

The mutual alloying behaviour of the later transition and early B sub-group elements

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A graphical method of plotting the compositions of families of compounds is used in investigations into the pattern of incidence of chlorides, oxides, aluminides etc, of the elements. In many instances the points representing compounds lie on hyperbolae either of normal valency or golden ratio type, and the significance of this is discussed with special reference to the compounds of the later transition and early B sub-group elements and the hypothesis that a particular type of combination is present. Another feature of the discussion relates to the variation of atomic/ionic radii, ionization energies, valencies, d-band occupation, and lattice distortion in solid solutions in the relevant part of the Periodic Table.

1. Introduction

Graphical methods often provide an elegant way of summarizing data and of revealing formal patterns in what may otherwise be a confusing mass of detail. In this paper, a particular method of plotting the compositions of binary compounds is developed, into which one may read implications regarding the underlying chemistry. The principle may be understood by reference to Fig. 1. The right-hand edge or ordinate stands for a series of elements whose pattern of compound formation we wish to analyse, in this instance the first elements in the First Long Period, and the left-hand edge represents a constant element, chlorine, so that we are here concerned with the family of chlorides. Chlorine content increases from right to left along tie-lines parallel to the abscissa, so that when we come to represent compounds, potassium chloride will be represented by a point midway between the ordinates, calcium chloride by a point on the appropriate tie-line defined by intercepts in the ratio 1:2, and so on. It will be readily seen that the points representing KCl, CaCl₂, etc, lie on a hyperbola, and conversely the drawing of a hyperbola is usually a test for the existence of a family of compounds of normal valency. In the following discussion, this property of such synoptic diagrams

is utilized in an unravelling of the mutual alloying behaviour of the later transition and early B sub-group elements. The use of this type of diagram is, however, likely to be of value in many situations,

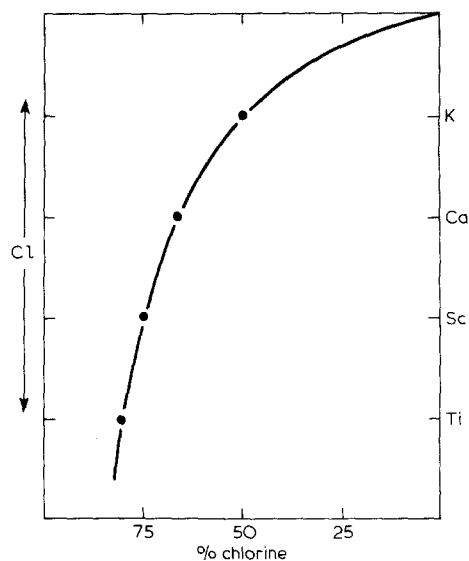


Figure 1 A diagrammatic representation of the chlorides of the elements at the beginning of the First Long Period, showing a characteristic hyperbola of normal valency. The left-hand ordinate stands for chlorine throughout; chlorine content increases from right to left. Each chloride is represented by a dot.

as for example in comparing solubilities in families of alloys, and the assessment of the probability of incidence in an unknown system of any given phenomenon. The procedure will be first to discuss the application of the diagrams to the incidence of oxides of the elements, secondly the application to the part of the Periodic Table

under discussion, and thirdly to relate an essential feature of the latter, which is revealed in the diagrams, to properties such as atomic/ionic radii, ionisation energies, valencies, d-band occupation, and lattice distortion in solid solutions. It is necessary to remind the reader on a point of terminology, namely, the notion of a divide [1-4]. A divide is a hypothetical line in the Periodic Table across which families of compounds form; for example, in alkali and alkali-earth salts (e.g. KCl, CaF₂) the components come from opposite sides of an ionic divide vertically through the noble gases, whereas GaAs is an example of an adamantine compound whose components lie on either side of a covalent divide which runs through group IV → IVB. At least one other divide (the composite divide) may be identified; this runs vertically between Cu/Zn and Ag/Cd, and is referred to in the following text.

