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Immiscibility in binary alloys of group IB metals (copper, silver and gold) – a semi empirical approach

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The paper shows that concepts of neither the Hildebrand parameter nor the Mott number are adequate to predict the occurrence of miscibility gaps in binary metallic systems. It shows that modified versions of these parameters which are closely integrated with the structure of liquid metals (now called the Kumar-Hildebrand and the miscibility syndrome respectively), statistically account for the occurrence of miscibility gaps. Whereas no rigorous and theoretical justification could be given, it is shown that miscibility in liquid binary metallic systems could be discussed in terms of the electronic configuration of valency electrons.

1. Introduction

Despite the advances made in the theory of alloys, founded on the well-established semi-empirical rules of Hume-Rothery, the existence of a region of liquid immiscibility in binary phase equilibria is not yet satisfactorily understood. The success of the concept of the size factor, measured by the difference in the atomic diameters of the pure binary components in predicting the formation of extensive or restricted solid solutions, created an indelible imprint on the early metallurgical opinion that the factors controlling the solubility of one liquid metal into another may essentially be the same as those determining the limits of primary solid solubility. Prominent amongst such attempts was that of Axon [1] who attempted to relate the nature of phase equilibria in about eighty simple binary systems in terms of two arbitrary parameters involving the size factor and a temperature factor When the size factor of the two metals was less than 30%, only those systems could be immiscible* in liquid state in which the constituent metals had widely different melting points. When the size factor was greater than 30%, the systems were about equally divided between the immiscible and the simple eutectic types. Since the Axon approach did not take into account the electro-chemical nature of the elements, it naturally had restricted applicability to metallurgical systems. It, nevertheless, showed that attempts can be made to rationalize the occurrence of liquid immiscibility in binary metallic systems. In view of a recent review [2] no attempt is made in this paper to present an up-to-date account of immiscibility in liquid metallic systems but it proceeds to modify the concepts of both Hildebrand [3] and Mott [2] in the light of the present knowledge of the structure of liquid metals and alloys and only a brief review of their concepts has necessarily been given here.

2. The Hildebrand and Mott criteria of immiscibility

Although considerations of the inter-atomic forces between neighbouring atoms failed to provide a mathematical theory of liquid state and were also inadequate to explain their macroscopic properties such as viscosity or melting and boiling characteristics, Hildebrand and Scott [3] attempted to develop a parameter to predict immiscibility in binary systems from fundamental considerations involving the intermolecular potential energy in liquid state. They obtained an expression for the energy of mixing in terms of the differences in the potential energy of the solution and that of its pure components and showed that the excess free energy of formation of a liquid solution was similar to the

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*The term immiscibility includes systems which are wholly immiscible and also those which only have a miscibility gap in their binary phase equilibrium.

expression for the energy of mixing (ΔE^{M}) of a regular solution. The following expression was derived:

$$\Delta E^{\mathrm{M}} = V\left[\left(\frac{\Delta E_{\mathrm{A}}{}^{\mathrm{V}}}{V_{\mathrm{A}}}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_{\mathrm{B}}{}^{\mathrm{V}}}{V_{\mathrm{B}}}\right)^{\frac{1}{2}}\right]^{2} \phi_{\mathrm{A}}.\phi_{\mathrm{B}} \quad (1)$$

In this expression, V is the average atomic volume of the solution, V_{A} and V_{B} the atomic volumes of the component metals, $\Delta E_{\mathrm{A}}{}^{\mathrm{V}}$ and $\Delta E_{\mathrm{B}}{}^{\mathrm{V}}$ their heats of vaporization and, ϕ_{A} and ϕ_{B} the volume fractions of the components. When $V_{\mathrm{A}} \neq V_{\mathrm{B}}$, an approximation can then be made for $V = (V_{\mathrm{A}} + V_{\mathrm{B}})/2$. The term $\Delta E^{\mathrm{V}}/\mathrm{V}$ or δ is called the solubility parameter. It is a measure of the binding energy of the component and was identified with the energy of vaporization on the assumption that the vapour of the pure liquid at ordinary temperatures is nearly ideal.

The thermodynamic conditions for liquid immiscibility can be derived from the activity versus molal fraction curves for the solution; a single phase may decompose into two liquid phases when $\mathrm{dln}\alpha/dx = 0$ and $\mathrm{d}^2\mathrm{ln}\alpha/\mathrm{d}x^2 = 0$ for both components. Applying the regular solution theory, Hildebrand and Scott evaluated the following condition for liquid state immiscibility for non-polar liquids:

$$\frac{(V_{\mathrm{A}} + V_{\mathrm{B}})}{2} \,.\, (\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 > 2RT \quad (2)$$

In other words, the algebraic sign of the Hildebrand excess energy or the Hildebrand parameter

$$\frac{(V_{\mathrm{A}} + V_{\mathrm{B}})}{2} (\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 - 2RT$$

determines the miscibility or otherwise in liquid state of binary components – a positive value foreshadowing immiscibility and a negative, miscibility. Whilst the Hildebrand parameter successfully accounted for the immiscibility in forty, out of some forty-seven known immiscible binary systems, it showed marked disagreement when applied to miscible systems; in fact the success of its prediction may not exceed 50%. Since most of such disagreeing systems contain electron and/or intermetallic compounds in solid state, the failure of the Hildebrand parameter in the case of complex systems was not unexpected. Subsequently, Mott [2, 4] suggested that the Hildebrand parameter was in itself inadequate to predict immiscibility because it did not take into account the effect of electro-chemical attraction on promoting randomization of the solute and solvent atoms. He proposed that the effect of electro-chemical attraction could be included in the Hildebrand expression by incorporating a term involving the electro-negativities of the component metals (χ_{A} and χ_{B}) and the maximum number of Pauling bonds, n, which could be formed in the liquid state. Thus, immiscibility could develop when:

$$\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 - 23060n(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^2 > 2RT \quad (3)$$

or

$$\frac{\tfrac{1}{2}(V_{\mathrm{A}} + V_{\mathrm{B}})(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 - 2RT}{23060(\chi_{\mathrm{A}} - \chi_{\mathrm{B}})^2} > n$$

provided $n \neq 0$; T represents the melting point in K of the more refractory metal. The ratio of Hildebrand term (the numerator) and the electronegativity term (the denominator) was called the Mott number and is a measure of the number of Pauling bonds, which the two metals could form in the liquid state; the maximum number of such bonds being six. Mott proposed that liquid immiscibility could be expected when the number of bonds which could form in a system was greater than six and miscibility when it was less than six. The statistical viability of the concept was increased by subjecting the behaviour of systems with a Mott number of between two and six to an arbitrary classification between the Mott number and size factor such that miscibility was not expected in the size factor range 15 to 50% [2]. A general weakness of this treatment was that for systems with identical Mott numbers, miscibility depended in an inexplicable manner on size factor. Of the 1401 binary systems thus analysed by him, 1181 conformed to the prediction from their Mott numbers [2].

