Alkali metal compounds have been known since antiquity. In 1807, Sir Humphry Davy surprised everyone by electrolytically preparing (and naming) potassium and sodium metals. In 1808, he noted their interaction with ammonia, which, 100 years later, was attributed to solvated electrons. After 1960, pulse radiolysis of nearly any solvent produced solvated electrons, which became one of the most studied species in chemistry. In 1968, alkali metal solutions in amines and ethers were shown to contain alkali metal anions in addition to solvated electrons. The advent of crown ethers and cryptands as complexants for alkali cations greatly enhanced alkali metal solubilities. This permitted us to prepare a crystalline salt of \( \text{Na}^- \) in 1974, followed by 30 other alkalides with \( \text{Na}^- \), \( \text{K}^- \), \( \text{Rb}^- \) and \( \text{Cs}^- \) anions. This firmly established the \(-1\) oxidation state of alkali metals. The synthesis of alkalides led to the crystallization of electrides, with trapped electrons as the anions. Electrides have a variety of electronic and magnetic properties, depending on the geometries and connectivities of the trapping sites. In 2009, the final surprise was the experimental demonstration that alkali metals under high pressure lose their metallic character as the electrons are localized in voids between the alkali cations to become high-pressure electrides!

1. Introduction

The alkali metals Li, Na, K, Rb, Cs, Fr occupy the first column of the periodic table. Their common oxidation state of +1 made their chemistry simple and predictable. Most general chemistry textbooks devote only three to four pages to this group. One can get the impression that, except for the fun that can be had with the addition of alkali metals to water, this group is boring! Here, we see that alkali metal chemistry can be full of surprises and hidden complexity that take the boredom out of this family of elements!
2. Davy’s surprising discoveries

In 1807, shortly after Volta’s disclosure that electrical current could be produced by a ‘pile’ of alternating copper and zinc plates, immersed in an acidic solution, Humphry Davy made an amazing discovery. He passed current through molten potash (potassium hydroxide), and noted that, at the negative platinum electrode, ‘small globules having a high metallic lustre, and being precisely similar to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed’ [1]. Davy referred to metallic potassium as ‘the basis of potash’, but, as with the ‘basis of soda’, he soon chose to name these new metals potassium and sodium. While he did not claim at the time that they were elemental, he probably felt this to be the case, as seems clear from his statement, ‘there seems, however every reason to believe that the metallic bases of the alkalies, and the common metals, will stand in the same arrangement of substances; and as yet we have no good reasons for assuming the compound nature of this class of bodies’.

The production of very low density, highly reactive, soft metals by electrolysis of stable, water-free alkali hydroxides came as a great surprise to scientists of the time. The alkali metal family suddenly became much more interesting! This discovery led to fame and knighthood for Humphry Davy, whose many other accomplishments were also major contributions to science and technology.

Davy continued to experiment with the properties and reactions of sodium and potassium metals. In 1808, just a year after its first preparation, he explored the interaction of potassium with ammonia gas. He found that potassium ‘assumed a beautiful metallic appearance and gradually became of a fine blue color’. Unfortunately, this first observation of metal-ammonia ‘solutions’ was recorded only in his laboratory notebook and not published [2]. But it provides the first observation of the second great surprise about alkali metals—that they can dissolve in liquid ammonia without chemical reaction to form solvated electrons.

3. Metal solutions and solvated electrons

The first published observation of metal-ammonia solutions was that of Weyl in 1864 [3], who called them ‘metal-ammoniums’. Until the extended studies of Charles Kraus, started in 1907 [4] and continuing for over 25 years [5], it was generally considered that the solution contained compounds between alkali metals and ammonia, although it was recognized that the metals could be recovered unchanged by evaporation of the ammonia [6]. Kraus concluded in a 1908 paper [7] that ‘the negative ion constitutes new species of anion. It consists of a negative charge, an electron, surrounded by an envelope of solvent molecules’. This description of the solvated electron contains about as much information as we know 106 years later about the structure of this species!

A remarkable feature of metal-ammonia solutions is the very large solubility range. As the concentration increases, the conductivity rises, changing from ionic to metallic, and including a remarkable phase separation at low temperatures. Lithium metal even forms a metallic compound Li(NH₃)₄ [8]. The alkali metals are soluble to various extents in a number of other solvents, although, except for lithium, the solubilities tend to be low. Lithium is highly soluble in methylamine and ethylamine and forms the compound Li(MeNH₂)₄ [9]. Compound formation with ethylamine is uncertain [10].

The formation of solvated electrons is not limited to alkali metal solutions. Alkaline earths, certain lanthanides and even aluminium can be dissolved in ammonia, either directly or by electrolysis to form solvated cations and solvated electrons [11,12]. Even solutions of tetraalkylammonium salts can be used to produce solvated electrons at the cathode. The only requirement seems to be non-reducibility of the counterion.

Although solvated electrons are powerful reducing agents and react rapidly with many solvents, the reactions are often slow enough to permit the formation of, and observation of, solvated electrons in many solvents by photolysis or pulse radiolysis of the solvent.
such as optical spectra can be obtained in microseconds or less after the pulse. Solvated electrons have been studied in this way in so many liquids that they compete with solvated protons as the most studied species in chemistry!

