DIFFUTOR©

DATA BANKS OF DIFFUSION KINETICS

VOLUME 1 : THERMALLY DRIVEN DIFFUSION IN PURE METALS

code : DIFFUTOR–01©

GDF DATABANKS BULLETIN , VOL. 2 , No. 3 (1998)

***Each chapter has the same structure ;**
FOM = Figure of Merit of diffusion experiments ;
see for details in : **GDF DATA BANKS BULLETIN ,VOL.3,No.1 (1999)**

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DIFFUTOR©-01

Databanks of Diffusion Kinetics in Pure Metals

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1. Diffusion – a basic process revealing materials' structure

Behaviour-structure relationship is an essential problem of technology, because the composition of a material cannot univocally define its behaviour in practical processing and/or operating conditions. This assumption is the basic purpose of GDF databanks created on the UNIVERSAL topoenergetic working principles [1].

UNIVERSAL procedure consists both in specific standard experiments in which a process is triggered and the retrieval of experimental from which three independent parameters formerly result, generically denoted as (N,M,Uo) having also UNIVERSAL assignments [1-4] and univocally defining the transforming process. These parameters give a considerably quitecence of the relationship between behaviour and structure of the tested sample.

DIFFUTOR© is a databank series based on diffusion process in materials and driven by different potentials.

DIFFUTOR©-01 is a databanks series belonging from **DIFFUTOR©** where the diffusion processes are thermally driven.

Diffusion process represents the mass transport of a suitably chosen diffusing element (DE) along a single direction through the tested material considered as host lattice (HL), so that a single experiment is driven only by the gradient of DE concentration. Experimental conditions are established in view the diffusion process does not involve pair interactions of DE. If DE is even the atomic, molecular or supermolecular species specific to HL, the diffusion process is called as self-diffusion. Self-diffusion process has correct meaning only for pure HL, i.e. where only one atomic, molecular or supermolecular species exists.

The driving potential defining databank's pattern represents the independent quantity, generally denoted by U, depending on which the series of identical experiments are repeated for the same tested sample. This represents a basic operating principle of the UNIVERSAL topoenergetic procedure.

Standard experimental procedures are essential in view to obtain accurate topoenergetic parameters with small experimental uncertainties and high phylogenies [1-4] representing highly efficient databanks.

This first volume of DIFFUTOR©-01 opens the DIFFUTOR© series by using classical and heterogeneous experimental data from a rich literature dealing with diffusion in pure metals. The experimental data obtained on so-called pure materials evidenced according to our experience that are not so dependent on standard procedure when the same eigenvalue is measured. Big differences appear for complex materials with many components and/or complex processing/operating conditions. This opening represents the first step to standardize in the next future experimental procedures for practical purpose of more complex materials, but considering these databanks as a reference one. There are many processes diffusion based and we can mention some of most known:

- Mechanical and dielectric losses;
- Chromatographic techniques;
- Phase transitions;
- Electrophoresis ;
- Sedimentation;

but, we can observe that all transforming processes based on component/phase separation are mainly based on diffusion. Data on vapor-liquid equilibria (VLE) express just the vapor-liquid separation process [3,4]. It is possible to standardize on of such measuring system in view to establish and create databanks for diffusion behaviour. In our previous comments on VLE experimental techniques have observed that most of them are useless sophisticated, but without considering topoenergetic requirements.

Classical non-equiilibrium thermodynamics evidenced in qualitative terms that in a general measuring system many elementary processes may contribute, but in specific proportions [5,6].

Topoenergetic theory of composite systems' behaviour gradually developed by energy circuit of a complex measuring system contains the contributions of elementary branches of transformation [7-14].

It is important to mention here that for temperature (thermally) driven processes expressed in Arrhenius representation these contributions appear as additive rule for activation energy [9], but taking into account the algebraic sign directly connected with the process polarity defined also by topoenergetic principles [10].

There is one important aspect of databanks including Arrhenius parameters also mentioned in many of the previous studies: complex processes of complex samples can be decomposed in simple contributions of reference samples.

UNIVERSAL parameters have higher advantages and we must mention at least two of them, namely:

a. UNIVERSAL representation can be applied for any kind of measuring system driven by any kind of potential, but considering the topoenergetic requirements [11];
b. Based on pyramidal structure of these UNIVERSAL parameters, it is possible to univocally identify the nature and the amplitude both of the overall tested sample and of the contributing elementary processes [7-9,12-14].

