

## MODELING TECHNIQUES FOR THE PREDICTION OF PHASE DIAGRAMS

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Most metallurgical reactions at high temperatures involve two or more phases. Therefore, the phase diagram, which describe the phase relations based on their thermodynamic properties are highly important. These diagrams display graphically a large amount of data on the behaviour of a system in a limited space. The variables that are plotted in most diagrams are temperature and composition. Also the diagrams showing the relations of temperature and pressure and several compositions at a given temperature for ternary systems are drawn in many instances. These diagrams are also known as equilibrium diagrams since the phase reactions are considered to be in thermodynamic equilibrium. However, non equilibrium diagrams, such as metastable phase diagrams and coherent phase diagrams are also available for some systems.

All metallurgists are familiar with Fe-C phase diagrams (Fig. 1). Both the equilibrium and non equilibrium diagrams of this system are available since this system has been extensively investigated in the area steelmaking, foundry and heat treatment. These two-component diagrams or binary phase diagrams are most widely available today. The ternary and higher order systems are also being studied, investigated and evaluated nowadays, either using a modeling technique or by direct experimental technique of equilibrium phase identification.

For the proper construction of a phase diagram, however simple or complex it may be, various rules have to be kept in mind. The most important one is the Gibbs phase rule. This can be used to determine the number of phases that must be present at equilibrium in a system when certain conditions are fixed. According to phase rule, if C is the number of component in the system, P, the number of phase present then the degree of freedom, F is related as follows:

$$F = C - P + 2 \quad (1)$$

where 2 represents the temperature and pressure of the system.

Most phase diagrams of interest to metallurgist drawn at a constant pressure of 1atm, such as the iron carbon diagram already shown. As a result the equation (1) can be rewritten as:

$$F = C - P + 1 \quad (2)$$

This indicates that in the single phase region of iron carbon diagram (e.g. austenite area), the possible degrees of freedom are two, the temperature and the composition of the phase. For conditions where two phases are present (e.g. austenite and cementite), there is only one degree of freedom, either the temperature or the composition of the phases. If the temperature is specified, the compositions of both phases are fixed. When three phases are present, there is no variance possible, i.e. there is no choice of either temperature or composition of phases. This condition is represented on the diagram as the intersection of three lines at the eutectic point.

The phase diagram is also based on the general condition for equilibrium of all phases in the system containing several components that the chemical potential of each component must be the same in every phase. This corresponds to the minimum Gibbs energy of the system. Here the phase diagram is a function of temperature,  $T$  and mole fraction of different components  $i$  in the phase  $j$  i.e.

$$G = f(T, x_i^j) \quad (3)$$

which can be transformed to:

$$T = g(x_i^j) \quad (4)$$

This function is normally used to plot a phase diagram.

Thus it is evident that the phase diagrams and thermodynamical quantities of phase are very much interconnected. Even the knowledge of free energy at one temperature can be very helpful for assessing possible phase reaction in the system. Whenever possible, the basic thermodynamic properties are obtained from different experimental methods such as calorimetry, vapour pressure, emf measurements, DTA, NMR, solubility measurements etc. Recently, these parameters are also being evaluated from the first principle. The experimental technique used for the determination of thermodynamic properties of metallic and oxide systems are rather complex. As a result there is lack of data in many systems. However, if the behaviour of one component is experimentally determined over a composition range, the behaviour of other component can be deduced through the Gibbs-Duhem equation. Besides, the phase equilibrium relationships along the appropriate interaction model can be used to construct the phase diagrams for binary and higher order systems. Here the equilibrium conditions and various interaction models will be elaborated.

## PHASE EQUILIBRIUM CONDITIONS

The maximum number of coexisting phases in system at a given pressure and temperature formed by  $m$  components is  $(m+1)$  as per phase rule. If  $j$  phases are formed, when  $1 < j < m + 1$ , the partial free energy of a component would be the same in all phases at equilibrium. Thus

$$\bar{G}_i^1 = \bar{G}_i^2 = \bar{G}_i^3 = \dots = \bar{G}_i^j \quad \text{for } i = 1 \text{ to } m \quad (5)$$

This set of  $m$  non-linear equations have to be resolved with respect to the molar fraction of the components ( $x_i^f$ ) in the different phases according to the interaction model employed.

