

Immiscibility in binary alloys of group IA metals (lithium, sodium and potassium)

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This paper evaluates the miscibility syndrome in order to predict the occurrence of miscibility gaps in the binary alloy systems of lithium, sodium, and potassium and compares its predictions with those from the Hildebrand, the Kumar-Hildebrand parameters or the concept of Mott number. It is shown that statistically, the predictions from the miscibility syndrome are most reliable. An attempt is also made to partially rationalize the nature of the binary liquid systems in terms of the electronic configuration of the valency electrons.

1. Introduction

In the previous paper [1], a concept of miscibility syndrome was introduced and it was shown that along with the size factor it could be used to predict the occurrence, or otherwise, of miscibility gaps in the binary alloy systems of the group IB metals. Although the alkali metals – lithium, sodium, and potassium – are of little commercial interest, and only a few of their binary systems with other metals are accurately known, this paper examines their alloying behaviour in liquid state to test if the same relationship between the miscibility syndrome and the size factor is valid for the miscibility gaps in the binary alloy systems of the group IA metals, which from the point of view of atomic and crystal structures, unlike those of group IB, do not conform to the hard sphere model as there is considerable difference between their ionic and atomic radii. The methodology adopted for this purpose is essentially the same as that of the previous paper [1].

2. Computations

As in [1], the Table I lists the values of the Hildebrand factor and the original Mott number calculated with the help of the Hildebrand solubility parameters. Similarly, Table II records the values of the Kumar-Hildebrand factor and the miscibility syndrome obtained with the help of the Kumar solubility parameter. Figs. 1 to 3 plot the relationships between the miscibility syndrome and the size factor and the line separating the bulk of the miscible systems

from the immiscible ones is drawn identically in all the systems, including those of the noble metals [1]. The nature of the binary systems in the liquid state is indicated in Figs. 4 to 6.

Predictions based respectively on the (i) Hildebrand factor (ii) Kumar-Hildebrand factor (iii) modified criterion of Mott number and (iv) miscibility syndrome are summarized in Table III in which the actual nature of the systems is also indicated. Table IV is a record of the number of successful predictions on the basis of each of the above criteria. The following observations can be made:

1. The concept of miscibility syndrome makes the largest number of successful predictions for the binary systems of lithium, sodium, and potassium with the metals of group IB and with metals of sub-group A of the periodic classifications.
2. When the binary systems of group IA metals are considered with the elements of the B sub-groups, the prediction is 100% correct for lithium and sodium. Of the nine known systems of potassium, only three – those with mercury, tin, and lead – are the dissenting systems.

Whereas the predictions of immiscibility from the concept of miscibility syndrome indicate the general reluctance of the two kinds of atoms to pack together to form a liquid, whether or not a system would actually show immiscibility depends on certain other not so well understood factors. Thermodynamically, miscibility is promoted by the entropy of mixing and also if the interaction

