CALCULATING MODELS OF MASS ACTION CONCENTRATIONS OF BINARY METALLIC MELTS INVOLVING SOLID SOLUTIONS①

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ABSTRACT Based on the appearance of minima of mixing free energy and maxima (or minima) of excess free energy, formation of compound or short-range order in the solid state, exhibition of miscibility gap, two phase region or eutectoid in the solid (or liquid) state as well as symmetrical or unsymmetrical deviations of activity relative to Raoultian behavior, calculating models of mass action concentrations for Si-Ge, Ni-Pb, Fe-Cr, Fe-Cu, Sb-Sn and Ag-Au as well as Ni-Pt, Cr-V and Ag-Pb metallic melts have been formulated. Good agreement between calculated and measured values shows that the calculating models reflect the structural characteristics of given metallic melts.

Key words: activity short-range order coexistence theory mass action concentration

1 INTRODUCTION

Coexistence theory of metallic melts involving compound formation in corresponding phase diagrams had been proposed[1], and showed its good agreement with practice in many conditions[2-5]. Meanwhile, calculating models of mass action concentrations of binary metallic melts involving eutectic had also been formulated[6], and got satisfactory application results in relation to 13 pairs of binary metallic melts, such as Cd-Bi, Ge-Al, Ag-Cu, Al-Sn etc. But for metallic melts involving solid solutions, for example, Si-Ge, Fe-Cu, Ag-Au, Ni-Pt etc., there isn't any ready-made model of mass action concentrations. This paper attempted to resolve the problem mentioned above.

2 CALCULATING MODELS

2.1 *Metallic Melts with Symmetrical Deviations of Activity*

The thermodynamic characteristics of Si-Ge, Ni-Pt, Fe-Cr, Fe-Cu, Sb-Sn and Ag-Au systems are shown in Table 1[7,8]. The free energies of mixing ΔG exhibit minima, and the excess free energies ΔG^{XS} exhibit maxima (or minima); furthermore, the majority of minima and maxima (or minima) of ΔG^{XS} is located at $x_i = 0.5$, showing obvious symmetrical character. The consistency of thermodynamic data with the structure of metallic melts[1] indicates the possibility of AB form compound formation in the melts mentioned above. It is worthwhile to notice that the excess free energies ΔG^{XS} of Sb-Sn and Ag-Au melts are negative, while that of the preceding four melts are positive which is a question left for further consideration.

The possibility of AB form compound formation can also gain enlightenment from the following facts:

(1) There is intermetallic compound σ phase (FeCr) formation in the Fe-Cr alloy system at low temperatures (below 830 ℃). In

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Table 1 The free energy of mixing ΔG and excess free energy ΔG^{XS} of several metallic melts (J/mol)

x_b	Si-Ge		Ni-Pb		Fe-Cr	
	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}
0.1	−4177	480	−4442	624	−3772	553
0.2	−6278	890	−6665	1130	−5694	963
0.3	−7535	1220	−8009	1511	−6871	1260
0.4	−8290	1350	−8729	1758	−7494	1465
0.5	−8465	1470	−8943	1859	−7628	1599
0.6	−8290	1350	−8683	1805	−7331	1629
0.7	−7535	1220	−7926	1591	−6649	1482
0.8	−6278	890	−6573	1227	−5527	1130
0.9	−4177	480	−4363	703	−3776	553

x_b	Fe-Cu		Sb-Sn		Ag-Au	
	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}
0.1	−1885	3077	−3052	−603	−4434	−783
0.2	−2345	5246	−4840	−1072	−7063	−1444
0.3	−2613	6653	−6008	−1407	−8826	−1964
0.4	−2776	7432	−6674	−1608	−9885	−2324
0.5	−2822	7691	−6896	−1675	−10287	−2504
0.6	−2772	7436	−6674	−1608	−10040	−2483
0.7	−2646	6619	−6008	−1407	−9102	−2240
0.8	−2428	5158	−4840	−1072	−7381	−1758
0.9	−1947	2981	−3052	−603	−4668	−1017

the Sb-Sn alloy system at 200～300 ℃, there is β' phase (SbSn compound) formed during peritectic reaction [7]

(2) In Au-Cu and Cd-Mg phase diagrams at low temperatures, there are clear indications of AuCu, CdMg compounds formation[9] with sharp peaks.

