A Model for Solutions of Non-metals in Liquid Alkali-metals

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A theoretical model is presented for solutions of non-metals in liquid alkali-metals. This is based upon the assumption that these dissolve in the form of negative ions. By use of a Born–Haber cycle the different quantities determining the enthalpy of dissolution are separated. One of these is the electrostatic energy of the dissolved ion imbedded in the electron gas of the metal. This is calculated by use of a slightly modified Thomas–Fermi screening potential. In cases where experimental data are available reasonable agreement with the calculated values is found.

THE liquid alkali-metals are interesting solvents,[1,2] mainly because of the availability of a large number of electrons of relatively high energy. A theoretical model for these solutions, however, has not yet been available. The theory of solid alloys is much better developed.[3,4] Ebisuzaki and O'Keeffe[5] have presented a theory for solutions of hydrogen in solid transition metals. We now suggest a similar model for non-metals in liquid alkali-metals. A primary aim is the calculation of the enthalpy of dissolution.

Thermodynamics of Dissolution.—As dissolution reaction of the non-metal we consider reaction (1), where

$$\tfrac{1}{2}\mathrm{X_2(g)} = \mathrm{X(M)} \qquad (1)$$

X(M) denotes X dissolved in the liquid metal M. In equilibrium we must have condition (2). We assume

$$\tfrac{1}{2}\mu_{\mathrm{X_2}} = \mu_{\mathrm{X}} \qquad (2)$$

that for the, generally very low, solubilities to be considered here the solution can be treated as ideal. Using the notation of Prigogine and Defay[6] we can then write equations (3). We shall use the convention that the

$$\mu_{\mathrm{X}} = \mu_{\mathrm{X}}^{\ominus} + RT\ln x_{\mathrm{X}} \qquad (3a)$$

$$\mu_{\mathrm{X_2}} = \mu_{\mathrm{X_2}}^{\dagger} + RT\ln p_{\mathrm{X_2}} \qquad (3b)$$

standard thermodynamic quantities for the elements are zero at all temperatures. Although this is strictly true only at 298 K the difference is in general small. We then find for the solubility by substituting (3) into (2), putting $\mu_{\mathrm{X_2}}^{\dagger} = 0$ and rearranging as in (4). In practice

$$x_{\mathrm{X}} = p_{\mathrm{X_2}}^{\frac{1}{2}} \exp(-\mu_{\mathrm{X}}^{\ominus}/RT) \qquad (4)$$

it is often not possible to choose $p_{\mathrm{X_2}}$ freely, namely, when a stable compound MX can be formed in the reaction (5). The dissociation pressure of MX is given

$$\mathrm{M(l)} + \tfrac{1}{2}\mathrm{X_2(g)} = \mathrm{MX(s)} \qquad (5)$$

by equation (6). Here it is assumed that the solubility of M and X_2 in MX is negligible.

$$p_{\mathrm{X_2}}^{\frac{1}{2}} = \exp(\mu_{\mathrm{MX}}^{\ominus}/RT) \qquad (6)$$

Combination of equations (4) and (6) gives for the limiting solubility x_{X}^{1} of X in the presence of MX equation (7) from which equation (8) is easily deduced.

$$x_{\mathrm{X}}^{1} = \exp\{(\mu_{\mathrm{MX}}^{\ominus} - \mu_{\mathrm{X}}^{\ominus})/RT\} \qquad (7)$$

$$\frac{\mathrm{d}\ln x_{\mathrm{X}}^{1}}{\mathrm{d}(1/T)} = -\frac{h_{\mathrm{X}}^{\ominus} - h_{\mathrm{MX}}^{\ominus}}{R} = -\frac{h_{\mathrm{S}}^{\ominus}}{R} \qquad (8)$$

Here $h_{\mathrm{MX}}^{\ominus}$ is the standard enthalpy of formation of MX, $h_{\mathrm{S}}^{\ominus}$ is the standard enthalpy of dissolution of MX in liquid M, and $h_{\mathrm{X}}^{\ominus}$ is the standard partial molar enthalpy of X in the solution.

