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A NEW APPROACH TO THE SOLID-LIQUID TRANSITION FOR SIMPLE BINARY
EUTECTIC SYSTEMS IN RELATION TO THE MELTING ENTROPY
AND THE PERIODIC TABLE

Pierre Guiraldenq*

SUMMARY

The author gives a description of simple binary eutectic alloys with a solid state insolubility between the two components. In this way, the transient entropy gain from the solid to the liquid state is studied for the eutectic compositions taking place during this isothermal transformation.

This order-disorder phenomenon is analysed by the classical thermodynamic values of the two basic elements and applied to the duplex structure, correlated with the diffusion mechanisms in the solid state, along the interfaces and in the bulk.

These selected binary alloys are divided into two groups: One, with a very low melting entropy excess, compared to each element, and a second one which shows an increasing melting entropy, whose level can be compared to some new materials (as quasi-crystal structures, high entropy or amorphous alloys) during the process.

1- INTRODUCTION

A long time ago, many studies have been carried on in order to understand the lamellar morphology obtained with the eutectic alloys from the liquid state in relation with industrial applications: solders or brazes, castability for complex shape metallic pieces, electronic devices, thermal engines, etc.

This typical lamellar microstructure, obtained from the liquid state and controlled by many physical parameters, is taken here as a reference before heat treatment up to the melting point. During this process, we have to take into account the atomic diffusion mechanisms along the interfaces and in the bulk for the two adjacent crystals (1 and 2).

Figure 1 gives a such classical binary diagram according to the classical thermodynamic laws and the Gibbs rule, with a such lamellar microstructure of the two solid phases (1+2) in a quasi-equilibrium state at room temperature taken as a reference.

In a first time, we have collected the melting entropy values for the different elements in the periodic Table at their melting temperatures T_m , which may be compared with other basic properties of the matter, with a classification taking into account the atomic numbers (Z).

2- CLASSIFICATION OF THE ELEMENTS IN THE PERIODIC TABLE BY THE MELTING ENTROPY (at the atmospheric pressure)

Taking the equilibrium state of one solid phase, the classical relation between the melting enthalpy (ΔH_m), the melting entropy (ΔS_m) and the melting temperature (T_m) is:

$$\Delta S_m = \Delta H_m / T_m$$

The ΔH_m values are given by the classical thermodynamic Tables (1). The evolution of the melting entropy as a function of the atomic number Z is presented in Figure 2. We note different periodic sequences, as well as for other properties of these elements (melting temperature, inter atomic distances in crystals, etc...) (2)

But the position of the maximum entropy values is here quite different: The melting entropy is the highest for C ($Z=6$) and Si ($Z=14$) in the second and third periods, then with Cl ($Z=17$)

, Br ($Z=35$), I ($Z=53$) just before the rare gas Ar ($Z=18$), Kr ($Z=36$), Xe ($Z=54$) at the limit of different periods;

For the classical metals, we have noticed the lower values for their melting entropy (between 5 and 10 J/mole) which are quite independent of their electronic configurations. On the contrary, for covalent elements, the results are in a gap of upper values (between 20 and 25 J/mole). These results are used in the next section for the binary eutectic systems without solubility in the solid state.

3- MELTING ENTROPY OF BINARY EUTECTIC SYSTEMS INSOLUBLE IN THE SOLID STATE

This binary eutectic group has been selected from the reference books by M. Hansen, M. Hansen and K. Anderko and F.A. Shunk, for each couple (3). The eutectic concentration CE is the lower point down for the two liquid solubility curves in the diagram, between the two melting temperatures T_{m1} , T_{m2} and TE (Figure 1). These two limit curves have no influence on the properties of the two solid state elements 1 and 2, except the position of CE on the isothermal eutectic line (TE).

We take the value CE coming from the experimental results obtained at atmospheric pressure, without discussion in a first time. This last point will be reviewed during the discussion and we take: $C_1 + C_2 = 100$ at. percent.

The position of TE will be discussed later with the influence of the nanostructure factor for eutectic alloys, more recently analysed.