2. Short description of DIFFUTOR©-01 databanks

The first volume of this series is devoted exclusively to self diffusion and (hetero) diffusion in pure metals. The annexed advertisement gives the main chapters of this volume. Each chapter is devoted mostly for one or a small group of pure metals. The first chapter gathers data for self-diffusion in all pure metals.
Self- and hetero- diffusion data are presented in four groups, namely:

a. databanks with the first UNIVERSAL and Arrhenius parameters and their associated experimental uncertainties estimated by linear regression according to the constitutive eqns [3,15,16]. Some additional data regarding the experimental procedures are given by: DE, temperature range over which the experiments are extended on, number of experiments (m) and the references from which the BED are taken from. As a typical example Table 1 (taken from the original Table 7.1) reproduces these data for diffusion in pure Ca.
b. The figures of merit (FOM) of diffusion experiments as resulted in UNIVERSAL and Arrhenius representations. These figures reveal the quality of experimental data more suggestively than correlation coefficients given in group a. For more details concerning the physical significance of FOM see references [15,16]. As a typical example Table 2 (taken from the original Table 7.3) gives these values for the diffusion experiments also in pure Ca.
c. BED considered and retrieved according to UNIVERSAL and Arrhenius eqns are also given. Table 3 (taken from the original Table 7.2) reproduces BED collected from literature for pure Ca.
d. In view to evidence the phylogeny of diffusion behaviour for each HL the graphic representations are given by considering the following main first phylogenies:

$$N = n1*M + m1 \qquad (2.1)$$
$$-N^2/M = ncs*M + mcs \qquad (2.2)$$
$$To = nfp*M + mfp \qquad (2.3)$$

$$E = n1A*\ln(Do) + m1A \qquad (2.4).$$

The physical significances of all these parameters are explained in all previous cited studies (see for instance [3,4]), but taken again shortly below for this particular case. Figures 1 (13.1), 13.2 and 2 (13.3) (these are graphs in chapter 13 from the original brochure of **DIFFUTOR©-01**) present some of above phylogenies for self- and hetero- diffusion in pure Nb. While the first phylogenies of type (2.1) and (2.2) exist for all types of HL and diffusion experiments, phylogenies of (2.3) and (2.4) types are in some cases broken like in Figure 2. Their explanation consists in above mentioned comments and considering also the physical significances of To [3,4] and E [7-10].

3. Upon some topoenergetic aspects

Even in highly accurate experimental conditions for pure diffusion processes, there are many elementary processes contributing to the final data. We try to reveal some of them.

According to an extensive and intensive experience, the calorimetric image of an experiment can evidence many details about it. In Figure 3 thermograms obtained in isothermal conditions for a sample in which an ideal diffusion process occurs is represented. His is similar to a melting process in a crystalline material (To=the melting/freezing point) [10]. The figure caption gives also the significances of the parameters.

The structural image of this process is given in Figure 4, where the inert, Cin, and the transforming, Ctr, components in diffusion process contain parts both from HL and DE. This image allows to us immediately remember the diffusion process in chromatographic techniques which will be a next topic of our discussions.

All pure metals considered in these databanks are highly crystalline, even as single crystals. Self- and hetero- diffusion take place mainly in the amorphous and/or local amorphous domains (see the series on the amorphous-crystalline coupling [9-14]. These amorphous domains consist in a more or less broad spectrum of behaviours, so each kind gives a specific contribution to the overall values. For instance, To is consistent with the melting point of intercrystalline ordered amorphous domains and also correlates with melting point of crystalline domains. Shortly, we may assert that the HL morphology has a specific porous structure developed by the overall diffusion process.

In view to evidence this important structural aspect of these databanks, we may select the suggestive case of aluminium. Its known porous structure significantly changes by adding small amounts of allying components.

The first phylogenic parameter m1 as a function of the mass of the crystalline unit cell of HL, Muc, is represented in Figure 5 for almost pure metals as HL including also a large series of Al-alloys with a good phylogeny of type (2.1). Muc is calculated according to the structure of the crystalline unit cell [17]. For instance, the symmetry of the unit cell of pure Al is K2 with 4 atoms, so ln(Muc(Al)) = ln(4*26.98) = 4.6814 considered the same for Al-alloys. According to the structural image given in Figure 4, it results that Cin = (structural factor)*Muc, where the structural factor defines the porosity of HL.

