Thermoelectric Power and Thermal Diffusion in Cubic Lithium Sulfate

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(Z. Naturforschg. **19 a**, 1058—1064 [1964]; eingegangen am 25. Mai 1964)

The thermocell Pt/Li_2SO_4/Pt has been studied over the temperature range 580 − 820 °C. The initial thermal emf of −0.7 mV/degr. is identified as the inhomogeneous thermoelectric power due to the temperature dependence of the salt/metal contact potential. Thermal diffusion increases the number of cations at the cold electrode. This causes a change in the thermal emf for which the characteristic time is found to be inversely proportional to the self-diffusion coefficient of the lithium ions. The total steady-state thermoelectric power is temperature-dependent

$$-\varepsilon_{\infty} = (0.03 \pm 0.25) + (1.95 \pm 0.34) \cdot 10^{-3}\, T_{\mathrm{m}} \quad \mathrm{mV/degr.}$$

where T_{m} is the mean absolute temperature and the errors are standard deviations.

The thermocell Zn/Li_2SO_4/Zn was found to have the same initial emf within experimental error.

The high temperature modification of lithium sulfate has a cubic lattice where the number of available cation positions is 50% higher than the number of lithium ions at electroneutrality[1]. α-Li_2SO_4 is further characterized by the cations being as mobile as else is typical for molten salts. This has been demonstrated by studies of electrical conductivity[2–4], self-diffusion[5], transport number[5] and isotope separation due to thermal diffusion[6]. As a further step in the investigation of this salt, we have now measured the thermoelectric power.

A number of measurements of thermoelectric powers in solid and molten salts (halides or nitrates) have been reported[7–24]. The usual arrangement is to have reversible electrodes. Irreversible electrodes were used in some early experiments, mainly qualitative ones[10, 7], but their use has in general been rejected, since Reinhold found for platinum electrodes in silver halides, that the emf was not steady until both platinum electrodes had been coated by a layer of silver, i. e. until reversible electrodes had been obtained[8]. (This was done by reversing the direction of the temperature gradient in the thermocell several times.) However, Nikitinskaya and Murin[12] chose noble metal electrodes (Pt, Pt-Rh, Au) when working with NaCl and KCl, since they meant that it was easier to interpret the measurements if the electrodes "did not react" with the salt. Their measurements show a pronounced straggling of the readings, which they assigned to indeterminable processes in the crystal. While our experiments were in progress two investigations with alkali halides have been reported, where platinum electrodes were used[21, 22]. The theory of solid and molten thermocells is usually confined to reversible cells[25, 26], but irreversible cells have been treated by Allnatt and Jacobs[27].

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It is difficult to arrange reversible metal or gas electrodes when working with lithium sulfate. Pure molten lithium would react with the salt. It might be possible to use a molten alloy, such as lithium-zinc, but there is a tendency that the salt-metal interface gets contaminated with reaction products (oxide, sulfide, etc.)[28] which means that the obtained emf corresponds to a combined thermal and concentration cell. A separation of the two contributions, e. g. by measuring the emf of the contentration cell separately, seems difficult in practice since the composition of the mixture of reaction products, which can contain some five different anions, hardly is reproducible from experiment to experiment, nor would it be constant with time[28]. (Preliminary experiments with a Li-Zn alloy showed that it was not practicable with the available equipment to handle this alloy at elevated temperatures.) Thus we found it necessary to use irreversible electrodes and to check carefully whether any observed time-dependence was due to changes of the electrode surfaces or had other causes.

Experimental

Reagent grade lithium sulfate (Hopkin & Williams AnalaR) was used in all experiments without further purification.