The Mott treatment is, of course, an approximate attempt to deal with a complex theoretical problem. As the Mott numbers become small, it is no longer permissible to identify them with metallic bond number. This conclusion is a rather unattractive feature of the scheme and raises a question as to the limits of the validity of the underlying physical picture. Further, in his evaluation of various binary systems, Mott disregarded the algebraic sign of the Mott number. He considered the systems miscible even though their numbers were negative. Since the Mott number is related to the number of bonds which the two metals could form in liquid state, a negative Mott number, on the same logic, would signify that the two constituent metals have not only no tendency to alloy but also repel each other; in other words, a negative Mott number should also be regarded as a manifestation of possible immiscibility in liquid state. Accordingly, computations strictly according to the procedure outlined in [2] will, henceforth, be qualified and called *"original Mott numbers"* and those in which the algebraic sign is also taken into consideration, and according to the concepts developed in this paper, as *"modified Mott criterion"*.

2.1. Limitations of the Hildebrand parameter

In evaluating the solubility parameter of the different metals, Hildebrand and Scott utilized the heats of vaporization as a measure of the binding energy in the liquid state. In effect, this implies that structurally liquid metals could be regarded as a version of condensed gases. Hildebrand [5] has been the principal advocate of such a concept of the structure of liquid metals since many of their properties and much of their behaviour could be adequately described by considering them as fluids. On the other hand, many of the physical properties of the metallic liquids are closer to those of their solids at corresponding temperatures than to their gaseous phases, for example, the molecular configuration changes little on melting [6, 7]. Thus the relative difference in the states of order between the crystalline and the liquid states on one hand is much smaller than between the liquid and the gaseous states on the other [7]. Critical appraisals of the X-ray investigations of the structure of liquid metals [8] have, in general, provided support to the concept that the atomic co-ordination in liquid state is only a little different from that of the corresponding crystalline structure. The liquid is, therefore, structurally closer to its solid than to its gaseous state not only in terms of atomic packing and co-ordination, but also in terms of order. In view of this, is it not more desirable to use the heats of fusion in place of the heats of vaporization for evaluating the solubility parameters of the various metals for the purpose of predicting the existence of immiscibility in liquid state with the help of either the (i) Hildebrand parameter or (ii) the original Mott number? This statistical study was primarily undertaken to provide the answer. The group IB metals – copper, silver, and gold – were first chosen as they may be regarded as built up of hard spheres (ions) held in contact by the valency electrons and their atomic and ionic radii are also nearly equal. Their alloying behaviour in terms of the occurrence of miscibility gaps with the solutes belonging to the A and B subgroups of the periodic classification of elements is discussed in this paper.

3. Concept of miscibility syndrome

Accordingly, values of the solubility parameters were first determined with the help of the heats of (i) vaporization and (ii) fusion and these have been respectively denoted as the Hildebrand and the Kumar solubility parameters, for the sake of clarity. Since this data has been used for subsequent computations, it is given in the master Tables I and II. In order to assess each binary system independently, their Hildebrand factors and the original Mott numbers were also calculated according to the stipulations of the original authors (i.e. on the basis of the heats of vaporization and the reference temperature being the melting point of the more refractory metal). These computations are summarized in Tables III and IV for the binary systems of copper, silver, and gold as solvents. In these tables, only the computed values of the Hildebrand factor and the Mott's electronegativity factors are shown along with the original Mott number. Similar factors calculated with the help of the Kumar solubility parameter and fusion temperature of the less refractory metal are summarized in Tables V and VI, but are now respectively called the Kumar-Hildebrand excess energy and the miscibility syndrome. When the logarithms of the numerical values of the miscibility syndrome are plotted as a function of the size factor, as in Figs. 1 to 3, an empirical demarcation between the miscible and immiscible systems becomes apparent; such a demarcation is simple to appreciate because a system is most likely to be miscible in all proportions if its point falls on the left of the empirical demarcation line and most likely to exhibit a miscibility gap if it is on the right. It is noteworthy that the graphical location of the demarcation line is identical in the three figrues. In view of the foregoing discussion, a negative Mott number has been regarded as an indication of the existence of miscibility gap in contradistinction with the computations of Mott himself. A positive Mott number value of less than six has been taken as an index of general miscibility in the present computations. Predictions on the basis of the (i) Hildebrand factor, (ii) Kumar-Hildebrand

TABLE I Data for the calculation of miscibility syndrome

Group	Element	Atomic volume (ml/g atom)	Melting point (K)	Electro-negativity*	Latent-heat† (cal/g atom)		Solubility parameter ($\text{cal}^{\frac{1}{2}}/\text{ml}^{\frac{3}{2}}$)	
					of vaporization	of melting	Hildebrand	Kumar
IA	Li	13.00	459	0.95	37000	715	54	7.42
	Na	24.00	371	0.90	26000	622	33	5.09
	K	45.00	336	0.81	21500	588	21	3.50
	Rb	55.90	312	0.78	20500	560	19	3.17
	Cs	70.00	301	0.76	18800	510	16	2.70
IIA	Be	4.96	1553	1.42	80000	2800	129	23.76
	Mg	14.00	923	1.16	35900	2140	50	12.36
	Ca	25.90	1123	1.03	42600	2070	40	8.94
	Sr	34.00	1043	0.99	39200	2400	34	8.40
	Ba	39.00	977	0.92	42000	1830	33	6.85
IIIA	Sc	18.00	1473	1.27	93000	3850	80	14.63
	Y	16.10	1763	1.20	103000	4100	72	15.96
	La	22.60	1099	1.17	88000	2750	63	10.03
IVA	Ti	10.60	2093	1.62	95000	4460	94	20.51
	Zr	14.00	2023	1.48	125000	4900	94	18.71
	Hf	15.70	1973	1.48	—	5790	—	19.20
	Th	20.20	2073	1.36	145000	4500	85	14.93
VA	V	8.50	2008	1.85	120000	5050	119	27.35
	Nb	10.80	2686	1.77	175600	6400	127	24.36
	Ta	10.90	3269	1.77	200000	5900	136	23.27
VIA	Cr	7.23	2163	2.15	84500	5000	108	26.30
	Mo	9.41	2898	2.05	156000	6650	128	26.58
	W	9.53	3683	2.05	201600	8092	145	29.11
	U	12.70	1403	1.30	128000	3250	100	16.12
VIIA	Mn	7.39	1518	1.69	68600	3500	95	21.76
VIII Transition element	Fe	7.10	1812	2.21	96700	3670	117	22.74
	Co	6.60	1768	2.26	10500	4100	126	24.93
	Ni	6.59	1728	2.24	101800	4210	124	25.28
	Ru	8.33	2773	2.12	160000	6200	139	27.28
	Rh	8.27	2239	2.12	138000	5200	129	25.07
	Pd	8.89	1827	2.08	93000	4200	102	21.74
	Ir	8.58	2727	2.10	165000	6300	139	27.10
	Pt	9.10	2047	2.07	135000	4700	121	22.72
Rare earths	Ce	20.90	1070	1.21	97600	2200	68	10.26
	Gd	20.20	1585	1.20	81300	3700	63	13.54

*Data from B. W. Mott, *J. Mater. Sci.* **3** (1968) 424.

†Data from either Kelley, Contributions to the Data on Theoretical Metallurgy, US Bureau of Mines Bulletin No. 584 or Kubaschewski and Evans, Metallurgical Thermochemistry, Pergamon Press.

