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**SOLVATION OF SOME NON - METALS IN  
LIQUID LITHIUM AND SODIUM**

**N.A. RUMBAUT**

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**BLG 536**

N.A. RUMBAUT  
BLG 536 (June 1980)

SOLVATION OF SOME NON-METALS IN LIQUID LITHIUM AND SODIUM

Summary. - Equations are presented which relate the thermodynamic activity of dissolved non-metals (H, C, O and N) to their chemical concentration in liquid lithium and sodium.

Partial molar enthalpies and - entropies of solvation are deduced and interpreted in terms of solute-solvent interaction.

N.A. RUMBAUT  
BLG 536 (June 1980)

SOLVATION OF SOME NON-METALS IN LIQUID LITHIUM AND SODIUM

Samenvatting. - Er worden vergelijkingen voorgesteld die het verband weergeven tussen de thermodynamische potentiaal van de opgeloste niet-metalen H, C, O en N in vloeibaar lithium en natrium en hun chemische concentratie.

De waarden van de partiële molaire vrije enthalpie en - entropie van solvatatie worden besproken in het kader van de interacties van deze metalloïden met vloeibare alkalimetalen.

N.A. RUMBAUT  
BLG 536 (June 1980)

SOLVATION OF SOME NON-METALS IN LIQUID LITHIUM AND SODIUM

Résumé. - Des équations sont présentées, liant la concentration chimique au potentiel thermodynamique des metalloïdes H, C, O en N en solution dans le lithium et le sodium liquide.

Les valeurs de l'enthalpie et de l'entropie de solvatisation sont discutées du point de vue des interactions de ces metalloïdes avec les métaux alcalins liquides.

## INTRODUCTION

The study of dissolved non-metals such as carbon, nitrogen, oxygen and hydrogen in liquid alkali metals is of technological interest, as these species enhance corrosion and mass transfer in the container materials used for cooling circuits in future fusion reactors.

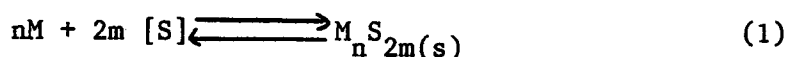
As chemical activities, rather than concentrations are the driving factors, there is a need for well-established relationships between these thermodynamic quantities and the existing concentrations in dilute solution.

In this paper, we deduced activity-concentration equations from "terminal" solubility relationships for H, C, O and N in liquid lithium and sodium. The latter were obtained from a statistical analysis of experimental data supplied by various authors.

Related thermodynamic quantities such as partial molar entropies and - enthalpies are deduced and indicate a similar solvation pattern for these non-metals in lithium as compared to sodium.

## 2. THERMODYNAMIC ANALYSIS

On saturating a solid or liquid metal M with a diatomic gas  $S_2$  until a precipitate  $M_n S_{2m}$  forms, following equilibrium exists in solution :



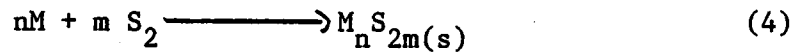
[S] represents the "free" dissolved gas atom in the metal solution and  $M_n S_{2m(s)}$  the precipitating solid. Applying the mass action law we find :

$$K = \frac{a_{M_n S_{2m(s)}}}{a_M^n \cdot a^m [S]} \quad (2)$$

If we relate activities to the pure components as standard states,  $a_{M_n S_{2m(s)}} = 1$ , and, since also  $a_M^n = 1$  in the dilute solutions considered here, we have :

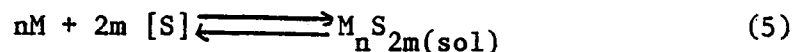
$$K = e^{-\frac{\Delta G_f^\circ}{R T}} \quad (3)$$

where  $\Delta G_f^\circ$  is the Gibbs free energy of formation for the reaction :



In this reaction, the physical state of  $S_2$  has to be the same as that of the standard state on which a  $[S]$  is based. This is usually the gas at 1 bar and the temperature of the system.

In unsaturated solutions eq. (1) becomes :



where the index "sol" stands for the dissolved state.