(3) Short-range order can be observed over a wide composition range of Ag-Au system[9], and in the 50at.-% alloy, evidence for a partial ordering of atoms can be found[10]. Magnetic, electronic, vibrational tests etc. show that significant short-range order is present in Ni-Pd melts. An anomalous rise in the heat capacity of Ni-50at.-% Pd can be found at about 350 ℃. The resistivity reaches a maximum at Ni-50at.-% Pd above 400 ℃[11].

Preceding facts show that at low temperatures, in this kind of melts, AB form compound or short-range order chemical cluster really forms. At high temperatures, according to Kulikov, Y S[12], these compounds formed in the solid state are capable to be retained in liquid after melting.

Take Si-Ge melts for example. Putting $b = \Sigma n_{Si}$, $a = \Sigma n_{Ge}$, $N_1 = N_{Si}$, $N_2 = N_{Ge}$ (Σn represents mole number calculated from results of chemical analysis; N_i are mass action concentrations, i. e. equilibrium mole fractions), if these melts are homogeneous, they will follow the regularity of metallic melts involving compound formation[1], then the equilibrium constant of formation of AB form compound would be:

$$K = [1 - (a + 1)N_1 - (1 - b)N_2] / (a - b + 1)N_1N_2 \quad (a)$$

If the melts consist of two phases, they should follow the behavior of metallic melts involving eutectic[6], then the equilibrium constant of formation of AB form compound is:

$$K = ab(2 - N_1 - N_2)/(a + b)N_1N_2 \quad (b)$$

Examination of four melt systems (Si-Ge, Ni-Pd, Fe-Cr and Fe-Cu) based on measured activity data[7, 8] showed that on account of their positive deviations of activities relative to Raoult's law, equilibrium constants calculated by Eq. (a) are negative, and hence are unreasonable. As for the other two melts, Sb-Sn and Ag-An, though their equilibrium constants of formation of AB form compound can be calculated by Eq. (a), they are not constant. Taking Ag-Au melts for example, as X_{Ag} ranged from 0.1 to 0.9, K_{AgAu} are 2.199 12, 1.833 92, 1.616 96, 1.449 94, 1.332 79, 1.254 59, 1.197 05, 1.163 40, 1.142 39 respectively. On the contrary, equilibrium constants of formation of AB form compound calculated by Eq. (b) for all six melts mentioned above remain constant.

Why the equilibrium constants of formation of AB form compound for metallic melts involving solid solutions should be calculated by equation of metallic melts involving eutectic? Firstly, there is immiscibility in Fe-Cu melts, even at temperatures above 1600 ℃[13]; secondly, the occurrence of two phase region in Cd-Mg[9], Ni-Pb[11] and Au-Cu[14] alloys and that of eutectoid in Au-Cu alloys can be discovered.

So with great possibility this kind of melts is not homogeneous but of two phase; it follows the regularity of two-phase melts.

Take Si-Ge melts for example. According to the calculating model of mass action concentrations for metallic melts involvng eutectic[6], the calculating model of mass action concentrations for this kind of melts can be written as:

$$\left.\begin{aligned} &Si_{(1)} + Ge_{(1)} = SiGe_{(1)} \\ &K = N_3/N_1N_2 \\ &N_3 = KN_1N_2 \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} &b = x + z \\ &N_1 + KN_1N_2/b = 1 \\ &N_1 = x/b \end{aligned}\right\} \quad (2)$$

$$\left.\begin{aligned} &a = y + z \\ &N_2 + KN_1N_2/a = 1 \\ &N_2 = y/a \end{aligned}\right\} \quad (3)$$

$$K = ab(2 - N_1 - N_2)/(a + b)N_1N_2 \quad (4)$$

$$N_2 = 1 - b(1 - N_1)/a \quad (5)$$

$$N_1 = (-[(a - b)K + ab] + \{[(a - b)K + ab]^2 + 4ab^2K\}^{1/2})/2bK \quad (6)$$

where $x = n_{Si}$, $y = n_{Ge}$, $z = n_{SiGe} = N_3$; n represents equilibrium mole numbers.