TABLE II Data for the calculation of miscibility syndrome

Group	Element	Atomic volume (ml/g atom)	Melting point (K)	Electro-negativity*	Latent-heat† (cal/g atom)		Solubility parameter ($cal^{\frac{1}{2}}/ml^{\frac{3}{2}}$)	
					of vaporization	of melting	Hildebrand	Kumar
IB	Cu	7.09	1356	2.00	81500	3120	107	20.98
	Ag	10.28	1234	1.90	69100	2855	82	16.67
	Au	10.20	1336	2.30	90500	2955	93	17.02
IIB	Zn	9.17	693	1.50	31200	1765	58	13.87
	Cd	13.00	594	1.55	26800	1450	45	10.56
	Hg	14.80	234	1.80	14500	542	31	6.05
IIIB	Al	9.99	933	1.48	75000	2570	86	5.07
	Ga	11.80	303	1.62	65000	1335	74	10.64
	In	15.70	429	1.48	57400	780	60	7.05
	Tl	17.24	573	1.46	42800	1020	49	7.69
IVB	Si	12.00	1703	1.82	90000	12100	88	31.76
	Ge	13.50	1231	1.77	78400	7600	76	23.73
	Sn	16.26	505	1.61	70000	1720	65	10.29
	Pb	18.27	600	1.56	48500	1140	51	7.90
VB	As	13.10	1087	2.04	58000	2490	66	13.79
	Sb	18.40	904	2.10	63000	4740	59	16.05
	Bi	21.30	544	1.78	49000	2600	48	11.05
VIB	Se	16.40	493	2.35	20600	1300	35	8.90
	Te	20.50	723	2.08	20000	4180	31	14.28

*Data from B. W. Mott, *J. Mater. Sci.* 3 (1968) 424.

†Data from either Kelley, Contribution to the Data on Theoretical Metallurgy, US Bureau of Mines Bulletin No. 584 or Kubaschewski and Evans, Metallurgical Thermochemistry, Pergamon Press.

factor, (iii) modified criterion of Mott number and (iv) miscibility syndrome are summarized in Tables VII and VIII in which the true nature of the various binary systems is also indicated. Table IX summarizes the relative evaluation of these parameters. The following observations can be made:

(*a*) The number of successful predictions is largest on a consideration involving the miscibility syndromes and the size factors and is closely followed by the Kumar-Hildebrand parameter. Predictions from either the modified Mott number or the Hildebrand parameter trail far behind.

(*b*) The concept of miscibility syndrome is cent per cent successful in its predictions for the B subgroup solutes in copper, silver, and gold – themselves belonging to the B subgroup with the exception of only the Ag-Se and Ag-Te systems.

(*c*) When their alloy systems with the metals of the A subgroups and the transition metals of group VIII are considered, the accuracy of prediction, though still high (57%) for the miscibility syndrome is highest for the Kumar-Hildebrand parameter (66%).

4. Discussion

Although the theoretical basis and the significance of the curious relation between the miscibility syndrome and the size factor is at present obscure, it is clear that a boundary condition involving electronic considerations of cohesion determines miscibility, or the lack of it. Although in the elements of the B subgroups, there is comparatively little change in atomic diameter on passing from Group IB to Group VB in any one period, except for the expansion in indium, tin and lead where the structures are incompletely

TABLE III Data computed according to Hildebrand and Mott for the evaluation of miscibility

GROUP	SOLUTE	SOLVENT								
		COPPER			SILVER			GOLD		
		Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number	Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number	Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number
I A	Li	23 000	25 400	0.9	4 200	20 900	0.2	12 400	42 000	0.3
	Na	–	–	–	35 900	23 100	1.6	55 900	45 200	1.2
	K	–	–	–	–	–	–	139 100	51 200	2.7
II A	Be	(–) 3 200	7 800	(–) 0.4	106 200	5 300	2.0	45 000	17 900	0.3
	Mg	28 900	16 300	1.8	7 900	12 600	0.6	(–) 3 067	30 000	(–) 0.1
	Ca	68 600	21 700	3.2	27 100	17 500	1.6	45 400	37 200	1.2
	Sr	–	–	–	44 900	19 100	2.4	–	–	–
	Ba	–	–	–	51 900	22 100	2.4	–	–	–
III A	La	23 300	15 900	1.5	1 000	12 300	0.1	9 500	29 400	0.3
IV A	Ti	(–) 6 800	3 300	(–) 2.1	(–) 6 800	1 800	(–) 3.8	(–) 8 300	10 700	(–) 0.8
	Zr	(–) 6 200	6 200	(–) 1.0	(–) 6 300	4 100	(–) 1.5	(–) 8 000	15 500	(–) 0.5
	Th	(–) 1 600	9 400	(–) 0.2	(–) 8 100	6 700	(–) 1.2	(–) 7 300	20 400	(–) 0.4
V A	V	(–) 6 900	500	(–) 13.8	4 900	60	82.0	(–) 1 600	4 700	(–) 0.4
	Ta	(–) 5 400	1 200	(–) 4.5	20 600	400	53.0	6 500	6 500	1.0
VI A	Cr	(–) 8 600	500	(–) 17.2	(–) 2 100	1 500	(–) 1.5	(–) 6 500	500	(–) 13.0
	Mo	(–) 7 900	60	(–) 132	9 300	500	18.6	600	1 500	0.4
	W	–	–	–	24 900	500	50.0	–	–	–
	U	(–) 5 100	11 300	(–) 0.5	(–) 1 800	8 300	(–) 0.2	(–) 5 000	1 100	(–) 4.5
VII A	Mn	(–) 5 100	2 200	(–) 2.3	(–) 4 500	1 000	(–) 4.5	(–) 6 000	8 600	(–) 0.7
VIII A	Fe	(–) 6 500	1 000	(–) 6.5	2 500	2 200	1.6	(–) 2 200	200	(–) 11.0
	Co	(–) 4 500	1 600	(–) 2.8	9 300	3 000	3.1	2 100	40	52.5
	Ni	(–) 4 900	1 300	(–) 3.7	8 000	2 700	3.0	1 300	80	16.2
	Ru	–	–	–	19 200	1 100	17.4	8 600	750	11.5
	Rh	–	–	–	11 700	1 100	10.6	3 100	750	4.1
	Pd	(–) 7 100	150	(–) 47	(–) 3 400	750	(–) 4.6	(–) 6 500	1 100	(–) 5.8
	Ir	–	–	–	19 900	450	21.6	9 200	10	920
	Pt	(–) 6 500	100	(–) 65	25 600	670	38.5	(–) 600	1 200	(–) 0.5
	Ce	–	–	–	–	–	–	3 800	27 400	0.1

TABLE IV Data computed according to Hildebrand and Mott for the evaluation of miscibility