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

GROUP	SOLUTE	SOLVENT LITHIUM					SODIUM					POTASSIUM				
		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	Hildebrand excess energy (cal/mol)	Mott's electronegativity factor (cal/mol)	Original Mott number			
IA	Li	-	-	-	6 300	60	105	-	6 300	60	105	29 800	450	66		
	Na	6 300	60	105	-	-	-	3 500	200	18	-	3 500	200	18		
	K	29 800	450	66	3 500	200	18	6 400	350	18	(-)	1 100	21	(-)		
	Rb	40 400	670	60	12 100	450	27	12 100	450	27	100	100	60	2		
	Cs	58 100	800	73	(-) 23	150	1	1 800	1 600	1	21 100	2 900	2 900	7		
IIA	Mg	(-) 3 450	150	(-) 4	(-) 3 100	400	(-) 8	-	-	-	-	-	-	-		
	Ca	(-) 650	150	0.6	-	-	-	-	-	-	-	-	-	-		
	Pd	18 000	30 000	-	-	-	-	-	-	-	-	-	-	-		
	Cu	23 000	25 400	0.9	-	-	-	35 900	23 100	2	-	-	-	-		
IB	Ag	4 250	20 800	0.2	55 900	45 200	1	55 900	45 200	1	-	-	-	-		
	Au	12 400	42 000	0.3	-	-	-	-	-	-	-	-	-	-		
	Al	8 100	6 500	1	44 000	7 800	6	44 000	7 800	6	112 500	10 400	11			
	Zn	(-) 2 600	7 000	(-) 0.3	7 600	8 300	1	7 600	8 300	1	34 800	11 000	3			
IIB	Cd	(-) 1 300	8 300	(-) 0.2	300	9 800	0.03	300	9 800	0.03	14 300	12 600	1			
	Mg	5 500	16 700	3.3	(-) 1 400	18 700	(-) 0.07	(-) 1 400	18 700	(-) 0.07	1 700	22 600	0.1			
	Ga	-	-	-	28 600	12 000	2	28 600	12 000	2	78 400	15 100	5			
	In	(-) 1 300	6 500	(-) 0.2	-	-	-	-	-	-	-	-	-	-		
IIIB	Tl	(-) 1 900	6 000	(-) 0.3	3 000	7 200	0.4	3 000	7 200	0.4	22 100	9 700	2			
	Si	7 700	17 500	0.4	-	-	-	-	-	-	-	-	-	-		
	Sn	(-) 1 230	10 000	(-) 0.02	18 600	11 600	2	18 600	11 600	2	57 300	14 800	4			
	Pb	(-) 2 250	8 600	(-) 0.3	4 500	10 000	0.5	4 500	10 000	0.5	26 100	13 000	2			
VIB	Sb	-	-	-	10 700	33 200	0.3	10 700	33 200	0.3	42 200	38 400	1			
	Bi	(-) 1 550	15 900	(-) 0.1	2 930	17 900	0.2	2 930	17 900	0.2	22 000	21 700	1			
VIB	Te	-	-	-	(-) 2 800	32 000	(-) 0.09	(-) 2 800	32 000	(-) 0.09	-	-	-			

TABLE II Computed data for the evaluation of miscibility according to the miscibility syndrome and Kumar-Hildebrand parameter

SOLUTE	SOLVENT				SODIUM				POTASSIUM			
	Kumar-Hildebrand energy	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand energy	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand energy	Miscibility syndrome	Size factor (%)	Kumar-Hildebrand energy	Miscibility syndrome	Size factor (%)
Li	-	-	-	(-) 1 400	23.66	22.3	(-) 1 400	23.66	18.2	(-) 900	1.96	34.1
Na	(-) 1 400	23.66	22.3	-	-	-	-	-	-	(-) 1 250	6.67	19.4
K	(-) 900	1.96	51.7	(-) 1 250	6.67	24.0	(-) 1 250	6.67	24.0	-	-	-
Rb	(-) 600	0.93	62.5	(-) 1 100	3.29	32.9	(-) 1 100	3.29	32.9	(-) 1 200	1.77	7.2
Cs	(-) 270	0.32	75.1	(-) 900	2.05	43.2	(-) 900	2.05	43.2	(-) 1 200	19.97	15.4
Mg	(-) 1 500	10.09	5.2	(-) 500	0.17	14.0	(-) 500	0.17	14.0	1 000	0.35	30.6
Ca	(-) 1 800	12.01	27.6	(-) 1 100	2.83	4.3	(-) 1 100	2.83	4.3	-	-	-
Pd	400	0.01	9.5	-	-	-	-	-	-	-	-	-
Cu	27	0.001	15.9	-	-	-	-	-	-	-	-	-
Ag	(-) 822	0.04	4.9	800	0.04	22.3	800	0.04	22.3	-	-	-
Au	(-) 750	0.02	5.1	1 000	0.02	22.4	1 000	0.02	22.4	-	-	-
Al	(-) 1 800	0.27	5.8	(-) 1 500	0.19	22.9	(-) 1 500	0.19	22.9	(-) 1 300	0.12	379
Zn	(-) 1 350	0.2	12.3	(-) 200	0.03	28.3	(-) 200	0.03	28.3	1 600	0.14	42.2
Cd	(-) 1 700	0.2	2.0	(-) 900	0.09	19.8	(-) 900	0.09	19.8	100	0.009	35.4
Hg	(-) 900	0.05	7.1	(-) 900	0.05	24.0	(-) 900	0.05	24.0	(-) 700	0.03	38.7
Ga	-	-	-	(-) 650	0.05	24.5	(-) 650	0.05	24.5	250	0.02	46.9
In	(-) 1 700	0.26	7.0	-	-	-	-	-	-	-	-	-
Tl	(-) 1 800	0.30	17.2	(-) 1 300	0.18	4.2	(-) 1 300	0.18	4.2	(-) 800	0.08	22.7
Si	5 600	0.32	22.6	-	-	-	-	-	-	-	-	-
Sn	(-) 1 700	0.17	0.6	(-) 900	0.08	18.7	(-) 900	0.08	18.7	80	0.005	34.4
Pb	(-) 1 800	0.21	15.2	(-) 1 300	0.13	5.8	(-) 1 300	0.13	5.8	(-) 600	0.05	24.1
Sb	-	-	-	1 100	0.03	9.5	1 100	0.03	9.5	3 700	0.1	27.0
Bi	(-) 1 600	0.1	2.4	(-) 700	0.04	6.3	(-) 700	0.04	6.3	550	0.03	24.5
Te	-	-	-	400	0.01	6.7	400	0.01	6.7	-	-	-