Many pure metals group themselves along a straight line showing a direct relationship between m1 and ln(Muc) considered as a reference behaviour. HL placed above to this line shows a more porous morphology, while the ones placed below it, shows a more compact morphology.

It is important to note, by considering the drawn given in Figure 4, that by increasing the sample porosity, Ctr decreases and subsequently interaction between HL and DE decreases.

Figure 6 shows the specific relationship between standard coupling strength (CS), mcs, as a function of ln(Muc). We must remember that CS means the strength of the interaction between Ctr and Cin. In other words, this represents the coupling between the crystalline (Cin) and intercrystalline amorphous domains participating to the diffusion process (Ctr).

Figure 7 shows the relationship between standard freezing point, mfp, and melting point of crystalline phase in HL. A good linear relationship results, although mfp characterizes the intercrystalline ordered amorphous domains (denoted in previous studies as T^1_m [9-14]).

4. Concluding remarks

4.1. **DIFFUTOR©-01** databank for pure metals represents reference data for any next data obtained for any more complex material obtained in other standard operating procedure.

4.2. The quality of a databank characterized by its pyramidal structure (high phylogenies and small uncertainties) results only for BED as obtained in the same measuring system (including also the same standard operating procedure).

4.3. Calorimetric methods have some major advantages, namely they are rapid, sensitive, available for any kind of samples and transforming process, allow to separate in accurate conditions the inert and transforming components, clearly show the process polarity. Visco/Dens Calorimeter (VDC-4) has specific softwares for such calorimetric measurements.

5. References

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Table 1. Typical results obtained in UNIVERSAL and Arrhenius representations for thermally driven experiments; eigenvalue (θ) = D (isothermal diffusion coefficient in m^2/s); the driving potential (U) = temperature (in Kelvin); host lattice = Ca.

No.	DIFFUSING ELEMENT	TEMP. RANGE (K)	NO. OF EXPTS. m	REF.	UNIVERSAL				ARRHENIUS			
					N u(N)	-M u(M)	To u(To)	correl	E u(E)	LnDo u(nDo)	Do u(Do)	correl
1	C 14	773 1023	12	95	1.268 0.002	35 2	754 71	0.882	76 2	-19 2	6.9E-09 1.8E-08	0.850
2	Fe 59	823 1073	12	10	8.8818 0.0005	91.1 0.5	411 17	0.996	123 4	-19.7 0.6	3.1E-09 1.5E-09	0.996
3	Ni 63	823 1073	12	10	7.3128 0.0006	79.4 0.6	495 22	0.993	121 5	-19.4 0.6	4.0E-09 1.5E-09	0.993
4	U 236	773 973	10	10	7.6395 0.0006	82.3 0.6	547 16	0.997	151 4	-17.4 0.6	2.9E-08 1.7E-08	0.997

REF = cited reference for basic experimental data (not available in this presentation);
UNIVERSAL representation according to the constitutive eqn: $\mathbf{\ln D = N * \ln(T - To) + M}$ (1),
To = the freezing point below which the diffusion process changes its nature;
E = the activation energy (in kJ/mol);
R = the gas constant;
u(A) = the experimental uncertainty of quantity A estimated according to the procedures previously described [2-4];
correl = correlation coefficient of the linear regression according to the constitutive eqns.

Table 2. Figures of merit (FOM) of diffusion experiments associated with UNIVERSAL and Arrhenius representations (HL : Ca).

No.	DE	REF.	v = m-1 n = 1	UNIVERSAL FOM(N) 1/(v*u(N))	ARRHENIUS FOM(E) 100/(v*u(E))
1	C 14	95	11	45	0.61
2	Fe 59	10	11	182	2.46
3	Ni 63	10	11	152	1.96
4	U 236	10	9	185	2.78

Table 3. Basic experimental data (BED) for thermally driven diffusion in pure Ca : T = temperature (K); D = bulk diffusion (m^2/s) (all values are given in scientific format with three decimal figures); the diffusion system of HL/DE and the references of BED are explicated in the top of the Table.