From the mass action law we have :

$$K = \frac{a_{M_n S_{2m}(sol)}}{a_{[S]}^{2m}} \quad (6)$$

In general, activities may be expressed as the product of a concentration and an "activity coefficient"  $\gamma$  :

$$a_{M_n S_{2m}(sol)} = \gamma \cdot x_{M_n S_{2m}(sol)} \quad (*) \quad (7)$$

When the solubility is low (Henry region) this relationship persists until the saturation point is reached :

$$a_{M_n S_{2m}(sol),sat} = \gamma \cdot x_{M_n S_{2m}(sol),sat} \quad (8)$$

since, by the convention adopted above,  $a_{M_n S_{2m}(sol),sat}$  is equal to  $a_{M_n S_{2m}(s)}$  or to unity, it follows :

$$a_{M_n S_{2m}(sol)} = \frac{x_{M_n S_{2m}(sol)}}{x_{M_n S_{2m}(sol),sat}} \quad (9)$$

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(\*) Mole fraction units are employed throughout this paper, so as to eliminate the configurational entropy of mixing of the standard state.

Finally, by combination of eq. (6) and (9) :

$$a^{2m} [S] = \frac{x_{M_n S_{2m}(\text{sol})}}{x_{M_n S_{2m}(\text{sol}), \text{sat}}} \exp (\Delta G^{\circ}_f / RT) \quad (10)$$

In determining the saturation solubilities of Table I, the total gas or C content of the saturated solution was analysed. Thus,  $x_{S, \text{sat}}$  was found rather than  $x[S], \text{sat}$  or  $x_{M_n S_{2m}(\text{sol}), \text{sat}}$ . Eq. (10) is therefore not directly applicable. However, in very dilute solutions a constant concentration ratio exists between the "free" species [S] and the "bonded" ones as  $M_n S_{2m}(\text{sol})$ .

This simply is because for dilute solutions eq. (6) may be written :

$$K' = \frac{x_{M_n S_{2m}(\text{sol})}}{x^m [S]} \quad (11)$$

And, if the solution is still sufficiently dilute at saturation :

$$K' = \frac{x_{M_n S_{2m}(\text{sol}), \text{sat}}}{x^m [S], \text{sat}} \quad (12)$$

By eq. (11) and (12) and the mass balance :

$$x_S = x[S] + 2m x_{M_n S_{2m}} \quad (13)$$

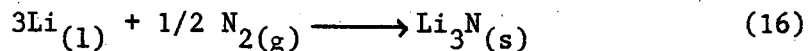
one obtains :

$$\frac{x_{M_n S_{2m}(\text{sol})}}{x_{M_n S_{2m}(\text{sol}), \text{sat}}} = \frac{x_S}{x_{S, \text{sat}}} \quad (14)$$

With this relationship eq. (10) reduces to :

$$a^{2m} [S] = (x_S / x_{S, \text{sat}}) \exp (\Delta G^{\circ}_f / RT) \quad (15)$$

For a gas such as  $N_2$ , dissolved in liquid lithium, eq. (4) can be written as :



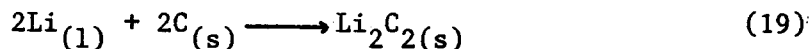
thus,  $m = 1/2$  and :

$$a_{[N]} = (x_N/x_{N,sat}) \exp (\Delta G^\circ_f/RT) \quad (17)$$

in which  $\Delta G^\circ_f$  is the Gibbs free energy of formation for reaction (16). In the case of monatomic gases or solids such as carbon, eq. (15) is equally valid when the appropriate value of  $m$  is inserted, as deduced from the chemical composition of the precipitate. E.g. for the case of carbon in liquid lithium,  $Li_2C_2$  precipitates, so  $m=1$  and :

$$a^2_{[C]} = (x_C/x_{C,sat}) \exp (\Delta G^\circ_f/RT) \quad (18)$$

in which  $\Delta G^\circ_f$  is the Gibbs free energy of formation of 1 mole of  $Li_2C_2$  :



### 3. TERMINAL SOLUBILITY DATA

Table I, column 3 gives the saturation or "terminal" solubility data for H, C, O and N in liquid lithium and sodium.