Now the computation of phase boundary involves following steps:

i) Calculation of thermodynamic properties as a function of components,  $x_i^f$ . Usually analytical expressions are obtained from numerical fitting of data or from statistical thermodynamics.

ii) Solution of set of non-linear equations:

For example for 2-phase region, the partial free energies of components in both phases can be written from equation (5) as:

$$D_i = \bar{G}_i^1 - \bar{G}_i^2 = 0 \quad (6)$$

where  $\bar{G}_i^1 = f(x_1^1, x_2^1, \dots, x_{m-1}^1)$  (7)

and  $\bar{G}_i^2 = g(x_1^2, x_2^2, \dots, x_{m-1}^2)$  (8)

Here, there are  $2(m-1)$  unknowns but only  $m$  equation. For a 2-component system, the solution would be unique. However, for the higher component systems the above equation can only be solved if  $(m-2)$  variables defined. The solution of such set of equations can be obtained by Newton-Raphson method.

Another approach is the 'hill climbing technique' developed by Nelder and Mead which searches the minimum of Gibbs energy of the system. Here the Gibbs energy of a multicomponent system is calculated at about 10 different coordinates. The point which has the highest value of the Gibbs energy is replaced by another one. The procedure is repeated till the minimum value is obtained.

## INTERACTION MODELS

There are various models available to express the thermodynamic properties of mixing as a function of composition and temperature. Some important models will be briefly reviewed here.

### IDEAL SOLUTION

Very few real systems behave ideally. However, because of its simplicity, this ideal solution model can be easily tried in a binary system to determine the liquidus and solidus line.

For example, in a two component system, say A and B, the chemical potential of B in the solution is given by:

$$\mu_B^L = G_B^L + RT \ln X_B^L \quad (9)$$

similarly in the solid solution,

$$\mu_B^S = G_B^S + RT \ln X_B^S \quad (10)$$

Since at equilibrium,  $\mu_B^L = \mu_B^S$  we can get:

$$G_B^L - G_B^S = \Delta G_B = RT \ln \frac{X_B^S}{X_B^L} \quad (11)$$

Rearranging,

$$X_B^S = X_B^L \exp(\Delta G_B / RT) \quad (12)$$

since  $X_B + X_A = 1$ , similar analysis for the component A would yield

$$1 - X_B^S = (1 - X_B^L) \exp(\Delta G_A / RT) \quad (13)$$

Free energy terms such as  $\Delta G_B$  may be expressed in terms of more readily available quantity, the enthalpy of fusion, i.e.  $\Delta H_B$  in the following way:

$$\Delta G_B = \Delta H_B - T \Delta S_B \quad (14)$$

and at fusion temperature of B,  $T_B^m$

$$\Delta G_B^m = 0 = \Delta H_B^m - T \Delta S_B^m \quad (15)$$

Otherwise, equation (12) and (13), containing two unknowns viz.  $X_B^L$  and  $X_B^S$  can be solved as follows, to determine the liquidus & solidus line respectively.

$$X_B^L = \frac{1 - \exp(\Delta G_A/RT)}{[\exp(\Delta G_B/RT) - \exp(\Delta G_A/RT)]} \quad (16)$$

and

$$X_B^S = \left\{ \frac{1 - \exp(\Delta G_A/RT)}{[\exp(\Delta G_B/RT) - \exp(\Delta G_A/RT)]} \right\} \exp(\Delta G_B/RT) \quad (17)$$

#### REGULAR SOLUTION

In this model, it is assumed that there is an ideal configurational entropy of mixing and the enthalpy of mixing is finite. Thus free energy of mixing is

$$\Delta G^m = RT(x_A \ln x_A + x_B \ln x_B) + RT(x_B \ln \gamma_B + x_A \ln \gamma_A) \quad (18)$$

and, enthalpy of mixing

$$\Delta H^m = \Delta G^{XS} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) \quad (19)$$

and the partial properties are expressed as:

$$\bar{\Delta H}_A^m = \bar{\Delta G}_A^{XS} = RT \ln \gamma_A = \alpha_A (1 - x_A)^2 \quad (20)$$

$$\text{and } \bar{\Delta H}_B^m = \bar{\Delta G}_B^{XS} = RT \ln \gamma_B = \alpha_B (1 - x_B)^2 \quad (21)$$

Again using the 2 component system and applying a 2 phase equilibrium condition the phase boundaries  $X_B^S$  and  $X_B^L$  are obtained from the following expressions:

$$RT \ln \frac{X_B^S}{X_B^L} + B(1-X_B^S)^2 - L(1-X_B^L)^2 + \Delta G_B^{L \rightarrow S} = 0 \quad (22)$$

and

$$RT \ln \frac{1-X_B^S}{1-X_B^L} + B X_B^{S2} - L X_B^{L2} + \Delta G_L^{L \rightarrow S} = 0 \quad (23)$$

where L and B are the regular solution interaction parameter for the phase reaction. For ideal solutions these parameters are zero.