Ca/C 14	95	Ca/Ni 63	10	Ca/Fe 59	10	Ca/U 235	10
T	D	T	D	T	D	T	D
773	4.20E-14	823	1.00E-16	823	5.00E-17	773	2.00E-18
773	3.10E-14	833	7.90E-17	823	4.00E-17	773	1.48E-18
823	1.20E-13	873	2.62E-16	873	1.55E-16	823	8.50E-18
823	8.50E-13	873	2.10E-16	873	1.35E-16	823	6.60E-18
873	2.10E-13	923	7.20E-16	923	3.45E-16	873	3.00E-17
873	1.70E-13	923	6.00E-16	923	3.10E-16	873	2.50E-17
923	4.30E-13	973	1.35E-15	973	7.80E-16	923	1.00E-16
923	3.50E-13	973	1.20E-15	973	7.20E-16	923	7.90E-17
973	8.50E-13	1023	2.35E-15	1023	1.40E-15	973	2.25E-16
973	7.80E-13	1023	2.00E-15	1023	1.20E-15	973	1.85E-16
1023	8.50E-13	1073	6.40E-15	1073	4.00E-15		
1023	1.10E-12	1073	5.30E-15	1073	3.20E-15		

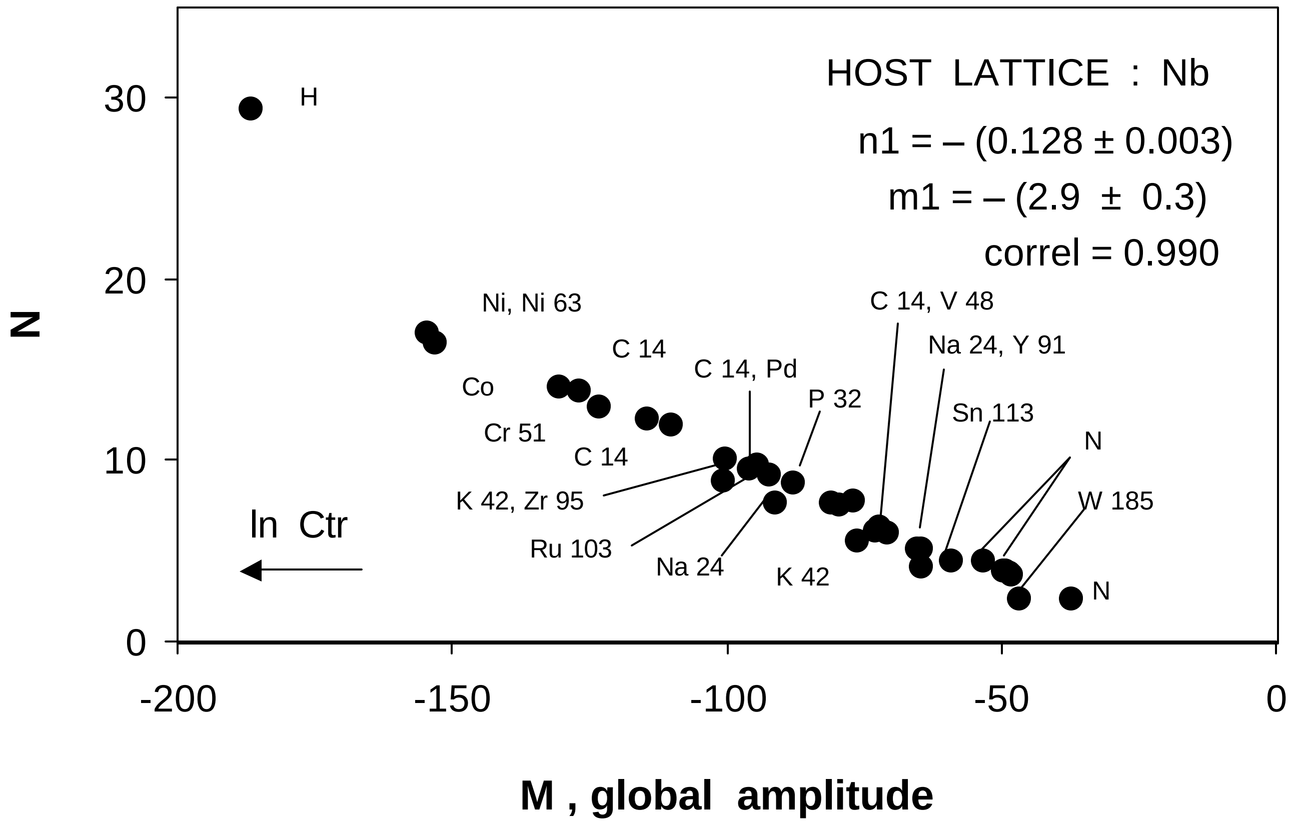

Figure 1. First phylogeny for thermally driven diffusion in pure Nb as HL.

