Invited Review

Solubilities and Solution Chemistry in Liquid Alkali Metals

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Summary. Experimental solubility data for metals and non-metallic substances in liquid alkali metals have been collected from literature, critically evaluated, and selected for recommendation. Sometimes results for a selected system at a selected temperature vary over more than an order of magnitude. This is not uniquely connected with a poor precision of the measurements. Some impurities may spectacularly modify the solubilities and, moreover, definition of a saturating solute phase is not always a simple task. Based on supplementary experiments one may explain several phenomena which often accompany dissolution processes. These accompanying processes are essentially the same as those frequently observed in solution chemistry.

Keywords. Alkali metals; Solubility; Solutions; Thermochemistry.

Introduction

The compatibility of construction materials with liquid alkali metals is of fundamental importance in the technology of energy production and conversion. The alkali metals are known as the most effective coolants of high temperature sources from atomic, fusion, and chemical reactors; they are also used in space technique. The construction of high energy electrochemical cells as well as thermionic and magneto-hydrodynamic converters is only possible using these metals. They could be also more effectively used in extraction metallurgy, especially in that of some precious metals from their ores and wastes.

The knowledge of solubility parameters is therefore essential for corrosion prediction for solid construction materials and all kinds of technology work-out in which liquid alkali metals are and will be used. A review of experimental methods used for the solubility determinations in solid-liquid metal system is presented in Ref. [1]. The majority of the techniques described therein may also be used for such determinations in the liquid alkali metal systems.

Within the framework of the IUPAC Solubility Data Commission, all available experimental results concerning the solubility of metals [2] and non-metallic

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substances [3] in liquid alkali metals were collected from literature. These data were critically evaluated and, after their selection, recommended, in case of poor reliability as tentative suggestions.

Graphical Representation of Solubilities

Selected solubility values in the five alkali metal solvents at 873 K ordered according to the atomic number of solute element are shown in Fig. 1. This way of presentation of solubility data is very compact (although its irregular shape may be confusing at first) and seems to be more impressive than tables. It allows to investigate changes of the solubility stepping from one element to another as well as to compare the solubilities of elements from the same group or period. Drastic changes of the solubilities of neighbouring elements are rarely observed. Strong variations appear between the solubilities of halogens and noble gases in liquid alkali metals. The changes generally reflect intermittent features of the elements, typical for the periodic table. The kind of solvent metal plays a secondary role in most cases; this fact causes proportional differences in the solubility of a selected solute element. For example, He is always less soluble than H in Li, Na, and K, but the difference between their solubilities decreases with the atomic number of the solvent. The low-melting metals (block s and p electrons) mix quite easily with liquid alkali metals; the high-melting metals (block d), however, have only a poor
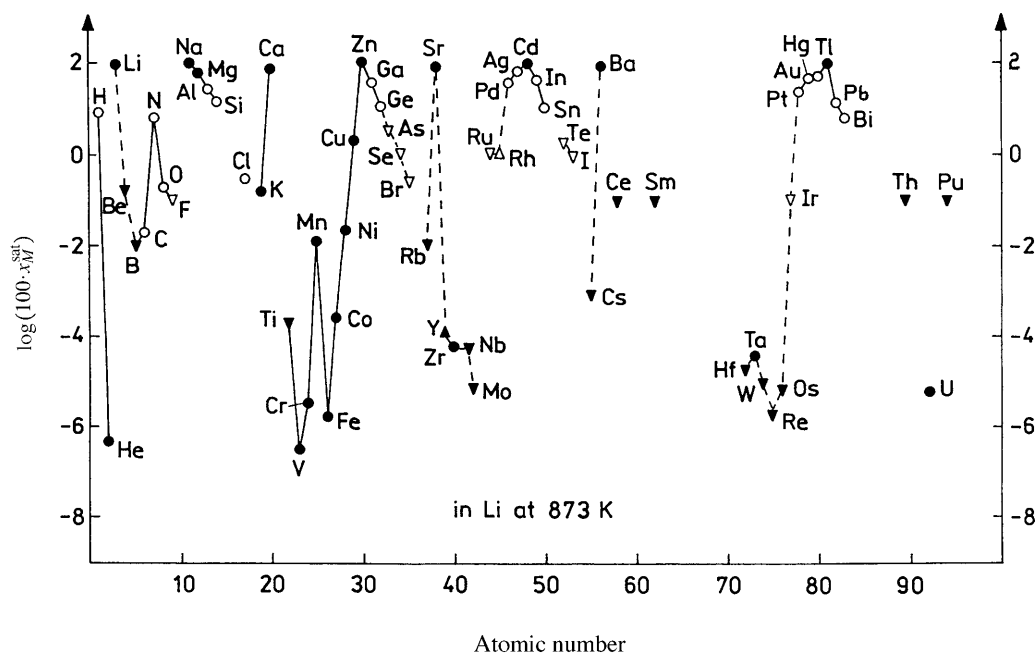

