volume, respectively; x is the mole fraction of the second component; P is pressure; and T is temperature. It follows from Eq. (2) that the spatial representation of coexisting phases is four-dimensional. The situation in a four-dimensional figure is normally discussed with the aid of G - P - T , G - P - x and G - T - x three-dimensional figures or their projections on the P - T , P - x and T - x planes, respectively. To clarify, for example, some features of the T - x projection, let us deduce a part of this figure from G - T - x diagram. Relative position of the solid (G^S), liquid (G^L) and vapor (G^V) surfaces can be considered using their isothermal (G^S-x) $_T$, (G^L-x) $_T$ and (G^V-x) $_T$ sections. These considerations are illustrated in Fig. 1, which represents plot of Gibbs energies (G^S , G^L , G^V) per g-atoms versus atomic fraction in the binary system A-B. Isotherms for the coexisting phases are given by

$$\begin{aligned} G^S(A_{1-x}B_x) &= (1-x^S)\mu_A^S + x^S\mu_B^S \\ G^L(A_{1-x}B_x) &= (1-x^L)\mu_A^L + x^L\mu_B^L \\ G^V(A_{1-x}B_x) &= (1-x^V)\mu_A^V + x^V\mu_B^V \end{aligned} \quad (3)$$

where μ_i^j stands for chemical potential. At $T=T_1 > T_{m,AB}^{\max}$ (Fig. 1a), the solid phase is not stable relative to the L + V two-phase system. The fundamental criterion for equilibrium between two phases (a fixed value of the chemical potential characteristic of each component) is met if a common tangent can be drawn to both G^L and G^V isotherms. The tangency points for given lines define composition of the coexisting liquid and vapor phases.

With decreasing temperature, the relative position of the G^S , G^L and G^V lines changes. The temperature dependence of the G plots is given by the entropy: $(\partial G/\partial T)_{P,x} = -S$. As the entropy of vapor essentially exceeds the entropy of solid ($S^V \gg S^S$), the G^V and G^L plots shift upward more quickly, than does the G^S curve, at further decreases of temperature. At $T=T_2=T_{m,AB}^{\max}$, one common tangent appears to the three curves (Fig. 1b). This temperature $T_{m,AB}^{\max}$ is called the maximum melting point of solid AB and the points of tangency for a given line define the compositions x_V^{\max} , x_L^{\max} and x_S^{\max} of the coexisting solid (S), liquid (L) and vapor (V) phases. Upon further cooling at temperature $T=T_3 < T_{m,AB}^{\max}$, two tangents can be drawn to the three G^V , G^L and G^S plots and there appear six points of tangency (x_V' , x_L' , x_S' , x_V'' , x_L'' and x_S'')

which define the compositions of the coexisting phases (Fig. 1c). The superscript (') corresponds to composition lying to the left, and superscript (''), to the right from the phase composition at $T=T_{m,AB}^{\max}$. Graphically, the $G=f(T, x)$ dependencies can be represented by three surfaces. Projections of the tangency points to these surfaces on the T - x plane define the solidus (S' S S''), liquidus (L' L L''), and vapor (V' V V'') lines (Fig. 1d). These lines represent the temperature dependence of the coexisting solid, liquid phases and vapor. The solidus lines defining the limits of the homogeneity range may include the stoichiometric composition as a stable phase over most of the temperature range in Fig. 1d the need not in general (see Section 3.3).

It is obvious from Fig. 1 that the solidus $S'SS''$ line or homogeneity region depends not only on the properties of the solid itself but on the properties (G) of coexisting phases. Points V' , L' , S' or V'' , L'' and S'' which represent the coexisting phases are called conjugate points. These points form conjugate lines $V'V$, $L'L$ and $S'S$ or $S'S''$, $L'L''$ and $V'V''$.

In the situation given in Fig. 1d, three nonvariant points may occur where the phase compositions are identical.