Most of the equations are the result of a least square analysis on the existing data. The equation for hydrogen in sodium is based on the results of five different publications (1 to 5).



For carbon in the same metal, only four sets of determinations from the many published data were retained (6 to 9).

The equation for oxygen in sodium is that of NODEN (10) who based it on 268 determinations. For N in sodium, no equation was found for the terminal solubility. However, the "Henry" constant was determined as a function of temperature by VELECKIS et al. (11), from which solvation properties can be deduced. The solubility of hydrogen in lithium was derived by ADAMS (12) and MARONI (20). For carbon, the publications show widely divergent results. The relationship that we retained correlates best with the other data and stems from GRISHIN (23). The equation for nitrogen in lithium is from ADAMS et al. (12) and YONCO et al. (13) and is based on 33 determinations between 181 and 435 °C. For the Li-O solubility, we used the equation of ADAMS et al. (14), who combined 15 measured values of three different groups of authors.

The solubilities are graphically represented in fig. 1. Table II shows the partial molar solution enthalpies and - entropies for C, H, O and N, calculated from these solubility equations. As can be seen on fig. 2, a  $\Delta\bar{S}_{\text{sol}} - \Delta\bar{H}_{\text{sol}}$  graph displays only a faint correlation between the thermodynamic solution properties of the non-metals in sodium as compared to lithium.

Instead, solvation properties have been determined, which give better insight into the nature of solute solvent interactions.

#### 4. SOLVATION PROPERTIES

For any of the non-metals considered here, it is possible to relate the activity in solution to the concentration and the Gibbs free energy of the precipitating solid as given by eq. (15).

Table III shows the Gibbs free energies which have been used to obtain the data of Table IV. Some of them are from the combined measurements of different authors.

By definition is  $RT \ln a_{[S]}$  for  $x_S = 1$  the non-mechanical work needed to bring the gas or non-metal out of the standard state into the dilute solution. It is also the solvation free energy for the neutral atoms or molecules :

$$\Delta \bar{G}_{\text{solv.}} = RT \ln a_{[S]} \quad (20)$$

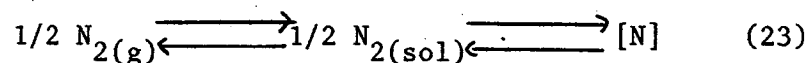
From

$$\Delta \bar{G}_{\text{solv.}} = \Delta \bar{H}_{\text{solv.}} - T \Delta \bar{S}_{\text{solv.}} \quad (21)$$

the partial molar enthalpies and entropies of solvation are deduced and tabulated in Table V. Although no terminal solubility for N in sodium is reported, it was possible to obtain the activity data and related quantities for this element from the "Henry" constant, determined as a function of temperature by VELECKIS et al. (11). These authors obtained for the gas content at 10 atmospheres :

$$\log S = - 7.18 - \frac{2780}{T} \quad (22)$$

S is the solubility in gramme of total nitrogen per gramme of sodium and per atmosphere. It was also proven that most of the nitrogen dissolved in the molecular form  $N_2$ . In order to obtain a  $[N]$  from this equation, it is necessary to consider the (minor) dissociation into free N atoms in the liquid sodium.



From this equilibrium, it follows for dilute solutions :

$$a_{[N]} = \gamma x_{[N]} = p^{1/2} N_2 \quad (24)$$

which implies that Sieverts' law is still obeyed, even when the gas dissolves mainly in the molecular form. It has been shown in section 2 that, in deducing activity equation (15), it is immaterial whether the free atom concentration is determined in solution or the total gas content, as long as the solution is dilute. Therefore eq. (22) can be transformed and  $a_{[N]}$  introduced in Table IV.