Fig. 1. Solubilities of elements in liquid Li (a), Na (b), K (c), Rb (d), and Cs (e). The circles denote definite solubility data, whereas triangles directed with their tops up point to lower detection limits, those with tops down to upper detection limits of analytical procedures used for solubility determinations. In the case that a compound between a solute and solvent is the equilibrium solid phase, the symbols are empty; full symbols are used for practically pure elements as the equilibrium saturating phase
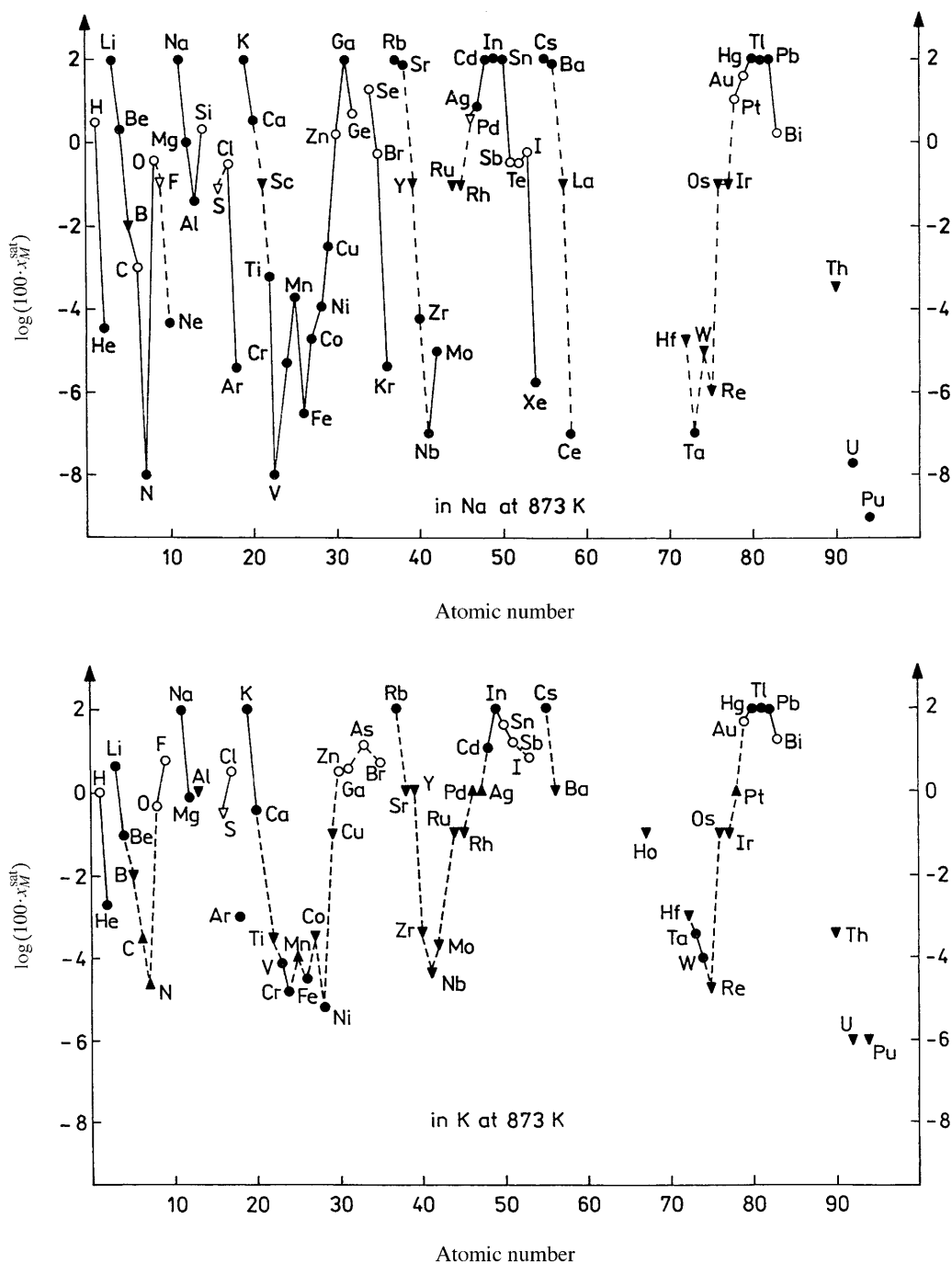
Fig. 1 (continued)