It has also been reported[13] that Cu_2 molecules are present in the vapor of Fe-Cu melts. The *fcc* → *bcc* transformation in Fe-Cu melts[15] may be a favorable condition for the formation of double-atom molecules, as one cell of *fcc* cube contains 2 atoms, and that of *bcc* cube contains 1 atom. For Fe-Cu melts, if the formation of double-atom molecules is considered, giving $b = \Sigma n_{Fe}$, $a = \Sigma n_{Cu}$, $x = n_{Fe}$, $y = n_{Cu}$, $N_1 = N_{Fe}$, $N_2 = N_{Cu}$, $N_3 = N_{Fe_2}$, $N_4 = N_{Cu_2}$, then the calculating model becomes:

$$\left.\begin{aligned} &2Fe_{(1)} = Fe_{2(1)} \\ &K_1 = N_3/N_1^2 \\ &N_3 = K_1N_1^2 \end{aligned}\right\} \quad (7)$$

$$\left.\begin{aligned} &2Cu_{(1)} = Cu_{2(1)} \\ &K_2 = N_4/N_2^2 \\ &N_4 = K_2N_2^2 \end{aligned}\right\} \quad (8)$$

$$\left.\begin{aligned} &b = x + 2K_1N_1^2 \\ &N_1 + 2K_1N_1^2/b = 1 \\ &N_1 = (-b + \sqrt{b^2 + 8K_1b})/4K_1 \end{aligned}\right\} \quad (9)$$

$$\left.\begin{aligned} &a = y + 2K_2N_2^2 \\ &N_2 + 2K_2N_2^2/a = 1 \\ &N_2 = (-a + \sqrt{a^2 + 8K_2a})/4K_2 \end{aligned}\right\} \quad (10)$$

$$\left.\begin{aligned} &K_1 = b(1 - N_1)/2N_1^2 \\ &K_2 = a(1 - N_2)/2N_2^2 \end{aligned}\right\} \quad (11)$$

For Fe-Cu melts, which of the two models(Eqs. (1)~(6) or Eqs. (7)~(11)) reflects the reality of this kind of melts better needs further verification from practice.

2.2 *Metallic Melts with Unsymmetrical Deviations of Activity*

The thermodynamic characteristics of Ni-Pt, Cr-V and Ag-Pd metallic melts in Table 2 show that the free energies of mixing ΔG and excess free energies ΔG^{XS} exhibit minima, but they are not symmetrical, which indicating the formation of chemical compound in this kind of melts, but not of single AB form compound. Nash, P and Singleton, M F pointed out that chemical compounds NiPt and Ni_3Pt were formed, in Ni-Pt alloy[16]. Formation of two intermetallic compounds in Ag-Pd alloy had also been reported[9]. Thus, it is possible to form AB and B_3A type chemical compounds in this kind of melts.

Comparing two calculating models(one of homogeneous melts, the other of two phase melts), it is shown that the calculating model of homogeneous melts agrees better with practice. Hence, taking Ni-Pt metallic melts for example, the calculating model of mass action concentrations can be deduced as follows.

Let $b = \Sigma n_{Ni}$, $a = \Sigma \nu_{Pt}$, $x = n_{Ni}$, $y = n_{Pt}$, $z = n_{NiPt}$, $w = n_{Ni_3Pt}$, $N_1 = N_{Ni}$, $N_2 = N_{Pt}$, $N_3 = N_{NiPt}$, $N_4 = N_{Ni_3Pt}$, then the chemical equilibria are:

$$\left.\begin{aligned} &Ni_{(1)} + Pt_{(1)} = NiPt_{(1)} \\ &K_1 = N_3/N_1N_2, \\ &N_3 = K_1N_1N_2 \end{aligned}\right\} \quad (12)$$

$$\left.\begin{aligned} &3Ni_{(1)} + Pt_{(1)} = Ni_3Pt_{(1)} \\ &K_2 = N_4/N_13N_2, \\ &N_4 = K_2N_13N_2 \end{aligned}\right\} \quad (13)$$

and the mass balance:

$$N_1 + N_2 + K_1N_1N_2 + K_2N_1^3N_2 - 1 = 0 \quad (14)$$

Table 2 The free energy of mixing ΔG and excess free energy ΔG^{XS} of several metallic melts (J/mol)