In the first series of experiments, called A, the salt was melted in a Vycor U-tube, and after solidification the two salt surfaces were covered with a layer of pure molten zinc. Tungsten leads were used to connect the zinc to the potentiometer, thus actually forming the cell W/Zn/Li_2SO_4/Zn/W. However, it was difficult to avoid that the metal-salt interface was contaminated by a certain amount of reaction products, giving a still more complicated cell (see below). This method with molten electrodes was soon abandoned, and two other arrangements, both with platinum electrodes, were preferred. The U-tube was used also in the next arrangement (B) where the platinum electrodes and Vycor tubes containing Chromel-Alumel thermocouples were immersed into the molten salt before it was allowed to solidify. Both arms of the U-tube were surrounded by auxiliary heating coils so that a temperature gradient could be obtained in either direction. This arrangement, was used for several of the measurements, before we went over to press slabs of lithium sulfate which had been dehydrated at 160 °C for some days. The slabs were stacked in a vertical Vycor tube with platinum discs at the bottom and top of the column, Fig. 1 (Method C). The height of the column was about 8 cm and its diameter was 1 cm. Miniature thermocouples (ext. diam. 1 mm) were in thermal contact with each platinum disc, but insulated electrically. In order to press the column together, a weight was placed on top of a tube that rested on the upper platinum disc. After the experiment it was always found that the column was completely homogenous without any traces of the origi-

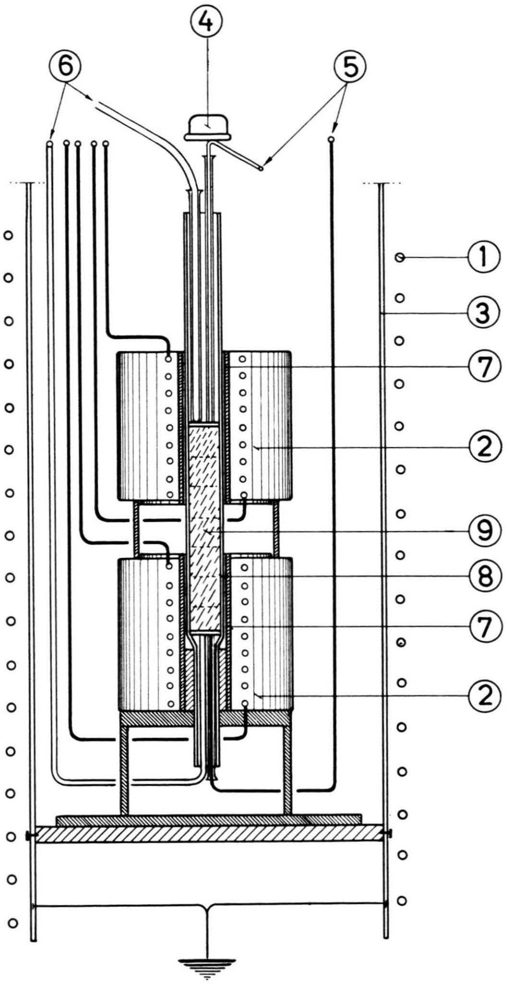

Fig. 1. Cell and furnace used for measuring the thermal emf of Li_2SO_4 with salt slabs (method C). 1) main heating coil. 2) auxilliary heating coils. 3) steel tube. 4) small weight. 5) electrode leads. 6) miniature thermocouples. 7) steel tube. 8) Vycor tube. 9) salt.

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[28] A. Lundén, Chalmers Tekn. Högskolas Handl., No. 289, Göteborg 1964.

nal boundaries between the slabs. The cell was heated in a furnace with a rather high heat capacity. The power input was controlled by means of a variable transformer, for which the input voltage was stabilized within ± 0.2%. The two heating coils surrounding the Vycor cell were fed with stabilized DC-current. The temperature of the room was also stabilized and the fluctuations of the furnace temperature were less than 1 degree during a day. The thermocouples were connected to a compensation bridge (Norma Model 317) with which temperature differences of 1/4 °C could be detected.

Thermal emf's are usually measured with compensation bridges, which arrangement in principle gives a high accuracy. However, since we were studying cells with irreversible electrodes, we found that the emf was sensitive to the small currents that passed through the cell before the bridge was balanced exactly, cf. ref. [21]. For this reason we preferred to use a microvoltmeter (Philips GM 6020) with an internal resistance of 1 or 100 M Ω, depending on measuring range. The accuracy of this instrument was stated to be 3%, but by calibrating the microvoltmeter against a compensation bridge it was possible to reduce the instrument error to 0.5%. It is possible to measure an emf much faster with the microvoltmeter than with a compensation bridge, which was an advantage when studying the time-dependence of the emf.

In order to check whether obtained potential differences could be influenced by induction from the AC-current in the main heating coil of the oven, measurements were made both with and without a grounded steeel cylinder shielding the cell. No disturbances could be detected.

