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Preface

It has again been possible, in Volume 5, to find authors for all chapters from amongst the inorganic chemists in the University of Nottingham, and the Senior Reporter would like to express his appreciation of the hard work to which they were prepared to commit themselves, and of the enthusiasm which they have shown. Because of financial pressures, we were called upon to produce a volume only two-thirds the length of Volume 4. The shorter the volume the more difficult becomes the task of choosing amongst the large number of worth-while research papers published during the year. Readers will detect a further move in the direction of structure and reactivity as against purely physical properties; for example, Chaper 4 no longer includes cover of binary and ternary intermetallic phases, which have been included in earlier volumes. All authors regret that much good work which merited mention has had to be omitted purely because of space limitation. Selection has to be based on originality and novelty, but also on the need to present a readable account, and thus to include reference to all published papers on any chosen theme. In this difficult task the authors have found that the opportunity to work as a team, and to maintain day to day discussion on possible overlap between chapters, has been of considerable advantage.

C. C. ADDISON

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Elements of Group I

BY P. HUBBERSTEY

1 Introduction

The definition of the limits of the literature search pertinent to the present Report is complicated by the extensive role of the alkali metals as simple counter-cations. In general, papers have been abstracted which are relevant to a number of broad subject groups in which the role of the alkali metals is unique. Consequently, the format of this Chapter is such that the inorganic chemistry of the alkali metals is considered collectively in sections which reflect topics presently of interest and importance.

For certain topics (*e.g.* cation solvation, molten salts, crown and cryptate complexes), the chemistry of the Group I and II metals is closely interwoven; in these cases, the data abstracted are considered once only in the relevant section in this Chapter.

The extraction of alkali-metal cations from salt solutions into organic solvents has been the subject of four papers.[1-4] The ion $[\pi\text{-}3\text{-}1,2\text{-}B_9C_2H_{11}]Co^-$ has been proposed as a nearly ideal hydrophobic anion for extraction of M^+ ions into $C_6H_5NO_2$ *via* formation of ion pairs.[1] Li^+ has been selectively extracted from nearly neutral aqueous solutions of alkali-metal salts *via* the formation of the trioctylphosphine adduct of a lithium chelate of fluorinated β-diketones; although high separation factors were obtained from Na^+, K^+, Rb^+, and Cs^+, selectivity from the alkaline-earth-metal cations was found to be poor.[2] The extraction of M^+ into $PhNO_2$ and $MeNO_2$ using hexafluoroacetylacetonate has also been investigated.[3,4] Dissociation constants of the alkali-metal enolates were determined, the extent of association of enolate ion with enol to give a dimeric ion was deduced, and the latter's formation constant calculated.

2 The Alkali Metals as Solvent Media

The role of liquid sodium as a heat-exchange medium in the fast breeder reactor, and that of liquid lithium as a prime candidate for use as the blanket medium in a deuterium–tritium-fuelled thermonuclear reactor, has maintained interest in the solution chemistry of these liquid metals.

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[1] J. Rais, P. Selucky, and M. Kyrs, *J. Inorg. Nuclear Chem.*, 1976, **38,** 1376.
[2] F. G. Seeley and W. H. Baldwin, *J. Inorg. Nuclear Chem.*, 1976, **38,** 1049.
[3] S. Tribalat and M. Grall, *Compt. rend.*, 1976, **282,** *C*, 457.
[4] S. Tribalat and M. Grall, *Compt. rend.*, 1976, **282,** *C*, 539.

Phase equilibria for Li–Li_3N dilute solutions have been investigated by two independent groups of authors.[5–7] Pulham *et al.*[5,6] have determined the hypoeutectic and hypereutectic liquidi by thermal[5] and by electrical resistance[6] methods, respectively. The freezing point of Li (453.64 K) is depressed by 0.25 K to 453.39 K at the eutectic composition 0.068 mol % N. The depression was used to calculate the solid solubility of Li_3N in Li (0.024 mol%N) at the eutectic temperature.[5] The solubility of Li_3N in liquid Li increases smoothly from the eutectic to 2.77 mol % N at 723 K.[6] Over a wide temperature range, the data can be represented by equation (1). These latter data are corroborated by those of Veleckis *et al.*[7] [equation (2)], who used a direct sampling technique. This agreement resolves the problem of the earlier inconsistent data[8] referred to in the previous Report.[9] Veleckis *et al.*[7] also measured the equilibrium nitrogen pressure over solid Li_3N at temperatures between 933 and 1051 K. From a thermodynamic analysis of the solubility and decomposition data, the standard free energy of formation of solid Li_3N ($\Delta G_f^\ominus$/kJ mol^{-1}) was estimated to be $138.9 \times 10^{-3}\ T/K - 163.6$. For dilute solutions of Li_3N in Li, the Sieverts law constant ($K_s/\mathrm{atm}^{-1/2} = x_{Li_3N}\, p^{-1/2}$) is given by $-13.80 + 14590\,(T/\mathrm{K})^{-1}$. The melting point of Li_3N was found to be 1086 K, in good agreement with the previously reported value of 1088 K.[7]