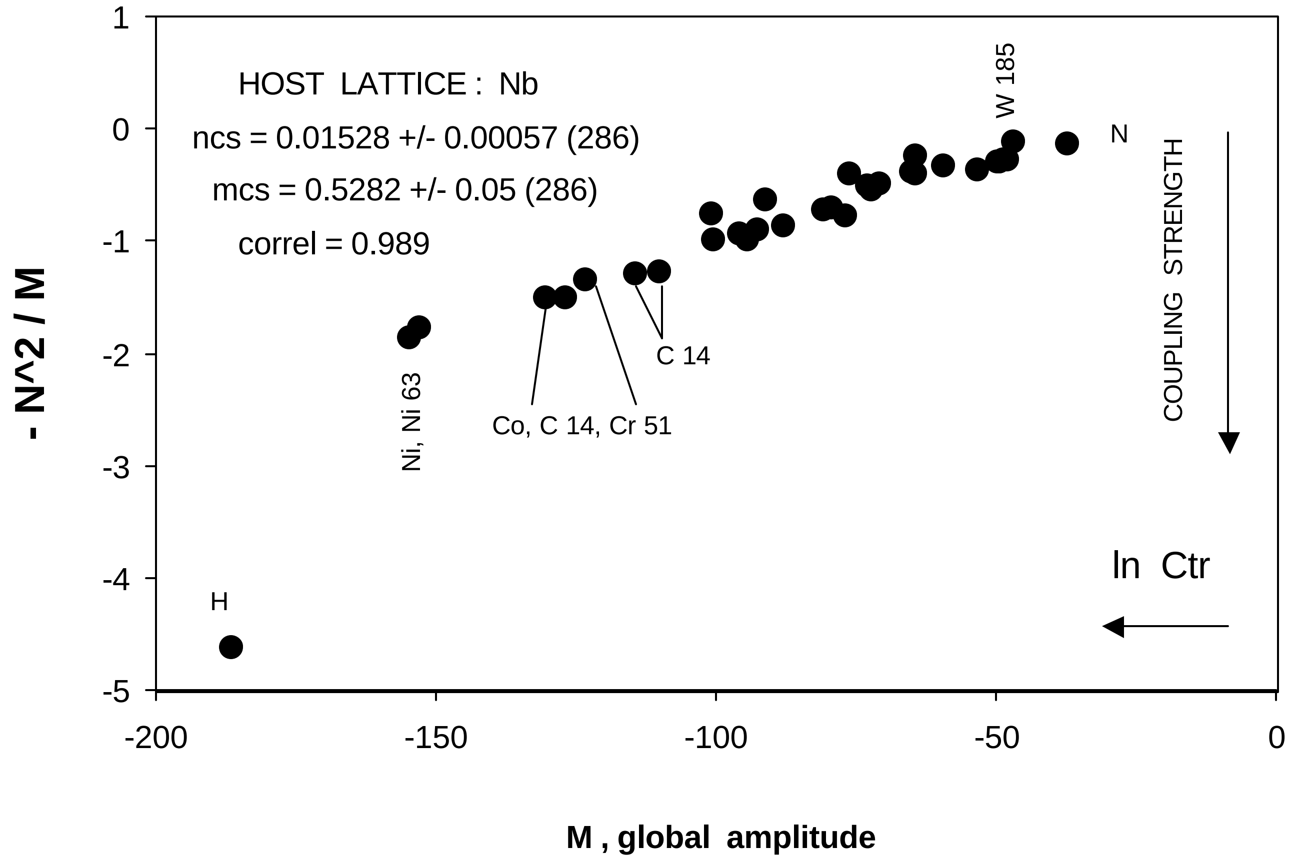

Figure 13.2. Phylogeny of the coupling strength for thermally driven diffusion in pure Nb as HL.