Results

The electrode on the hot side became negative, i. e. the thermal emf has the same direction in solid lithium sulfate as in nearly all other solid and molten salts investigated so far.

The measurements with the $W/Zn/Li_2SO_4/Zn/W$ cell (method A) gave a thermal emf of -0.7 mV/degr. A calculation of the emf for $Zn/Li_2SO_4/Zn$ from this measured emf would require that also the emf of the cell W/Zn (molten)/W is known. It is probable that this latter emf is negligible in comparison with the measured emf, since the emf's of all-metal cells usually are at least an order of magnitude less than for metal-salt-metal cells. E. g. the emf for W/Pb(molten)/W is about 20 μV/degr. at 600 °C [23], and the absolute thermoelectric powers of nearly all investigated molten metals are less than this value [29]. However, even if a correction for metal-metal emf's is done the measurements with method A are to be considered as less accurate than those with platinum electrodes (B or C), since isothermal concentration cell emf's might interfere with the pure thermal emf's. The reason for this is that the zinc-salt interfaces seemed to be contaminated by reaction products, the amount of which is likely to be temperature dependent.

The platinum electrode cells (B and C) were used for a great number of measurements of the potential difference, ΔV, as a function of the temperature difference, ΔT, of time, t, and of the mean temperature, T_m, cf. Fig. 2 – 5. With cell B the measurements were always repeated with the reversed temperature gradient in order to compensate for the isothermal emf that could be very large, up to 38 mV, with this type of cell. On the other hand, the vertical C-cells did not show any detectable isothermal emf's, i. e. their upper limit was well below 1 mV.

Nikitinskaya and Murin do not give any information on the magnitude of the isothermal emf's they found for solid halides [12]. Allnatt and Jacobs report the same magnitude and behaviour of the isothermal emf's in KCl as we have found for the B-cells [21], except that in their case this emf could be removed by annealing at a sufficiently high temperature. In NaCl, however, the

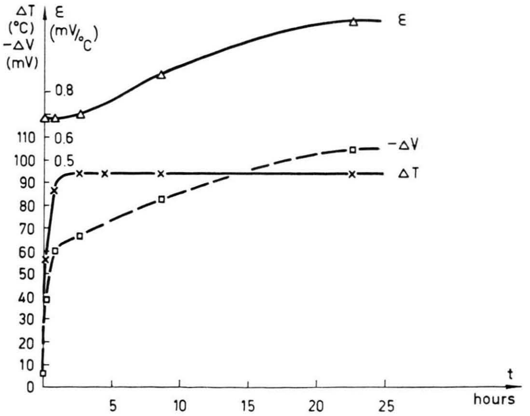

Fig. 2. Variation with time of temperature difference (ΔT), potential difference (ΔV) and thermoelectric power (ε). The heater was switched on at $t=0$. $T_m=725$ °C for this measurement. N.B. The minus sign for ε and ε_∞ has been dropped in Fig. 2 and 5.

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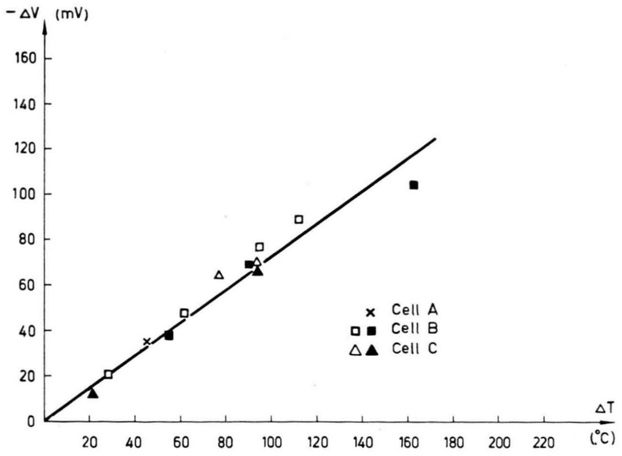

Fig. 3. Proportionality of the voltage difference (ΔV) against temperature difference (ΔT), measured as soon as the electrode temperatures had become constant. The values given are examples of results obtained with the $Zn/Li_2SO_4/Zn$ thermocell (A) and with the two different types of $Pt/Li_2SO_4/Pt$ thermocells (B and C). Two cells of each of the latter types were investigated. The results for the A and B cells are the averages of two measurements with reversed temperature gradient, while single measurements are given for the C cells. The straight line is a least-squares fit $\Delta V = -0.725\ \Delta T$.

