

Isotopic Effect on the Melting Point of Lithium Nitrate

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The techniques of segregation during normal freezing and of zone melting have been used to establish that the melting point of $^6\text{LiNO}_3$ is higher than that of $^7\text{LiNO}_3$. The difference is of the order of 0.03°C . The isotope shift of the melting point is in the opposite direction of the isotope effects found previously for phase transitions in solid lithium metal and lithium sulfate. For the latter salt a recalculation based on a more accurate value for the self-diffusion coefficient shows that the temperature of transition at about 575°C to a fcc structure is about 0.08 degr. lower for $^6\text{Li}_2\text{SO}_4$ than for $^7\text{Li}_2\text{SO}_4$.

Soon after the discovery of deuterium it was found that the isotope effect on transition points (phase transitions, melting, boiling) was large for many inorganic as well as organic compounds¹⁻³. Small isotope effects on transition points have been detected for other elements and some of their compounds, and such effects have been utilized for the separation of isotopes by various distillation methods. However, little is known on the isotope effects of ionic compounds. A few years ago we could report for lithium sulfate that the transition at about 575°C to a face centered cubic phase occurs at a higher temperature for $^7\text{Li}_2\text{SO}_4$ than for $^6\text{Li}_2\text{SO}_4$, i. c.^{4, 5}.

(SNYDER has found a shift in the same direction for the bcc-hcp transition in lithium metal⁶.) We have extended the study to other lithium compounds and can now report our observations regarding the melting point of lithium nitrate.

Segregation During Normal Freezing

In the previous investigation a zone refining technique was used⁴. In principle large separations can be obtained by passing the zone many times. If this is to be done in practice, it is a disadvantage if the substance has a large volume change on melting, such as 21.4% for LiNO_3 . In comparison with a single-pass experiment a larger fractionation can be obtained by normal freezing.

The abundance of ^6Li is sufficiently low to permit the application of equations derived for dilute solutions⁷. The following symbols are to be used.

k_0 = equilibrium distribution coefficient,
 k = effective distribution coefficient,
 C_0 = initial concentration of the solute,
 C = concentration of solute at the location where a fraction g of the original liquid has frozen,
 D = diffusion coefficient,
 f = growth rate,
 δ = thickness of diffusion layer.

The solute distribution caused by normal freezing is

$$C/C_0 = k(1 - g)^{k-1}. \quad (1)$$

In our case both C/C_0 and k are close to unity, thus

$$\begin{aligned} C/C_0 - 1 &= (R_0 - R)/(1 + R) \\ &= (k - 1)[1 + \ln(1 - g)] \end{aligned} \quad (2)$$

where R is the isotope abundance ratio $^7\text{Li}/^6\text{Li}$.

According to the BURTON-PRIM-SLICHTER theory^{7, 8}

$$\ln(1 - 1/k) = \ln(1 - 1/k_0) - f\delta/D. \quad (3)$$

In order to calculate k_0 it is thus necessary to determine δ . If experiments are made with different growth rates but the same stirring conditions, both δ/D and k_0 can be calculated from Eq. (3). We decided to use this procedure, although the accuracy becomes low when k is close to unity.

¹ A. FARKAS, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge Univ. Press 1935.

² A. H. KIMBALL, Bibliography of Research on Heavy Hydrogen Compounds, Nat. Nucl. Energy Ser. III-4 C, McGraw-Hill, New York 1949.

³ V. S. KOGAN, Usp. Fiz. Nauk **78**, 579 [1962]; Sov. Phys. Usp. **5**, 951 [1963].

⁴ A. LUNDÉN, E. SVANTESSON, and H. SVENSSON, Z. Naturforsch. **20 a**, 1279 [1965].

⁵ There is a numerical error in cit. ⁴. Thus, those calculations gave that the temperature difference is of the order of 0.07°C .

⁶ D. D. SNYDER, Bull. Am. Phys. Soc. **11**, 47 [1966].

⁷ W. G. PFANN, Zone Melting, 2nd Ed., J. Wiley & Sons, New York 1966.

⁸ The equations are quoted only for the case $k > 1$.



A sealed glass ampoule containing molten lithium nitrate was hanging in a furnace. It was pulled upwards slowly, so that the salt started to solidify from the top. Afterwards samples from selected positions in the salt column were analysed several times in our mass spectrometer. According to our usual procedure to reduce the influence of charges in the measuring conditions⁹, only samples measured the same day were compared with each other. Within each such sequence of measurements there was a tendency that the ⁶Li abundance was slightly higher in the samples from the upper part than in those from the lower part. The probability that the observed trend would be due the stochastic error in the mass analysis was estimated by means of a rank test¹⁰. For all three experiments together, this probability was less than 0.1%, i. e. the distribution coefficient deviates significantly from unity. The probabilities estimated for the individual experiments are quoted in Table 1.

Two experiments were made, and, as said above, for both of them selected samples were analysed in several sequences. For each such sequence the least squares method was used to calculate $k-1$ according to Eq. (2). As weighted averages we obtained

$$k-1 = (2.52 \pm 0.56) \times 10^{-3}$$

for the experiment with $f = 4.26$ mm/h, and

$$k-1 = (3.03 \pm 0.45) \times 10^{-3}$$

for the one with $f = 1.90$ mm/h.

It follows from Eq. (3) that

$$\delta/D = 2.8 \times 10^3 \text{ s/cm} \quad \text{and} \quad k_0 - 1 = 3.5 \times 10^{-3}.$$

To test the plausibility of this result, we extrapolated the diffusion coefficient for lithium in lithium nitrate¹¹ to the melting point; obtaining $D = 1.36 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which gives $\delta = 0.038$ cm.