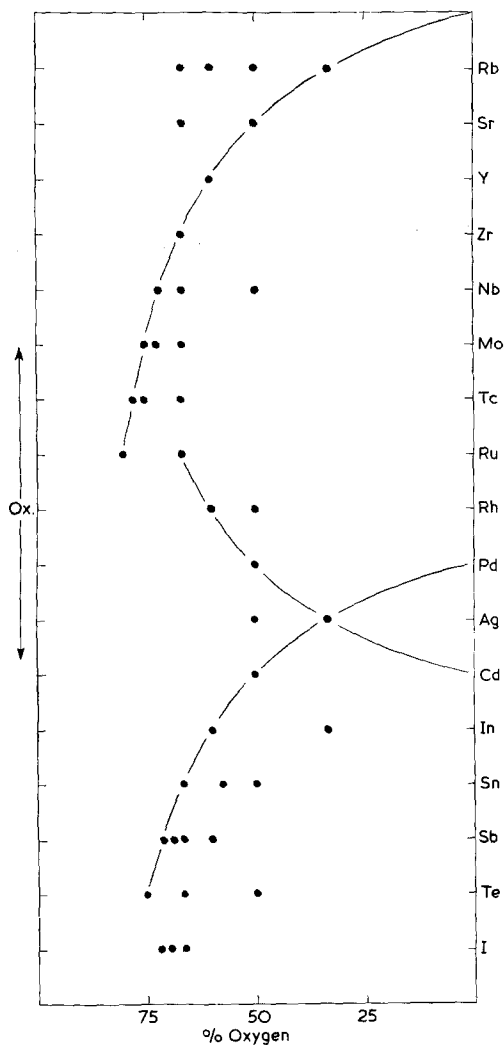


Figure 2 Summary diagram of the same type as Fig. 1 indicating how the points representing oxides of the elements from Rb to Te lie on well-defined hyperbolae. Notes (1) For clarity, two oxides of compositions between MoO₂ and MoO₃ [14] have been omitted. (2) Maximum heat of formation per g/atom [15] occurs approximately along a line expressed by $O/M \approx 2$ for metals of the second and third transition series, but at the equiatomic ratio for the First Long Period. (3) A line of p-n neutrality in the First Long Period [16, 17] falls between the hyperbolae and the heat of formation line (i.e. a compromise between the thermal and the valency or integral requirements).

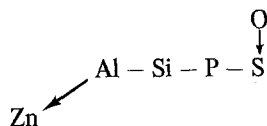
2. Valency hyperbolae

We may begin by plotting extended diagrams of the above type, and Fig. 2 illustrates a section out of a complete strip representing all oxides. Many of the points representing compounds lie on one of several hyperbolae, hyperbolae of normal valency, as noted previously. That beginning at krypton is a typical example. It runs to ruthenium, in conformity with the tendency for maximum valency to be shown in some compounds of ruthenium and osmium, after which a break occurs. A hyperbola of negative valency runs from RuO₂ (or MoO₃), continuing to Ag₂O and meeting the ordinate at cadmium. The oxide Ag₂O also lies on another hyperbola which runs to Sb₂O₅ and TeO₃. A summary of well-marked hyperbolae of positive and negative valency for elements up to the end of the Third Long Period is given in Table I; note that there is no distinct hyperbola of negative valency at the end of the first transition series. This kind of exercise with synoptic diagrams may be repeated with alternative, common

TABLE I Valency hyperbolae for oxides

	Positive valency	Negative valency
Short period,		
First	He to C (or N)	
Second	Ne to Cl. Also Mg to S	
Long period,		
First	A to Cr. Also Ni to Se	
Second	Kr to Ru. Also Pd to Te and Cd to I	Cd to Mo
Third	Xe to Os. Also Hg to Po	Pb to Re

(in the sense of constant) components, of which the following sequence well illustrates changes in the pattern of compound formation.



Proceeding from oxides, the finding of valency hyperbolae becomes successively more difficult, slightly so on passing to sulphides, markedly with silicides and compounds of the more metallic elements mentioned, although aluminium and zinc compounds still tend to occur preferentially along a mixed positive/negative valency line [2, 4]. Oxides are formed from the generality of elements, but for silicon, aluminium and zinc, compounds form only with elements on the left-hand side of the composite divide.