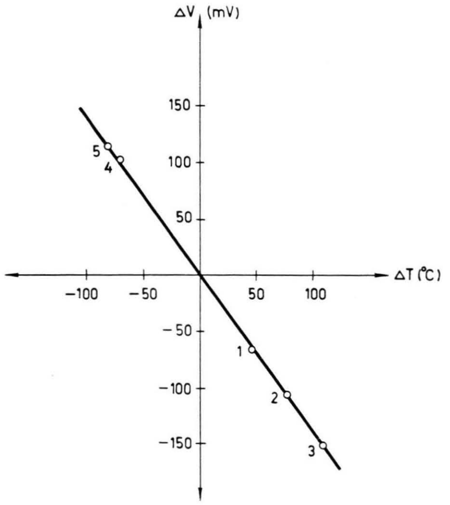

Fig. 4. Proportionality in the steady state of the voltage difference (ΔV) against temperature difference (ΔT) studied with a C-cell kept at the mean temperature $T_m \cong 755$ °C. The measurements were done in the order 1 to 5, i. e. the first three were done with the high temperature at the upper electrode, whereafter the temperature gradient was reversed.

isothermal emf was persistant at all temperatures[22]. When Pt electrodes were used for measurements on AgBr an isothermal emf occurred when the salt was doped but not when it was pure[22]. In comparison with the observations for irreversible cells, the isothermal emf's found for reversible cells are negligible, i. e. a few

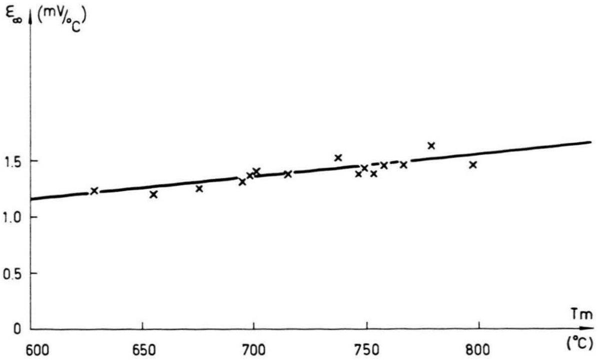

Fig. 5. Temperature dependence of the steady state thermoelectric power (ε_∞), cf. eq. (1), measured with a C-cell. ΔT is 30 to 80 degrees.

tens of microvolts for molten nitrates[16, 17]. For these melts as well as for aqueous solutions[30] the isothermal emf's are attributed to the small differences that are likely to exist between the surface properties of the two electrodes, however carefully they are prepared. When preparing the B cells the platinum electrodes are in contact with molten sulfate for a while, and a slight corrosion might take place in the melt causing some change of the electrode properties. This change need not be identical for the two electrodes, and an isothermal emf might thus be created, but it should hardly be of the observed magnitude. Another possible cause of the isothermal emf is the uneven temperature distribution of the B cells. Thus while for a C-cell the temperature gradient is the same the whole way between the top and bottom electrode, there are to be considered two sources of temperature gradients for the U-shaped B-cells. There is always the slight temperature gradient which is nearly unavoidable in furnaces with a vertical main heating coil, and then there is the temperature difference produced when the coil surrounding one of the arms is heated. The resulting temperature distribution might well be such that the bottom of the U-tube is at a lower temperature than the "cold" electrode. In principle, the more or less pronounced irregularities in the temperature distribution should not cause any observable "isothermal emf" between the two electrodes, but the uncertainty about the temperature gradient should be considered as a disadvantage of the B cells. A third possibility is that the isothermal emf is due to the presence of an inhomogenously distributed impurity[21, 22]. Still other explanations of the isothermal emf's are possible, but no special efforts were made to determine their cause, since it was noticed that their contribution to the total measured emf could easily be corrected for by taking the average of two measurements with reversed temperature gradient, cf. Fig. 3.