Born–Haber Cycle for Dissolution.—In order to make it possible to calculate $h_{\mathrm{S}}^{\ominus}$ (or $h_{\mathrm{X}}^{\ominus}$) from a molecular model we consider reaction (1) to be separated into the steps shown in the Born–Haber cycle of equation (9).

$$\begin{tikzcd}
\tfrac{1}{2}\mathrm{X_2(g)} \arrow[r, "h_{\mathrm{X}}^{\ominus}"] \arrow[d, "(1)"', "\tfrac{1}{2}D"] & \mathrm{X(M)} \\
\mathrm{X(g)} + \mathrm{e^-} \arrow[r, "(2)", "E_{\mathrm{F}} + E_{\mathrm{A}}"'] & \mathrm{X^-(g)} \arrow[u, "(3)", "Q"']
\end{tikzcd} \qquad (9)$$

In step (1) the dissociation enthalpy D has to be supplied. In step (2) an electron is taken from the electron gas of the metal at the expense of the work function E_{F} and put upon the X atom forming the ion X^-, which liberates the electron affinity E_{A}. Finally the X^- ion is put into the metal, where the interaction of this ion with the electron gas gives rise to the electrostatic energy Q. According to Hess' law this leads to equation (10). For

$$h_{\mathrm{X}}^{\ominus} = \tfrac{1}{2}D + E_{\mathrm{A}} + E_{\mathrm{F}} + Q \qquad (10)$$

D, E_{A}, and E_{F} experimental values are available (*e.g.*, ref. 7). In order to find $h_{\mathrm{X}}^{\ominus}$ it is therefore only necessary to calculate Q.

Electrostatic Energy of the Ion in the Electron Gas.—The calculation of the electrostatic energy of an ion dissolved in a metal will be based upon the free-electron model of the metal which is thus considered as an electron gas in which positive charges are distributed homogeneously. If a negative ion is immersed in the electron gas the

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[4] A. Blandin, Alloying behavior and effects in concentrated solid solutions, Metallurgical Society Conferences, vol. 29, Gordon and Breach, New York, 1965, p. 50.

[5] Y. Ebisuzaki and M. O'Keeffe, *Progr. Solid-State Chem.*, 1967, **4**, 187.

[6] I. Prigogine and R. Defay, 'Chemical Thermodynamics,' translated by D. H. Everett, Longmans Green, London, 1954.

[7] Handbook of Chemistry and Physics, 48th edn., Chemical Rubber Co., Cleveland, Ohio.

electron density therein will be decreased owing to the electron–ion repulsion. This leads to a net energy gain as the net positive charge of the metal is then on the average closer to the dissolved ion than the electrons.

The change of the potential caused by the dissolved ion was calculated for a point charge by use of the Thomas–Fermi approximation by Mott.[8,9] This calculation is completely analogous to that used[10] in the theory of strong electrolytes according to Debye and Hückel. Similar to the last mentioned theory we use a model with a finite radius a of the dissolved ion which is considered to be more realistic than a point-charge model. Also we then avoid the difficulty, noted by Alfred and March,[11] that the very high potentials close to the point charge would lead to the impermissible result of electrons with a negative kinetic energy.

For the screened potential around an ion of radius a and charge ke we then find, combining the derivations of Mott[8,9] and MacInnes,[10] equation (11), where λ^{-1} is

$$\psi = \left(\frac{ke}{r}\right)\frac{\exp\{\lambda(a-r)\}}{a\lambda + 1} \qquad (11)$$

the so called screening length, which is given in the Thomas–Fermi approximation by equation (12), where

$$\lambda^2 = \frac{4me^2}{h^2}\left(\frac{3N_0}{\pi}\right)^{\frac{1}{3}} \qquad (12)$$

N_0 is the electron density in the undisturbed metal.

In the charging process of the X^- ion as given in step (2) of cycle (9) the electron affinity E_A contains the energy necessary for building up the potential field given by equation (13) around the ion in a vacuum. When the

$$Q = \frac{ke}{r} \qquad (13)$$

charging process is carried out in the metal, however, the potential field is given by equation (11). Therefore the electrostatic energy of dissolution is given by the difference between the energies necessary for building up the potential fields (11) and (13). This gives equation (14), where $\Delta\psi$ is given by equation (15), and finally

$$Q = \int_0^{ke} \Delta\psi \, dq \qquad (14)$$

$$\Delta\psi = \frac{q}{r}\left(1 - \frac{\exp\{\lambda(a-r)\}}{\lambda a + 1}\right) \qquad (15)$$

leads to equations (16). The second form (16b) is valid

$$Q = -\tfrac{1}{2}\cdot\frac{k^2e^2}{a + \lambda^{-1}} \qquad (16a)$$

$$= -\frac{165k^2}{a + \lambda^{-1}}\ \text{kcal mol}^{-1} \qquad (16b)$$

if a and λ^{-1} are expressed in Ångström units.