$$\log_{10}x_N = 1.168 - 2036(T/\mathrm{K})^{-1} \qquad (473 \leqslant T/\mathrm{K} \leqslant 708) \qquad (1)$$

$$\log_{10}x_{Li_3N} = 1.323 - 2107(T/\mathrm{K})^{-1} \qquad (468 \leqslant T/\mathrm{K} \leqslant 714) \qquad (2)$$

Phase equilibria of Li–LiH and Li–LiD dilute solutions have also been studied by Pulham *et al.*[5,6,10,11] The maximum depression of the freezing point of Li by LiH[5] (LiD)[10] is 0.08 K (0.075 K), corresponding to a eutectic composition of 0.016 mol%H (0.013 mol%D). These data, which indicate negligible solid solubility of the salts in Li, have been used to show that both hydrogen and deuterium dissolve in liquid Li as monatomic solute species.[11] Typically, the depression caused by small LiH concentrations (Figure 1) follows quite closely the line derived theoretically for monatomic solutes. The theoretical line for a diatomic species is included in the Figure for comparison. The solubilities of LiH[6] and of LiD[10] in liquid Li have been determined by electrical resistance methods at temperatures up to 824 K (5.68 mol%H), and 729 K (2.63 mol%D), and can be represented over a considerable part of the temperature range by equations (3) and (4), respectively. The hydrogen–deuterium isotope effect has been discussed and the experimental data have been extrapolated to predict the behaviour of tritium in liquid Li.[10,11]

$$\log_{10}x_H = 1.523 - 2308(T/\mathrm{K})^{-1} \qquad (523 \leqslant T/\mathrm{K} \leqslant 775) \qquad (3)$$

$$\log_{10}x_D = 2.321 - 2873(T/\mathrm{K})^{-1} \qquad (549 \leqslant T/\mathrm{K} \leqslant 724) \qquad (4)$$

---

[5] P. Hubberstey, R. J. Pulham, and A. E. Thunder, *J. C. S. Faraday I*, 1976, **72,** 431.

[6] P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, *J. Less-Common Metals*, 1975, **42,** 325.

[7] R. M. Yonco, E. Veleckis, and V. A. Moroni, *J. Nuclear Materials*, 1975, **57,** 317.

[8] P. F. Adams, P. Hubberstey, and R. J. Pulham, *J. Less-Common Metals*, 1975, **42,** 1.

[9] R. J. Pulham, in 'Inorganic Chemistry of the Main-Group Elements' (Specialist Periodical Reports), ed. C. C. Addison, The Chemical Society, London, 1976, Vol. 4, Ch. 1.

[10] P. F. Adams, P. Hubberstey, R. J. Pulham, and A. E. Thunder, *J. Less-Common Metals*, 1976, **46,** 285.

[11] P. Hubberstey, P. F. Adams, R. J. Pulham, M. G. Down, and A. E. Thunder, *J. Less-Common Metals*, 1976, **49,** 253.

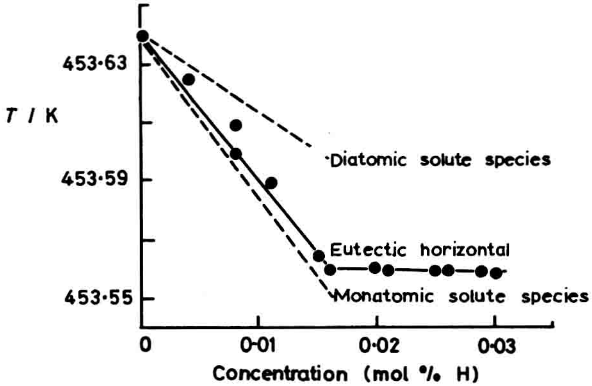

Figure 1 *Depression of the freezing point of lithium by small concentrations of hydrogen, showing evidence for monatomic solute species*
(Reproduced by permission from *J. Less-Common Metals*, 1976, **49,** 253)