A further variation in the plotting of synoptic diagrams is illustrated in Fig. 3. This is suitable for showing the alloying pattern of elements near a divide in cases where (cf. oxygen in Fig. 2) one common element does not form compounds with elements on both sides of the divide. In effect, there are two synoptic strips with a common series of elements down the centre; the zinc strip allows the marking in of the compound pattern of the transition elements, and the copper strip does the same for the B-group elements. We first note, in the lower right-hand section, a series of normal valency compounds with narrow ranges of stoichiometry, from CuBr to Cu₃As. Further up in the diagram are indicated the many compounds of Cu with Ge, Ga and Zn. Although the latter clearly lie on a hyperbola, it will be realized that this is not of the normal valency type (the latter, which has its centre at "a" (Fig. 3) is represented by the dashed line towards "Ni") but on a tighter hyperbola with its centre at "b". The course of the latter, actual, hyperbola is marked by the well known electron compounds with their characteristic e/a ratios. For clarity, only lines for which e/a equals 21/13 are indicated in Fig. 3, starting near "Cu₄Ge" and continuing to the left and upwards. The course of the 21/13 line into the upper part of Fig. 3 may be realized by counting the valencies from Ge to Ni as 4 to 0. From nickel, proceeding towards metals of lower atomic number, it may be argued that negative valencies

are as acceptable as are positive, so that two possibilities exist and two lines may be drawn, corresponding respectively to $0 \rightarrow -1 \rightarrow -2$ and $0 \rightarrow 1 \rightarrow 2$ etc. For positive values, a 21/13 line reverts towards the transition metal axis, cutting it between Co and Fe; for negative values, a line continues near the zinc ordinate and is "reflected" beyond the upper frame of Fig. 3 to a point between K and Ca. The area between the lines (not drawn) representing e/a ratios of 3/2 and 7/4

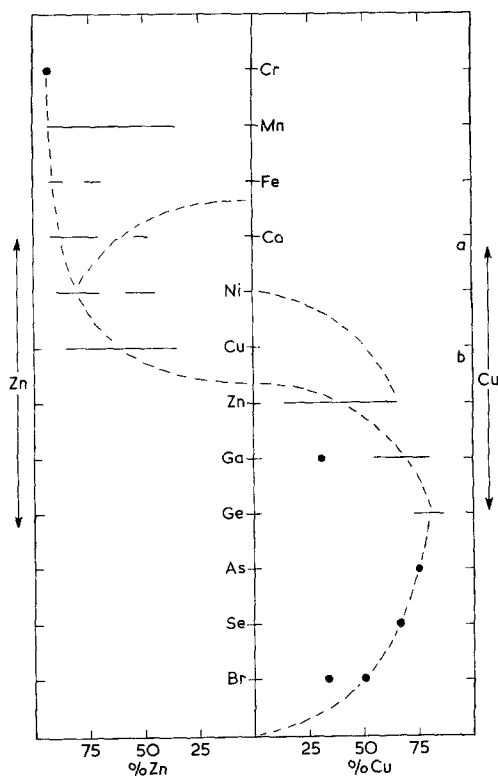


Figure 3 Duplex summary diagram indicating how binary compounds of zinc and copper with the elements chromium to bromine inclusive lie on either normal valency or golden ratio type hyperbolae. The method of representation is an extension of that used in Fig. 1 and 2; as a consequence, the Cu-Zn system appears twice. The dashed line in the lower right hand corner links compounds of normal valency, and the line to the right from nickel is for hypothetical normal valency; the remaining dashed lines indicate the electron/atom ratio of 21/13 calculated from the assumed valencies Zn 2, Cu 1, Ni 0, Co ± 1 , Fe ± 2 , Mn ± 3 , Cr ± 4 . An assumption of zero valency for Ni, Co and Fe will give a reasonable fit for the structures of gamma brass type, as is well known. Compounds ZnAs₂, Zn₃As₂, ZnSe and ZnBr₂ have been omitted for clarity; there are no compounds of Cu with Ni to Cr inclusive. A similar exercise to the above for the Second Long Period with Ag in place of Cu shows a 21/13 hyperbola continuing to Group VB(Sb)(cf.As).

respectively (taking the extremes of the positive and negative choices) includes the majority of compounds in the First Long Period; furthermore, gamma brass type compounds occur along lines intermediate between the positive and negative branches. This type of graphical presentation illustrates both the similarities and differences of the composite as compared to the ionic divide between groups VIIB and IA (as at krypton, Fig. 3 lower part). A feature of the differences may be noted from Fig. 2 where valency hyperbolae in opposite senses begin from palladium and cadmium respectively, rather than from one element; in a way, we may say that an offset type of behaviour occurs at Pd → Cd and analogous places.