Through the periodic Table, we find approximately between ten and fifteen examples, corresponding to Figure 1. In this group, we have included a limit case with the presence of a primary solid solution (Ge 32 – Ag 47 with 9.6 at.percent Ge) to control a possible solubility effect of Ge in Ag, or not, seen during the discussion.

This selected group is given below with, for each couple, their atomic numbers, as a marker.

Be (4) – Al (13) TE=918K 1103K	Be (4) – Si (14) TE=1363K	B (5) -Pt (78) TE =
Al (13)- Ge (32) TE=697K =1103K	Al (13)-Sn (50) TE=501K	Si (14) -Ag(47) TE
Si (14)-Au (79) TE=643K TE= 921K	Ga (31)-Sn(50) TE=293K	Ge (32) -Ag(47)
Ge (32)-Au (79) TE=620K TE=1708K	As (33)-Pb(82) TE=561K	Nb (41) -Th(90)
Ag (47) - Bi (83) TE=535K		Cd (48) – Bi (83) TE = 417 K

We recognize some systems obtained with metals and semi-conductors (Si, Ge) and we notice the famous Si-Au diagram, the first amorphous alloy discovered by Pol Duwez after a high speed cooling from the liquid state.

For this group, we have calculated the increasing entropy $\Delta S E (1+2)$, taking as a reference the self-melting entropy of each element 1 and 2 at T_{m1} and T_{m2} with the two concentrations $C1$ and Δ

$$\Delta S E (1+2) = (\Delta S1 / TE - \Delta S1 / T_{m1}) C1 + (\Delta S2 / TE - \Delta S2 / T_{m2}) C2$$

$$\Delta S E (1+2) = (\Delta H_{m1}/TE - \Delta H_{m1}/T_{m1}) C1 + (\Delta H_{m2}/TE - \Delta H_{m2}/T_{m2}) C2$$

with the condition: $C1+C2 = 100$ at per cent

Using the melting enthalpy and the melting temperature for each element, the eutectic temperature (at atmospheric pressure), we have obtained two groups with distinct values for $\Delta S E (1+2)$:

A first group, with a small increasing melting entropy ($\Delta S E \leq 3$ J/mole):

$$\text{Be (4) – Al (13) } \Delta S E = 0.7 \quad \text{Be (4) – Si (14) } \Delta S E = 2.8 \quad \text{Al (13) – Sn (50) } \Delta S E = 0.3$$

$$\text{Ga (31) – Sn (50) } \Delta S E = 1.1 \quad \text{Nb (41) -Th (80) } \Delta S E = 1.5 \quad \text{Ag (47) – Bi (83) } \Delta S E = 0.9$$

A second group is obtained with an higher increasing melting entropy ($\Delta S E \geq 3$ J/mole):

$$\text{B (5) – Pt (78) } \Delta S E = 15.3 \quad \text{Al (13) – Ge (32) } \Delta S E = 11.4 \quad \text{Si (14) – Ag (47) } \Delta S E = 3.4$$

Si (14) – Au (79) $\Delta S E=22$ Ge (32) – Ag(47) $\Delta S E = 4.7$ Ge (32) – Au (79) $\Delta S E=15.4$

Cd (48) – Bi (83) $\Delta S E = 5,2$ As (33) – Pb (82) $\Delta S E = 7.6$

As noted before, couples with semi-conductors and metals are observed in the two groups. We see also, like a numerical chain, diagrams crossing the all periodic Table, with the same topology, and only a single case with a very large gap between their Z numbers (Si (14) – Au (79), without other numerical relation with the periodic Table:

Be(4) – Si(14) ----- Si(14) – Ag(47) ----- Ag(47) – Bi (83)
 Al(13) – Ge(32)..... Ge(32) – Ag(47)..... Ag (47) – Bi(83)
 Si (14)..... Au (79)

To describe the increasing entropy at the eutectic temperature, we introduce the properties of each element in relation with the self-diffusion mechanisms in the two solid phases and solid defects.