tendency to miscibility with alkali metals. Still we do not know much about reliable quantitative solubility data of lanthanides and actinides (block f), but generally their solubilities are expected to be rather low. It seems that bivalent lanthanides (Eu and Yb) display relatively higher solubilities (at levels comparable with those of Ca, Sr, and Ba as it was found in other metallic solvents [4]). It is
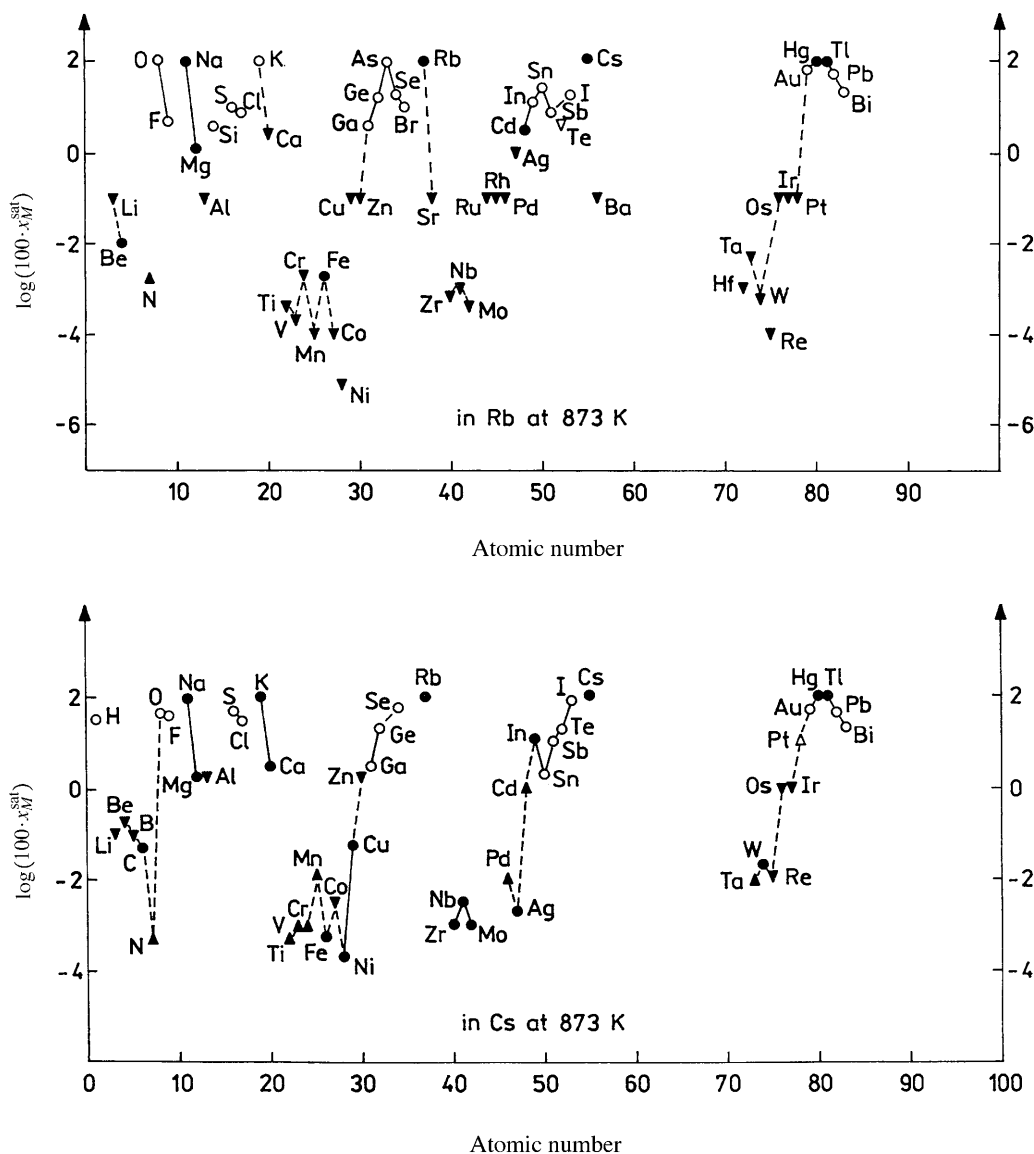
Fig. 1 (continued)

quite characteristic that Mn (with the half-filled d electron level) is always better soluble than the neighbouring metals Cr and Fe. The relatively best solvent for the metals, in general, is Cs, and the worst Na. From the thermodynamic point of view one should observe a successive decrease of solubility (especially of high-melting metals) from Li to Cs.

Influence of Non-Metallic Elements on Solubilities

Anomalies are observed for many temperature dependencies of the solubility of selected transition metals. The slopes of such dependencies (logarithm of solubility vs. reciprocal temperature) have distinctly too small negative values, and, for

example, the solubilities of Ce in Na or Ti in K even decrease with temperature. Since the pure dissolution process must be endothermic from the thermodynamic point of view, the exothermic enthalpy of solution implies that the dissolution is connected with a chemical reaction. In fact, many transition metals form stable oxides, nitrides, carbides, and these compounds or their derivatives (mixed oxides or nitrides) were observed to be the equilibrium solid phases in systems which are only slightly contaminated. Thus, we actually measure a sum of solubilities of absolutely pure metal (S_M^{pure}) and metal bonded to a non-metallic impurity (S_M^{bonded}), where $S_M = 100 \cdot x_M^{\mathrm{sat}}$.

$$S_M = S_M^{\mathrm{pure}} + S_M^{\mathrm{bonded}} \tag{1}$$

Most of the analytical methods used cannot distinguish between the components of Eq. (1), since many analytical procedures are carried out at room temperature with frozen samples in which equilibrium may be quite different from that in the high temperature region. It seems incidental that both terms of Eq. (1) are of the same order of magnitude. No methods to purify alkali metals down to levels below 10^{-4} mol% of impurities are available. In addition, the purity of any solute metal is rarely above 99.9999 mol%. Therefore, we measure, particularly in the case of transition metals, only the apparent solubilities, and such experimental values are needed for practical applications of these metals as constructional materials. The unknown S_M^{pure} value may be sometimes several orders of magnitude lower than S_M^{bonded}. Predictions of S_M^{pure} may be best obtained from the cellular model of *Miedema* and coworkers [4, 5] and of S_M^{bonded} from thermodynamic considerations according to *Grundy* [6]. Many investigators have observed that an impurity may originate from either the solute or the solvent, but the final equilibrium, reached in hours or days, is the same. In this way we approached the phenomenon of partitioning, which is a standard problem in the extraction step of solution chemistry. It may be applied in an analogous manner in systems in which the solvent is a liquid metal in contact with a solid one.