GROUP	SOLUTE	SOLVENT								
		COPPER			SILVER			GOLD		
		Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number	Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number	Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number
IB	Cu	–	–	–	85	200	0.4	(–) 3 700	2 100	(–) 1.8
	Ag	100	250	0.4	–	–	–	(–) 4 100	3 700	(–) 1.1
	Au	(–) 3 700	2 100	(–) 1.8	(–) 4 100	3 700	(–) 1.1	–	–	–
IIB	Al	(–) 1 600	6 200	(–) 0.3	(–) 4 700	4 100	(–) 1.2	(–) 4 800	55 500	(–) 0.3
	Zn	14 100	5 800	2.4	700	3 700	0.2	6 600	14 800	0.4
	Cd	33 200	4 700	7.1	11 000	2 800	3.9	21 400	13 000	1.7
	Hg	57 800	900	64.2	27 700	200	139	42 700	5 800	7.4
IIIB	Ga	4 900	3 300	1.5	(–) 4 200	1 800	(–) 2.3	(–) 1 300	10 700	(–) 0.1
	In	19 800	6 200	3.2	1 400	4 100	0.3	8 800	15 500	0.6
	Tl	35 800	6 700	5.3	10 100	4 500	2.3	21 300	16 300	1.3
IVB	Si	(–) 3 400	700	(–) 4.9	(–) 6 400	150	(–) 43.1	(–) 6 500	5 300	(–) 1.2
	Ge	4 500	1 200	3.8	4 500	400	(–) 11.2	(–) 1 900	6 500	(–) 0.3
	Sn	15 200	3 500	4.3	(–) 1 100	1 900	(–) 0.5	5 100	11 000	0.5
	Pb	34 400	4 400	7.8	8 800	2 700	3.3	19 900	12 700	1.6
VB	As	11 600	40	290.0	(–) 1 900	450	(–) 4.2	3 200	1 600	2.0
	Sb	24 000	200	120	2 700	900	3.0	11 300	900	12.5
	Bi	44 000	1 100	40	13 400	300	44.7	26 600	6 200	4.3
VIB	Se	55 500	2 800	20	25 600	4 700	5.3	22 600	60	390
	Te	74 300	150	495	36 700	750	49	53 700	1 100	48.1

TABLE V Computed data for the evaluation of miscibility according to the proposed modification

GROUP	SOLUTE	SOLVENT								
		COPPER			SILVER			GOLD		
		Kumar-Hildebrand excess energy	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand excess energy	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand excess energy	Miscibility syndrome	Size factor (%)
I A	Li	27	0.001	18.9	(–) 800	0.04	5.2	(–) 800	0.02	5.4
	Na	–	–	–	–	–	–	1 000	0.02	28.9
	K	–	–	–	–	–	–	3 700	0.07	59.8
	Rb	–	–	–	–	–	–	6 000	0.11	71.3
	Cs	–	–	–	–	–	–	7 900	0.15	84.5
II A	Be	(–) 5 300	0.69	13.6	(–) 4 500	0.85	23.6	(–) 1 000	0.06	23.5
	Mg	(–) 2 900	0.18	25.0	(–) 3 400	0.27	10.7	(–) 700	0.02	10.9
	Ca	(–) 2 100	0.095	51.7	(–) 3 400	0.19	34.2	(–) 3 300	0.09	34.4
	Sr	–	–	–	(–) 2 600	0.14	45.7	–	–	–
	Ba	–	–	–	(–) 1 500	0.07	50.5	(–) 1 300	0.03	50.7
III A	La	(–) 4 200	0.26	44.3	(–) 3 600	0.30	27.6	(–) 3 300	0.11	27.9
IV A	Ti	(–) 5 400	1.62	12.0	(–) 4 700	2.62	0.9	(–) 5 200	0.49	0.7
	Zr	(–) 5 300	0.85	22.3	(–) 4 800	1.20	8.2	(–) 5 300	0.34	8.4
	Th	(–) 4 900	0.51	39.2	(–) 4 900	0.72	23.1	(–) 5 200	0.26	23.3
V A	V	(–) 5 100	9.76	2.6	(–) 3 820	0.28	9.2	(–) 4 200	0.90	9.1
	Ta	(–) 5 300	4.37	11.9	(–) 4 400	11.37	1.0	(–) 4 900	0.70	0.8
VI A	Cr	(–) 5 200	10.0	2.3	(–) 4 100	2.83	13.5	(–) 4 600	8.77	13.4
	Mo	(–) 5 120	88.34	6.6	(–) 3 900	7.57	5.7	(–) 4 400	3.06	5.5
	W	(–) 4 800	83.34	7.2	(–) 3 400	6.48	5.1	(–) 5 300	0.23	6.2
	U	(–) 5 200	0.46	19.8	(–) 4 900	0.60	6.0	(–) 5 100	0.56	7.5
VII A	Mn	(–) 5 400	2.43	4.4	(–) 4 700	4.59	7.6	(–) 5 000	26.85	12.0
VIII A	Fe	(–) 5 400	5.27	0.7	(–) 4 500	2.02	12.1	(–) 4 800	12.91	13.1
	Co	(–) 5 300	3.38	2.0	(–) 4 300	1.45	13.3	(–) 4 700	57.00	13.6
	Ni	(–) 5 300	3.96	2.5	(–) 4 300	1.60	13.7	(–) 4 300	5.79	8.1
	Ru	–	–	–	(–) 3 800	3.45	8.3	(–) 4 400	5.86	6.7
	Rh	–	–	–	(–) 4 200	3.80	6.9	(–) 5 100	4.56	4.6
	Pd	(–) 5 400	36.33	7.6	(–) 4 700	6.23	4.8	(–) 4 400	4.72	5.9
	Ir	–	–	–	(–) 3 900	8.56	6.0	(–) 5 000	4.09	3.8
	Pt	(–) 5 400	47.42	8.5	(–) 4 500	6.82	4.0	(–) 2 800	0.10	23.7
	Ce	–	–	–	–	–	–	–	–	–

TABLE VI Computed data for the evaluation of miscibility according to the proposed modification

GROUP	SOLUTE	SOLVENT								
		COPPER			SILVER			GOLD		
		Kumar-Hildebrand energy term	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand energy term	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand energy term	Miscibility syndrome	Size factor (%)
IB	Cu	–	–	–	(–) 4 700	20.54	11.5	(–) 5 200	2.49	11.4
	Ag	(–) 4 700	20.54	13.0	–	–	–	(–) 5 300	1.44	0.2
	Au	(–) 5 200	2.49	12.8	(–) 4 800	1.30	0.2	–	–	–
IIB	Al	1 600	0.26	12.0	(–) 2 300	0.56	0.9	(–) 2 300	0.15	0.7
	Zn	(–) 2 300	0.41	4.3	(–) 2 700	0.72	7.7	(–) 2 700	0.18	7.6
	Cd	(–) 1 300	0.27	16.3	(–) 1 900	0.68	3.1	(–) 1 900	0.14	3.3
	Hg	1 500	1.64	10.5	500	2.1	2.2	600	0.10	2.1
IIIB	Ga	(–) 200	0.058	4.4	(–) 800	0.44	2.9	(–) 800	0.07	2.7
	In	1 800	0.29	27.2	(–) 500	0.12	12.5	150	0.01	12.7
	Tl	(–) 100	0.019	39.4	(–) 1 200	0.26	23.3	(–) 1 100	0.07	23.5
IVB	Si	(–) 4 300	5.72	8.0	(–) 2 400	15.95	18.6	(–) 2 900	0.54	18.5
	Ge	(–) 4 100	3.37	4.2	(–) 4 300	11.01	15.2	(–) 4 400	0.67	15.0
	Sn	(–) 700	0.19	18.2	(–) 1 400	0.75	4.6	(–) 1 400	0.13	4.8
	Pb	(–) 200	0.05	36.9	(–) 1 300	0.48	21.2	(–) 1 200	0.10	21.4
VB	As	(–) 600	15.27	20.0	(–) 4 200	9.33	9.3	(–) 4 200	2.69	9.5
	Sb	(–) 3 300	14.18	13.6	(–) 3 600	3.89	0.5	(–) 3 600	3.88	0.7
	Bi	(–) 800	0.68	36.2	(–) 1 700	5.16	7.7	(–) 1 600	0.26	7.9
VIB	Se	(–) 240	0.09	35.5	(–) 1 300	0.25	19.9	(–) 1 400	24.31	20.1
	Te	(–) 2 300	15.22	35.7	(–) 2 800	3.72	20.4	(–) 2 900	2.56	0.7