x_b	Ni-Pt		Cr-V		Ag-Pd	
	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}	ΔG	ΔG^{XS}
0.1	−7034	−2642	−5062	−871	−3454	−209
0.2	−11664	−4903	−8106	−1654	−5602	−607
0.3	−14964	−6703	−10245	−2366	−7331	−1231
0.4	−17070	−7972	−11681	−3002	−8738	−2022
0.5	−17995	−8625	−12414	−3475	−9743	−2822
0.6	−17689	−8591	−12343	−3663	−10170	−3450
0.7	−16044	−7787	−11338	−3458	−9705	−3605
0.8	−12904	−6138	−9253	−2801	−8068	−3073
0.9	−7963	−3567	−5845	−1650	−5007	−1758

$$b = x + z + 3w = \Sigma n(N_1 + K_1N_1N_2 + 3K_2N_1^3N_2) \quad (15)$$

$$\Sigma n = b/(N_1 + K_1N_1N_2 + 3K_2N_1^3N_2)$$

$$a = y + z + w = \Sigma n(N_2 + K_1N_1N_2 + K_2N_1^3N_2) \quad (16)$$

$$\Sigma n = a/(N_2 + K_1N_1N_2 + K_2N_1^3N_2)$$

From Eqs. (15) and (16):

$$aN_1 - bN_2 + (a - b)K_1N_1N_2 + (3a - b)K_2N_1^3N_2 = 0 \quad (17)$$

Adding Eq. (14) to Eq. (17) gives:

$$\left.\begin{aligned} &1 - (a+1)N_1 - (1-b)N_2 \\ &= (a - b + 1)K_1N_1N_2 \\ &\quad + (3a - b + 1)K_2N_1^3N_2 \\ &[1 - (a+1)N_1 - (1-b)N_2] \\ &\quad /(a - b + 1)N_1N_2 \\ &= K_1 + K_2(3a - b + 1)N_1^2/(a - b + 1) \\ &[1 - (a+1)N_1 - (1-b)N_2] \\ &\quad /(3a - b + 1)N_1^3N_2 \\ &= K_2 + K_1(a - b + 1)/(3a - b + 1)N_1^2 \end{aligned}\right\} \quad (18)$$

Eqs. (14), (17) and (18) are the calculating models of mass action concentrations for this kind of metallic melts, whose validity will be verified by measured activities.

3 RESULTS AND DISCUSSION

3.1 *Metallic Melts with Symmetrical Deviations of Activity*

By use of measured activities from literatures[7, 8] and Eq. (4), the equilibrium constants and standard free energies ΔG^0 of intermetallic compound formation in this kind of metallic melts at definite temperatures were calculated (Table 3). It can be seen from Table 3 that the equilibrium constants of intermetallic compound formation for this kind of metallic melts are fairly constant, this in turn explains that this kind of chemical reaction rigorously obeys the mass action law. Calculated mass action concentrations by Eqs. (1), (5) and (6) are compared with measured activities as shown in Fig. 1 and Fig. 2. It can be seen that, irrespective as to whether posi-

Table 3 Equilibrium constants and standard free energy of intermetallic compound formation in metallic melts at definite temperatures

x_b	Equilibrium constants		
	Si-Ge	Ni-Pd	Fe-Cr
0.1	0.685 714	0.659 607	0.656 768
0.2	0.706 553	0.668 398	0.679 985
0.3	0.717 608	0.677 968	0.690 000
0.4	0.733 696	0.686 009	0.690 868
0.5	0.726 583	0.687 376	0.684 232
0.6	0.733 696	0.682 768	0.678 067
0.7	0.717 608	0.673 791	0.650 635
0.8	0.706 553	0.657 530	0.617 149
0.9	0.685 714	0.631 392	0.568 254
K	0.712 636	0.669 427	0.657 329
ΔG^0/ J·mol^{-1}	4856	6253	5585
T/K	1723	1873	1600