New solubility data for NaH in liquid Na have been determined by Whittingham[12] in a detailed study (610—677 K) of the thermodynamic and kinetic properties of the liquid Na–H_2 system. Comparison with some previous data has been effected and a composite solubility equation (5) formulated.

$$\log_{10}x_H = 1.818 - 3019(T/K)^{-1} \quad (435 \leqslant T/K \leqslant 673) \qquad (5)$$

These new solubility data for hydrogen isotopes have been collated and compared to the corresponding solubilities in NaK and K;[11] surprisingly, hydrogen is least soluble in sodium.

Solubility data have been used[6,10,11] to determine solvation enthalpies, U_x, [defined as in equation (6)] for N^{3-}, O^{2-}, H^-, and D^- in Li and for H^- in Na and K. The values of U_x are collected in Table 1. Those for H^- and D^- in Li are lower than those for O^{2-} and N^{3-} by factors of *ca.* 2^2 and 3^2, respectively, corresponding to increasing U_x with increasing charge of solute. Those for H^- in Li, Na, and K are very similar, that in Li being the greatest.[11] Solvation enthalpies have been derived[13] in *ab initio* M.O. calculations of solvation clusters in Li and Na. By comparison with experimental data, the best model was deduced to be that of a tetrahedral solvation sphere of cations supplemented by a further metal tetrahedron positioned on the three-fold axes of the first solvation sphere. Other incidental results to emerge from the calculations are the effective radii for Li (0.1675 nm), Na (0.1715 nm), and H (0.0525 nm in Li and

Table 1 *Solvation enthalpies for non-metal solutes in liquid alkali metals*

Solvent	Potassium	Sodium	Lithium	Lithium	Lithium	Lithium
Solute	Hydrogen	Hydrogen	Hydrogen	Deuterium	Oxygen	Nitrogen
U_x/kJ mol^{-1}	−362	−365	−427	−413	−1960	−3473

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[12] A. C. Whittingham, *J. Nuclear Materials*, 1976, **60,** 119.
[13] A. Mainwood and A. M. Stoneham, *J. Less-Common Metals*, 1976, **49,** 271.

0.0535 nm in Na) and the effective charges on the H (−0.45 in Li and −0.25 in Na).[13]

$$X^{n-}(g) + M \xrightarrow{U_x} X^{n-}(M) \tag{6}$$

The chemistry of liquid alkali metal–hydrogen solutions has been surveyed.[11] Whereas hydrogen and nitrogen act independently in Li at 693 K, hydrogen and oxygen interact in Na at 673 K, according to equilibrium (7). Hydrogen–oxygen interactions in the other alkali metals are also considered and rationalized in terms of the enthalpy changes of the corresponding solid-state reaction. Furthermore, Y has been shown to react with hydrogen in Li at 673 K to form a mixture of Y(H) solid solution and YH_2 according to reaction (8).[11]

$$O^{2-} + H^- \rightleftharpoons OH^- + 2e^- \tag{7}$$

$$Li(H) + Y \rightarrow Li + Y(H) + YH_2 \tag{8}$$

Enrichment of deuterium in the gaseous phase above dilute Li–LiD solutions ($x_D = 10^{-5}$) has been observed by Ihle and Wu[14] at temperatures above 1240 K. This supports the contention that deuterium can be removed from highly dilute solutions in Li by distillation. The results are of importance in the context of the technology of thermonuclear reactors and have been extrapolated to Li–LiT solutions.[14]