According to Ref. [7], if O is introduced in the practically immiscible system of solid Zr and liquid K at 1088 K, its partition coefficient K_{p} is expressed by Eq. (2), where $[O_{\mathrm{Zr}}]$ and $[O_K]$ are concentrations of O in the Zr and K phases, respectively.

$$K_{\mathrm{p}} = [O_{\mathrm{Zr}}]/[O_K] = 2000 \tag{2}$$

The law expressed by Eq. (2) has a simple thermodynamic background and is obeyed if the concentrations of oxygen in Zr and K are below their solubility limits. From a strictly thermodynamic point of view one ought to use the O activities in both phases (Zr and K) instead of concentrations. Thus, under equilibrium conditions the majority of O is gettered into the Zr phase (finally forming ZrO_2), and a very small amount of O remains in liquid K. However, in the case of the equilibration of Nb with Li the majority of O will be collected in the liquid Li phase.

Another example is the Cs sorption from a solution in Na by graphite or charcoal introduced into the liquid Na. Cs is partially adsorbed on the C surface, but generally Cs forms a stable Cs-C intercalation compound; the reaction proceeds even if Cs vapour over liquid Na is in contact with graphite [8]. Thus, the partitioning of elements opens a possibility to absorb impurities (N, C, O, H, some

metals), a fact which may be used for the purification of materials as well as for the determination of the content of contaminants.

As mentioned above, O present even as a minor impurity in a transition metal-alkali metal system leads frequently to a specific ternary interaction in the liquid metal which causes enhanced solubility of that metal according to the exemplary reaction

$$Cr + 2O + Na \rightleftharpoons NaCrO_2 \tag{3}$$
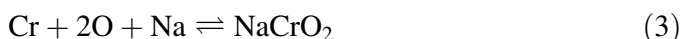
Such a reaction is analogous to complexation, well known in inorganic and analytical chemistry; O plays the role of the complexing agent. If the value S_M^{bonded} increases according to Eq. (3), the analytically determined apparent S_M also increases. Many compounds of salt-like character $NaVO_2$, $KNbO_3$, Rb_2MoO_4, Cs_2UO_4) have been detected as solid equilibrium phases or corrosion products instead of pure metals. Most frequently, $S_M^{bonded} > S_M^{pure}$ in such cases. It has been best shown in case of the solubility of Ta in liquid K that increasing O concentration causes an increase of apparent Ta solubility up to 3 mol% Ta if the O concentration reaches 1 mol% O, whereas the solubility of absolutely pure Ta in absolutely pure K should be distinctly below the limit of Ta detection (10^{-4} mol% Ta at 1273 K). The interaction product in this system was identified as K_3TaO_4, and this substance should be treated as the real solute instead of pure Ta. A presence of Hf (which is a very strong O getter) in Ta alloy substantially decreases the Ta solubility because less O is available for Ta to form K_3TaO_4. Or in other words: the thermodynamic activity of O decreases in the presence of Hf.

Since the majority of such ternary solid equilibrium phases are typical salts known from inorganic chemistry, one can imagine that anions and cations, after their dissociation in the metallic solution, are solvated by polarized alkali metal atoms; a formation of ion pairs seems also to be possible. Monoatomic and diatomic ions of non-metals were found in the alkali metals (for example H^-, O^{2-}, N^{3-}, CN^-, C_2^{2-}) [9]. The solvation enthalpies measured for H^-, O^{2-}, and N^{3-} increase roughly in the order 1:4:9 as would be expected for ions of increasing charge. Small ions (F^-) have a coordination number of 6, those of comparable size with the solvating (Cl^-) atom have number 8, and large ions (I^-) reach even number $8 + 6$ in liquid Na solutions.

Due to the strong interaction of Li with O, formation of ternary Li-*M*-O salts has not been detected in Li medium. However, N as an impurity acts as a complexing agent, thus enhancing solubilities of transition metals by formation of *e.g.* Li_3FeN_2. The existence of Mo-N-Li complexes formed in liquid Li has been investigated by electro-transport experiments [10], and the solubility of Mo in Li contaminated with N has been observed to be higher than in pure Li. Generally, a ratio of non-metallic impurity to solute metal concentrations in a liquid metal is higher than the stoichiometric ratio in the ternary complex formed as the reaction product. An introduction of Ba, Ca, or Sr into liquid Li increases the solubility of N, probably due to the complexation of N by the alkaline earth metals [11].

Sometimes a decrease of the solubility upon addition of a third element to a binary system is observed. Si and N are moderately soluble in Li (both about 2 mol% at 723 K), but due to Eq. (5), virtually insoluble Li_5SiN_3 is formed [12].

$$5\,Li + Si + 3N \rightleftharpoons Li_5SiN_3 \tag{4}$$
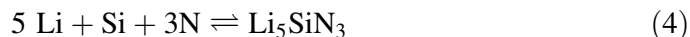
Equilibria of such reactions have been described by typical solubility products in the case of Hg [13] or Pb [14] as solvents; however, an analogous behaviour was not yet documented experimentally in the case of binary (ternary) compounds precipitated in alkali metals. Equations (3) and (4) are analogous to the dissolutive and the precipitative complexation, both well known in inorganic and analytical chemistry.

The dissolution of the majority of metals with p, d^8, d^9, and d^{10} electrons in alkali metals is frequently connected with the formation of intermetallic compounds as the equilibrium solid phases. No influence of impurities (O, N) on such equilibria has been reported. Analyzing values of diffusion coefficients of such metals in liquid alkali metals (Li, Na, K) one may come to the conclusion that the solute metals exist in the liquid phase as solvates of similar composition as in the equilibrium solid phase [15].

