THE RULE ON PHASE CONSTRUCTION OF THE BINARY ALLOYS

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1. Introduction

We have tried to relate the construction of binary phase diagram to both absolute difference between the melting temperatures of two components, ϕ, and one between the melting temperature of the less fusible component and the eutectic temperature, σ[1)~3)].

The object of the present investigation is to show how the various types of the phase diagram[4)] and heats of mixing in the binary molten alloys[5) 6)] may be classified by the ϕ-σ relationship, while a pioneer contribution in this field has made by Hume-Rothery *et al.*[7)] who noted the importance of electron ratios, difference in atomic volumes etc. to interpret the binary phase diagrams.

2. Classification of the Phase Diagrams According to ϕ

Table 1 shows that occurrence of two phase liquid systems with one common

TABLE 1. ϕ for the two phase liquid systems.

System	ϕ	System	ϕ
Cr - Sn	1643	Cu - Cr	792
Cr - Bi	1604	Cu - Tl	780
Cr - Pb	1548	Cu - Pb	756
Fe - Bi	1263	Al - K	596
Fe - Tl	1231	Al - Na	562
Fe - Pb	1207	Al - In	504
Bi - Fe	1263	Ag - Fe	573
Bi - Co	1224	Ag - Co	534
Bi - Si	1141	Ag - Ni	492
Tl - Fe	1231	Al - Bi	389
Tl - Co	1192	Al - Tl	357
Tl - Ni	1150	Al - Cd	339
Tl - Si	1109	Al - Pb	333
Tl - Mn	940	Ga - Pb	297
Co - Bi	1224	Ga - Cd	291
Co - Tl	1192	Ga - Tl	273
Co - Pb	1168	Ga - Bi	241
Pb - Fe	1207	Li - Cs	150
Pb - Co	1168	Li - Rb	141
Pb - Ni	1126	Li - K	111
Pb - Si	1085	Li - Na	82
Pb - Mn	916	Zn - Bi	149
Si - Bi	1141	Zn - Tl	117
Si - Tl	1109	Zn - Pb	93
Si - Pb	1085		

component may be attributed to similarity in ϕ. As a consequence, Table 1 leads naturally to the idea that a series exists in those systems with one common component. That is, the table can be regarded to be classified by the series belonging to the common components on the left. It seems however possible that these series are not only established belonging to the one component but also to the other.

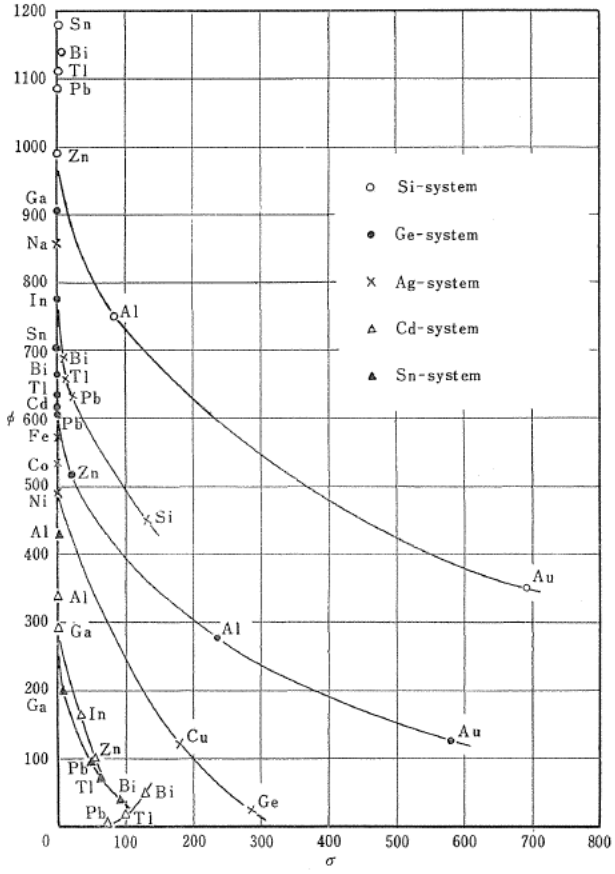


FIG. 1. ϕ-σ relationship for the two phase liquid and the eutectic systems. (a)

Fig. 1 shows the ϕ-σ relationship in the systems forming the two phase liquid and the eutectic, from which the transition series on passing from the former system to the latter may be observed. In Fig. 2 by the common elements reversed Fig. 1, the curves are shaped differently from Fig. 1 and it is, in particular, attracted attention that there are some crossings in the curves for Pb-systems.