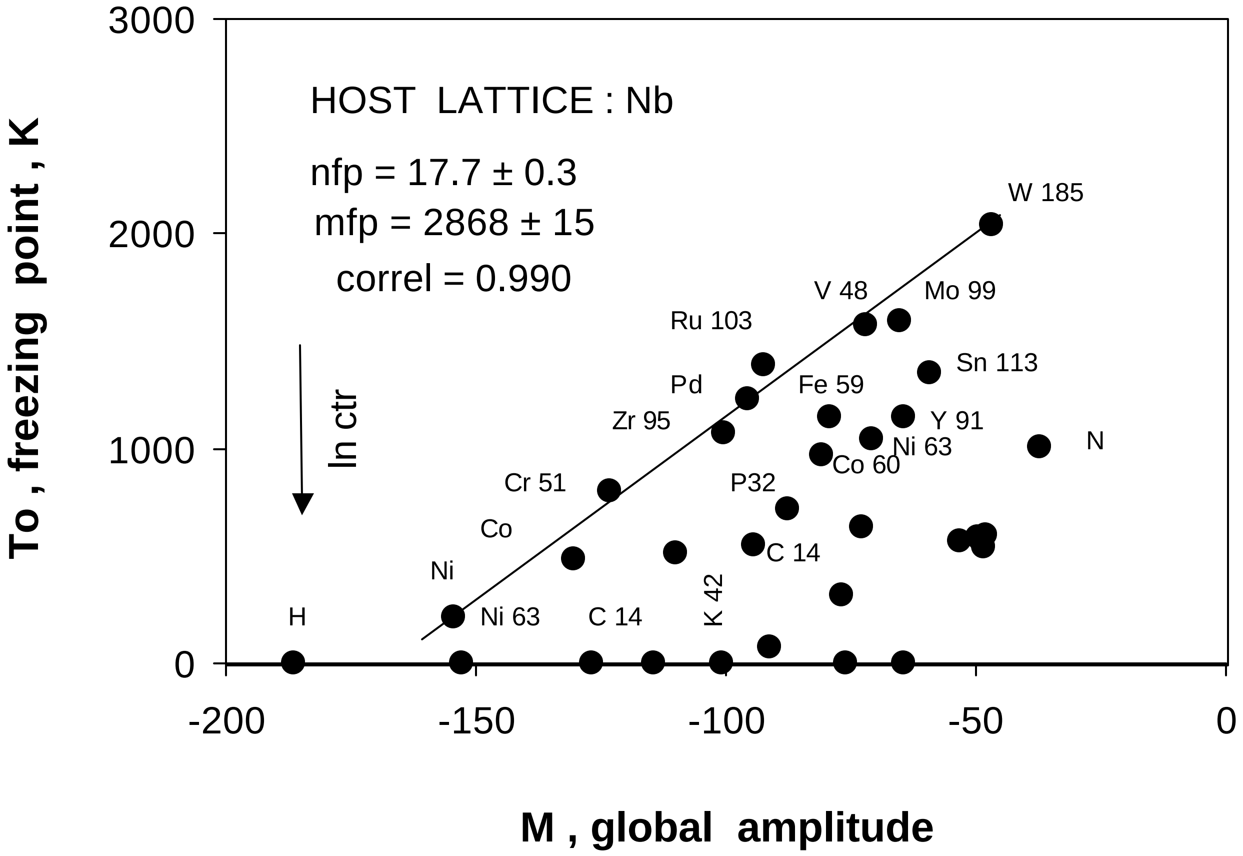

Figure 2. Phylogeny of freezing point for thermally driven diffusion in pure Nb as HL.

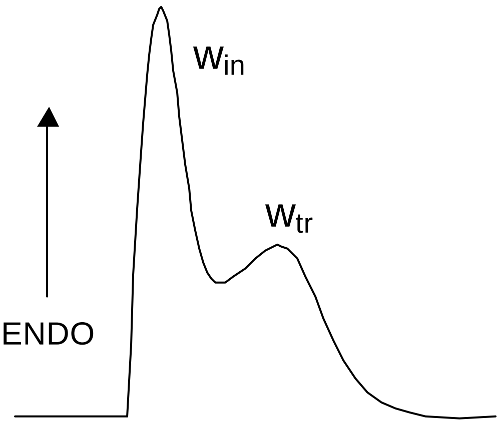

Figure 3. Calorimetric representation of temperature driven diffusion process. The test specimen is transferred from an initial temperature T1 < To to a final temperature T2 > To (To is the freezing point below which the diffusion is practically inhibited).