## DISCUSSION

The solids  $\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$  both have the  $\text{CaF}_2$  structure with a 4-8 surrounding. When these solids dissolve in the liquid alkali metals, the same rearrangements of bonds must take place in going from  $\text{Na}_2\text{O}$  to the Na-O solution, when compared to  $\text{Li}_2\text{O}$  going in Li-O solution. This can be seen by the nearly equal energy changes of solution as displayed by fig. 2. It is therefore likely that these interstitials have a similar co-ordination sphere, the difference in entropy in fig. 2 being the result of the difference in "free" volume disposable to the non-metal atom. This is further supported by fig. 3, where the entropy changes involved in the solvation of oxygen molecules in the same metals are very similar, while on the other hand the energy differences are much larger because of the difference in electro negativity of the alkali metals involved. These statements are in accordance with the calculations of THOMPSON (26) who regarded a octahedrally arranged co-sphere as the most probable for oxygen in both, lithium and sodium. The very similar energy and entropy of solvation for hydrogen in Li and Na (fig. 3) reveals analogous structure changes, the 6-6 surrounding in the solids being probably retained in solution, as displayed by the rather small enthalpy difference in fig. 2.

The rather large entropy difference for  $\text{Na}_2\text{C}_2$  and  $\text{Li}_2\text{C}_2$  dissolving in sodium and lithium respectively (fig. 2) is probably caused by the difference in crystal structure of these solids at higher temperatures. Indeed, GRISHIN et al. (22) and FEDOROV and MEIN TSUNG SU (24) report allotropic modifications for  $\text{Li}_2\text{C}_2$  at 410,440 and 560 °C, a fact that is not accepted by SECRIST (25). However, the points here discussed are in favour of the former authors. As to the binding structure in solution, fig. 3 procures evidence that carbon has a similar co-ordination sphere in the two liquid alkali metals.

The interpretation of the solute-solvent interactions for N can only be based on the solvation properties as displayed by fig. 3, since the terminal solubility equation in sodium is unknown.

But in view of the similarity in entropy changes during solvation, it can be assumed that this non-metal is bonded in an analogous manner in the two solvents. The fact that the enthalpy of solvation has a positive value of + 12 750 cal/mole N indicates a very loose binding of N to sodium. In fact, as already mentioned, a great part of the total dissolved gas has been shown to be in the molecular form (11).

ACKNOWLEDGEMENT

The author thanks Prof. Dr Ir. M. BRABERS for his stimulating criticism and Dr Ir. F. CASTEELS for valuable suggestions.

TABLE I

Terminal solubility of H, C, O and N in liquid lithium and sodium

|           |                                | Lithium                              |          |
|-----------|--------------------------------|--------------------------------------|----------|
| non-metal | precipitating phase            | solubility equation                  | refer.   |
| hydrogen  | LiH                            | $\ln x_H = 3.33 - \frac{5\,208}{T}$  | (23,20)  |
| carbon    | Li <sub>2</sub> C <sub>2</sub> | $\ln x_C = 0.618 - \frac{3\,855}{T}$ | (23)     |
| nitrogen  | Li <sub>3</sub> N              | $\ln x_N = 2.80 - \frac{4\,714}{T}$  | (12,13)  |
| oxygen    | Li <sub>2</sub> O              | $\ln x_O = 1.791 - \frac{6\,310}{T}$ | (14)     |
|           | Sodium                         |                                      |          |
| hydrogen  | NaH                            | $\ln x_H = 4.375 - \frac{7\,118}{T}$ | (1 to 5) |
| carbon    | Na <sub>2</sub> C <sub>2</sub> | $\ln x_C = 2.99 - \frac{12\,991}{T}$ | (6 to 9) |
| nitrogen  | Na <sub>3</sub> N              | —————                                |          |
| oxygen    | Na <sub>2</sub> O              | $\ln x_O = 0.960 - \frac{5\,631}{T}$ | (10)     |