3. Offset behaviour at the composite divide

The nature of the offset may be illustrated in several ways. The trend of elements of maximum atomic radius in their respective periods runs from zinc to lead, whilst the elements of maximum ionic radius are those of group IB (Table II). Alternatively we may synthesize an offset situation, for example from data on ionization energies [5, 6]. In Fig. 4a are plotted the ionization energies and electron affinities of the elements adjoining argon. Now if the onset of minimum electron affinity be delayed to higher atomic numbers, as is probably the situation towards the ends of the transition series, an offset would exist; the counterpart of this situation in Fig. 4 is where the energies for P → A are moved to the right relative to A → Sc. Addition of the two portions now gives the full line in Fig. 4b, which is in reasonable agreement with the actual energies indicated by the dashed line. Increasing degrees of offset may be simulated as in Fig. 4c and d. The curve obtained from 2-offset is nearer in shape

TABLE II Lines of maximum atomic and ionic radius

Ni	Cu	Zn	Ga	Ge	
Pd	Ag	Cd	In	Sn	
Pt	Au	Hg	Tl	Pb	Bi
	I			A	

Notes:

A = line connecting elements of maximum atomic radius in their period for the elements indicated.

I = as A, but ionic radius (Third Long Period – for complete ionization)

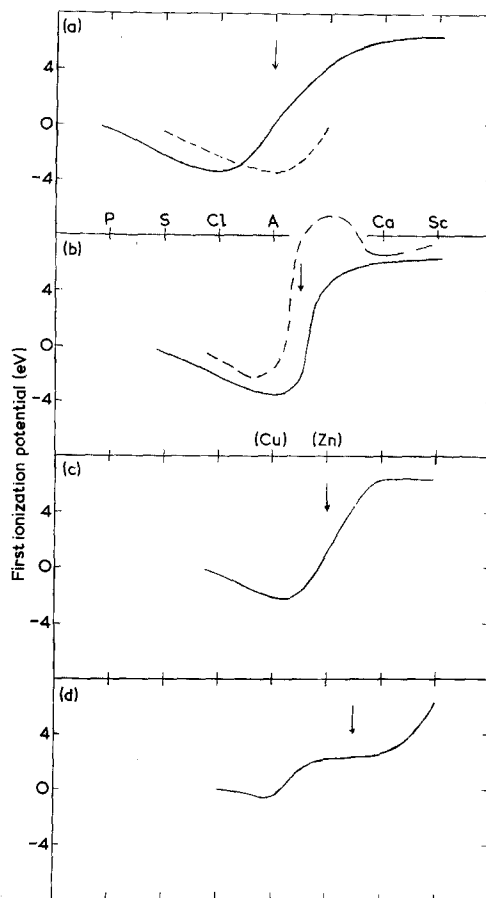


Figure 4 An exercise in the addition of ionization potentials: the synthesis of hypothetical ionization potential/atomic number curves for some transition and other elements from data for the elements phosphorus to scandium inclusive. The latter are represented by the full line in (a). The dashed line in (a) represents an offset by one atomic number of the negative part of the full line (i.e. the electron affinity); the full lines in (b), (c) and (d) are obtained by summing part-curves for one, two and three atomic number offsets respectively. The arrow in each case indicates the point of half offset. The dashed line in (b) illustrates published data for potentials (affinities for Cu, Ni and Co) of elements of the First Long Period, placed to conform with the indications (Cu) and (Zn). Quoted values [5] for elements of the Third Long Period are not consistent with interpretation (d).

to the source curve than to that in the 1-offset case, and for this reason (c) may reflect the situation in the Second Long Period, with the marked univalency of silver. However that may be, the 3-offset with its quite different form does appear to be an accurate counterpart to the situation in the Third Long Period – inspection of binary inter-Third Long Period equilibrium diagrams from platinum to bismuth (contrasted with