θ = D [m^2/s];

U = T [K];

N > 0, n1 <0, P+

Sign(win*wtr) > 0, (win, wtr) ENDO

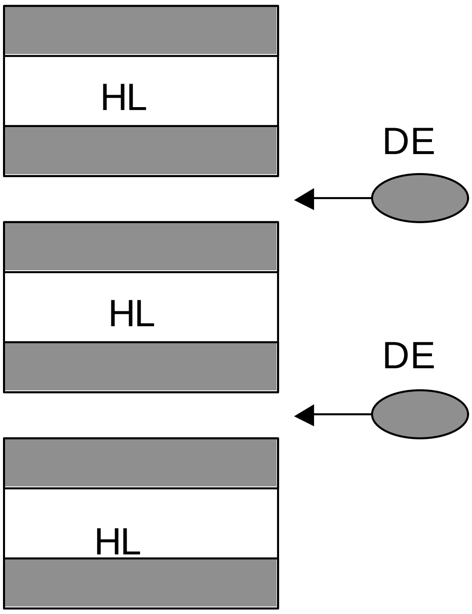

Figure 4. Structural drawn in topoenergetic terms of the diffusion process of diffusing element (DE) through the host lattice (HL).

☐ Cin, the inert component

▨ Ctr, the transforming component

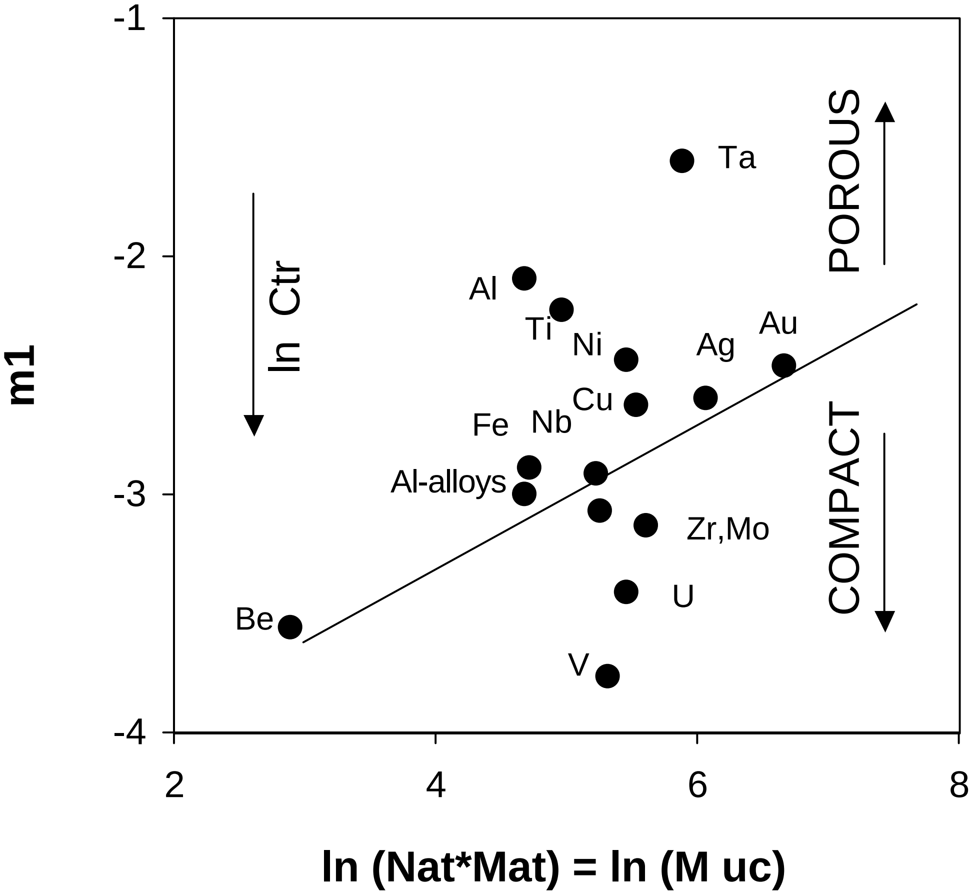

Figure 5. Dependence of standard phylogenic amplitude of diffusion process over several pure metals as HL as a function of the estimated inert component.