Several papers pertinent to the elucidation of the corrosive properties of very dilute solutions of non-metals in liquid alkali metals have been published.[15—21] The corrosion of V,[15] Nb,[15] Ta,[15] Mo,[16] and W[16] plates suspended in dynamic liquid sodium, containing more than 5 p.p.m. oxygen, has been examined at 873 K; the products were analysed through a matrix of Na by *X*-ray diffraction techniques. The ternary oxides Na_4VO_4 and $NaVO_2$ were formed on V, together with a V(O) solid solution.[15] For Nb and Ta, only a single ternary oxide Na_3MO_4 (M = Nb or Ta) was observed, together with a M(O) solid solution.[15] Although corrosion of Mo was found to be independent of oxygen concentration, no ternary oxide products being observed, that of W was found to be strongly influenced by initial oxygen concentration in the Na. At low oxygen levels, the cubic phase Na_3WO_4 was identified; at very high oxygen levels in static Na, however, the orthorhombic phase Na_6WO_6 was observed. Inclusion of labile carbon in the system containing Mo caused the formation of Mo_2C.[16] The closely related solid-state reaction of Na_2O with Mo and W under vacuum gave the ternary phases Na_4MoO_5 and Na_6WO_6, respectively, together with unreacted refractory metal and Na vapour.[16]

Barker and Hooper[17] have reinvestigated the products of the reaction of liquid Na with CrO_3 at temperatures up to 873 K; CrO_2, Cr_2O_3, and Na_2CrO_4 were also studied as substrates. The ternary oxide $NaCrO_2$ is found in each case in which reaction took place. The previously accepted reaction product, Na_2CrO_3, was not formed; the error has been rationalized in terms of the experimental procedure, and improved techniques have been developed.[17] Gellings *et al.*[18] have also studied

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[14] H. R. Ihle and C. H. Wu, *J. Phys. Chem.*, 1975, **79,** 2386.

[15] M. G. Barker and C. W. Morris, *J. Less-Common Metals*, 1975, **42,** 229.

[16] M. G. Barker and C. W. Morris, *J. Less-Common Metals*, 1976, **44,** 169.

[17] M. G. Barker and A. J. Hooper, *J. C. S. Dalton*, 1976, 1093.

[18] H. van Lith, E. G. van den Broek, and P. J. Gellings *Inorg. Nuclear Chem. Letters*, 1975, **11,** 817.

the reaction of CrO_3 with liquid Na, their results corroborating the identification of $NaCrO_2$ as product. The product of these reactions, $NaCrO_2$, together with the other ternary oxides Na_3CrO_4 and Na_4CrO_4, has been prepared by Barker *et al.*[19] by the reaction of Na_2O and Cr_2O_3 or Cr, and it has been characterized by *X*-ray powder diffraction techniques. $NaCrO_2$ decomposes reversibly to the simple oxides at *ca.* 1068 K.[19]

The reaction of pure liquid Li with MO_2 ($M = Ti$, Zr, Hf, or Th) has been shown to follow thermodynamic predictions.[20] TiO_2 and ZrO_2 give rise to Li_2O and the appropriate transition metal; HfO_2 yields Hf metal, Li_2O, and a tetragonal phase, which may be the ternary oxide $LiHfO_2$; ThO_2 does not react. Reaction with liquid Li doped with dissolved nitrogen, however, converts all four oxides, in differing degrees, into either the mononitride or a ternary nitride Li_2MN_2 ($M = Zr$, Hf, or Th).[20]

Liquid K reduces NiO to Ni metal at 458 K with the concomitant formation of the ternary oxides K_2NiO_2 and K_2NiO_3; thermomagnetic analysis indicates that the reaction occurs in a single step.[21] K_2NiO_2 was also prepared by the reaction of equimolar quantities of K_2O and NiO; K_2NiO_3 was produced by the reaction of K_2O and NiO in O_2 or by heating K_2NiO_2 in a stream of O_2.

The reaction between Ba and N_2 in liquid Na has been investigated at 573 K.[22,23] Solubility studies[22] showed that the reaction of a 4.40 mol % Ba solution occurs in two stages; (i) dissolution of N_2 (N_2 is insoluble in pure liquid Na), and (ii) precipitation of Ba_2N, the initial product of the reaction. The occurrence of these two processes is reflected in the resistivity studies[23] effected on a number of Na–Ba solutions (between 0.34 and 6.89 mol % Ba). The extent of the solution process was found to be a linear function [equation (9)] of the initial Ba concentration, the solubility limit corresponding to an overall reaction composition approximating to Ba_4N. This ratio, and the decrease in resistivity which invariably occurred during the solution process, leads to the concept of strong preferential solvation of the nitride ion by Ba cations, perhaps in the form of a 'Ba_4N' solvated unit.[23]