After confirming the ϕ-σ relationships to be held strictly in the systems forming the two phase liquid and the eutectic, whether or not, the tendency to such rule exists for the systems forming stable intermediate compounds, is investigated

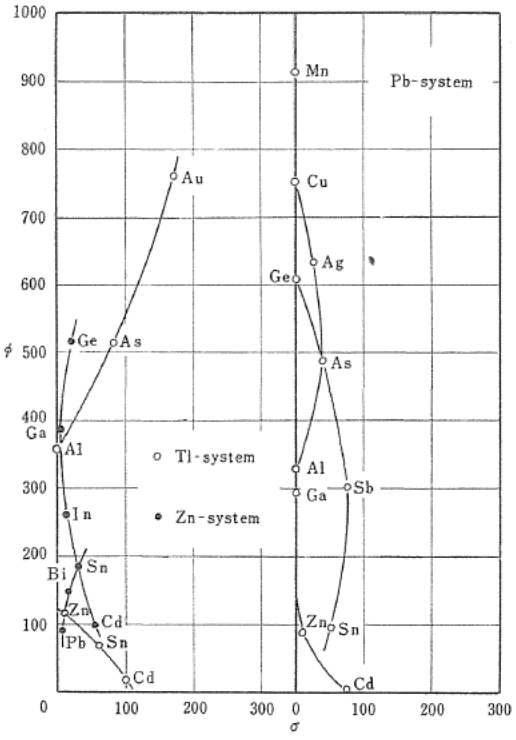


FIG. 2. ϕ-σ relationship for the two phase liquid and the eutectic systems. (b)

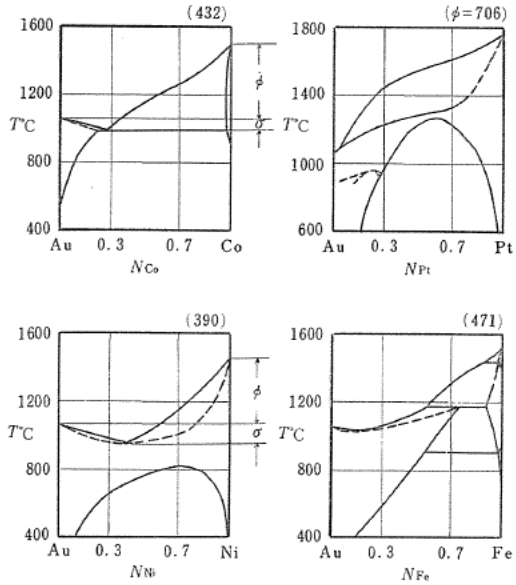


FIG. 3. Series of the continuous solid solution and the eutectic systems.

in the following section.

Fig. 3 shows a series of schematic diagrams representing transition from the diagram of continuous solid solution to the one on passing through the eutectic diagram. In this case, relationship like the ϕ-σ relationship in the eutectic systems can be obtained as shown in Fig. 4, if use congruently minimum melting point instead of the eutectic temperature, the graph of σ against ϕ being normally a smooth curve. This fact gives a valid of the transition series that the rule of ϕ-σ relationship is also held for the continual transitions of the solid solution and eutectic diagrams.

Fig. 5 shows the transition series of systems forming intermediate phase with comparatively wide solid solubility, and there seems be a continual transition in changes of form of the intermediate phase β and position of forming the compounds.

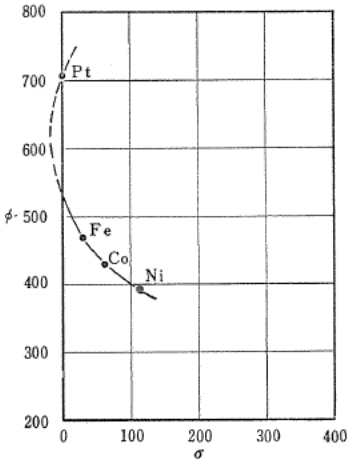


FIG. 4. ϕ-σ relationship for the series of continuous solid solution and eutectic systems. (Au-system)