x_b	Equilibrium constants		
	Fe-Cu	Sb-Sn	Ag-Au
0.1	0.084 198	2.180 61	2.036 31
0.2	0.096 768	2.045 03	1.962 42
0.3	0.112 537	1.943 76	1.904 98
0.4	0.121 073	1.893 90	1.874 88
0.5	0.122 875	1.875 00	1.871 22
0.6	0.120 033	1.893 90	1.906 35
0.7	0.109 618	1.943 76	1.979 94
0.8	0.095 751	2.045 03	2.131 90
0.9	0.090 485	2.180 61	2.398 20
K	0.105 926	2.000 18	2.007 36
ΔG^0/ J·mol^{-1}	34 046	−5219	−7856
T/K	1823	905	1350

tive or negative deviations relative to Raoultian behavior, the agreement between calculated and measured values is fairly good, which in turn showing that the models mentioned above really reflect the characteristics of this kind of melts.

For the sake of comparison, in Fig. 1(c), the results calculated by Eqs. (9)～(11) with consideratin of the formation of double atom molecules Cu_2 and Fe_2 are given by dotted lines; their agreement with practice is not worse than that calculated by Eqs. (1), (5) and (6). Hence, for Fe-Cu melts, which of the two models agrees better with practice still needs further investigations.

3.2 *Metallic Melts with Unsymmetrical Deviations of Activity*

According to Eqs. (14), (17), (18), and using measured activities of literature [7], mass action concentrations for Ni-Pt, Cr-V and Ag-Pd melts can be calculated. Their comparison with practice is show in Fig. 3. Their equilibrium constants and standard free energies of formation ΔG^0 are given in Table 4. It is clear from the figure that the agreement between calculated and measured values is

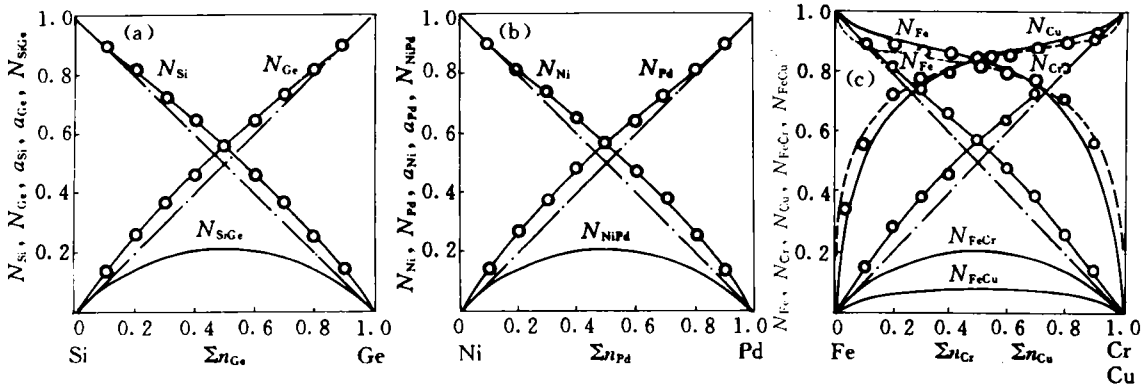

Fig. 1 Comparison of calculated mass action concentrations with measured activities
(Solid line—calculated values; circles—measured values)
(a)—Si-Ge melts, 1 723 K; (b)—Ni-Pd melts, 1 873 K;
(c)—Fe-Cr melts, 1 600 K; Fe-Cu, 1 823 K

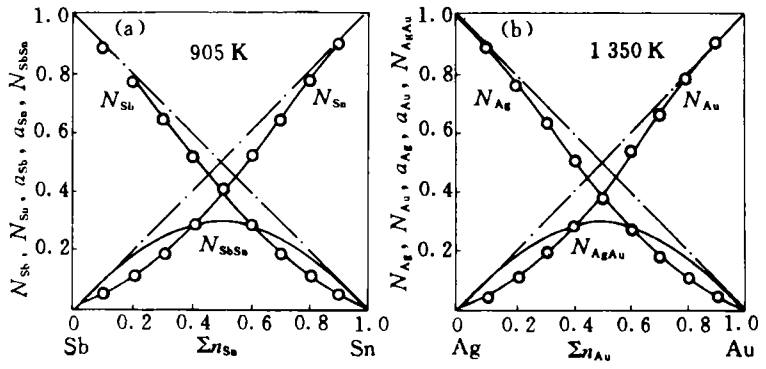

Fig. 2 Comparison of calculated mass action concentrations with measured activities
(Solid line—calculated values; circles—measured values)
(a)—Sb-Sn melts; (b)—Ag-Au melts

quite good, i. e., the deduced model can reflect the structural reality of this kind of melts.