4. The third surprise: alkali metal anions

Although elemental alkali metals have an oxidation state of zero, when they dissolve in ammonia they become $M^+$ with transfer of $e^-$ to the solvent. It was noted as early as 1918 that solutions of alkali metals or alkaline earths in methyamine had an absorption maximum at 650 nm in addition to the increased infrared (IR) absorption of the solvated electron [13]. Many other studies since that time have shown this peak in Li, Na, K, Rb and Cs solutions in amines and polyethers. This peak was seen in addition to that of solvated electrons and other intermediate peaks and shoulders in K, Rb and Cs solutions. The nature of the species responsible for this metal-independent peak at 650 nm was the subject of much speculation for 50 years. The mystery was cleared up in 1968 by Golden and co-workers [14] at Brandeis, who noted that the peak is always due to the presence of sodium in the solutions. When no sodium metal or salt is added, the solutions of Li, K, Rb or Cs react with the Pyrex (sodium borosilicate) flasks used to prepare the solutions to produce dissolved sodium. It soon became apparent [15,16] that the 650 nm absorption was that of the anion, $Na^-$, and that the other intermediate peaks were due to $K^-$, $Rb^-$ and $Cs^-$ anions, whereas the common IR peak at approximately 1200 nm was due to solvated electrons. Li$^-$ was not (and has not been) seen in any solution. Alkali metal anions had been proposed earlier as candidate species in solution [17]. The ‘Pyrex anomaly’ had confused the metal–amine community for a half-century!

While the $-1$ oxidation state of the alkali metals had been observed in the gas phase for some time, and, after 1968 appeared to be a major species in alkali metal solutions in solvents other than ammonia, no salts of the alkali metal anions had yet been isolated. Except for lithium and caesium in primary amines, which gave only $M^+$ and $e_{solv}^-$, metal solubilities were low. This changed dramatically in 1970 when Dye et al. [18] showed that the addition of cation complexants, such as crown ethers [19] and cryptands [20] (figure 1) greatly increased alkali metal solubility via the equilibria

\[
M^+ + C \leftrightarrow M^+C, \quad (4.1)
\]

\[
2M(s) \leftrightarrow M^+ + M^- \quad (4.2)
\]

and

\[
M(s) \leftrightarrow M^+ + e_{solv}^- \quad (4.3)
\]

For example, potassium is not perceptibly soluble in dimethyl ether. The high extinction coefficients of $K^-$ and $e_{solv}^-$ suggest that the saturation concentration is less than $10^{-6}$ M in the absence of a complexant. The addition of cryptand (222) increases the potassium concentration to greater than 0.1 M, and the optical spectrum indicates that the major species is $K^-$. During the period 1970–1974, we studied the optical, electron paramagnetic resonance and nuclear magnetic resonance (NMR) spectra of the alkali metals in a number of amine and ether solvents [21,22] and found that evaporation of the solvent produced gold, metallic-looking solid films. This led, in 1974, to the formation and crystal structure determination of the first crystalline salt of an alkali metal anion, $Na^+$(C222)$Na^-$ [23]. The solid-state $^{23}$Na NMR spectrum [24] confirmed the identification of $Na^-$ as the anion. Comparison with the structure and interatomic distances in the compound $Na^+$(C222)I$^-$ [25] provided us further confirmation that $Na^-$ is a large spherical anion. Since the crystallization of this first alkalide, we have crystallized and determined the structures of 26 sodides, four potassides, four rubidides and three cesides [26,27].

Most of these alkalide salts contain separated spherical alkali metal anions in isolated sites (table 1). However, not all alkalides contain just complexed cations and separated alkali metal anions. For example, the complexation of $Na^+$ by hexamethyl hexacyclen (the aza analogue of 18-crown-6) forms a contact ion-pair between $K^+$ and $Na^-$ without perceptible charge transfer from $Na^-$ to $K^+$ [26]. In the compounds $K^+$(C222)$K^-$, $Rb^+$(C222)$Rb^-$ and $Ba^+$(HAza222)$Na^-$,
the anions form dimers in which the M− to M− distances are about 1 Å shorter than those expected for isolated anions. Theoretical calculations show that such dimers (and chains), although unstable to dissociation in the gas phase, can be stabilized by the image positive charges of the nearby complexed cations [28]. The cesides, Li+(C211)Cs− and Cs+(C222)Cs− form zig–zag linear chains of Cs− anions with shortened Cs–Cs distances [29]. The structure of Rb+(18C6)Rb− is remarkable in that it not only forms Rb− chains, but each Rb− also forms a contact pair with a complexed Rb+ cation that is incompletely encapsulated in the 18-crown-6 ring [30].