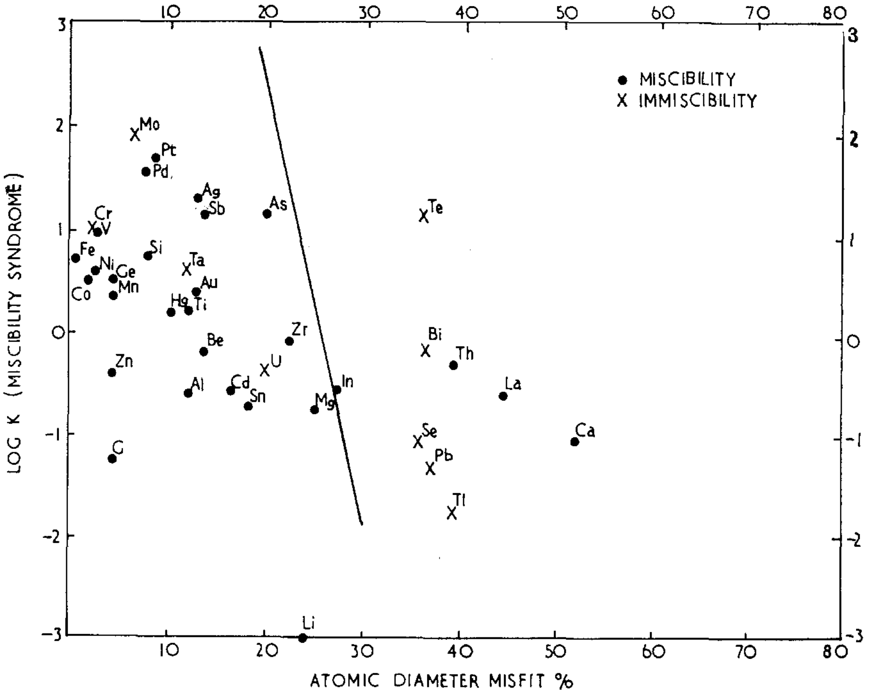


Figure 1 Indicator diagram for liquid state miscibility in copper.

ionized, the success of the concept of miscibility syndrome is particularly significant because the B subgroup metals exhibit an assortment of crystal structures from typically metallic close-packed structures to those governed by the (8-N) rule. This can be regarded as lending support to the concept that the forces involved in metallic and covalent bonding are closely similar.

In the case of binary alloy systems of copper, silver, and gold with the metals of the A sub-groups and with those of the Group VIII transition metals, the concept of miscibility syndrome, unlike the Hildebrand parameter, errs mostly in predicting miscibility for systems which are known to be immiscible.

Individually, silver shows the largest number of dissenting systems. This is in conformity with the evidence from spectra [9] that the penultimate 18 group of electrons is more stable when the principal quantum number is 4 (silver) than when it is 3 (copper). According to Grimm and Sommerfeld [10], the removal of an electron from the 18 group of electrons requires at least 40 kcal more per gram ion with Ag^+ than with Cu^+. Further, some of the electrons of the imperfect 18 group can be utilized as valency electrons in copper and gold (1 for Cu and 2 for Au thereby imparting valencies of 1 and 2 for Cu, and 1 and 3 for Au). The reason for this difference in the behaviour of copper and gold is not yet known. A consideration of the systems dissenting from the predictions from the concept of miscibility syndrome shows that these metals can essentially be categorized under the following two groups:

1. Those whose outer valency electrons exhibit the "ds" electronic configuration in the isolated atoms.
2. The low melting alkali metals like lithium, sodium, and potassium in which the ionic and the atomic radii are significantly different from the IB metal.

Since the expression for the miscibility syndrome does not incorporate terms related to the electronic configurations and their interactions or the degree of ionization of the atoms, its failure to predict liquid state alloying characteristics of binary constituents differing widely in terms of electronic structure is not surprising. These considerations are further complicated by the existence of interactions between the valency shells of the solute and solvent atoms; it is known that such interactions are responsible for the variation of the atomic sizes and of

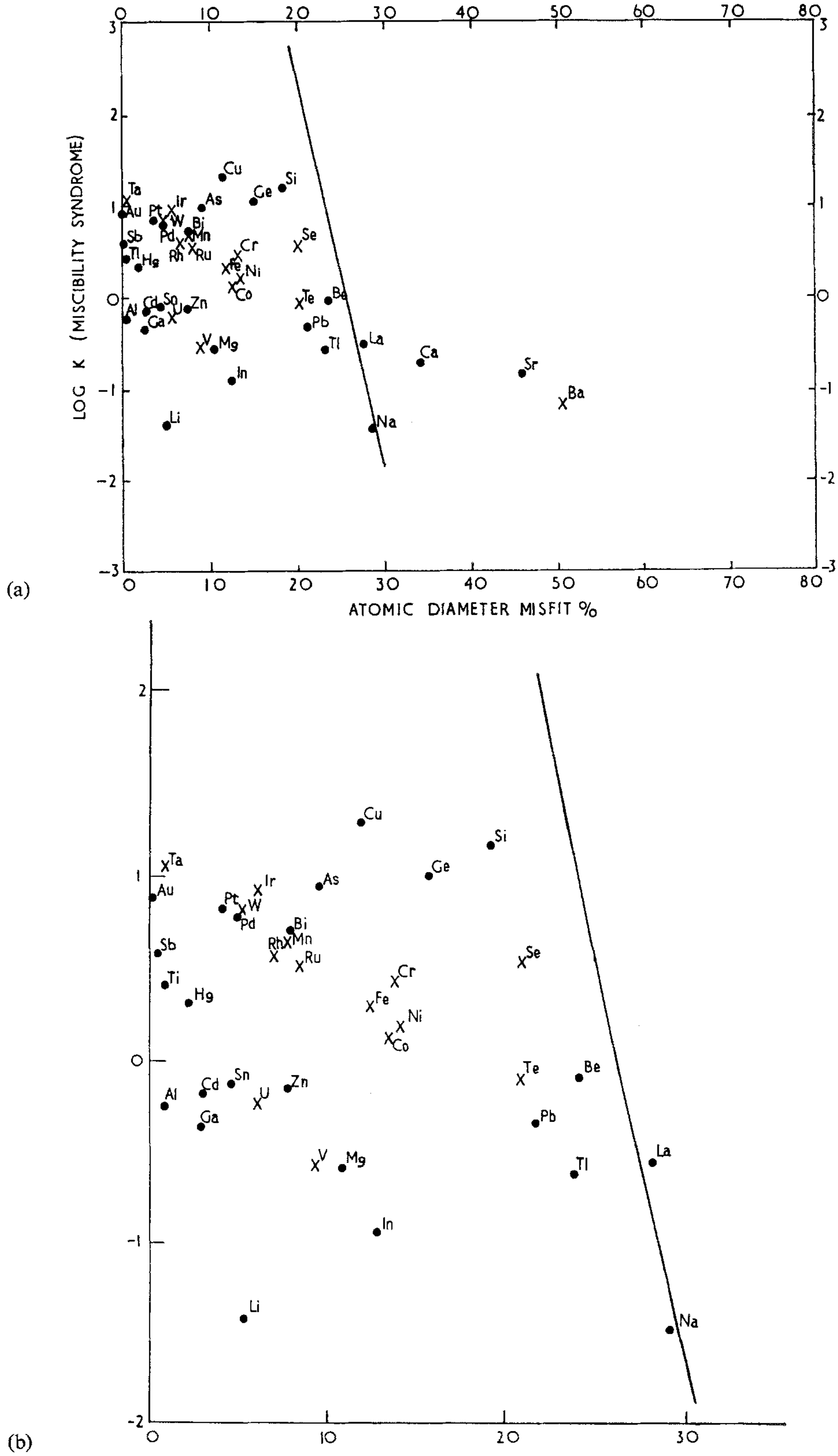


Figure 2 (a) Indicator diagram for liquid state miscibility in silver. (b) Enlarged left-hand side of (a).