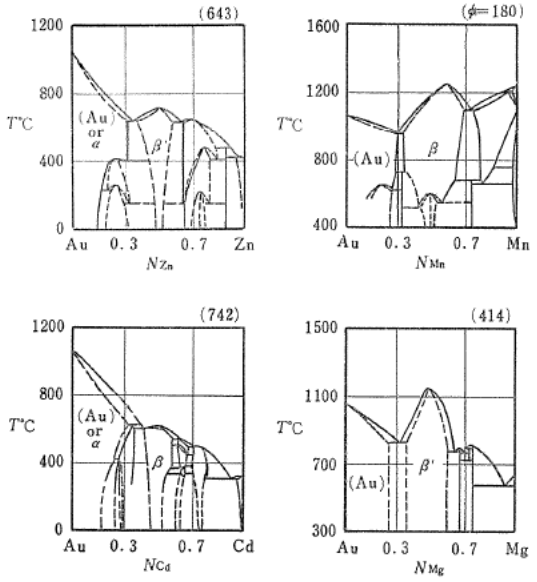


FIG. 5. Series of the intermetallic phase, the compound and the solid solution systems.

Fig. 6 is an example of Au-systems forming one compound or two and when they are arranged in order of ϕ, the diagrams are found to change regularly. System Au-Bi forms compound A_2B and on passing to the system Au-Pb one more compound AB_2 forms, and then following the system Au-Te in which the com-

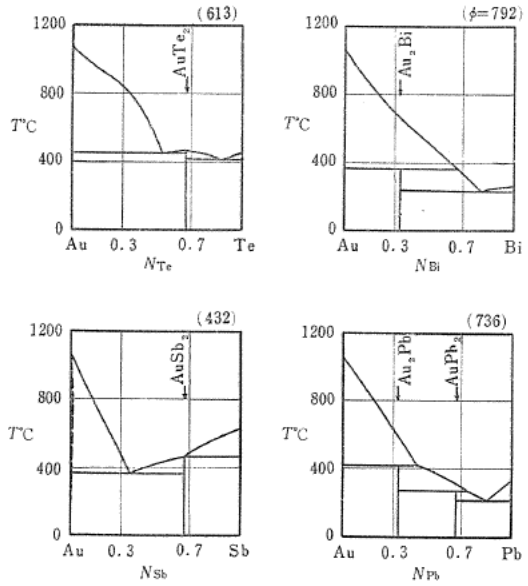


FIG. 6. Series of the compound systems.

pound A_2B disappears, system Au-Sb tends to decay the compound AB_2.

There are no more than some examples, but tendency to the similar series would be observed in nearly every cases for the phase diagrams if examined in detail. Although these series are, of course, not judged qualitatively but intuitionally, from the fact that a number of series may be observed, it may be said that there is no room for doubt on the series.

The Pb-systems are investigated in some details as a typical example, a number of phase diagrams of the two phase liquid and the eutectic being available. It is of some interest to note from Fig. 7 that we may understand the transition series best by considering first the systems such as Pb-systems.

When the Pb-systems are arranged in the order of ϕ, the rule of continuity is broken because of existence of a system by which discontinuity occurs, *e. g.* it is not continued on passing to system Pb-Al. However, as a first approximation, it is found convenient to take linear arrangement on ϕ but loop arrangement as shown in Fig. 7. This arrangement was derived from continual changes of magnitudes of solid solubility and of liquidus. Although we cannot reach a definite decision which the loop arrangement is correct because series made by many systems forming the two phase liquid and the eutectic are few, such loop arrangement would be probably applied for all series. That is, it is only natural to expect that this classification by ϕ may be extended to all metallic systems. Apart from the metallic systems of the common element of one kind, it is unfortunate that at present no complete method exists for classifying all series. However, when we observe Fig. 7 again, it comes now under our notice that metals formed a pair of Pb were arranged regularly in order on ϕ of large, small and large in spite of slight irregularity. We can arrive at the idea that the reasonable classification may be possible in which metallic elements are arranged on