4- INTERPRETATION AND DISCUSSION

We know the importance of defects (vacancies, dislocations, grain-boundaries, surfaces and interfaces, etc) on the melting mechanism, described a long time ago by D. Kuhlmann-Wilsdorf (4) and other authors by the diffusion processes (5) (6) (7) (8)

In particular, from a large set of experimental results, it has been shown, for grain boundaries and incoherent interfaces at the melting temperature, that the atomic diffusion coefficients are quite the same as in the liquid state, independently of the crystal structures. This fact concerns a wide number of elements. On the contrary, the bulk self-lattice diffusion results show the lowest diffusivities, with an order of two or three decades and higher activation energies.

Besides, in the temperature range between room and melting temperature T_m , different structural mechanisms are present for each element: surface diffusion at low temperatures, then grain boundaries or interface diffusion at medium temperatures and, at higher temperatures, only bulk diffusion: Applied to eutectic diagrams, the ratio T/T_m and the place of TE in the diagram are important factors to analyse the evolution of each couple according its topology (Figure 3). For instance, if this ratio is lower or equals 0,5, the grain boundary diffusion is widely present and for upper values, intergranular and bulk diffusion are acting at the same time.

We have applied this classical concept to the interfaces of the lamellar eutectic alloys, each interface between the two solid phases being considered as the place where the solid-liquid transition takes place by the diffusion processes, if TE is low compared to the melting points T_{m1} , T_{m2} .

To describe this effect on $\Delta S E$, we use the parameter $P = T_E / T_{m1} + T_E / T_{m2}$ (unitless number) which takes into account the cumulative diffusion effects of the two elements at the nano scale.

If $P \leq 1$ (with small values of T_E / T_m for 1 or 2, the diffusion process will be dependent on defects with the disorder created in all the interfaces 1-2 at T_E).

If $P \approx 1.3-1.5$ (with intermediate values of T_E/T_m for 1 and 2, the diffusion processes will be combined (by the interfaces and the bulk disorder)

If P is near the limit 2, the process will be only like a bulk process, with vacancies and other defects created at that time, for example by a nano Kirkendal effect between the two elements through the interfaces (with crystals relaxation and a low increasing entropy $\Delta S E$).

Figure 4 gives the results obtained with the different systems seen before:

$$\Delta S E (1+2) = f (T E / T_{m1} + T E / T_{m2})$$

We recognize the two series, with lower and higher values for $\Delta S E (1+2)$ when P is decreasing to 0.85 (with Si(14)-Au(79)) : 22 J/mole at T_E). This increasing evolution of $\Delta S E$ for the second group is quasi linear and the slope value is 26 J/mole (approximately: 3 R or 3kN).

In a general way, this result shows that the entropy gain associated with the melting of such eutectic binary structures should be characterized by a high degree of defects during the isothermal solid \rightarrow liquid transformation, beginning in the incoherent zones (with the classical amorphous structure) like a liquid, predicted a long time ago by authors, like Spaepen (9). We can mention here the work of Shechtman and al. (10) on the entectic binary Ag-Cu system, showing by TEM a high density of dislocations in bands structures for the eutectic composition obtained after a rapid solidification velocity.

Another question concerns the theoretical problem of nanophase eutectic alloys, compared to the bulk classical diagrams: In the case of the Ge-Au system, which has been studied and used to elaborate semiconductor nanowires of Ge, Lu and Meng (11) have developed an unified model to describe the dimensionality dependent equilibrium phase diagram, with a new shape for liquidus curves and the position of CE at the eutectic temperature. This model shows that the value of CE is not influenced at the nanoscale level, but the eutectic temperature is lowered ($\Delta T = -45$ K), compared to the bulk classical diagram. In Figure 4, this influence shall give a better position of $\Delta S E (1+2)$ for Ge-Au system on the computed straight line.

The question is also to consider the diffusion processes with a new dimensionality concept of the interfaces and grain boundaries, just at the solid-liquid transition. Some past results obtained on this subject, correlated with the fractal dimension for the grain boundaries diffusion, could be used at the melting point T_E , giving a quasi-fractal tridimensional process (12) (13) (14) in which the geometrical distortions for icosahedral structures, or others, should be possible.

This dynamic role of atomic diffusion processes for the two elements at T_E should have an impact to generate new transient structures, like quasi-amorphous or quasi-crystals, by a higher entropic effect during the melting transformation of binary eutectic structures, without bulk solubility.