When comparing the merits of the B and C cells it is found that preference should be given to the

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[30] H. J. V. Tyrrell, Diffusion and Heat Flow in Liquids, Butterworths, London 1961, p. 263.

latter. Thus in the B-cells both the platinum electrodes and the thermocouples were immersed to a depth of about one mm in the solid salt, and it is difficult to avoid a temperature gradient along this bare stretch of the electrode. This means that the measured emf does not correspond exactly to the temperature difference indicated by the thermocouples. This error should however be fairly small if sufficient precautions are taken. A source of error which surely is negligible is the influence on the emf from the small amount of impurities present in the B-cell due to corrosion of the Vycor glass while the sulfate was molten.

The time-dependence of ΔV is demonstrated in Fig. 2. It took about two hours after the heating coil had been switched on until the final temperature difference had been obtained, while ΔV continued to increase slowly and reached its final value after several days. In several experiments with C-cells the heating was switched over to the other coil after the final emf ε_∞ had been obtained. After a few hours the temperature difference was constant again, but the emf continued to decrease, went through a minimum and then increased until it became ε_∞ again. This behavior of the emf upon reversal of the temperature gradient rules out the possibility that the instability of the emf in the beginning of an experiment is due to a change in the electrode properties, e. g. the formation of a lithium electrode consisting of a thin layer of lithium on the platinum surface in analogy with REINHOLD's explanation of the behaviour of platinum electrodes in contact with silver salts. It is instead obviously a diffusion-controlled process.

The measured potential difference, ΔV, is proportional to the temperature difference ΔT. This was found both for the ΔV measured as soon as the temperature became stable, Fig. 3, and for the final ΔV_∞, Fig. 4. Within experimental error the same emf is obtained for the three different cell types, Fig. 3. The study of ΔV_∞ is of course time-consuming, thus it took nearly one month to make the five measurements reproduced in Fig. 4. As seen from this figure there was no isothermal emf in the vertical C-cells, cf. above.

The final emf, ε_∞, was studied as a function of the mean temperature ΔT_m over the range 628 – 797 °C, see Fig. 5. A least squares fit gives the following relation

$$-\varepsilon_\infty = (0.03 \pm 0.25) + (1.95 \pm 0.34)\, 10^{-3} \cdot T_m \text{ mV/degr.} \quad (1)$$

The errors are standard deviations[31]. Although it may be fortuitous the thermal emf is thus found to be directly proportional to the absolute temperature within the limits of error.

ε_i is estimated to be -0.69 mV/degr., cf. Fig. 2. The accuracy is not sufficient to decide whether ε_i is temperature dependent.

Discussion

The dependence of the emf ε_t on time t suggests a relation of the type

$$\varepsilon_t - \varepsilon_i = (\varepsilon_\infty - \varepsilon_i)\,(1 - C\, e^{-t/\Theta}) \quad (2)$$

where ε_i is the initial and ε_∞ the final emf, and Θ is a characteristic time. The constant C is 1 according to DE GROOT but $8/\pi^2$ in the long-time $(t > \Theta/3)$ approximation of an equation derived by BIERLEIN[32]. The corresponding short-time approximation $(t < \Theta/2)$ is

$$\varepsilon_t - \varepsilon_i = 4 \left(\frac{t}{\pi^3\, \Theta}\right)^{1/2} (\varepsilon_\infty - \varepsilon_i)\,. \quad (3)$$

The characteristic time is related to a diffusion coefficient D and the distance a between the two electrodes. (In all our formulas it is assumed that the concentration changes with the same rate at both electrodes, i. e. there are no large end volumes, and the temperature dependence of D is neglected.)

$$\Theta = a^2/\pi^2 D\,. \quad (4)$$

The diffusion coefficients estimated by means of equations (3) and (4) are to be considered as very approximate due to the difficulty to determine ε_i with the same accuracy as ε_∞. Nevertheless the obtained diffusion coefficients are found to be in good agreement with the previously measured self-diffusion coefficient of lithium ions in α-Li_2SO_4, see Table 1. Thus it is evident that the time-dependent part of the emf is due to thermal diffusion of lithium ions in the sulfate lattice producing an excess of cations at the cold electrode. At equilibrium the thermal diffusion emf is $\varepsilon_d = \varepsilon_\infty - \varepsilon_i$, which is to be identified

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[31] A. HALD, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522.

[32] J. N. AGAR and W. G. BRECK, Trans. Faraday Soc. **53**, 167 [1957].