This model has been widely used for computation of binary and ternary phase diagrams in metallic system. The calculated diagrams showed excellent agreement with the phase diagrams obtained experimentally.

Some real systems, such as Cu-Mn, do not follow this regular solution behaviour, where the interaction parameter are assumed to be independent of composition. As a result, this model can be further modified to a subregular solution, where the same binary system can be represented by the following equations:

$$RT \ln \frac{X_B^S}{X_B^L} + (A + B X_B^S)(1-X_B^S)^2 - (C + D X_B^L)(1-X_B^L)^2 = \Delta G_B^{L \rightarrow S} \quad (24)$$

and

$$RT \ln \frac{1-X_B^S}{1-X_B^L} + (A' + B' X_B^S) X_B^{S2} - (C' + D' X_B^L) X_B^{L2} = \Delta G_A^{L \rightarrow S} \quad (25)$$

where the constants are related as follows:

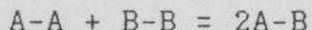
$$\begin{aligned} A' &= A - B/2 & C' &= C - D/2 \\ B' &= B & D' &= D \end{aligned} \quad \text{and}$$

Many other binary systems such as Fe-Mn, Co-Pt follow this model.

#### QUASICHEMICAL SOLUTION

The regular solution model assumes excess entropy to be zero. However, it is known for many solutions that the entropic drive for randomness is controlled by the lowering of potential energy of the solution through preferential formation of low energy bonds. On this basis, Guggenheim proposed this model.

Considering the case of mixing of  $n_A$  moles of A and  $n_B$  moles of B in a fixed lattice for the following reaction:



the enthalpy of mixing, can be expressed as

$$\Delta H^m = z w x_A x_B \quad (26)$$

where

$z$  = coordination number  
 $w$  = interaction energy,  $\frac{1}{2}(w_{AB} - w_{AA} - w_{BB})$

In case of ideal solution  $w$  is zero i.e. the attraction between unlike atoms is same as that between like atoms. If the like atoms attract more strongly than unlike atoms, is  $w > 0$  there will be preferential formation of A-A and B-B cluster. This is positive deviation from ideality. The activity coefficient of A of quasichemical binary solution can be obtained as:

$$\gamma_A = \left[ \frac{a-1 + 2x_A}{x_A(1+a)} \right]^{z/2} \quad (27)$$

where  $a = \left[ 1 - 4x_A x_B (1 - e^{-2w/RT}) \right]^{1/2}$

### CENTRAL ATOMS MODEL

The quasichemical model takes care of nonrandom or configurational excess entropy. However it ignores the thermal or vibrational entropy and assumes that the bond energy between two atoms is independent of their surrounding.

This model considers the cluster of an atom and its nearest neighbour shell to represent the configuration of the solution. The thermodynamic properties are expressed in terms of partition function of solution which is derived from classical statistical mechanics considering the all probabilities of different configurations in the nearest neighbour shell and influence of those configurations on the field acting on the central atom.

It can be shown that the partition function of a solution is,

$$Q = \sum \Omega; \frac{V_A^{N_A} V_B^{N_B}}{V_i^{N_i}} e^{-E_i/kT} \quad (28)$$

where  $q_i$  = average partition function of atom  $i$

$\Omega_i$  = number of quantum states possessing energy,  $E_i$

Considering a binary solution, the free energy can then be expressed as:

$$G = -kT \ln \left[ \frac{q_A^{N_A} q_B^{N_B}}{\bar{\Omega}} e^{-\bar{E}/kT} \right] \quad (29)$$

or

$$G = \bar{E} - kT (\ln \bar{\Omega} + \ln q_A^{N_A} q_B^{N_B}) \quad (30)$$

In the above expression, it can be readily noticed that  $\bar{E}$  corresponds to enthalpy term,  $\ln \bar{\Omega}$  relates to configurational ideal entropy part and the  $\ln q_A^{N_A} q_B^{N_B}$  the excess entropy.