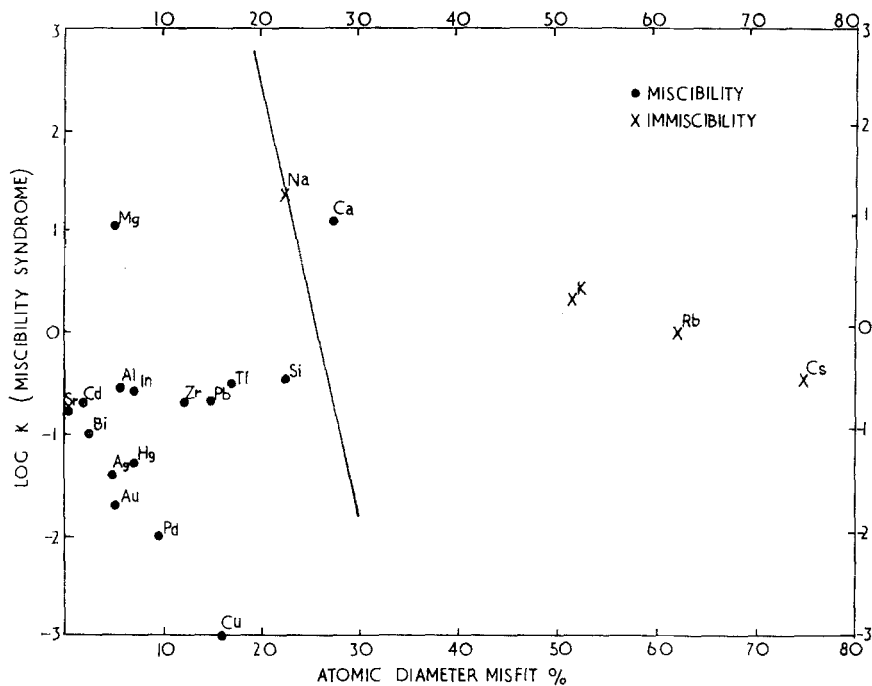


Figure 1 Indicator diagram for liquid state miscibility in lithium.