T_m °C	$D \cdot 10^5$ $cm^2 sec^{-1}$	
	From eqn. (4)	From ref[5]
654	6.9	5.0
720	11.4	7.3
725	9.3	7.5
755	9.4	8.8

Table 1. Comparison of self diffusion coefficients as estimated from the time dependence of the emf with those calculated from the relation[5] $D^+ = 0.015 \cdot \exp(-10\,500/R\,T)$.

as the homogeneous thermoelectric power in α-Li_2SO_4, while the initial thermal emf, ε_i, is to be considered as the inhomogeneous thermoelectric power caused by the dependence of the Li_2SO_4/metal contact potential on temperature.

The cubic lattice of α-Li_2SO_4 contains an excess of cation positions since the number of available positions is 50% higher than the actual number of cations[1]. Thus the lattice might be considered as an extreme example of SCHOTTKY defects, and it should be instructive to apply here the theory for thermal diffusion in ionic crystals with lattice defects[26]. Since the mobility of the anions is negligible in comparson with that of the cations, the relation

$$\varepsilon_d = (Q^* + \tfrac{1}{2}\,h)\,e\,T \tag{5}$$

should be valid. Q_1^* is the heat of transport of the cation vacancies and h is the "heat of formation of a defect pair". (e is the elementary charge.) Due to the uncertainty about ε_i all calculations are very approximate. By taking ε_i to be -0.69 mV/degr. over the whole temperature range, the estimations shown in Table 2 were made. The cation heat of transport (including $\frac{1}{2}\,h$) is thus of the same order of magnitude as the activation energy of cation self-diffusion 10.5 kcal/gramequiv. (Standard deviation 27%)[5], and might well be larger. The latter possibility is in quantitative conflict with the thermal diffusion theory of WIRTZ, according to which the activation energy always should be larger than the corresponding heat of transport, but such a disagreement has been noticed also for halides[21]. There is, however, at least qualitative agreement with WIRTZ' theory regarding the direction of the thermal diffusion effect, since the concentration of lithium ions increases at the cold side, which is expected if the main part of the activation energy for a jump is required to remove the ion from its original position, and the energy required to form a hole at the new position is small in comparison, cf. e. g. thermal diffusion of C in Fe[33, 34].

Temp. °C	$-\varepsilon_d$ mV/degr.	$-\varepsilon_d\,T$ eV	$-\varepsilon_d\,e\,T$ kcal/ gramequiv.
600	0.46	0.40	9.3
800	0.85	0.91	21

Table 2. Estimations of the homogeneous thermoelectric power, ε_d, and of heats of transport, cf. eq. (5). It is assumed that ε_i is -0.69 mV/degr. over the whole temperature range.

The thermal diffusion process studied here consists of a displacement of the cations relative to the sulfate ion, while the isotope effect described previously[6] corresponds to a displacement of the two isotopes relative to each other within this bulk transport of lithium ions. The heat of transport for the isotope effect was estimated to 0.17 kcal/gramequiv. at 750 °C[35]. Another type of thermal diffusion process causing a time-dependent emf has been studied for aqueous solutions of electrolytes[32, 36] where the concentration of the solute changes at the electrodes until the steady state has been obtained. In the interpretation of the more recent investigations of thermal emf's in solid halides, the homogeneous thermoelectric power is considered to be due to a displacement of ions and vacancies by thermal diffusion[11, 18, 21, 22, 24, 26]. Only in one case was a time-dependence reported[22], and it has recently been stated for a previous measurement that sufficient time had not elapsed to establish a complete SORET effect[37]. On the other hand, work in progress with α-AgI, where the cation self-diffusion coefficient is of the same order of magnitude as in Li_2SO_4, indicates that there is a time-dependence of the thermal emf for irreversible (Pt) but not for reversible (Ag) electrodes[38].

The total thermal emf (correctly $-\varepsilon_\infty$) increases with temperature for cubic Li_2SO_4, eqn. (1), while the emf is temperature independent for KCl[22], and decreases with increasing temperature for NaCl[21], CuCl[24], AgCl[22], AgBr[22] and AgI[14, 38]. For the

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[33] P. G. SHEWMON, Diffusion in Solids, McGraw-Hill, New York 1963, p. 189.

[34] For a more complete discussion of current theories of thermal diffusion in crystals see L. A. GIRIFALCO, Phys. Rev. **128**, 2630 [1962].