TABLE II

Enthalpies and entropies of solution of C, H, O and N - precipitates in liquid lithium and sodium

|                                | $\bar{\Delta S}_{\text{sol}}$ cal/mole . K | $\bar{\Delta H}_{\text{sol}}$ cal/mole |
|--------------------------------|--|--|
| sodium                         |  |  |
| NaH                            | 8.69                                       | -14 143                                |
| Na <sub>2</sub> C <sub>2</sub> | 5.94                                       | -25 813                                |
| Na <sub>2</sub> O              | 1.91                                       | -11 189                                |
| Na <sub>3</sub> N              | -  | -                                      |
| lithium                        |  |  |
| LiH                            | 6.62                                       | -10 348                                |
| Li <sub>2</sub> C <sub>2</sub> | 1.23                                       | - 7 660                                |
| Li <sub>2</sub> O              | 3.55                                       | -12 538                                |
| Li <sub>3</sub> N              | 5.56                                       | - 9 367                                |

TABLE III

Gibbs free energy of formation for the precipitating solids at 1 atm.

| Solid                   | Sodium                                    | Reference         |
|-------------------------|---|-------------------|
| $\text{Na}_2\text{C}_2$ | $\Delta G^\circ_f = - 10\ 581 + 12.57\ T$ | (15)              |
| $\text{NaH}$            | $\Delta G^\circ_f = - 13\ 630 + 19.70\ T$ | (16)              |
| $\text{Na}_2\text{O}$   | $\Delta G^\circ_f = - 96\ 945 + 30.8\ T$  | (17)              |
| $\text{Na}_3\text{N}$   | -----                                     |                   |
|                         | Lithium                                   |                   |
| $\text{Li}_2\text{C}_2$ | $\Delta G^\circ_f = - 14\ 200 + 11.2\ T$  | (18,19)           |
| $\text{LiH}$            | $\Delta G^\circ_f = - 19\ 500 + 18.05\ T$ | (20,21)           |
| $\text{Li}_2\text{O}$   | $\Delta G^\circ_f = - 144\ 350 + 32.8\ T$ | (22)              |
| $\text{Li}_3\text{N}$   | $\Delta G^\circ_f = - 39\ 947 + 34.09\ T$ | adapted from (13) |

TABLE IV

Activities of H, C, O and N in liquid sodium and lithium

| Non-metal | Activity based on the stable state at 1 atm                  |
|-----------|--|
|           | Sodium   |
| C         | $\ln a_{[C]} = 1/2 \ln x_C + 1.67 + \frac{3\ 833}{T}$        |
| H         | $\ln a_{[H]} = \ln x_H + 5.54 + \frac{258}{T}$               |
| O         | $\ln a_{[O]} = \ln x_O + 14.54 - \frac{43\ 158}{T}$          |
| N         | $\ln a_{[N]} = \ln x_N + 14.88 + \frac{6\ 402}{T} \quad (*)$ |
|           | Lithium  |
| C         | $\ln a_{[C]} = 1/2 \ln x_C + 2.51 - \frac{1\ 630}{T}$        |
| H         | $\ln a_{[H]} = \ln x_H + 5.751 - \frac{4\ 605}{T}$           |
| O         | $\ln a_{[O]} = \ln x_O + 14.76 - \frac{66\ 337}{T}$          |
| N         | $\ln a_{[N]} = \ln x_N + 14.36 - \frac{15\ 390}{T}$          |

(\*) Calculated from the Sieverts' constant as determined by VELECKIS et al. (11) see text.



TABLE V

Partial molar enthalpies and -entropies of solvation of H, C, O and N in liquid sodium and lithium

|         | $\Delta\bar{S}_{\text{solv}}$ cal/mole . K | $\Delta\bar{H}_{\text{solv}}$ cal/mole |
|---------|--|--|
| Sodium  |  |  |
| C       | - 3.32                                     | + 7 616                                |
| H       | - 11.0                                     | + 513                                  |
| O       | - 29.0                                     | - 85 755                               |
| N       | - 29.5                                     | + 12 720                               |
| Lithium |  |  |
| C       | - 4.98                                     | - 3 239                                |
| H       | - 11.5                                     | - 9 150                                |
| O       | - 29.3                                     | - 131 800                              |
| N       | - 28.5                                     | - 30 580                               |