1. At point $T=T_{m,AB}^c$ the conjugate solidus and liquidus lines cross and the composition of liquid and solid appear to be identical: $x^L=x^S \neq x^V$. Point $T=T_{m,AB}^c$ is called the congruent melting point of the nonstoichiometric solid AB.
2. At point $T=T_S^c$, the composition of the solid is equal to that of the vapor: $x^S=x^V \neq x^L$. The temperature T_S^c is called the maximum sublimation point.
3. At point $T=T_{ev}^c$, the composition of the liquid is equal to that of the vapor: $x^L=x^V \neq x^S$. The temperature $T_{ev}^c(S)$ is called the maximum evaporation point.

For systems which are held in sealed evacuated ampoules under their own pressure, the relation $T_{m,AB}^{\max} > T_{m,AB}^c > T_S^c > T_{ev}^c$ is fulfilled.

The composition of the mentioned points do not correspond to the stoichiometric composition $\delta=0$.

Whenever possible, the synthesis of nonstoichiometric AB should be carried out, at or near the congruent points to avoid complex transport problems near the growth interface due to different nutrient (vapor, melt) and solid compositions.

Knowledge of the features of phase diagrams which have been discussed here, enables one to select the temperature, nutrient composition and pressure for growth of nonstoichiometric compounds: for example, chalcogenides of the second ($A^{II}B^{VI}$), the fourth ($A^{IV}B^{VI}$) groups of the elements with specific composition from the liquid or vapor phase [2].

3.2. Difference between the compositions of the solid, liquid and vapor at the maximum melting point of compound AB

It is usually believed that at the maximum point the liquidus and solidus possess a common composition. But this is not always the case and is just observed in particular cases under a fixed total pressure. When the system is held at a fixed volume under its own pressure (which often occurs in the synthesis of volatile compounds), this does not necessarily hold true. It follows from thermodynamic considerations [3,4] of the three-phase equilibrium in a two-component system that maxima in pressure at $T = \text{const}$ and in temperature at $P = \text{const}$ may exist when

$$\begin{aligned} (x^L - x^S) / (x^V - x^S) &= (V^L - V^S) / (V^V - V^S) \\ &= (S^L - S^S) / (S^V - S^S). \end{aligned} \quad (4)$$

According to Eq. (4), the difference between the liquid, vapor and solid compositions $x^L \neq x^S \neq x^V$ at the maximum melting point (Fig. 1d) is created by the difference between the molar volumes (V^L, V^S, V^V) and entropies (S^S, S^L, S^V) of the solid (S), liquid (L) and vapor (V). This is important for the synthesis of compounds with composition-sensitive properties, such as the nonstoichiometric semiconducting gallium arsenide

GaAs [5], cadmium (CdTe) and lead (PbTe) tellurides [2,6]. Cases can be found in practice in which the vapor is almost entirely one component, so that $x^V - x^S \sim 1/2$. At pressures of the order of 1 atm, $V^V - V^S \cong 10^3 V^S$, so that $x^L - x^S \sim -5(10^{-4})(V^L - V^S) / V^S$. For open crystal structures, one might expect $V^L - V^S \sim 0.1 V^S$, so that $x^L - x^S \sim 5 \times 10^{-5}$.

3.3. The width and position of the homogeneity range relative to the stoichiometric composition $\delta = 0$

If a nonstoichiometric compound is in equilibrium with one of the pure components

$$A_S + B_S = AB_S \quad (5)$$

at each limit of the homogeneity range, the width of this range can be estimated from

$$f(\delta''/k) - (\delta'/k) = -2\Delta_f G^\circ / RT \quad (6)$$

where f is a monotonically increasing function of deviation from stoichiometry δ , k is temperature-dependent constant of the solid AB, single- and double-prime superscripts at δ correspond to the A-rich and B-rich limits of the homogeneity range, R is the gas constant and T is the temperature. Eq. (6) states that the more negative the Gibbs energy ($\Delta_f G^\circ$ per g-atom) of formation of solid AB from the pure components, the larger is