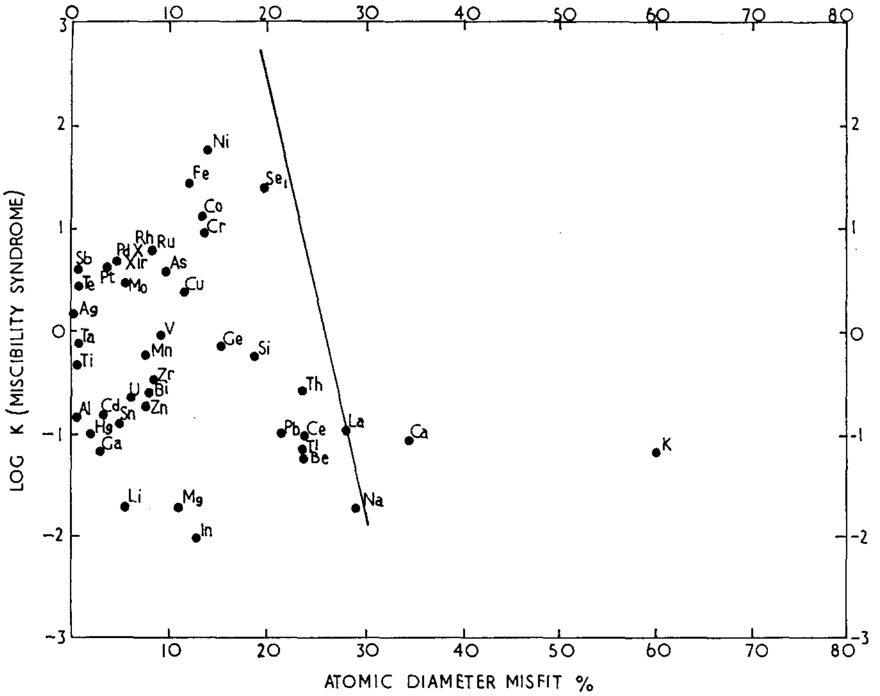


Figure 3 Indicator diagram for liquid state miscibility in gold.

valency of the solute or solvent atoms in the condensed states. An attempt to explain interaction between components in binary systems was made by Samsonov [11-13] and his co-workers including Upadhaya [14] on the basis of the stability of the outer most valency electron shells of isolated atoms. This model has been successfully applied to explain the nature of binary phase equilibrium, stability, crystal defects, diffusion etc. [14]. This concept is based on the fact that the valency electrons of a metal in condensed state can be divided into the localized and non-localized parts. The localized fraction of these electrons forms a fairly broad spectrum of configurations of varying energetic stabilities so that the stable configurations simultaneously coexist with those which are less stable or even unstable. The model visualizes that exchanges between the stable configurations and the non-localized fraction of the valency electrons are responsible for the bonds between pairs of stable configurations. On the basis of the electronic configuration of the valency electrons the metals could be classified into three groups ds-, s- and sp-elements. Orgel [15] has shown that the decreasing order of the stabiliy of the electronic configurations for the "d" metals is d^5, d^{10} and d^0. So far, it has been possible to calculate the statistical weight of atoms having the stable d^5 configurations (SWASC) in the metallic crystals of the transition metals only and the data is recorded in Table X from Upadhayaya [14]. Upadhayaya and Samsonov [13] have shown that when elements have similar SWASC values, the constituent metals form solid solutions.

The alkali and alkaline earth metals form the stable s^2-configurations. Some of the features of sp elements are [14]: (i) most stable configurations are the s^2p^3 and s^2p^6 (ii) the energetic stability of the unitypic sp-configurations is reduced with the increase in the principal quantum number of the valency electrons, (iii) in elements having the s^2p^4 or s^2p^5 configuration, s^2p^6 stable configuration is formed and (iv) s^2p^1 or s^2p^2 electron configurations tend to acquire the quasi-stable sp^3 configuration owing to s-p transitions.

The existence of miscibility gaps, or otherwise, in the alloy systems of copper, silver, and gold is shown in Figs. 4 to 6 in which the nature of the electronic configuration of the valency electrons is also indicated. Although satisfactory theor-

TABLE VII Relative performance of the Hildebrand, Kumar-Hildebrand, Mott number and miscibility syndrome for the prediction of miscibility

GROUP	SOLUTE	SOLVENT														
		COPPER					SILVER					GOLD				
		Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	System	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	System	Hildebrand	Kumar Hildebrand	Modified Mott criterion	Miscibility syndrome	System
I A	Li	x	x	0	0	0	x	0	0	0	0	x	0	0	0	0
	Na	–	–	–	–	–	x	x	0	x	0	x	x	0	x	0
	K	–	–	–	–	–	–	–	–	–	–	x	x	0	x	0
II A	Be	0	0	x	0	0	x	0	0	0	0	x	0	0	0	0
	Mg	x	0	0	0	0	x	0	0	0	0	0	0	x	0	0
	Ca	x	0	0	x	0	x	0	0	x	0	x	0	0	x	0
	Sr	–	–	–	–	–	x	0	0	x	0	–	–	–	–	–
	Ba	–	–	–	–	–	x	0	0	x	x	–	–	–	–	–
III A	La	x	0	0	x	0	x	0	0	x	0	x	0	0	x	0
IV A	Ti	0	0	x	0	0	0	0	x	0	0	0	0	x	0	0
	Zr	0	0	x	0	0	–	–	–	–	–	0	0	x	0	0
	Th	0	0	x	x	0	–	–	–	–	–	0	0	x	0	0
V A	V	0	0	x	0	0	x	0	x	0	x	0	0	x	0	0
	Ta	0	0	x	0	x	x	0	x	0	x	x	0	0	0	0
VI A	Cr	0	0	x	0	x	0	0	x	0	x	0	0	x	0	0
	Mo	0	0	x	0	x	–	–	–	–	–	x	0	0	0	0
	W	–	–	–	–	–	x	0	x	0	x	–	–	–	–	–
	U	0	0	x	0	x	0	0	x	0	x	0	0	x	0	0
VII A	Mn	0	0	x	0	0	0	0	x	0	x	0	0	x	0	0
VIII A	Fe	0	0	x	0	0	x	0	0	0	x	0	0	x	0	0
	Co	0	0	x	0	0	x	0	0	0	x	x	0	x	0	0
	Ni	0	0	x	0	0	x	0	0	0	x	x	0	x	0	0
	Ru	–	–	–	–	–	x	0	x	0	x	x	0	x	0	0
	Rh	–	–	–	–	–	x	0	x	0	x	x	0	0	0	x
	Pd	0	0	x	0	0	0	0	x	0	0	0	0	x	0	0
	Ir	–	–	–	–	–	x	0	x	0	x	x	0	x	0	x
	Pt	0	0	x	0	0	x	0	x	0	0	0	0	x	0	0
	Ce	–	–	–	–	–	–	–	–	–	–	x	0	0	0	0