In the end, the transient new semi-solid structures embedded within the residual initial crystals 1 and 2, before the final liquid phase, should involve the presence of a degenerated zone, including tie-triangles in the topological diagram, as proposed by Palatnik and Landau and analysed by Prince in 1963 (15). For this case, Gibbs rule is to be reviewed (16).

5- CONCLUSION

Using the classical thermodynamic relations for binary diagrams obtained with different elements of the periodic Table, we have focalized on the typical case of eutectic structures obtained with insoluble elements in the solid state and analysed the entropy of these alloys at their melting temperature.

We have noticed a group of binary couples in which the entropy during the melting process seems in relation with the presence of transient phases between the initial lamellar solid state eutectic structure and the final liquid state. It should be interesting to confirm these remarks by a structural comparison between different cases, for example Si-Au / Si-Ag, or Ge-Au / Ge-Ag at a nanoscale level, to note the new possible appearing phases during this solid→liquid transition.

At the end, we recall the linear relationship between the entropy gain and the ratio TE / T_m , with a factor like the higher heat capacity value in the Einstein theory for solids (3kN) (17) for some binary systems: Accordingly this result, the vibration frequencies of the two elements should be interesting to measure, giving so the correct eutectic melting process.

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KEYWORDS: binary eutectic alloys, melting entropy, diffusion mechanisms, interfaces grain-boundaries, solid-liquid transition, high-entropy alloys., amorphous clusters, quasi-crystals, nanoeutectic alloys.

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FIGURES:

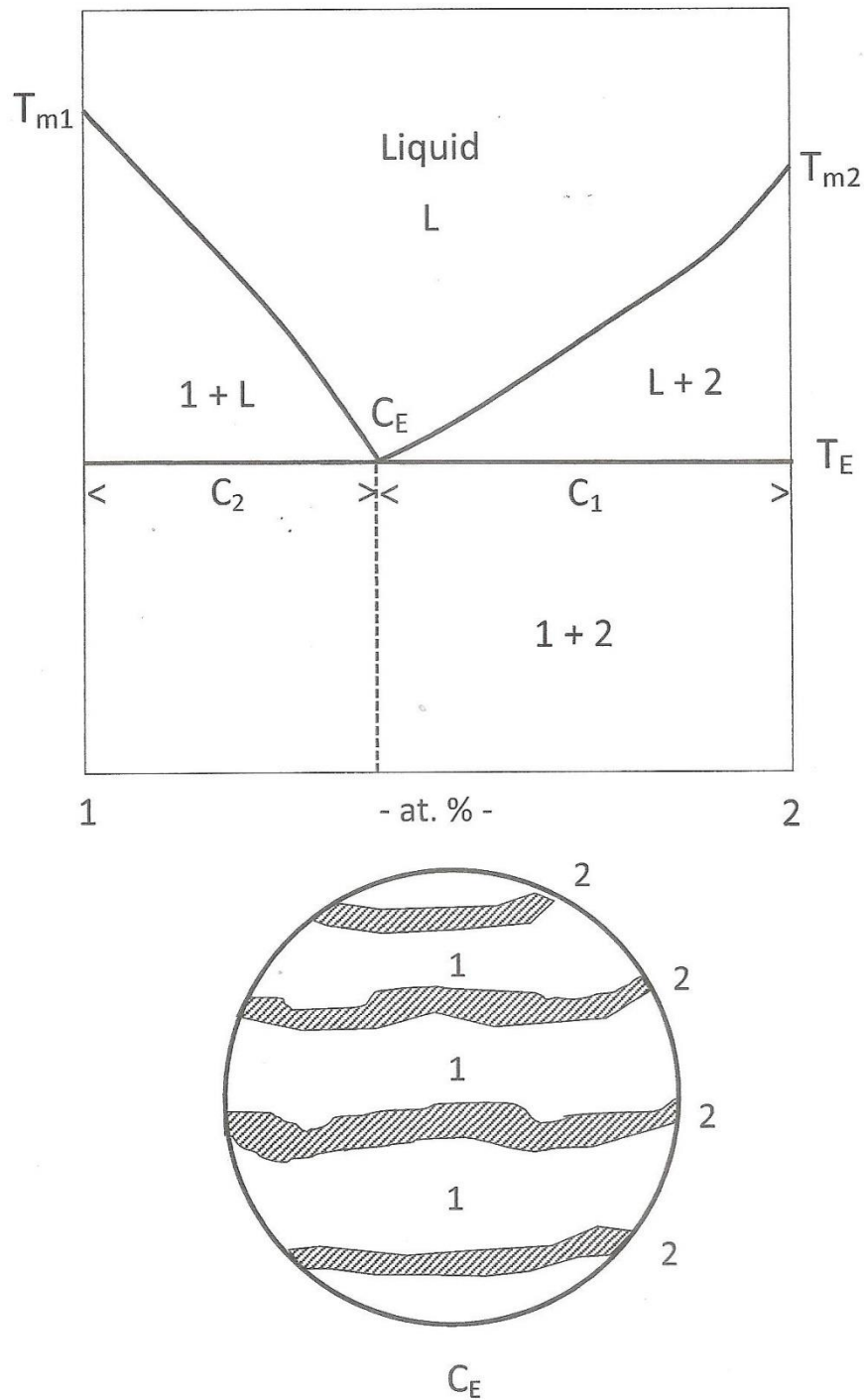


Figure 1

Fig. 1: Schematic representation of a simple binary eutectic system, without solubility in the solid state and with only an eutectic alloy CE: The lamellar optical microstructure ($\approx \times 500$) is given here for the two phases 1 and 2 in a quasi-equilibrium state after low cooling speed from the liquid state (and without impurities), like a Turing structure morphology.