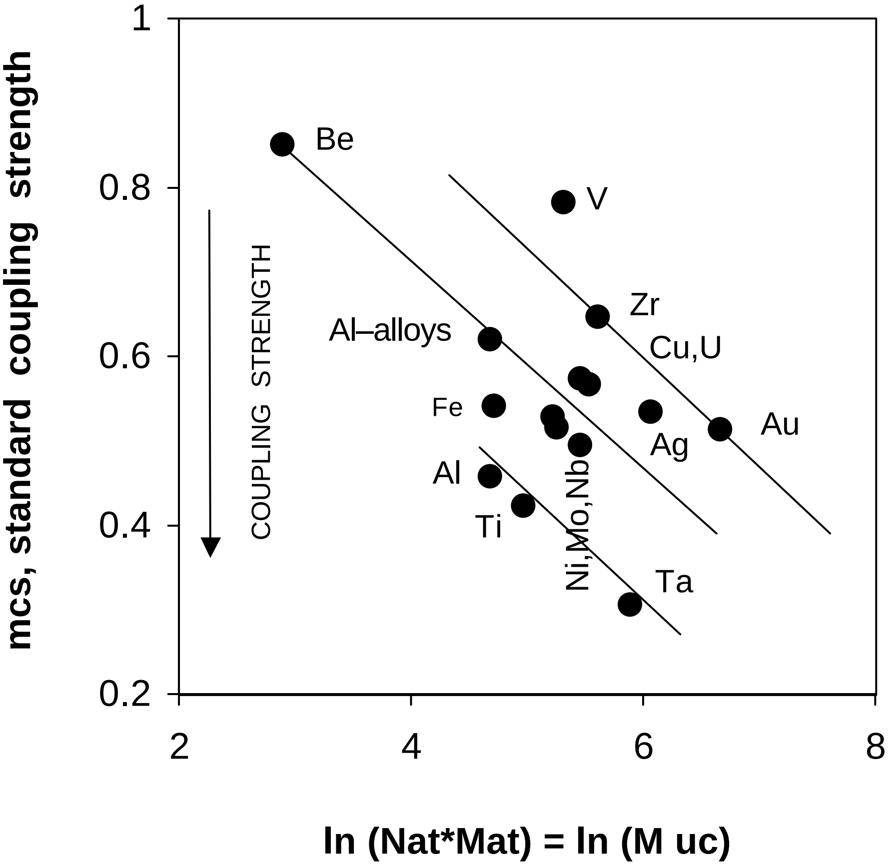

Figure 6. Dependence of phylogenic coupling strength for several pure metals as HL as a function of Cin .

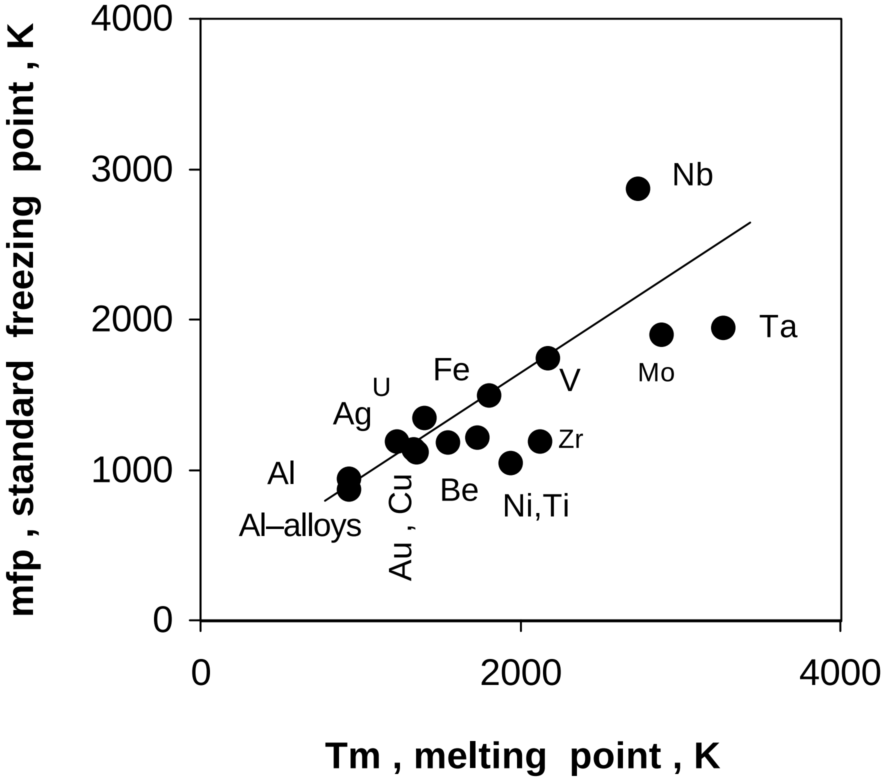

Figure 7. Dependence of standard freezing point defined over several series of pure metals as HL as a function of melting point of crystalline phase.