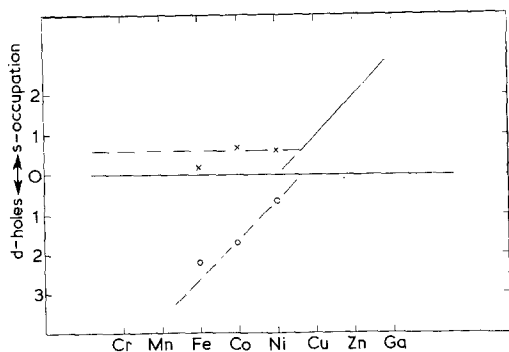


Figure 5 Offset or fault behaviour in the electronic constitution of some transition elements as revealed by a diagrammatic representation of electron states of the elements iron to zinc. The full horizontal line indicates a division between d-states below (expressed as d-holes) and s-states above. The values of the holes in the d-band for Ni, Co and Fe respectively [8] are essentially $\phi - 1$, ϕ and $2\phi - 1$ where ϕ is the golden ratio; the expression for iron probably enters as it has the next value in ascending order of $n\phi \pm 1$.

inter-First and inter-Second Long Period analogues) shows that a major difference exists between the Third and the earlier Long Periods in this respect. The areas below zero potential level in Fig. 4 (the integrated electron affinities) are approximately in the ratio 80:28:7 for 1, 2 and 3-offset respectively; the latter two figures are in fair agreement with the relative magnetic susceptibilities of palladium and platinum respectively [7], though clearly the area parameter may mirror only part of the conditions for high susceptibility.

Instead of summation of ionization energies, we may allot valency numbers and proceed as follows: the rows below the first are obtained by moving the block of numbers to the left of the asterisk bodily to the right and adding:

-3	-2	-1*	0	1	2	3
	-3	-2	-1	1	2	3
		-3	-2	0	2	3
			-3	-1	1	3

Alternatively we may delete the negative signs and continue as previously; this may better represent the cases where higher (covalent type) valencies are brought into play. A comparison of the lower lines obtained thus with the common valencies of some Third Long Period elements is of interest:

Pt	Au	Hg	Tl	Pb	Bi
4	3	2	3	4	3
2	1		1	2	

As a final illustration, Fig. 5 schematically represents in stratigraphical fashion the state of electronic energy levels for elements from iron to zinc. The sketch has been built up from quoted values of 3d and 4s occupancy [8] for iron, cobalt and nickel coupled with the simple electronic increase of unity per atomic number. Again the offset character is evident.

4. Conclusion

The self-consistency of Fig. 5 is achieved for an offset of approximately 0.62 electrons, not an integral number (cf. Fig. 4), and this reminds us that ratios near to or related to the golden ratio occur several times in the present context, not only in the estimates of d-level occupancies [8, 9], but also in the geometry of Fig. 3. Also, numbers from the Fibonacci series (the ratio of successive terms of which tends to the golden ratio) are integers commonly used in formulating electron compounds. (Fibonacci numbers also occur prominently in the formulae of beryllides.) Lines of "golden ratio" e/a occupy key positions in Fig. 3, and they probably coincide with minimum energy and strongest chemical binding (as shown by thermochemical data [10] and hardnesses [2, 4]) in the several systems; the difference between 4CuZn and 4CuZn.CuZn_4 [2] represents the accommodation in atomic terms which has to be offered in moving from the type of situation in the ionic to that in the composite divide. Paradoxically, at the stage of alloying of copper represented by beta-brass, we have, according to the present hypothesis (which in its insistence on separate d and s functions resembles [11]), ionic binding into the d-shell of copper simultaneously with promotion and increase in free electrons. Behaviour near the composite divide may be likened in some respects to a mechanical system on two fulcra, fulcra which occur, in the First Long Period, near nickel and between copper and zinc respectively. Examples of inter-fulcra behaviour are probably the solubilities, in copper, of nickel as contrasted with iron and cobalt, and secondly the different ordering behaviour noted [12] for beta-brass (CuZn) compared with other electron compounds.

Appendix. Solid solutions in copper, silver and gold

This work, in contrast with the remainder of the paper, has solid solutions as its subject. The information is on lattice distortion, as summarized by Hume-Rothery [13], and it will be noted that the relevant part of the Periodic Table is that near the composite divide. It is possible here only to outline the argument. For the general reader the essential point is that once again we have a parameter which varies near the composite divide in a manner which suggests offset behaviour, just as in the previous illustrations.