Also it can be shown that for random mixing, the excess functions are:

$$H^{XS} = \omega Z X_A X_B \quad (31)$$

$$\text{and } G^{XS} = \omega Z X_A X_B (1 - T/\tau) \quad (32)$$

where  $\tau$  is a constant and for most metallic system it is around 3000 K.

Beside all these models, various analytical expressions in series form are available to represent the thermodynamic properties of mixing of solution for different experimental data. The list is quite exhaustive and beyond the scope of this paper. However, one important example is of Redlich-Kister expression which can be written for binary phase as:

$$G = \sum_{i=1}^2 x_i G_i^0 + RT \sum_{i=1}^2 x_i \ln x_i + x_1 x_2 \sum_{j=0}^n (A_j - B_j T) (x_1 - x_2)^j \quad (33)$$

We should keep in mind, that these expressions should be used after examining carefully, since some equations may be valid for lower order systems. In ternary or quaternary systems, either the model may fail or become unwieldy for proper solution.

At this point, it should be clear that the computation of proper phase diagram calls for a selection of a model which needs to be solved with proper set of thermodynamic data. In some cases, prior thermodynamic information indicate the nature of the model to be selected. However, the generated diagrams should be checked with the reliable experimental data for consistency and accuracy. It is quite likely that different phase boundaries need to be determined by different models depending on the phase reactions, temperature and compositions.

For example, one hypothetical binary A-B system is considered. The necessary thermodynamic relations are given in the table I for constructing the phase diagram. The vapour - liquid phase reactions are considered to be ideal. However, the lower temperature condensed phase relations are regular in nature. The corresponding free energy - composition diagram is shown in fig.2. Any phase stability experimental evidence can be used to check the consistency of the data and the model used here. The calculated phase diagram in fig. 3 shows all the phase reactions considered in the table.

Manual computation of phase diagram is very laborious and also the analysis of the generated data is almost impossible without the suitable graphic visualization software. As a result, various computer software are being developed both for the computation of the phase diagram and the graphical display of data. Different organizations such as CALPHAD, FACT, ASM alloy phase diagram committee, SGTE, have already developed different softwares and are still carrying out active research in this area. Also, one international alloy phase diagram committee has been formed with members from various countries for systematic evaluation and compilation of thermodynamic data and phase diagrams (Fig. 4).

## Conclusions

The underlying thermodynamic principles employed for computation of phase diagrams are discussed here. The phase rule and the conditions of equilibrium form the basis of construction of equilibrium phase diagram. Depending on the complexity of the system and the availability of data, various models can be used to predict a phase diagram. Some important thermodynamic models having distinguished features are covered. The most complex models may not be the best model in many instances. Mostly, the selection of a model is mainly dependent on the available information on that system and the nature of the similar systems concerned.

Because of the importance of phase diagram, the world wide activities are being pursued to compile, assess and generate phase diagrams by different techniques. Many diagrams in the literature show inconsistencies due to the complexities and inaccuracies involved in a technique. It is expected that such an international effort would enable to obtain consistent and accurate phase diagrams.

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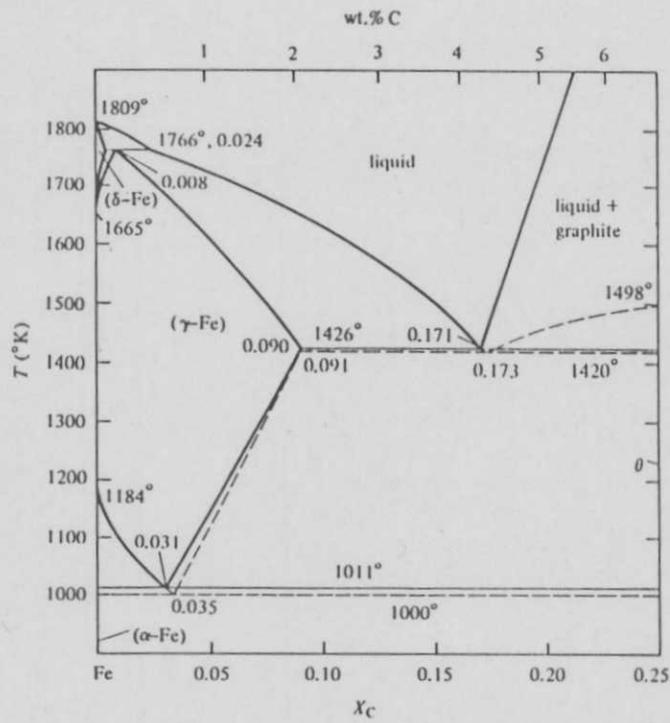


Figure 1 . Phase diagram of the iron-carbon system [1]. The dashed lines correspond to equilibria with respect to cementite ( $\theta$ ) rather than graphite.