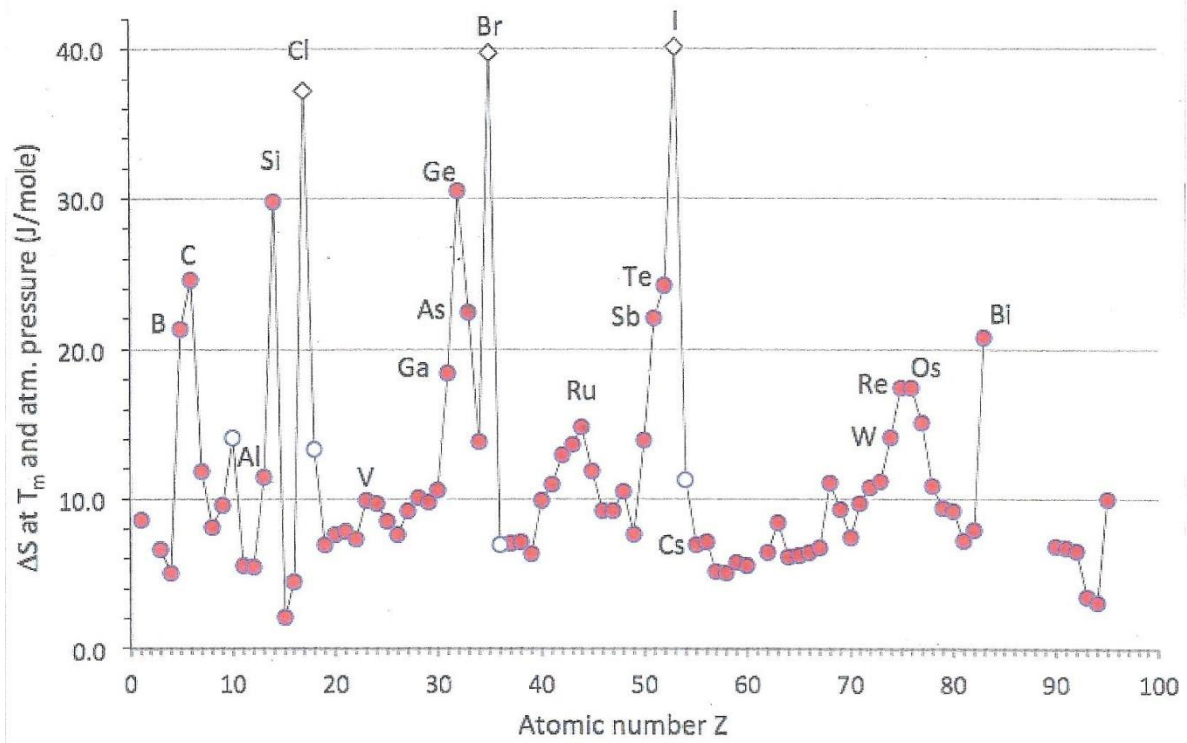


Figure 2

Fig.2: Evolution of the melting entropy ΔS_m at T_m with the atomic number Z (J/mole) at the atmospheric pressure.