The data has been replotted schematically in Fig. 6 which is based on Hume-Rothery's Fig. IV.58. The Cu/Zn,Ga line extrapolates to zero lattice distortion at group VIII B, and the Ag/Cd, In to group VIII C; the hypothetical Au/Hg, Tl (solubilities do not allow realization) would become zero at group I. On the other hand, the Cu/Ge, As line extrapolates to a point halfway between groups I and II, and the Ag/Sn, Sb to group II. Intercepts on the abscissa between firm lines and their accompanying extrapolations are variable in a systematic manner; this finding, and the inference from Fig. 6 that there are three regimes with nil, intermediate and greater slopes respectively, is consistent with the suggestion of

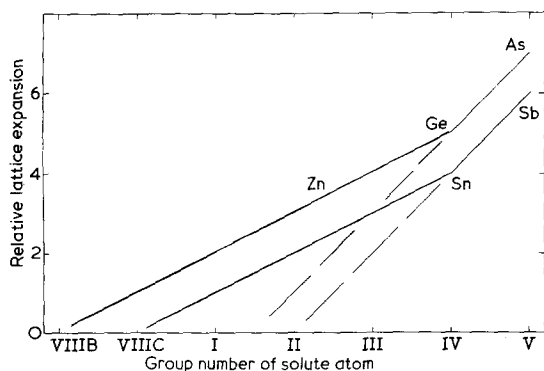


Figure 6 A possible manifestation of offset behaviour at the composite divide, as shown by variations in the relative lattice expansions. The figure gives the expansions [13] of (a) copper produced by equiatomic percentages of Zn, Ga, Ge and As in solution, indicated by the upper firm line, and (b) silver with Cd, In, Sn and Sb, lower firm line, versus group number of solute atom. The continuations of the firm lines to the left of group I have been inserted by the writer.

another offset effect. The existence of a zone of intermediate slope is interesting; possibly it may be accounted for by the presence of ionic pairs (for example CuZn) in the solid solutions.

Acknowledgement

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References

1. H. E. N. STONE, *J. Mater. Sci.* 9 (1974) 607.
2. *Idem, ibid* 10 (1975) 923.
3. *Idem, ibid* 7 (1972) 1147.
4. *Idem, ibid* 11 (1976) 1108, 1576.
5. R. M. TENNENT, Ed., "Science Data Book" (Oliver and Boyd, Edinburgh, 1971) p. 56.
6. G. W. C. KAYE and T. H. LABY, "Tables of Physical and Chemical Constants", 13th Edn. (Longmans Green, London, 1966) p. 200.
7. N. F. MOTT and H. JONES, "The Theory of the Properties of Metals and Alloys" (Dover reprint, New York, 1958) p. 195.
8. W. HUME-ROTHERY, "Atomic Theory for Students of Metallurgy", (The Institute of Metals, London, 1946) p. 259. See also W. Hume-Rothery and B. R. Coles, "Atomic Theory for Students of Metallurgy" (The Institute of Metals, London, 1969 reprint) p. 391.
9. W. HUME-ROTHERY, "Atomic Theory for Students of Metallurgy", (The Institute of Metals, London, 1946) p. 267.
10. O. KUBASCHEWSKI and E. LI. EVANS, "Metallurgical Thermochemistry" (Pergamon, London, 1958) pp. 177, 199, 350, but cf. the same volume, p. 68.
11. N. F. MOTT and H. JONES, "The Theory of the Properties of Metals and Alloys" (Dover reprint, New York, 1958) p. 192.
12. W. HUME-ROTHERY, R. E. SMALLMAN and C. W. HAWORTH, "The Structure of Metals and Alloys", (The Metals and Metallurgy Trust, London, 1969) p. 228.
13. *Idem, ibid*, p. 193.
14. O. KUBASCHEWSKI and B. E. HOPKINS, "Oxidation of Metals and Alloys" (Butterworths, London, 1962).
15. O. KUBASCHEWSKI and E. LI. EVANS, "Metallurgical Thermochemistry" (Pergamon, London, 1958).
16. H. E. N. STONE, Ph.D. Thesis, University of London (1966).
17. H. E. N. STONE and N. A. LOCKINGTON, *J. Mater. Sci.* 2 (1967) 112.

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