TABLE 1

THERMODYNAMIC PROPERTIES OF THE HYPOTHETICAL SYSTEM A-B

	<u>Component A</u>	<u>Component B</u>
Melting point (K)	1200	1300
Standard Gibbs Energy of Melting, $\Delta G_M^0$ (cal mol <sup>-1</sup> )	3600 - 3T	3900 - 3T
Standard Boiling Point (K)	1400	1600
Standard Gibbs Energy of Vaporisation, $\Delta G_V^0$ (cal mol <sup>-1</sup> )	2800 - 20T	32000 - 20T

Gas phase: Ideal monomeric

Liquid phase: Gibbs energy of mixing =  $\Delta G_L^{MIX} = RT (X_A \ln X_A + X_B \ln X_B) + G^E$

$$\text{where } G^E = \Delta H - T s^E$$

$$\text{and } \Delta H = X_A X_B (950 + 5500 X_B) \text{ cal mol}^{-1}$$

$$s^E = -0.05 X_A X_B \text{ cal mol}^{-1} \text{ K}^{-1}$$

Solid phase  $\alpha$ : A Henrian solution of solute B in solvent A.

$$G_A^E = RT \ln \gamma_A = 0$$

$$G_B^E = RT \ln \gamma_B = 5800 \text{ cal}$$

(that is,  $G_B^E$  is independent of composition),

Solid phase  $\beta$ : Stoichiometric solid pure component B. (Negligible solubility of component A)

Solid phase  $\gamma$ : A stoichiometric compound of the formula  $A_{2/3}B_{1/3}$  whose Gibbs energy of formation from pure solid A and B according to  $2/3 A_{(sol)} + 1/3 B_{(sol)} = A_{2/3}B_{1/3}(sol)$