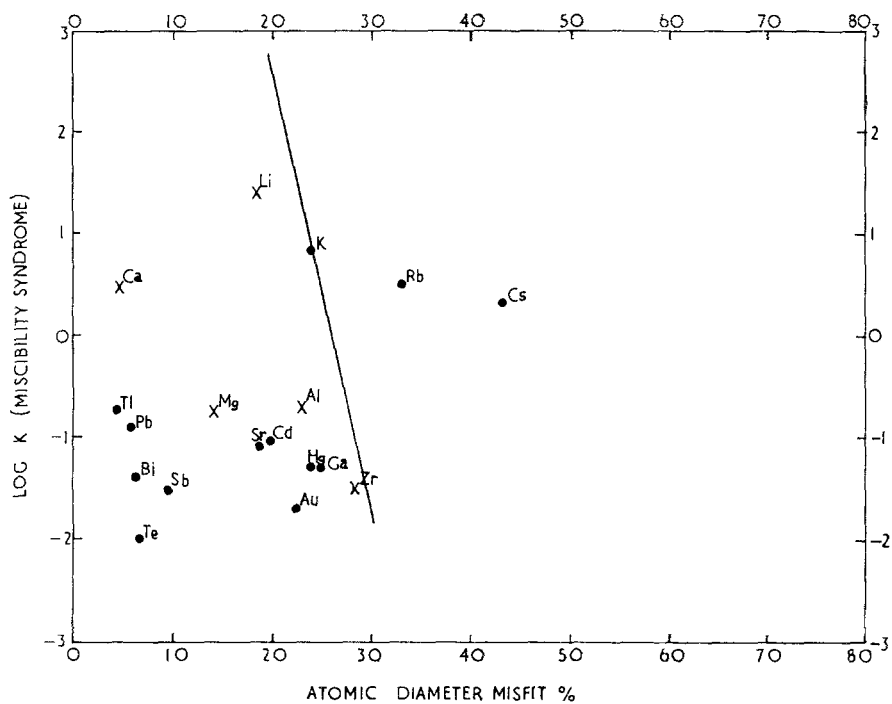


Figure 2 Indicator diagram for liquid state miscibility in sodium.

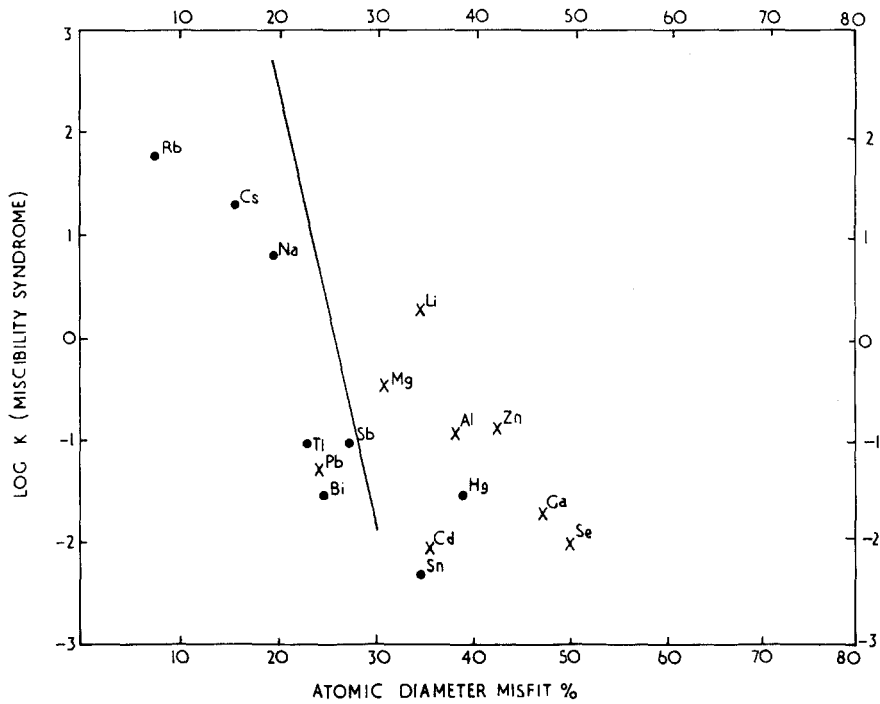


Figure 3 Indicator diagram for liquid state miscibility in potassium.

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

□ — s BONDING X — IMMISCIBLE SYSTEM
 ■ — d s BONDING ○ — MISCIBLE SYSTEM
 REST—sp BONDING

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

between unlike atoms is stronger than between like atoms.

However, Hume-Rothery and Anderson [2] showed that if the interaction between unlike atoms is profound, it may ultimately lead to the

formation of liquid immiscibility unless interrupted by the formation of solid phases. Thus geometrical considerations of atomic packing during the formation of a liquid of great stability can also contribute to the formation of misci-

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

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

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

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

bility gaps in certain binary systems. This factor is not taken into account, in either of the four parameters of miscibility discussed in this or the earlier paper. Since the strong interaction between unlike atoms responsible for the formation of intermetallic compounds in solid state, is not suddenly destroyed on melting [3], the occurrence of KHg_2 (mp $270^\circ C$) and KSn_2 (mp

$750^\circ C$) in the K-Hg and K-Sn systems could increase the stability of single-phase liquid and render the systems miscible, otherwise predicted to be immiscible from the concept of miscibility syndrome. The immiscibility of the K-Pb system could likewise be attributed to the (i) geometrical considerations of atomic packing and (ii) profound interaction between the solvent-