Approximate calculations have shown that *e.g.* In diffuses (and exists) in liquid Na as InNa. This fact was unambigously proved for amalgams for which we know plenty of diffusion coefficients with the highest accuracy. Thus, probably $HgNa_3$ (in the Na-rich), certainly Hg_4Na (in the Hg-rich) [16], and surely Hg_2Na molecules (in transitional composition) [17] are present in these liquid alloys. Depending on the difference of electronegativities, the bonding in such molecules varies from covalent to ionic character. If the electronegativity difference reaches a maximum, as in the case of Au and Cs, AuCs resembles NaCl (for the exactly stoichiometric 1:1 alloys) and behaves as an electrical insulator in the solid and a typical ionic conductor in the liquid state, since Au^- and Cs^+ ions are only present therein.

If a solute metal does not interact specifically with either a non-metallic impurity or a solvent alkali metal, it should exist in atomic form as reflected by the fact that its experimentally measured diffusion coefficient is equal (within the precision of its determination) to the diffusion coefficient predicted by the simple equation of *Sutherland-Einstein*. There are not many experimental examples of diffusion coefficients in the alkali metals (li, Na, K), but this concept is particularly well documented for Hg as solvent metal [15].

Another interesting phenomenon observed by some investigators is the adsorption of metals on the surface of another metal introduced into the liquid alkali metal. For example, Sb has been observed to adsorb on the surface of stainless steel foil, and the amount adsorbed was proportional to the Sb content in liquid Na [18]. Such a method of determination of concentrations avoids difficulties of the sampling procedure, the presence of a suspension of a solute, and allows monitoring the approach to equilibrium.

The most spectacular discrepancies, which are observed for the most comprehensively investigated system, concern the solubility data of Fe in liquid Na [2]. At low temperatures and high O concentrations, the apparent solubility of Fe is high (between 10^{-4} and 10^{-3} mol% Fe) and weekly dependent on temperature, the most probable equilibrium phase being $NaFeO_2$ in this case. Between 760 and 900 K Fe solubility changes more strongly with temperature, and the most probable equilibrium phase is then Na_4FeO_3. Above 900 K and at very low O concentrations in Na, the Fe solubility was observed to be between 10^{-7} and 10^{-6} mol% Fe, the values almost approaching the theoretical solubility prediction of [15].

In the case of non-metals dissolved in the alkali metals one may also observe some peculiarities. Li is the best solvent to p^2 and p^3 elements and H, whereas for the rest of non-metals Cs is the best solvent medium. N in Li forms a quite stable compound Li_3N being relatively well soluble in liquid Li. The nitrides of other alkali metals are unstable. Consequently, in Na, K, Rb, and Cs the dissolved species is the N_2 molecule with a solubility as low as those of noble gases. This has been concluded from the completely different dissolution behaviour of N in the heavier alkali metals. A good solubility of P in liquid Li was manifested during the decomposition-dissolution of Fe_3P in the liquid metal at 1073 K; after the reaction, P remained dissolved in Li, whereas Fe formed a precipitate [19].

Systems with P and As are not well known; however, it is sure that especially in the case of alkali metals several compounds of various stoichiometries are formed. Very different equilibrium solid phases are observed in case of C: Li_2C_2 is formed in Li, graphite is the most stable phase in Na, and in K, Rb, and Cs one observes the formation of series of intercalation phases starting from KC_8, RbC_8, and CsC_8, respectively. Na_2C_2 is a metastable phase, and the stability of K_2C_2, Rb_2C_2, and Cs_2C_2 is certainly even smaller. Some authors claim an equilibrium between graphite and Na_2C_2 in liquid Na. A formation of carbonyls, carbonates, carbides, alkylates, alkanes, and cyanides is possible when other impurities as O, transition metals, H, or N are present in Na containing C (Fig. 2). Thus, even in slightly contaminated systems the solubility of C in Na may be the sum of the concentrations of all species being present therein, from which only the solubilities of Li_2C_2, Na_2CO_3, and NaCN in liquid Na have been determined [3]. Na also dissolves C out of Fe based alloys as steels or precipitates C on such materials if the chemical activity of C in the solid is lower than in molten Na.
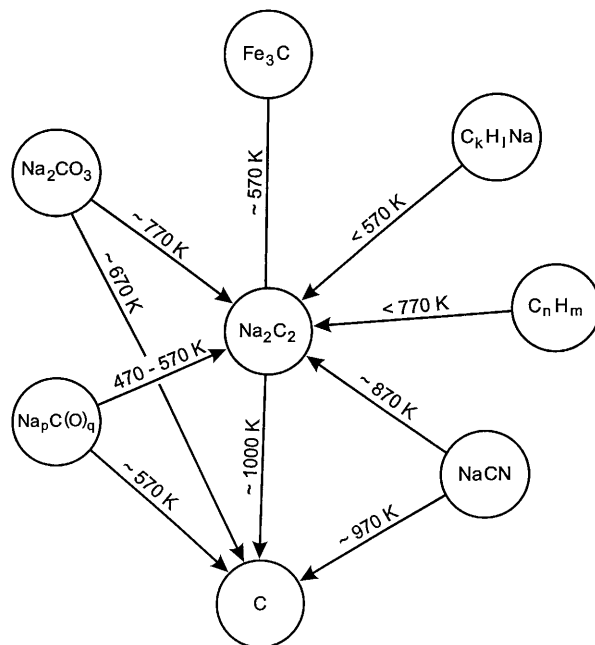