$$\text{is given by: } \Delta G^0 = -1000 + 0.5 T \text{ cal}$$

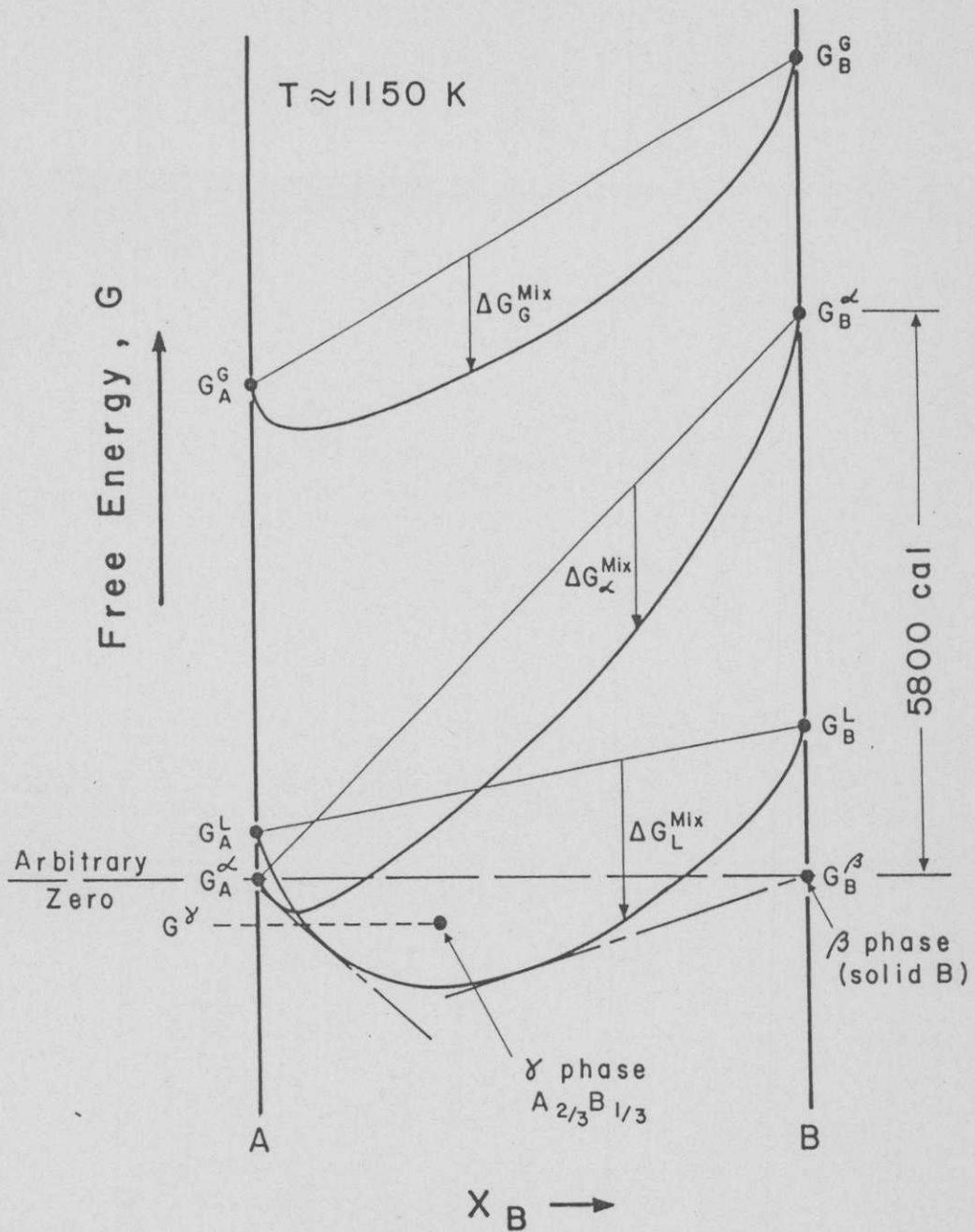


FIG.2 Gibbs energy-composition curves (schematic) for the phases in the hypothetical system A-B corresponding to the phase diagram of FIG.3 at  $T \approx 1150 \text{ K}$ .

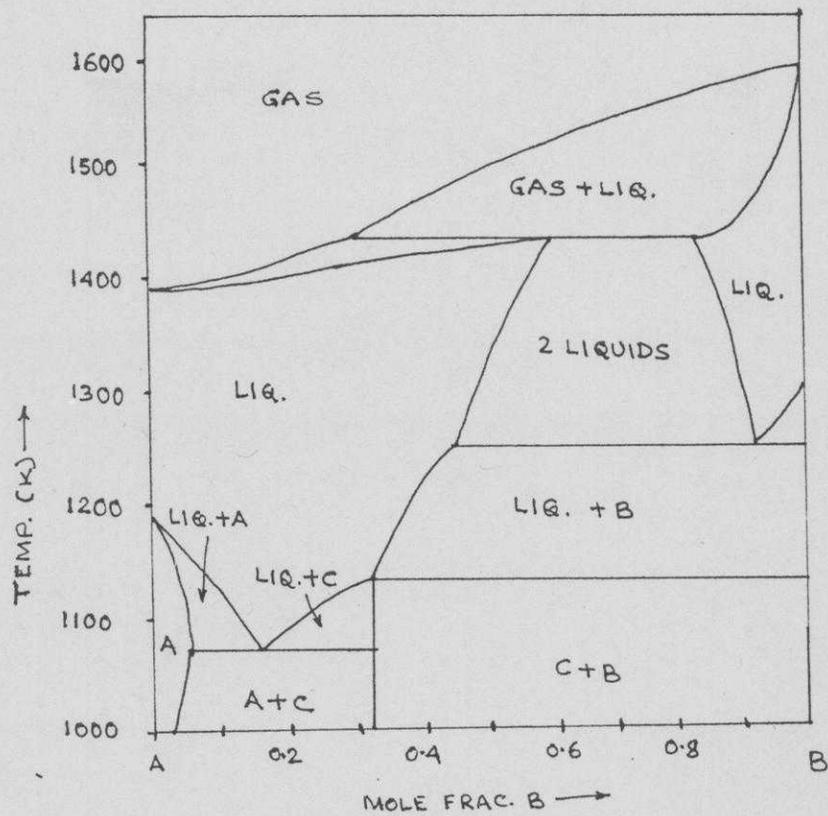


Fig.3 Binary temperature-composition phase diagram at constant pressure for a hypothetical system A-B calculated from the thermodynamic properties listed in the table.



Fig. 4 — Binary phase diagram assessments in the framework of international cooperation.