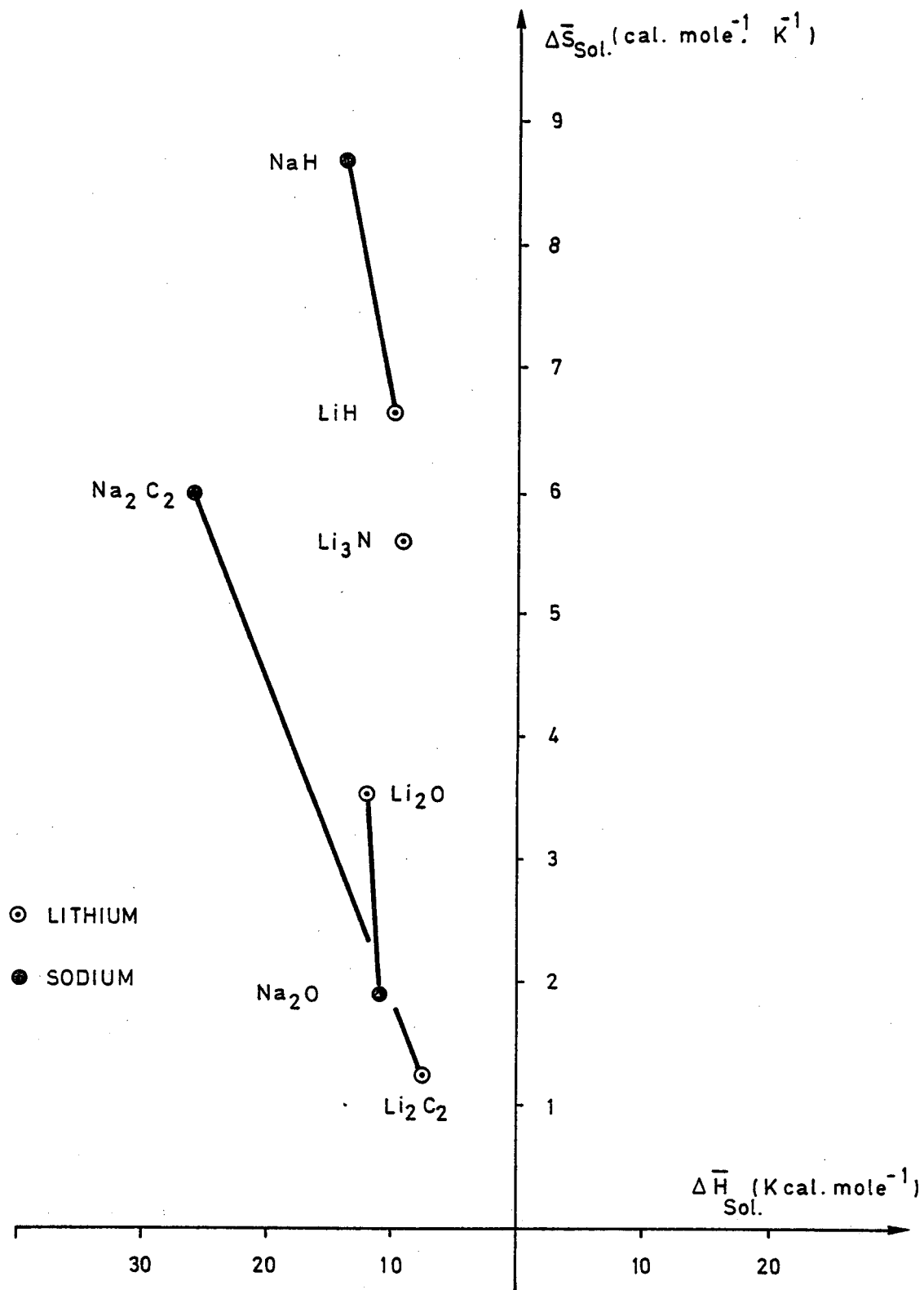


Fig. 2. ENTROPY AND ENTHALPY OF SOLUTION  
 FOR C,H,O AND N IN LIQUID SODIUM AND LITHIUM