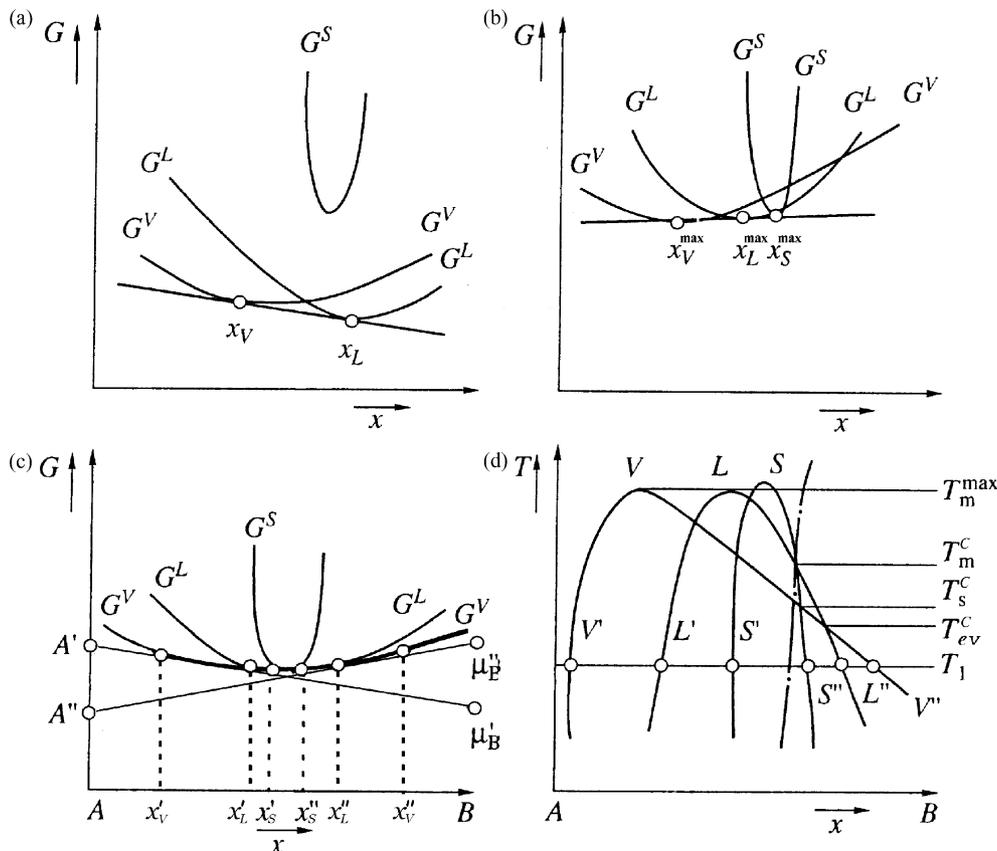


Fig. 1. $(G-x)$ -sections of $G-T-x$ diagram: (a) $T_1 > T_{m,AB}^{\max}$; (b) $T_2 = T_{m,AB}^{\max}$; (c) $T_3 < T_{m,AB}^{\max}$; (d) a part of $T-x$ projection of a $P-T-x$ diagram.

the difference $f(\delta''/k) - (\delta'/k)$ and hence $(\delta'' - \delta)/k$. Of course, $\Delta = \delta'' - \delta'$ is the width of the homogeneity range (Table 1).

The homogeneity range may or not include the stoichiometric composition $\delta = 0$. Let us compare the position of $\delta = 0$ and the midpoint of the stability range of AB^S , using Eq. (7)

$$\frac{f(\delta''/k) + f(\delta'/k)}{[\mu_B(B) - \mu_A(A)]/RT - [\mu_B(\delta = 0) - \mu_A(\delta = 0)]/RT} \quad (7)$$

Note that $\delta'' + \delta'$ is a measure of the centre of the homogeneity range and is positive or negative as the centre of the homogeneity range occurs at $\delta > 0$ or $\delta < 0$.