0 indicates miscibility

x indicates miscibility gap in liquid state

TABLE VIII Relative performance of the Hildebrand, Kumar-Hildebrand, Mott number and miscibility syndrome for the prediction of miscibility

GROUP	SOLUTE	SOLVENT														
		COPPER					SILVER					GOLD				
		Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	System	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	System	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	System
IB	Cu	–	–	–	–	–	x	0	0	0	0	0	0	x	0	0
	Ag	x	0	0	0	0	–	–	–	–	–	0	0	x	0	0
	Au	0	0	x	0	0	0	0	x	0	0	–	–	–	–	–
IIB	Al	0	x	x	0	0	0	0	x	0	0	0	0	x	0	0
	Zn	x	0	0	0	0	x	0	0	0	0	x	0	0	0	0
	Cd	x	0	x	0	0	x	0	0	0	0	x	0	0	0	0
	Hg	x	x	x	0	0	x	x	x	0	0	x	x	x	0	0
IIIB	Ga	x	0	0	0	0	0	x	x	0	0	0	0	x	0	0
	In	x	x	0	0	0	x	0	0	0	0	x	x	0	0	0
	Tl	x	0	x	x	x	x	0	0	0	0	x	0	0	0	0
IVB	Si	0	0	x	0	0	0	0	x	0	0	0	0	x	0	0
	Ge	x	0	0	0	0	0	0	x	0	0	0	0	x	0	0
	Sn	x	0	0	0	0	0	0	x	0	0	x	0	0	0	0
	Pb	x	0	x	x	x	x	0	0	0	0	x	0	0	0	0
VB	As	x	0	x	0	0	0	0	x	0	0	x	0	0	0	0
	Sb	x	0	x	0	0	x	0	0	0	0	x	0	x	0	0
	Bi	x	0	x	x	x	x	0	x	0	0	x	0	0	0	0
VIB	Se	x	0	x	x	x	x	x	x	0	x	x	0	x	0	0
	Te	x	0	x	x	x	x	0	x	0	x	x	0	x	0	0

0 indicates miscibility

x indicates miscibility gap in liquid state

TABLE IX Statistical performance of the Hildebrand, Kumar-Hildebrand, Mott and miscibility syndrome parameters of miscibility gaps in the binary alloy systems of copper, silver, and gold.

	Solvent	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	Number of systems
Subgroup A solutes	Copper	11	14	8	12	19
	Silver	11	9	16	7	23
	Gold	13	21	10	19	25
	Total	35 (52%)	44 (66%)	34 (51%)	38 (57%)	67
Subgroup B solutes	Copper	8	10	11	18	18
	Silver	9	15	9	16	18
	Gold	6	16	8	18	18
	Total	23 (43%)	41 (76%)	28 (52%)	52 (96%)	54

TABLE X Statistical weight of stable electronic configurations of transition metals (without considering intermediate spectra).

Metal	Valence electron configuration in isolated atoms	Statistical weight of configurations, %		
		d^0	d^5	d^{10}
Sc	$3d^14s^2$	84	16	0
Ti	$3d^24s^2$	57	43	0
V	$3d^34s^2$	37	63	0
Cr	$3d^54s^1$	27	73	0
Fe	$3d^64s^2$	0	54	46
Co	$3d^74s^2$	0	28	72
Ni	$3d^84s^2$	0	12	88
Cu	$3d^{10}4s^1$	0	8	92
Y	$3d^15s^2$	73	27	0
Zr	$4d^25s^2$	48	52	0
Nb	$4d^44s^1$	24	76	0
Mo	$4d^55s^1$	12	88	0
Ru	$4d^75s^1$	0	80	20
Rh	$4d^85s^1$	0	60	40
Pd	$4d^{10}5s^0$	0	18	82
Ag	$4d^{10}5s^1$	0	4	96
La	$5d^16s^2$	70	30	0
Hf	$5d^26s^2$	45	55	0
Ta	$5d^36s^2$	19	81	0
W	$5d^46s^2$	0	96	4
Re	$5d^56s^2$	0	94	6
Os	$5d^66s^2$	0	84	16
Ir	$5d^76s^2$	0	68	32
Pt	$5d^96s^1$	0	40	60
Au	$5d^{10}6s^1$	0	10	90

etical explanations are not available, the following observations can be made:

1. The interactions of the ds-metals of Group IB with the s-metals favour miscibility in liquid state with the exception of the Ag-Ba system. In this system, however, the existence of miscibility gap has not yet been established beyond shadow of doubt.

2. The ds-metals of Group IB are generally miscible with the sp-metals of Groups IIIB to VB, the exceptions are the Cu-Tl, Cu-Pb and Cu-Bi systems; the isolated atoms of these solutes respectively have the s^2p^1, s^2p^2, and s^2p^3 configurations. Since they may have tendency to acquire the quasi-stable sp^3 configuration, they have a potential tendency to form immiscible systems. On the other hand, thallium, lead, and bismuth form miscible systems with gold probably because gold can permit two electrons from the penultimate shell of eighteen electrons to take part in the valency bonding. Their binary systems with silver are also miscible in the liquid state despite the greater stability of the eighteen groups of electrons in silver. This difference in the behaviour of copper, silver, and gold can probably be accounted in terms of the size factor; a large difference ($> 21 \sim 23\%$) augments the tendency for the formation of miscibility gaps:

Solvent	Solutes % difference in atomic size		
	Tl	Pb	Bi
Cu	39	37	21
Ag	23	21	20
Au	23	21	21

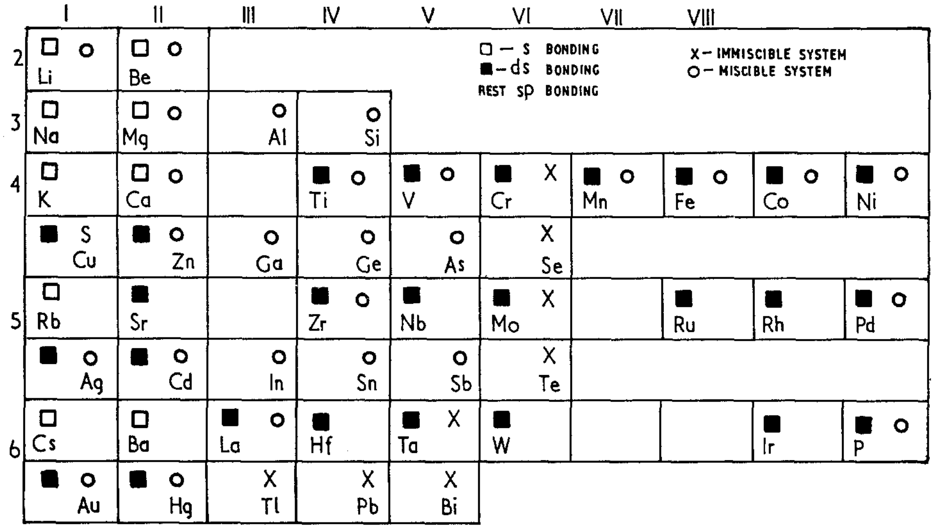
3. The miscibility characteristics of the IB metal with the d-metals can be discussed in terms of the relative difference in the SWASC values of the d^5 and d^{10} configurations of the solute and solvent metals. It appears that liquid state immiscibility may develop when this difference for the d^5 configuration exceeds sixty for the binary alloy

systems of copper and forty for those of silver, irrespective of the SWASC values of the d^{10} configuration. In case of gold, however, the SWASC values of the d^{10} configuration also assume importance; all metals with the SWASC values $d^{10} = 0$ are miscible in liquid state irrespective of the difference in SWASC d^5; but those whose SWASC d^{10} value is 50% or more, may be immiscible in gold if the relative difference in their SWASC d^5 exceeds 50%.