At last, it is necessary to clarify why chemical compounds absent in phase diagrams can form in liquid state? Why chemical compounds formed in solid state still exist in the liquid state? The answer to the first question is that the majority of standard free energies of formation ΔG^0 of this kind of chemical compound is positive, hence their formation condition requires energy supply from outside. High temperatures of liquid just answer this condition and facilitate their formation; in other words, their favorable environment of stability is high temperatures in the liquid state, but not low temperatures in the solid state. The answer to the later question is that in the process of melting and temperature raising, the majority of long-range order structures is destroyed, but it has little effect on the short-range order clusters, thus a considerable amount of them have been reserved. The so called short-range order structures observed over a wide composition range in phase diagrams[9] are most probably this part of short-range order chemical clusters or compounds being little affected by melting and temperature raising.

From the foregoing discussion, it can be concluded that metallic melts involving solid solutions contain chemical compounds too, hence they also belong to metallic melts involving compound formation.

4 CONCLUSIONS

(1) Based on the thermodynamic characteristics, phase diagrams as well as the devia tions of activity relative to Raoultian behav -

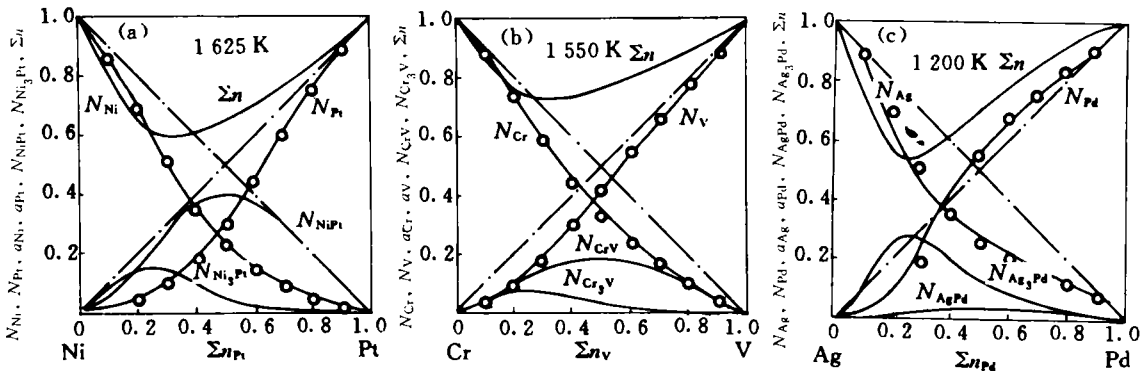

Fig. 3 Comparison of calculated mass action concentrations with measured activities
(Solid line—calculated values; circles—measured values)
(a)—Ni-Pt melts; (b)—Cr-V melts; (c)—Ag-Pd melts

Table 4 T, K and ΔG^0 values of Ni-Pt, Cr-V and Ag-Pd melts

Binary systems	Ni-Pt		Cr-V		Ag-Pd	
	NiPt	Ni_3Pt	CrV	Cr_3V	AgPd	Ag_3Pd
K	5.790 06	12.323 49	1.294 954	2.003 042	0.236 886	11.483 18
ΔG^0/ J · mol^{-1}	−23 739	−33 950	−3 333	−8 957	14 555	−24 366
Correlation coefficient r	0.984 916		0.991 936		0.790 987	
T /K	1 625		1 550		1 200	

ior, calculating models of mass action concentrations for metallic melts involving solid solutions have been formulated. Good agreement between calculated and measured values shows that the calculating models reflect the structural characteristics of given metallic melts.

(2) The activities of binary metallic melts involving solid solutions exhibit either positive or negative deviations from Raoultian behavior; their deviations have either symmetrical or unsymmetrical form. For metallic melts with unsymmetrical negative or positive deviations from Raoult's law, selection of calculating models depends on whether the melts are homogeneous or of two phase.

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