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

SOLUTE	SOLVENT LITHIUM				SODIUM				POTASSIUM							
	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome
Li	-	0	-	-	x	0	x	0	x	x	0	x	0	0	x	x
Na	x	0	x	x	-	-	-	-	-	x	-	-	-	0	x	0
K	x	0	x	x	x	0	x	0	-	x	-	-	-	-	-	-
Rb	x	0	x	x	x	0	x	0	0	0	x	0	0	0	0	0
Cs	x	0	x	x	x	0	x	0	0	0	x	0	0	0	0	0
Mg	0	0	x	0	x	0	0	0	x	x	x	x	x	x	x	x
Ca	0	0	x	0	0	0	x	0	x	-	-	-	-	-	-	-
Pd	x	x	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Cu	x	x	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Ag	x	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0
Au	x	0	0	0	0	x	0	0	0	-	-	-	-	-	-	-
Al	x	0	0	0	x	0	0	0	x	x	0	x	0	0	x	x
Zn	0	0	x	0	x	0	0	x	x	x	x	0	x	x	x	x
Cd	0	0	x	0	x	0	0	0	0	x	0	0	x	x	0	0
Hg	x	0	0	0	0	0	x	0	0	x	0	0	x	0	x	0
Ga	-	0	-	-	x	0	0	0	0	x	0	0	x	x	x	x
In	0	0	x	0	-	-	-	-	-	-	-	-	-	-	-	-
Fl	0	0	x	0	x	0	0	0	0	x	0	0	0	0	0	0
Si	x	x	0	0	-	-	-	-	-	-	-	-	-	-	-	-
Sn	0	0	x	0	x	0	0	0	0	x	0	0	x	x	0	0
Pb	0	0	x	0	0	0	0	0	0	x	0	0	0	0	0	0
Sb	-	-	-	-	x	x	0	0	0	x	x	0	0	x	0	0
Bi	0	0	x	0	x	0	0	0	0	x	0	0	0	x	0	0
Te	-	-	-	-	0	x	x	0	0	-	-	-	-	-	-	-

0 - indicates miscibility
 x - indicates immiscibility

TABLE IV Statistical performance of the Hildebrand, Kumar-Hildebrand, Mott and miscibility syndrome parameters of miscibility gaps in the binary alloy systems of lithium, sodium, and potassium.

	Solvent	Hildebrand	Kumar-Hildebrand	Modified Mott criterion	Miscibility syndrome	Number of systems
Subgroup A solutes	Li	6	2	5	6	7
	Na	2	3	2	1	6
	K	3	4	3	5	5
	Total	11 (63%)	9 (50%)	10 (56%)	12 (67%)	18
Subgroup B solutes	Li	7	11	6	13	13
	Na	4	7	9	12	13
	K	5	5	6	7	10
	Total	16 (44%)	23 (64%)	21 (58%)	32 (89%)	36

solute atoms. An important weakness of this discussion is that much of it is speculative.

The existence of miscibility gaps can also be discussed in terms of the electronic configuration of the valency electrons. On this basis, the following observations can be made:

1. The s-bonded alkali metals, in general, tend to have good miscibility with the ds-bonded elements of the group IB and IIB provided the size factor is less than about 22 to 23% and are likely to be immiscible if the size factor exceeds 28%.

2. The interactions of the alkali metals with the sp-bonded elements almost invariably lead to the formation of intermetallic compounds of relatively greater stability and the fusion temperatures of the intermetallic compounds increase in the direction indium → tin → antimony and thallium → lead → bismuth. It is difficult to establish any criterion of size factor, but it appears that a system is likely to be immiscible if the size factor exceeds 22 to 23%. But the important exception are the systems of potassium with the tin, antimony or bismuth.

3. The interaction of the s-bonded alkali metals with the other s-bonded elements of the group IA and IIA is difficult to predict. Thus Na-Ca system is immiscible with a size factor of only 4% but Na-Rb is miscible with a size factor of 33%.

3. Conclusions

These observations indicate that the concept of miscibility syndrome can account for the occurrence of miscibility gaps statistically in the binary system of metals of diverse atomic and crystal structures. It is significant that it commands almost the same degree of success for the alloy systems of both the alkali and the noble metals, although these metals are different from one another from the point of view of electronic and atomic structures. So far it has only been possible to make only a partial rationalization of the miscibility gaps in terms of the electronic configuration of the solvent and solute elements.

Acknowledgement

The author wishes to record his thanks to Professor V. A. Altekar, Director, National Metallurgical Laboratory for his interest in the project on liquid metals and permission to publish the paper.

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Received 26 October 1971 and accepted 9 February 1972.