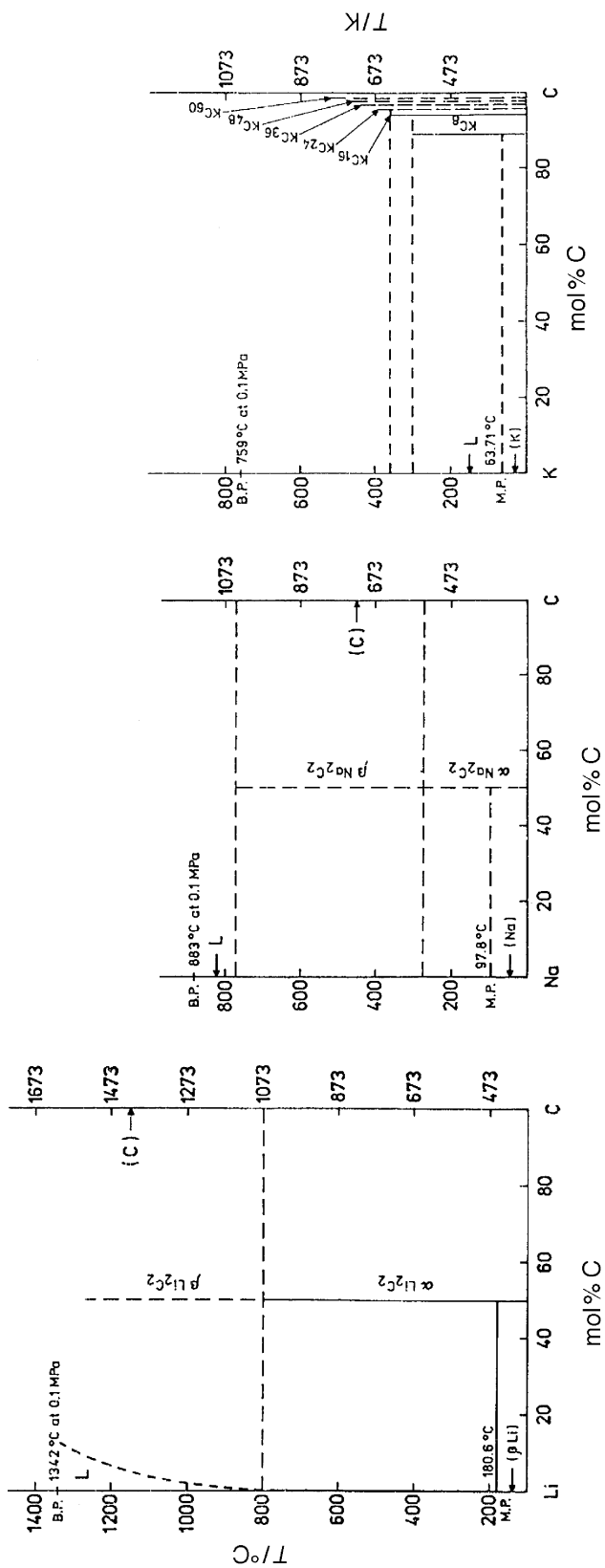**Fig. 2.** Scheme of reactions of C with impurities in liquid Na

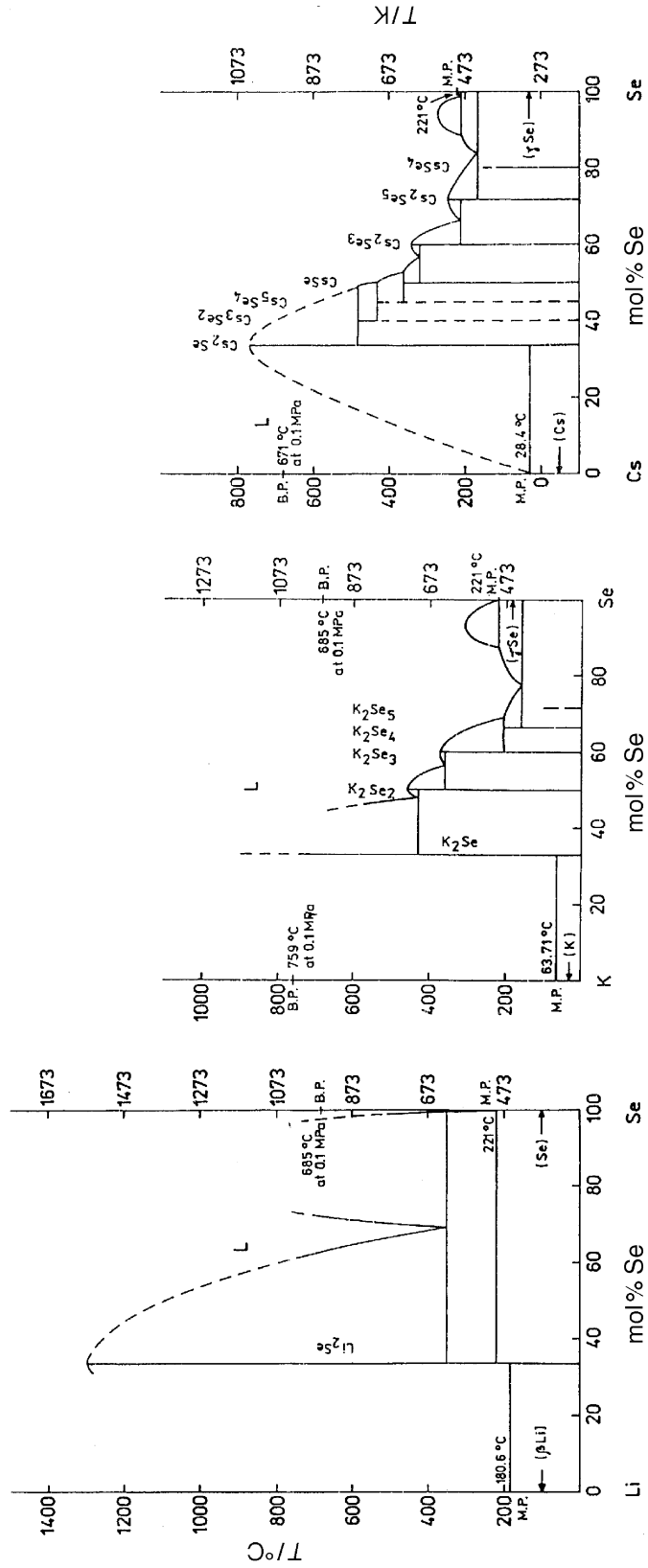**Fig. 3.** Phase diagrams of the Li-C, Na-C, and K-C systems [3]