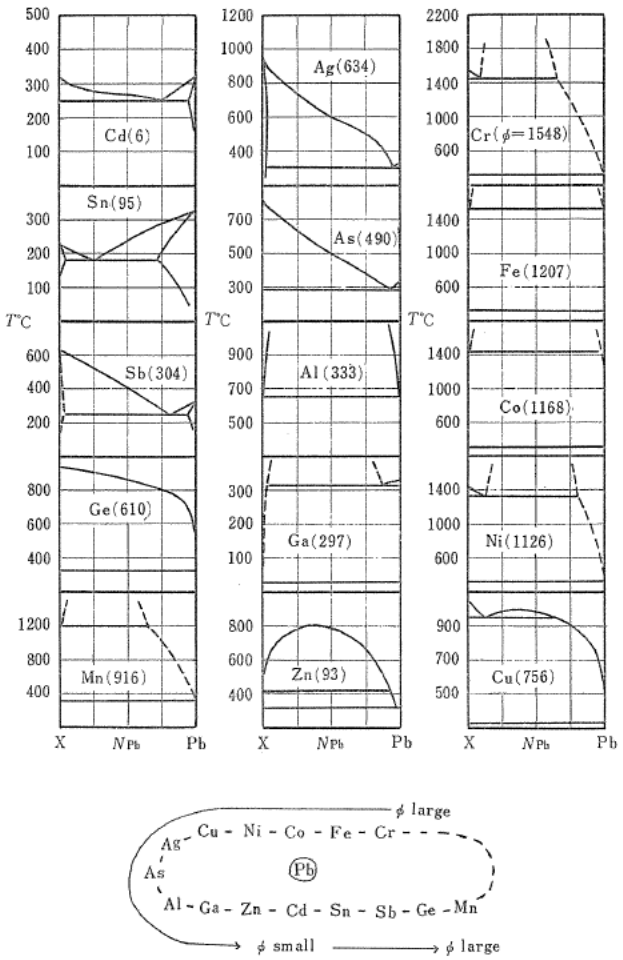
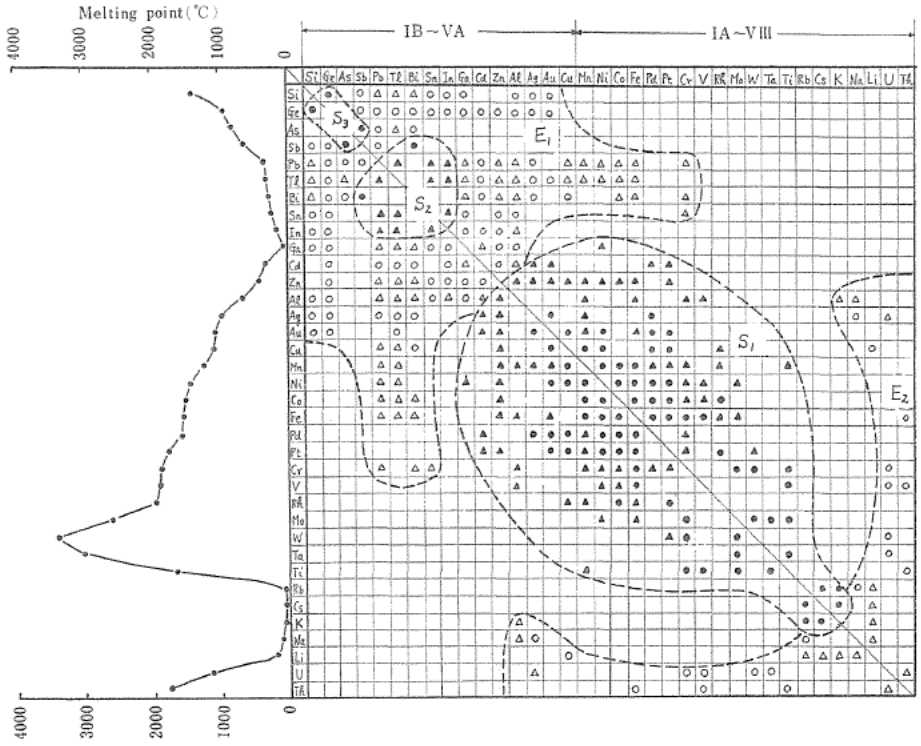


FIG. 7. Loop arrangement for the two phase liquid and the eutectic systems. (Pb-systems)

the melting temperatures in the shapes of loop and wave provided that the classification according to ϕ is difficult. Investigating the systems forming compound as well as the systems forming the two phase liquid and the eutectic, as guessed easily from arrangement of the loop shape, the two phase liquid and the eutectic systems can become the series but series changed on passing through the compound system from the eutectic one is, in general, assumed to be impossible. However, as shown from Fig. 3, the transition series containing the eutectic and the solid solution systems seems possible naturally, the systems having solid solubility of wide range being conveniently called the solid solution system here.