Eq. (7) states that the larger the right-hand member of the equation, the larger $f(\delta''/k) + (\delta'/k)$ and, hence, $(\delta'' + \delta')/k$ larger. The right-hand side of Eq. (7) is the difference of two terms, one $[\mu_B(B) - \mu_A(A)]$ is the difference between the Gibbs energies of the pure components relative to the isolated atoms on their ground states, and the second is the difference in the chemical potentials of B and A in the stoichiometric ($\delta = 0$) solid AB. Neglecting the second term in a related series of compounds, one can conclude that the centre of the homogeneity range $(\delta'' + \delta')/2$ shifts in the same direction as $[\mu_B(B) - \mu_A(A)]$. Examples of a homogeneity range shifted to the nonmetal component and not including the stoichiometric composition are found for the compounds $ZnTe_{1+\delta}$, $GeTe_{1+\delta}$ [2], $GaN_{1+\delta}$ [7,8], $GaSe_{1+\delta}$ [9].

4. Nonstoichiometry and defects

Synthesis of a nonstoichiometric compound AB can be represented as the transfer of A and B atoms from nutrient N (vapor, melt or another solid) to their sites (A_A^x, B_B^x) in the crystal lattice of AB:



The site-conservation rule explains the creation of V_B^x and V_A^x vacancies, where the superscript (x) indicates

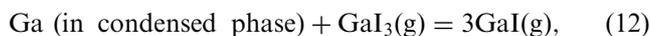
the neutral charge of the imperfection relative to the surrounding crystal lattice. Because of the crystal difference between all species involved in Eqs. (8) and (9), the equilibrium constants $K \propto \exp((\Delta_r G^0/RT))$ and, hence, the number of the A and B atoms are not identical. Thus, the deviation from stoichiometry (δ) is created, i.e., the difference between the atom ratio B to A in the real crystal and in a precisely stoichiometric crystal. It should be emphasized that the physical properties of a crystalline solid do not depend on the nonstoichiometric atoms A_A^x and B_B^x that occupy their own sites. Rather, they depend on the defects V_A^x and V_B^x , which are generated by interfacial transfer reactions such as (8) and (9). As a matter of fact, species A_A^x and B_B^x add to the number of lattice sites but do not change the energy diagram of the crystal. Defects, such as vacancies or interstitial atoms A_i^x and B_i^x



which disturb the energy field of the solid and, therefore, change the electrical, chemical, mechanical and other properties of the crystalline solid. Thus, defects generated by nonstoichiometry have an effect on all properties of a crystal [1,2,5,6,8].

5. New vapor pressure method in the investigation of the phase diagrams

The pressure measurement techniques, e.g. zero-manometric method, are widely applied in examinations of the P - T - x phase diagrams. However, low partial pressure of components frequently make it impossible to use these methods. A new null-manometric method for scanning of the phase diagrams and homogeneity regions of low-volatile binary compounds has been designed [9]. In this method a third component with a negligibly small solubility in condensed phases e.g. the iodine in the form of GaI_3 is put in contact with the investigated Ga- Se system and interacts with one of the components (Ga) of a weakly volatile compound ($GaSe$ or Ga_2Se_3)



where $\Delta_r H > 0$ — enthalpy of the reaction (12). Thus Ga is converted into vapor in the form of the volatile compound GaI and the composition of a condensed phase is changed. Because of the high GaI and GaI_3 volatilities total pressure is increased and can easily be measured by null-manometer. The equilibrium (12) is strongly shifted to the right with an increase in temperature. Such a shift decreases the gallium content in a condensed phase

Table 1
The Gibbs energy ($\Delta_r G^0$) of formation of solid AB and the homogeneity range (Δ) for Ge, Sn and Pb monotellurides at 800 K [3]

	$-\Delta_r G^0$ (kJ/gm atom)	Δ at. % Te
GeTe	330.1	1.0
SnTe	316.3	0.8
PbTe	275.7	0.1

(GaSe or Ga₂Se₃), while the equilibrium pressure is sharply increased. Controlling the equilibrium by adjusting the temperature makes it possible to control the disappearance of some of the condensed phases and the formation of the others. By measuring the temperature dependence of the total pressure it is possible to determine P – T — and T – x — projections of the P – T – x diagram. Using this method the P – T diagram and the homogeneity region of GaSe have been determined [9,10].

Acknowledgements

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