Fig. 4. Phase diagrams of the Li-Se, K-Se, and Cs-Se systems [3]; the solubility of Se in Cs as estimated from the phase diagram ($\log(100 \cdot x_{Se}^{sat}) = 1.3$) differs from the value in Fig. 1e which is based on different methods
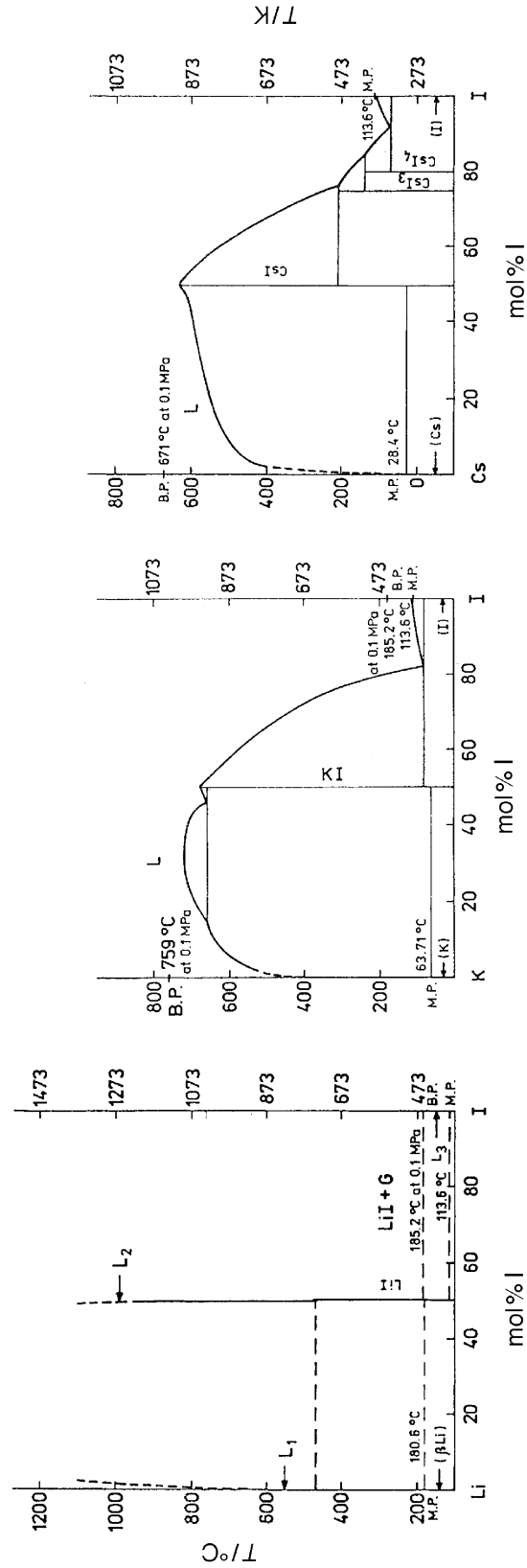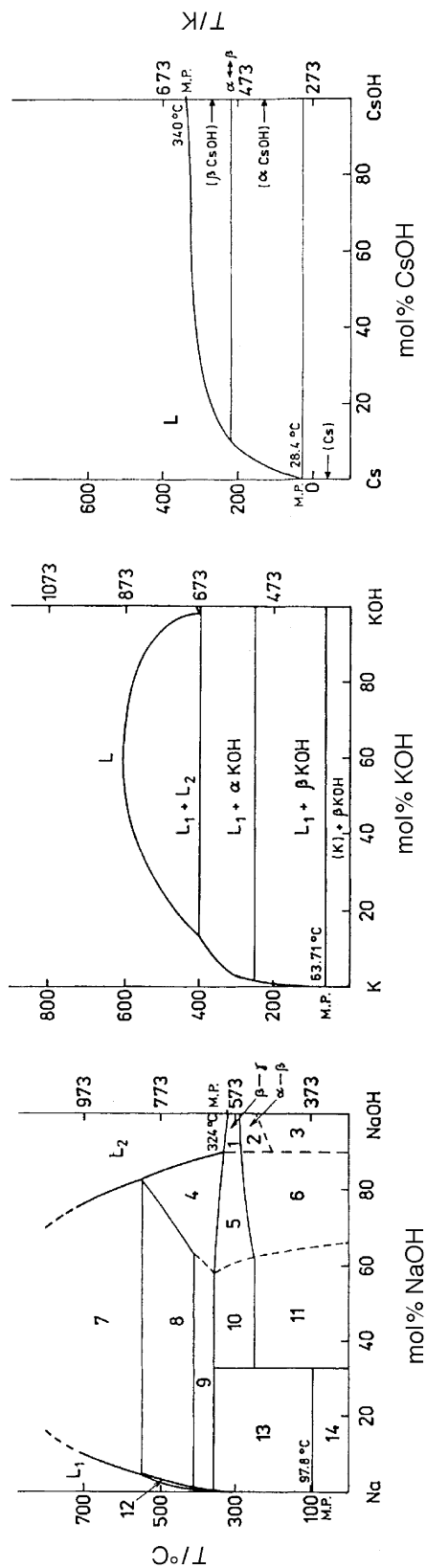
Fig. 5. Phase diagrams of the Li-I, K-I, and Cs-I systems [3]; the solubility of I in Cs as estimated from the phase diagram ($\log(100 \cdot x_{KI}^{sat}) = 103$) differs from the value in Fig. 1e which is based on different methods