The three conditions are then given all of which must be satisfied in order to obtain the classification.

(1) The series is not established belonging to which one component but to both of components in the systems.



○ Eutectic system
△ Two phase liquid system
● Continuous solid solution system
▲ Solid solution system (Max. solid solubility: more than 25 atomic per cent)

FIG. 8. Classification for the two phase liquid, the eutectic and the solid solution systems.

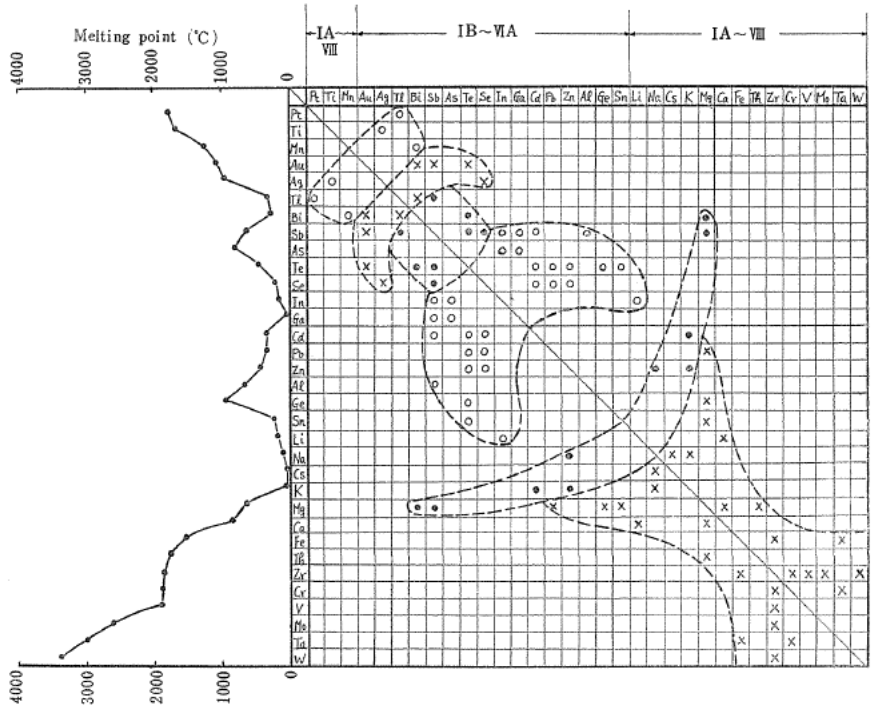
(2) The series becomes loop shape and also wave shape.

(3) The series for the two phase liquid, the eutectic and the solid solution systems has no relation to the series for compound systems.

Based on these assumptions various interesting arrangements such as Figs. 8 and 9 were devised. Fig. 8 shows the case of systems as much as possible of the two phase liquid, the eutectic and the solid solution systems[4], showing the relation between component elements arranged in loop and wave shapes on the melting temperatures of metallic elements, from which it is evident that these systems were separated and classified clearly. The two phase liquid and the eutectic systems are opposed on the solubility to the solid solution system and this tendency appeared as separation between groups S_1 and E_1 or E_2. But continuation between the both is observed as S_2 or S_3 in E_1.

We use the term "solid solution system" conveniently to denote the system having wide solid solution even if the compound is stable. The system in which the eutectic and the solid solution systems coexist, is indicated as the system of wider existing range.

In 181 of possible total metallic pairs, 171 pairs were illustrated in Fig. 8



○ AB type compound system
× AB_2 type compound system
● System forming compound of more than five atoms

FIG. 9. Classification for the one compound systems.

with the exception of 10 pairs containing 7 of abnormal Ag-systems.