$$x_N = 0.25 x_{Ba} \qquad (0 < x_{Ba} \leqslant 0.0689) \tag{9}$$

The reaction of C_2H_4 with liquid K has been studied in the range 503—671 K.[24] At low temperatures, self-hydrogenation occurs precisely according to equation (10). The surface reaction is explained by dissociative adsorption of C_2H_4 into H adatoms, which are subsequently employed in hydrogenation. With increasing temperature, progressively less C_2H_6 is produced, which is attributed to the loss of H from the surface by solution in the metal.[24]

$$3C_2H_4 \xrightarrow{K} 2C_2H_6 + 2C \text{ (or } K_2C_2) \tag{10}$$

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[19] M. G. Barker and A. J. Hooper, *J. C. S. Dalton*, 1975, 2487.
[20] M. G. Barker, I. Alexander, and J. Bentham, *J. Less-Common Metals*, 1975, **42,** 241.
[21] M. G. Barker and A. P. Dawson, *J. Less-Common Metals*, 1976, **45,** 323.
[22] C. C. Addison, R. J. Pulham, and E. A. Trevillion, *J. C. S. Dalton*, 1975, 2082.
[23] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. C. S. Dalton*, 1976, 1105.
[24] G. Parry and R. J. Pulham, *J. C. S. Dalton*, 1975, 2576.

3 Metallic Solutions and Intermetallic Compounds

The nature of the bonding in intermetallic phases has been discussed,[25,26] and an attempt has been made to demonstrate qualitatively the dependence of both the number of phases in a binary system and their relative thermal stabilities on the electronic configurations of the component atoms. Particular attention has been devoted to compounds of the alkali metals with Hg,[25] Sn,[26] Pb,[25] Sb,[25] and Bi.[25]

The preparation of the novel compounds K_2Cs and K_7Cs_6 by precipitation from solid K–Cs solutions at temperatures below 183 K has been reported.[27] Structural analysis has shown that K_2Cs ($a = 0.9065$, $c = 1.4755$ nm at 178 K) is isotypic with the hexagonal Laves phase Na_2K, whereas K_7Cs_6 ($a = 0.9078$, $c = 3.2950$ nm at 178 K) forms hexagonal crystals with a novel kind of Frank–Kasper structure. Although the K atoms in K_7Cs_6 are sited in two 12-co-ordination polyhedra, the Cs atoms occupy one of four sites with 14-fold, 15-fold (×2), and 16-fold co-ordination. The $K \cdots K$, $Cs \cdots Cs$, and $K \cdots Cs$ distances vary from 0.454 to 0.461, from 0.501 to 0.546, and from 0.466 to 0.574 nm.[27]

The Li–In phase diagram has been exhaustively re-examined by Alexander *et al.*,[28] using thermal and *X*-ray diffraction analysis. The work has confirmed the liquidus data of Grube and Wolf[29] and delineated the solid-state relationships. Eleven new phases (Table 2), together with the previously known LiIn phase (which extends from *ca.* 46 to between 55 and 63 mol % Li, depending on temperature), have been observed. The discovery of new phases, of which only five are stable at room temperature, has removed the apparent anomaly between the Li–In and the Li–Ga and Li–Tl systems. The solid solubility of Li in In is low (*ca.* 1.5 mol % Li at 432 K) and that of In in Li is very small.[28]

Intermetallic phases of the Li–Pd[30] and Li–Pt[31] systems have been synthesized

Table 2 *Intermetallic phases of the* Li–In *system*[28]

Phase	*Model fomula*	*Composition*/mol % Li		*Phase transformation temperatures (approx.)*/K	
		derived	*observed*		
β	LiIn	50.0	46.5—63.0	—	903[a]
γ	Li_7In_4	63.6	63.6	—	583[b]
δ	Li_2In	66.7	66.8	—	743[c]
ε	Li_5In_2	71.5	71.8	353[d]	670[b]
ζ	Li_8In_3	72.8	71.9	—	353[b]
η	$Li_{73}In_{27}$	73.0	—	618[d]	698[c]
θ	$Li_{11}In_4$	73.4	—	608[d]	658[b]
ι	Li_3In	75.0	75.8	—	686[c]
κ	Li_4In	80.0	80.7	—	583[e]
λ	Li_4In	80.0	80.7	583[e]	673[c]
μ	Li_6In	85.7	85.5	398[d]	573[c]
ν	$Li_{12}In$	92.3	92.6	413[d]	533[c]

[a] Melting point; [b] peritectoid decomposition; [c] peritectic decomposition; [d] eutectoid formation; [e] phase transformation

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[25] V. I. Kober and I. F. Nichkov, *Russ. J. Phys. Chem.*, 1975, **49,** 829.