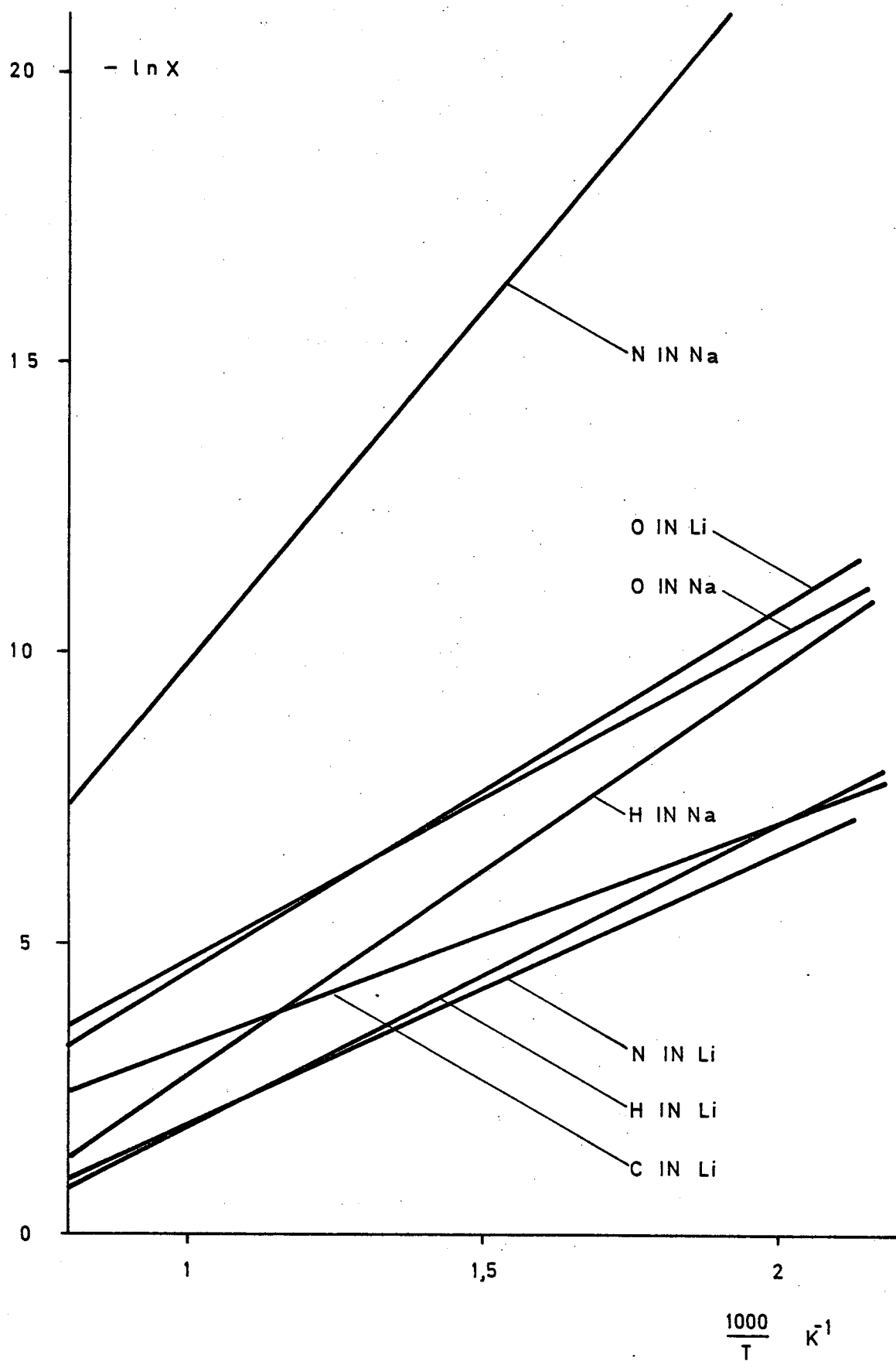


FIG. 1 SOLUBILITY OF C,H,O AND N IN LIQUID SODIUM AND LITHIUM

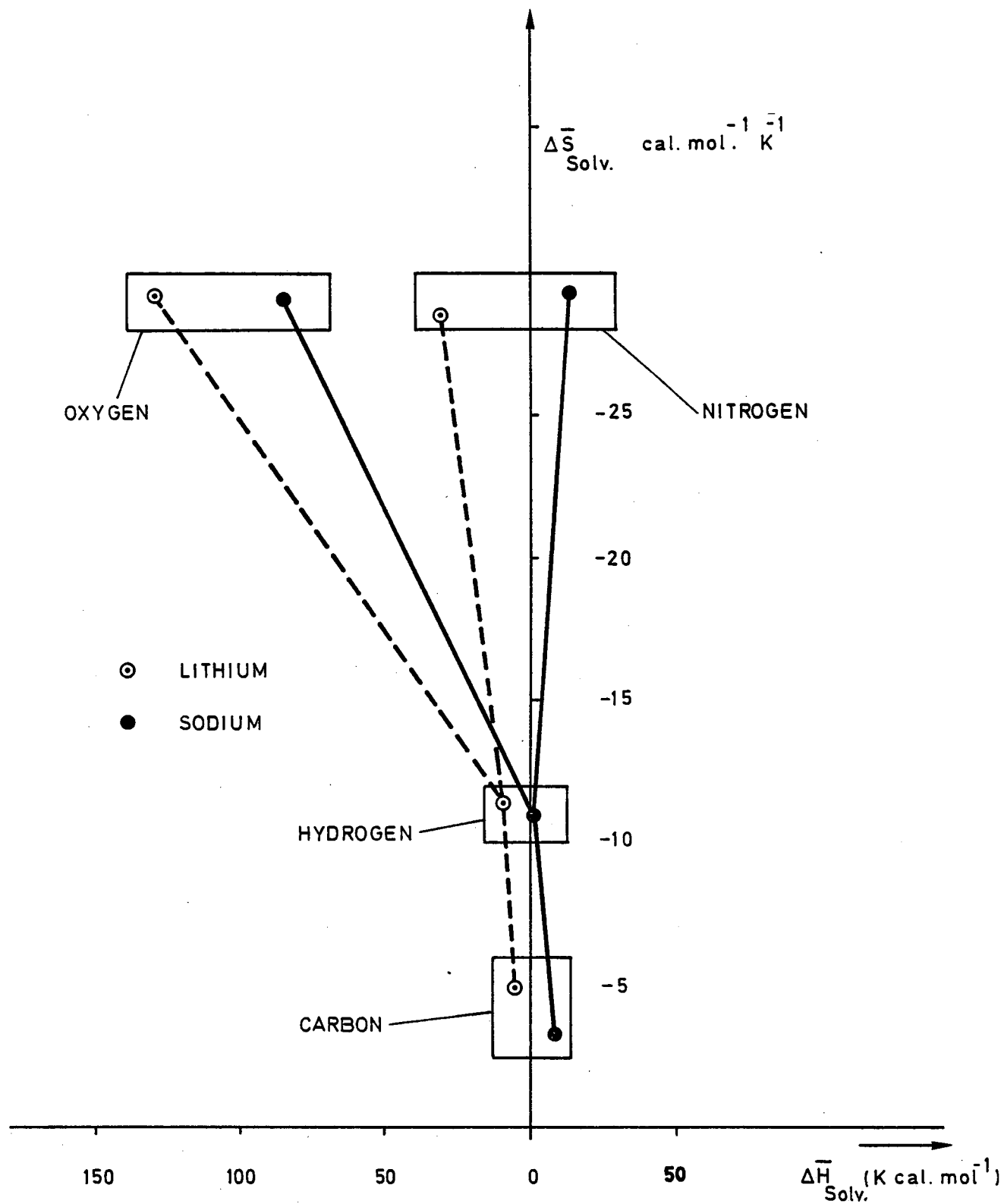


FIG.3 ENTROPY AND ENTHALPY OF SOLVATION FOR C,H,O  
 AND N IN LIQUID SODIUM AND LITHIUM

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