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Fig. 6. Phase diagrams of the Na-NaOH, K-KOH, and Cs-CsOH systems [3]

It would seem that O forms simple oxides (as Li_2O) with all alkali metals; however, with increasing atomic number of the alkali metal several peroxides (Na, K, Rb, Cs) and suboxides (Rb, Cs) are formed as the solid equilibrium phases. By analogy, Na, K, Rb, and Cs form polysulfides, -selenides, or -tellurides. F, Cl, and Br form always 1:1 compounds with the alkali metals, but I affords additionally RbI_3, CsI_3, and CsI_4. These differences are illustrated on exemplary phase diagrams in Figs. 3–5.

Further differences between the alkali metals are observed if two non-metals are simultaneously present therein. Li_2NCN are found in Li, but in Na or K typical cyanides were identified if the alkali metals contained C and N. Hydroxide, carbonate, nitrate, and amide of Li do not exists in liquid Li, and all these salts are decomposed to simpler compounds (hydride, nitride, oxide, acetylide). Na displays a very complicated equilibrium with NaOH, Na_2O, and NaH, but KOH, RbOH, and CsOH are well soluble and quite stable in solvent metals (Fig. 6). It has been found in some experiments that carbonates and amides of Na, K, and Cs are stable in the corresponding alkali metals.

Solubilities in Mixed Solvents

The solubilities of a few metals in mixed K-Na melts have been investigated. However, the experimental conditions, in the sense of temperature and impurity levels, were different, making any comparison impossible [2]. In the case of non-metallic elements we collected the corresponding data which are shown in Fig. 7. As the solubilities of Cl, H, and He increase smoothly and slightly with the K content in the melt, the irregular changes of solubility of O indicate that O is preferentially solvated by K. Thus, once again this phenomenon resembles the well known preferential solvation observed for ionic species in mixed solvents.
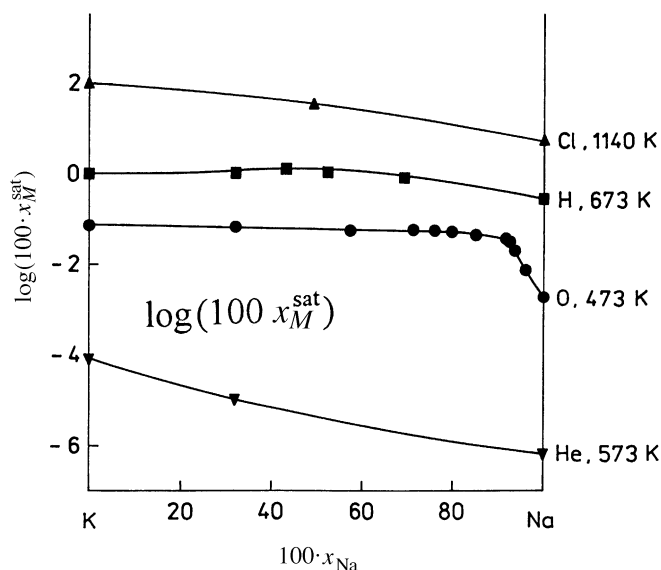

Fig. 7. Solubilities of He, O, H, and Cl in K-Na alloys [3]

Conclusions

Taking into account all the mentioned effects, which have not always been considered by the respective investigators, it is easy to explain why experimental data for a selected system scatter sometimes for several orders of magnitude. Summing up the observations, one may easily observe the significant specifity of interactions of alkali metals with dissolved metals as well as with non-metals, although many chemists have the impression that the alkali metals display identical chemical features differing only in their physical properties. In each particular case we quoted individual examples, but there are plenty of instances allowing to generalize this point of view.

Acknowledgements

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