Comparison with Experiment.—Bredig *et al.*[12–16] have studied the solubilities of a number of alkali-metal halides in the corresponding liquid alkali-metals. Addison *et al.*[17] studied the solubility of sodium hydride in molten sodium. The experimental results, together with the partial molar enthalpy of dissolution calculated from equations (10) and (16) are given in Table 1.

TABLE 1

Experimental and calculated dissolution parameters. All enthalpies in kcal mol^{-1}

M	X	$h_S^\ominus$ [a]	$h_{MX}^\ominus$ [b]	$h_X^\ominus$ Found	$h_X^\ominus$ Calc.
Na	F	25	−136	−111	−90
	Cl	22	−98	−76	−68
	Br	23	−86	−63	−61
	I	31	−71	−40	−50
	H	23 [c]	−14	+9	+13
K	F	18	−134	−116	−88
	Cl	23	−104	−81	−67
Rb	Cl	26	−103	−77	−70
	Br	23	−93	−70	−63
Cs	F	9	−127	−116	−96
	Cl	19	−104	−85	−76
	I	18	−81	−63	−58

[a] From refs. 12—16. [b] From ref. 7. [c] From ref. 17.

The enthalpies of dissolution $h_S^\ominus$ have been calculated by us from the experimental results as published using a least-squares method and in some cases differ slightly from the literature values. From the least-squares calculation it was found that the accuracy of $h_S^\ominus$ is not better than ±3 kcal mol^{-1}. The enthalpies of formation $h_{MX}^\ominus$ show differences of up to ±2 kcal mol^{-1} between different tabulations. This means that the accuracy of the experimental $h_X^\ominus$ values is not better than ±5 kcal mol^{-1}.

The electron affinities and work functions as given by different authors show differences of several kcal mol^{-1}. This leads to an uncertainty in $h_X^\ominus{}_{\text{calc}}$ from this source of approximately ±5 kcal mol^{-1}. Thus differences of up to ±10 kcal mol^{-1} between the calculated and experimental values of $h_X^\ominus$ are probably not significant.

TABLE 2

Properties of alkali-metals

	Atomic [a] weight	Density [a] / g. cm^{-3}	E_F/eV [a]	λ^{-1}/Å [b]
Li	6·939	0·534	2·49	0·6112
Na	22·99	0·97	2·28	0·6756
K	39·102	0·86	2·24	0·7531
Rb	85·47	1·532	2·09	0·7792
Cs	132·9	1·8785	1·81	0·8107

[a] From ref. 7. [b] Calculated from equation (12).

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The quantities used in the calculations are put together in Table 2 for the metals and Table 3 for the non-metals.

TABLE 3

Properties of non-metals (all data from ref. 7)

	r_{X^-}/Å	E_A/kcal mol^{-1}	D/kcal mol^{-1}
F	1·33	−79·5	37·8
Cl	1·81	−83·3	57·8
Br	1·96	−77·5	53·4[a]
I	2·20	−70·6	51·0[a]
H	1·54	−17·2	104·2

[a] Including the enthalpy of vaporization.

DISCUSSION

Comparison of the experimental and calculated values of the partial molar enthalpy of solution for the systems considered shows a reasonable agreement both as to the trends within the groups and to the absolute values. This agreement is particularly striking when the experimental uncertainties and the approximate nature of the theory are considered.

The explanation suggested by Bredig *et al.*[12] for the minimum in $h_S^{\ominus}$ for dissolution of NaCl seems to be unnecessary when considering $h_X^{\ominus}$. The main cause is the large difference between $h_{NaF}^{\ominus}$ and $h_{NaCl}^{\ominus}$. When considering solubilities in those cases where stable compounds are formed it is thus better to compare the $h_X^{\ominus}$ values than the enthalpies of solution $h_S^{\ominus}$ themselves.

As Alfred and March[11] and Fujiwara[18] have shown, equation (11) based on the Thomas–Fermi approximation differs markedly from a more exact solution of the Poisson equation. Secondly a possible direct interaction between the positive ion cores in the metal and the dissolved ion has not been taken into account.

Work is in progress to incorporate these factors in the theory and to extend its application to other systems. Very few systems have been studied experimentally with enough accuracy to form a reliable test.

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