[26] V. I. Kober and I. F. Nichkov, *Russ. J. Phys. Chem.*, 1975, **49,** 962.

[27] A. Simon, W. Bramer, B. Hillenrotter, and H.-J. Kullman, *Z. anorg. Chem.*, 1976, **419,** 253.

[28] W. A. Alexander, L. D. Calvert, R. H. Gamble, and K. Schinzel, *Canad. J. Chem.*, 1976, **54,** 1052.

[29] G. Grube and W. Wolf, *Z. Electrochem.*, 1935, **41,** 675.

[30] J. H. N. van Vucht and K. H. J. Buschow, *J. Less-Common Metals*, 1976, **48,** 345.

[31] W. Bronger, B. Nacken, and K. Ploog, *J. Less-Common Metals*, 1975, **43,** 143.

and their structures elucidated; pertinent structural data for seven Li–Pd phases (including Li_2Pd and LiPd), as determined in *X*-ray diffraction studies, and for Li_2Pt and LiPt, as determined using neutron-diffraction techniques, are collected in Table 3.

Table 3 *Pertinent structural parameters for intermetallic phases in the* li–Pd *and* Li–Pt systems

Phase	*Space group*	*Structure type*	*a*/nm	*c*/nm	*Ref.*
$LiPd_7$	$Fm3m$	$LiPt_7$	0.7660	—	30
$LiPd_2$	hexag. P	—	0.3836	0.4336	30
$LiPd^a$	$P6$	LiRb	0.2741 0.2767	0.4280 0.4131	30 30
LiPd	$Pm3m$	CsCl	0.2977	—	30
Li_2Pd	$P6/mmc$	AlB_2	0.4227	0.2732	30
Li_3Pd	$Fm3m$	BiF_3	0.6187	—	30
$Li_{15}Pd_4$	$I43d$	$Cu_{15}Si_4$	1.0676	—	30
Li_xPd^a ($6<x<10$)	cubic F	—	1.9009 1.9347	— —	30 30
LiPt	hexag.	—	0.2728	0.4226	31
Li_2Pt	—	AlB_2	0.4186	0.2661	31

[a] LiPd and Li_xPd exhibit wide homogeneity ranges

Thermodynamic properties of liquid Li–Tl[32] and of liquid Na–X[33] (X = Cd, Hg, In, Tl, Sn, Pb, Sb, Bi, S, Se, or Te) have been studied. The unsymmetrical form of the nature of the dependence on concentration of the thermodynamic characteristics of the Li–Tl system, which exhibits negative deviations from Raoult's Law, is thought to be consistent with the equilibrium diagram.[32] The dependence on concentration of the entropy of mixing in the Na–X systems is S-shaped, the point of inflexion corresponding to formation of intermetallic compounds.[33] This behaviour is attributed to a high degree of short-range order in the liquid, and of partial ionic character of the bonds in these intermetallic compounds. Short-range order has also been studied in liquid Li–Pb solutions by neutron-diffraction techniques.[34] The data indicate a preference for unlike nearest neighbours; this is manifest in a reduction of distance between unlike neighbours (0.295 nm) as compared with the mean distances between the pure components ($Li \cdots Li = 0.300$ nm; $Pb \cdots Pb = 0.340$ nm). It has been suggested that the short-range order is probably due to salt-like $Li \cdots Pb$ bonding. No evidence for the existence of isolated Li_4Pb clusters was obtained; indeed, in liquid Li_4Pb, each Pb atom is surrounded by *ca.* 10 Li atoms.[34]

4 Solvation of Alkali-metal Cations

The majority of data published on the solvation (both aqueous and non-aqueous) of alkali-(and alkaline-earth-)metal cations is of but peripheral interest to the inorganic chemist. Consequently, the papers abstracted for this section of the Report are quite selective, dealing principally with the structural and spectroscopic properties of these solutions.

[32] S. P. Yatsenko and E. A. Saltykova, *Russ. J. Phys. Chem.*, 1975, **49,** 292.

[33] A. G. Morachevskii, E. A. Maiorova, and A. I. Demidov, *Russ. J. Phys. Chem.*, 1975, **49,** 1093.

[34] H. Ruppersberg and H. Egger, *J. Chem. Phys.*, 1975, **63,** 4095.