Although it must be remembered that this value of δ is very approximate, it is satisfying that it falls within a range that can be expected for this entity. Thus, it is estimated that δ can be as low as 10^{-3} cm for vigorous stirring and that it is about 0.1 cm for very slow stirring⁷.

Zone Melting Experiment

We also made an experiment where a molten zone passed once over a horizontal column of lithium nitrate. Assuming ideal conditions, C , the solute concentration in the solid at the distance x from the starting point, becomes

$$C/C_0 = 1 - (1-k) \exp(-kx/l) \quad (4)$$

where l = the length of the molten zone.

This equation is valid for all but the last zone length, where we instead have normal freezing.

In our experiment the growth rate (f) was 4.2 mm/h, the zone length l was 7 ± 3 mm, and the length of the ingot was 74 mm. For selected samples the isotope abundance ratio was determined in five different sequences.

By means of Eq. (4) we obtained for the beginning of the ingot

$$k_b - 1 = (3.37 \pm 1.47) \times 10^{-3}.$$

This is a weighted average of 11 calculated values of $k-1$; the quoted error is the standard deviation of the mean. [Two extreme values were omitted; if they also are included one obtains 1.23 ± 2.42 for $(k_b - 1) \times 10^3$.]

For the normal freezing in the last zone length one obtains as the weighted mean of 13 values

$$k_e - 1 = (3.09 \pm 0.77) \times 10^{-3}.$$

Experiment	f mm/h	P %	k	k_0 calculated for δ equal to		
				0.038 cm	0.1 cm	0.001 cm
1. normal freezing	4.26	3.7	1.0025	1.0035	1.0060	1.0027
2. normal freezing	1.90	40	1.0030	1.0035	1.0045	1.0031
3. zone beginning end	4.20	0.6	1.0034	1.0047	1.0079	1.0037
			1.0031	1.0043	1.0073	1.0034

Table 1. Summary of experimental and calculated data. f =growth rate, P =probability of getting the observed find if the measured isotope distribution is random, i. e. when $k_0 = 1.0000$, k =measured effective distribution coefficient, k_0 =equilibrium distribution coefficient calculated under the assumption that the thickness of the diffusion layer (δ) has the given value.

⁹ A. LUNDÉN, Chalmers Tekn. Högskol. Handl. No. 289, Göteborg 1964.

¹⁰ We are indebted to Dr. H. JÖNRUP of the Department of Mathematics for doing the rank testing for us.

¹¹ A. S. DWORKIN, R. B. ESCUE, and E. R. VAN ARTSDALEN, J. Phys. Chem. **64**, 872 [1960].

Calculation of Equilibrium Distribution Coefficient and Temperature Difference

The four $k-1$ values quoted above are weighted means where the weights correspond to estimates of the reliability of the individual values. Of course deviating results can be obtained depending on how the weighing is done. However, this choice is not critical in our experiments, since in all four cases reasonable assumptions regarding the weights all give averages that coincide within 20% or better with the values chosen by us.

The equilibrium distribution coefficient k_0 was calculated for three different values of the thickness of the diffusion layer: the one obtained from the normal freezing experiments as well as for $\delta = 0.01$ cm and 0.001 cm. The results are given in Table 1. Our conclusion is that k_0 is of the order of 1.004. It is of little meaning to try estimate e. g. the standard deviation, but it seems from Table 1 as if 1.003 is to be considered as a lower limit and 1.008 as an upper limit for k_0 .

The difference between the melting points of $^6\text{LiNO}_3$ and $^7\text{LiNO}_3$ can be estimated by means of the equation¹²

$$\Delta T = N_2 R T^2 (k_0 - 1) / \Delta H \quad (5)$$

where N_2 is the mole fraction of $^6\text{LiNO}_3$, R the gas constant, T the melting point and ΔH the heat of fusion.

Using recent literature values¹³ $T = 527^\circ\text{K}$ and $\Delta H = 6.12$ kcal/mole we obtain $\Delta T = 0.03^\circ$ for $k_0 = 1.004$, while the lower and upper limits of k_0 correspond to 0.02° and 0.05° , respectively.

The result of the present experiment is thus that the melting point is of the order of 0.03°C higher for $^6\text{LiNO}_3$ than for $^7\text{LiNO}_3$. The isotopic effect thus has the opposite direction to the one we have reported previously for the phase transition in lithium sulfate at 575°C . The evaluation of those experiments had to rely upon a crude estimation of the self-diffusion coefficient D_{Li} in fcc Li_2SO_4 . More accurate diffusion data are now available¹⁴, according to which $D_{\text{Li}} = 1.83 \times 10^{-5} \text{ cm}^2/\text{s}$ at the transition point. A reevaluation based on this diffusion coefficient indicates that k_0 is likely to be about 0.995, which corresponds to the transition point of $^6\text{Li}_2\text{SO}_4$ being 0.08° lower than that of $^7\text{Li}_2\text{SO}_4$, l. c.¹⁵

Work is in progress to study the isotopic effect on the melting points of other lithium salts (LiF , LiCl , Li_2SO_4). According to the preliminary results k_0 is very close to unity for all these salts.

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¹² A. HAYES and J. CHIPMAN, AIME Techn. Publ. No. 988 [1938].

¹³ G. J. JANZ, Molten Salts Handbook, Academic Press, New York 1967.

¹⁴ A. KVIST and U. TROLLE, Z. Naturforsch. **22a**, 213 [1966].

¹⁵ With the new value for D_{Li} the discrepancy becomes larger than before between a 10-pass run on one hand and two single pass runs on the other. We have given the latter two ones a much larger weight than the 10-pass run. If only the latter were considered k_0 would be of the order of 0.95 and ΔT 0.8°C .