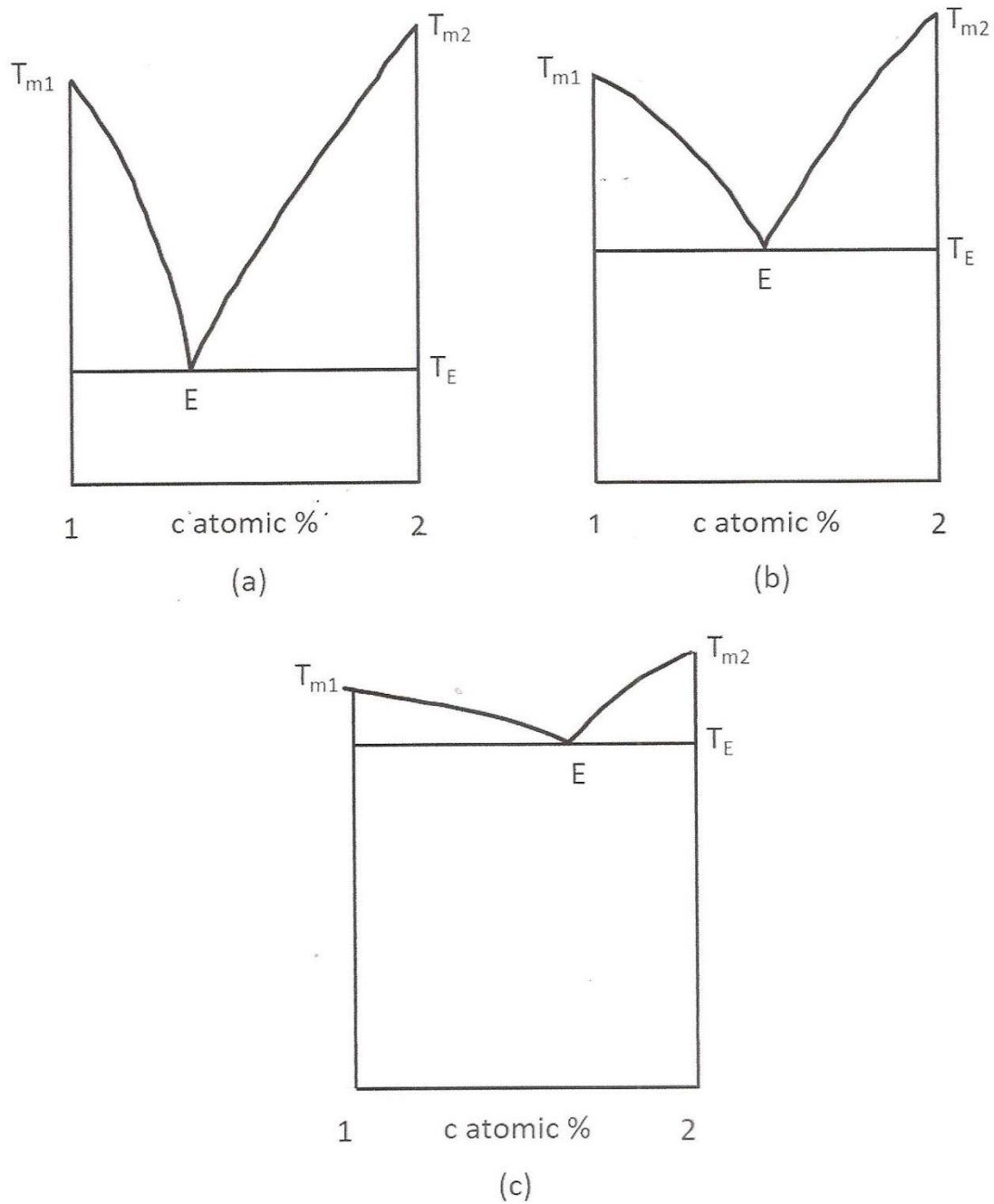


Figure 3

Fig.3: Binary eutectic alloys of the same group with different eutectic temperatures T_E compared to T_{m1} , T_{m2} and for different positions of CE:

a- Lower T_E : Interfacial diffusion: T_E/T_{m1} and $T_E/T_{m2} = 0.4 - 0.5$

b- Medium T_E : Interfacial and bulk diffusion: T_E/T_{m1} and $T_E/T_{m2} = 0.6 - 0.7$

c- Higher T_E : Only bulk diffusion: T_E/T_{m1} and $T_E/T_{m2} = 0.8 - 0.9$

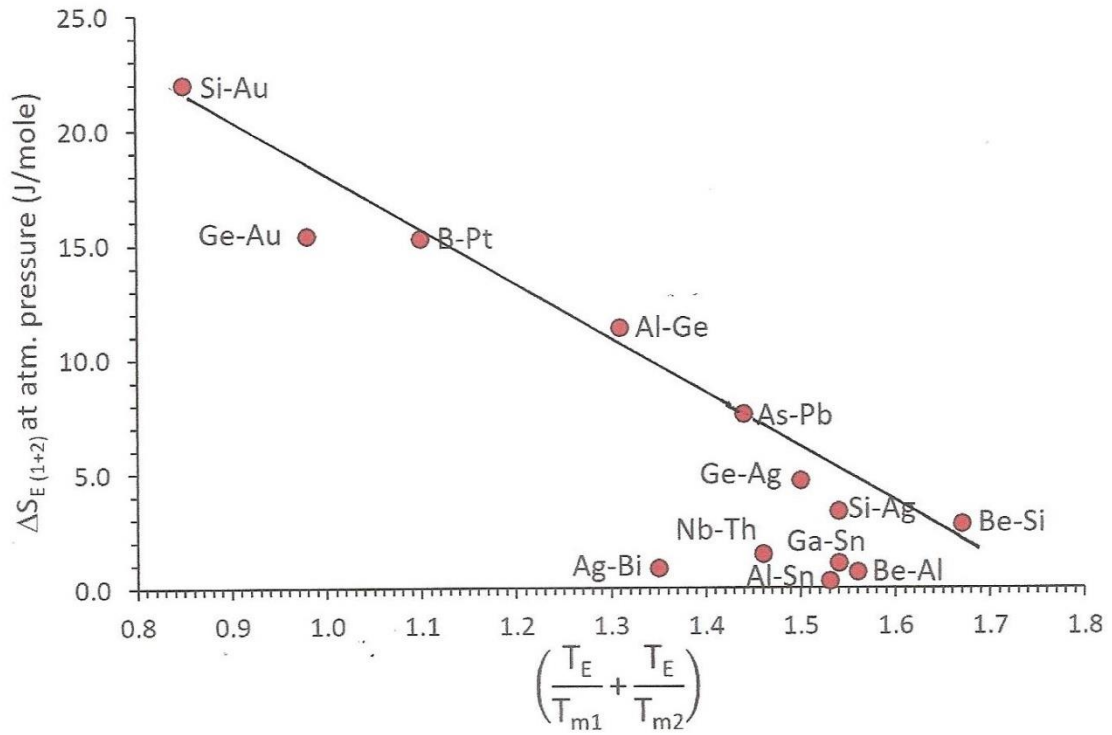


Figure 4

Fig.4: Increasing entropy $\Delta S E (1+2)$ obtained at the eutectic temperature during the transformation solid \rightarrow liquid as a function of the numerical factor $\left(\frac{T_E}{T_{m1}} + \frac{T_E}{T_{m2}}\right)$ for the two groups of binary alloys.