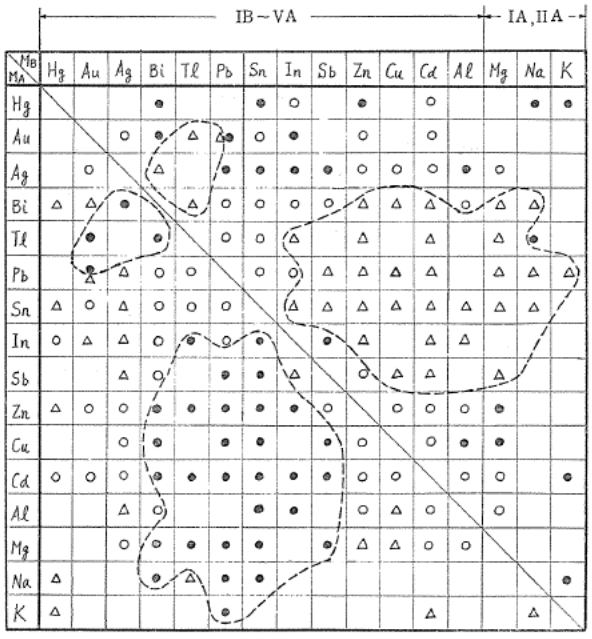
From the point that the present classification was made by the arrangement of the loop and wave shapes concerning not ϕ but the melting temperatures of metals, the present classification is approximate and true relation among these systems must be really more complicated. However, from the fact the classification is satisfactory for 94 per cent of the possible systems, there seems little doubt that the relation is the first character in estimating the two phase liquid, the eutectic or the solid solution system or not. When the arrangement of metallic elements is observed upon comparison with periodic table of the elements, a clear relation with the position in the periodic table is shown. The metals of Mn to Th belong to groups IA to VIII in the periodic table shown in Table 2 and are of strong metallic properties. On the other hand, the metals Si to Cu belong to groups IB to VA and are week metallic. The solid solution systems fallen in group S_1, are those resulted between metals of comparatively high melting temperatures and differ in character from those fallen in groups S_2 and S_3 which are considered resulted between analogous metals.

Next, let us consider case of the compound systems. In like manner it may be shown that similar relations are applied to the compound forming systems. In the compound systems, the arrangement of the metallic elements was rexami-

TABLE 2. Periodic table of the elements.

IA	IIA							H			IIIA	IVA	VA	VIA	VIIA	He
Li	Be										B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB	——VIII——			IB	IIB	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La ~ Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac ~ No															

nated from the standpoint that the compound systems belong to series which is independent of the two phase liquid, the eutectic and the solid solution systems. Fig. 9 illustrates the arrangement of the compound systems[4] by grouping them according to melting point-element relationship, showing many waves compared with Fig. 8. In this case, the metallic elements corresponding to groups IA to VIII in the periodic table part right and left in Fig. 9, but it is by no means improper arrangement and a similarity related to the periodic table exists in Figs. 8 and 9. Since the compound system of AB_3 type is only $InMn_3$, it was excluded here. The present figure classified 47 pairs in 48 of possible metallic pairs. That is, the excluded pair is only one. The metallic system by a common element, system of which is difficult to form one compound, is, in general, easy to form



△ $N_A < 0.45$ ○ $N_A = 0.45 \sim 0.55$ ● $N_A > 0.55$

FIG. 10. Classification for heats of mixing in the binary molten alloys.

many compounds and the system such as Si-, Ni-, La-, Pr-, Ce-systems tends to form the many compounds.

There are some exceptions, but the general tendency for becoming the series is very clear from the above-mentioned.

Although reported in another paper[8], maximum or minimum concentrations of heats of mixing in the binary molten alloys play an important role in the properties of the molten alloys. Therefore, its significance would be large if these concentrations can be assumed from classification on the heats of mixing similar to the foregoing. Fig. 10 shows classified the max. or min. concentrations of the heats of mixing[5)6)] in the series. It is evident that considerable classification is possible although loop and wave shapes are not clear because available systems are not so many.

3. Conclusion

Based on idea of the arrangement of the loop and wave shapes on the melting temperatures of metallic components derived from the ϕ-σ relation rule, various phase diagrams were classified systematically.

The results obtained seem to justify the following three assumptions:

(1) The series may belong to both components in the alloy system.

(2) The series is loop and wave shapes.

(3) The series for the two phase liquid, the eutectic and the solid solution systems is independent of it for the compound systems.

The method similar to the solid alloys can be applied for the heats of mixing in the binary molten alloys and the classification on their max. or min. concentrations was carried out.

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