5. From solvated electrons to electrides

Alkali metals in ammonia contain solvated electrons in dilute solutions and metallic electrons in concentrated solutions. While ion-pairs, M+ · e− and ion-triples, e− · M+ · e−, may exist in M-NH3 solutions, there is no evidence for ‘genuine’ alkali metal anions. As described above,
Figure 2. Molar susceptibility versus T for three electrides. The largest channel cross-sectional areas increase from 5 to 12 to 22 Å² for Cs⁺(15C5)²e⁻ to Cs⁺(18C6)²e⁻ to K⁺(C222)²e⁻, respectively.

however, other solvents, such as amines and polyethers, and solutions that contain cation complexants, generally contain both solvated electrons and alkali metal anions. The relative amounts of e⁻ₘₖ and M⁻ in a saturated solution depend only on the solvent and the metal. Lithium produces only e⁻ₘₖ in all solvents, whereas sodium tends to favour the formation of Na⁻. In an unsaturated solution, the addition of a cation complexant can shift the equilibrium,

\[ M^- + C \leftrightarrow M^+ C + e^-_{\text{solv}} \]  \hspace{1cm} (5.1)

to the right, increasing the concentration of e⁻ₘₖ relative to M⁻. By the appropriate choice of alkali metal, solvent and complexant, it is often possible to prepare concentrated solutions that contain predominantly the complexed cation and solvated electrons. Evaporation of the solvent forms blue films that we tentatively identified as ‘electrides’ [31]. By cooling such solutions, we were able to crystallize the first solvent-free electride [32]. We have been able to prepare and determine the structures of eight crystalline electrides [27], in each of which the counter ion to M⁺ is an electron trapped in the void spaces formed by packing of the complexed cations. In most cases, these trapping sites are similar to those occupied by alkali metal anions in the corresponding alkalides, and by halide ions in the corresponding halide salts. Trapped electrons in electrides behave as anions, much as solvated electrons in solution exhibit anionic character.

Of course, the position of an electron can be specified only as a probability density and this electron density can extend throughout the structure. The calculated electron density distribution in the electride Cs⁺(15C5)₂·e⁻ [33] has its maximum in the centre of the cavity and extends through the connecting channel to overlap slightly with the electrons in adjacent cavities. Just as some alkalides can form dimers and chains [30], trapped electrons in electrides can interact to form anti-ferromagnetic dimers and chains. The interelectron coupling constants depend on the sizes of the channels that connect adjacent trapping sites [34,35]. As shown in (figure 2), the molar susceptibility varies from nearly Curie–Weiss behaviour for Cs⁺(15C5)²e⁻ to strong spin–spin coupling for K⁺(C222)²e⁻. The coupling constant in electrides increases in the same order as the minimum cross-sectional area (‘pinch-point’) of the channels between electron-trapping sites [34]. The electrical conductivity, which is defect-dominated, also follows this general order, increasing by 12 orders of magnitude from Cs⁺(15C5)²e⁻ to K⁺(C222)²e⁻ as the area of the ‘pinch point’ increases by a factor of 10 [34].
The structure of the space occupied by electrons in stoichiometric electrides mimics that of ordinary anions. A salt such as Cs$^+(15C5)_2e^-$ is very similar in structure to that of Cs$^+(15C5)_2Na^-$, which, in turn, is very much like that of Cs$^+(15C5)_2I^-$. All dissolve in suitable solvents to yield Cs$^+(15C5)_2^+$ and $e_{\text{solv}}^-$, Na$^-$ or I$^-$. 

6. The final surprise: alkali metals at high pressure

Until the beginning of this century, sodium was viewed as a prototypical simple metal. Valence electrons were considered to form a homogeneous and isotropic electron gas. At ambient pressures, the tightly bound core electrons are like those in the free atom. This picture began to change in 1999 when Neaton & Ashcroft [36] predicted that lithium under pressure would form a less symmetric semi-metallic structure. Changes in the reflectivity and conductivity of lithium under pressure were observed in 1999 that suggested a decrease in conductivity [37]. The predicted changes in structure under pressure [36] were generally confirmed in 2000 [38]. In 2001, Neaton & Ashcroft [39] predicted that sodium would become an insulator at high pressures. Compressed lithium was found to be superconducting at 20 K [40,41]. Between 2002 and 2008, a number of phase transitions of sodium at pressures up to 160 GPa were observed [42–44].

In 2009, in three letters to Nature in the same issue [45–47], it was shown that both lithium and sodium lose their metallic character under pressure. Ma et al. [45] reported that thin slices of sodium became transparent insulators at about 200 GPa, whereas Matsuoso & Shimizu [46] showed that lithium at 80 GPa has an increase in resistivity by a factor of more than $10^4$. These effects were summarized by Ashcroft [47].

The summary by Ma et al. [45] of the structure of sodium under pressure is particularly intriguing. They note that ‘this novel dielectric consists of ionic cores and localized interstitial electron pairs, in analogy to electrides, where the interstitial electron density maxima play the role of anions’. Thus, even the sodium metal of Sir Humphry Davy, at pressures about half those at the centre of the earth, can be viewed as Na$^+$ cations imbedded in an electride matrix of anionic electron-pairs! In view of the extensive role that electrons play as anions, the remaining question is, ‘Where should electrons be placed in the periodic table?’!

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