5. Conclusions

Considering the above, the following conclusions can be tentatively drawn:

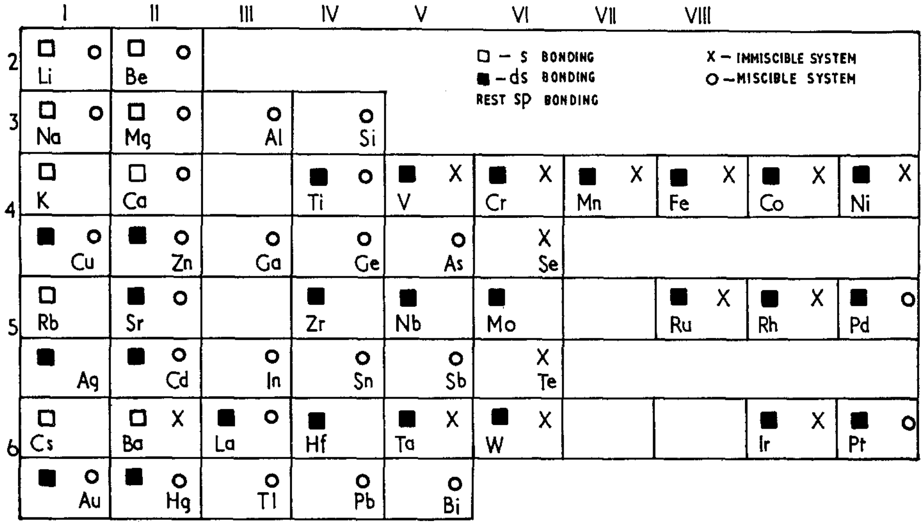
(*a*) Concepts of neither the Hildebrand parameter nor the Mott number are adequate to



	I	II	III	IV	V	VI	VII	VIII		
2	□ ○ Li	□ ○ Be								
3	□ Na	□ ○ Mg	○ Al	○ Si						
4	□ K	□ ○ Ca		■ ○ Ti	■ ○ V	■ X Cr	■ ○ Mn	■ ○ Fe	■ ○ Co	■ ○ Ni
	■ S Cu	■ ○ Zn	○ Ga	○ Ge	○ As	X Se				
5	□ Rb	■ Sr		■ ○ Zr	■ Nb	■ X Mo		■ Ru	■ Rh	■ ○ Pd
	■ ○ Ag	■ ○ Cd	○ In	○ Sn	○ Sb	X Te				
6	□ Cs	□ Ba	■ ○ La	■ Hf	■ X Ta	■ W			■ Ir	■ ○ P
	■ ○ Au	■ ○ Hg	X Tl	X Pb	X Bi					

□ — s BONDING
■ — ds BONDING
REST sp BONDING
X — IMMISCIBLE SYSTEM
O — MISCIBLE SYSTEM

Figure 4 Classification of the binary systems of copper with the various solutes arranged according to the periodic table.



	I	II	III	IV	V	VI	VII	VIII		
2	□ ○ Li	□ ○ Be								
3	□ ○ Na	□ ○ Mg	○ Al	○ Si						
4	□ K	□ ○ Ca		■ ○ Ti	■ X V	■ X Cr	■ X Mn	■ X Fe	■ X Co	■ X Ni
	■ ○ Cu	■ ○ Zn	○ Ga	○ Ge	○ As	X Se				
5	□ Rb	■ ○ Sr		■ Zr	■ Nb	■ Mo		■ X Ru	■ X Rh	■ ○ Pd
	■ Ag	■ ○ Cd	○ In	○ Sn	○ Sb	X Te				
6	□ Cs	□ X Ba	■ ○ La	■ Hf	■ X Ta	■ X W			■ X Ir	■ ○ Pt
	■ ○ Au	■ ○ Hg	○ Tl	○ Pb	○ Bi					

□ — s BONDING
■ — ds BONDING
REST sp BONDING
X — IMMISCIBLE SYSTEM
O — MISCIBLE SYSTEM

Figure 5 Classification of the binary systems of silver with the various solutes arranged according to the periodic table.

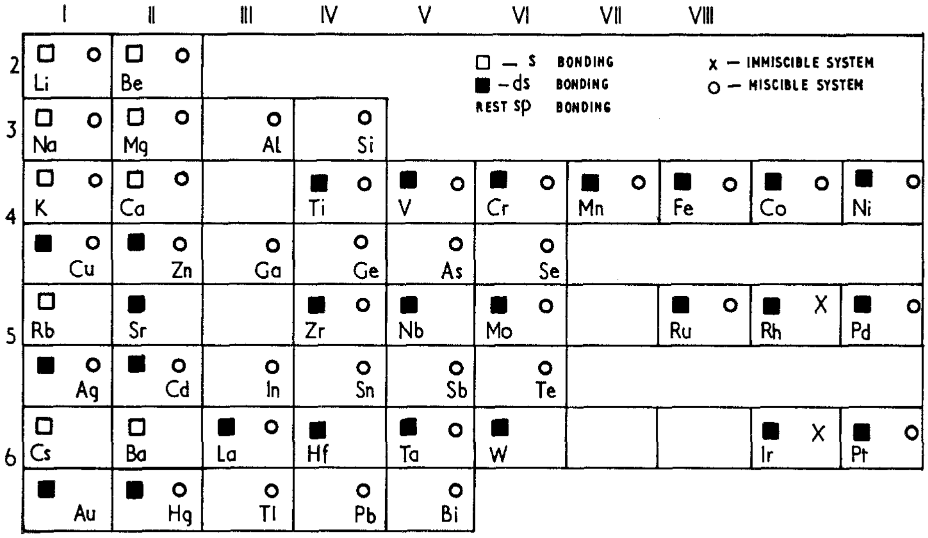


Figure 6 Classification of the binary systems of gold with the various solutes arranged according to the periodic table.

predict adequately the occurrence of miscibility gaps in binary systems.

(*b*) Statistically the Kumar-Hildebrand parameter and the concept of miscibility syndrome, which respectively integrate the Hildebrand parameter and the Mott number with the structure of liquid metals, offer much better prediction.

(*c*) The miscibility in liquid state can be discussed in terms of the electronic configuration of the valency electrons.

(*d*) It may be possible to predict the presence, or otherwise, of miscibility gaps in the unknown binary systems with the help of the numerical value of the miscibility syndrome and the position of the solute in the periodic table.

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