[35] S. GUSTAFSSON and A. LUNDÉN, Z. Naturforschg. **17 a**, 550 [1962].

[36] R. HAASE and G. BEHREND, Z. Phys. Chem., N.F. (Frankfurt) **31**, 375 [1962].

[37] A. W. LAWSON, J. Appl. Phys., Suppl. **33**, 466 [1962].

[38] A. KVIST, unpublished.

latter salt Weiss claims to have found an irregular temperature dependence[20], which, however, might be doubted already when the spread of his emf values is considered. A difference regarding the temperature dependence of the thermal emf between cubic Li_2SO_4 and all the solid halides investigated so far is not surprising, since Li_2SO_4 differs from most other solid salts also when several other properties are considered. A similarity between Li_2SO_4 and AgI might have been expected, since these two salts have an unusually high cation mobility, which is of the same order as for molten salts. Although an increase of the thermal emf with increasing temperature seems to be more common for melts, both the opposite behavior and temperature-independence has been found[23].

Acknowledgements

This work has been supported by "Wilhelm och Martina Lundgrens Vetenskapsfond".

Kalorimetrische Neubestimmung der Halbwertszeit von RaD (^{210}Pb)

Von H. Ramthun

Mitteilung aus der Physikalisch-Technischen Bundesanstalt, Braunschweig

(Z. Naturforschg. **19 a**, 1064—1069 [1964]; eingegangen am 4. Juni 1964)

The half-life of RaD has been evaluated from calorimetric measurements of the specific rate of energy emission of two radium sources with different ages of enclosure. The result $\tau = 21{,}96$ years agrees well with the value, recommended in 1931 by the international radium standard commission. The uncertainty (threefold standard deviation) of the result amounts to ±0,51 years.

Wie Tab. 1 zeigt, haben die in den letzten Jahren zur Halbwertszeit von RaD veröffentlichten Messungen die in ihrer Kenntnis bestehende Unsicherheit nicht wesentlich vermindert. Diese Feststellung überrascht angesichts der allgemeinen Verbesserung der Zählmethoden und Geräte selbst dann, wenn man bedenkt, daß RaD Glied der natürlichen Radium-Zerfallsreihe (Abb. 1) ist und die zeitliche Abnahme der Strahlungsintensität wegen des Anwachsens der ebenfalls radioaktiven Folgeprodukte RaE und RaF (Abb. 2) nicht direkt gemessen werden kann. Die Tabelle zeigt weiter, daß viele Fehlerangaben zu optimistisch sind und daß die wahre Unsicherheit der publizierten Halbwertszeit durch sie nur mangelhaft charakterisiert wird.

τ in Jahren	Jahr und Autor der Veröffentlichung
16,5 ± 0,5	1910 G. N. Antonoff[1]
22	1931 Intern. Radium-Standard-Kommission[2]
25,4 ± 1,5	1950 F. Wagner[3]
19,4 ± 0,35	1955 J. Tobailem[4]
22,4 ± 0,4	1957 W. F. Merritt u. a.[5]
20,4 ± 0,3	1959 G. Harbottle[6]
23,3 ± 0,5	1959 B. D. Pate u. a.[7]
21,4 ± 0,5	1960 W. R. Eckelmann u. a.[8]
22,85 ± 0,7	1963 L. Imre u. a.[9]
21,96 ± 0,51 *	1964 diese Arbeit

* Dreifacher Wert der in der Fehlerrechnung abgeleiteten Standardabweichung.

Tab. 1. Veröffentlichte Halbwertszeiten von RaD.

Die Neubestimmung beruht auf der Messung der zeitlichen Zunahme der Wärmeleistung von emanationsdicht eingeschlossenem Radium. Aus dieser Zunahme folgerten Curie und Yovanovitch[10] schon 1925, daß der damals geltende Wert von 16 Jahren zu klein sein müßte. Die geringere Meßgenauigkeit und die unsichere Kenntnis der mittleren Zerfallsenergien erlaubten jedoch keine genaueren Angaben über den wahren Wert.

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[1] G. N. Antonoff, Phil. Mag. **19**, 825 [1910].

[2] International Radium-Standards Commission Report, M. Curie u. a., Rev. Mod. Phys. **3**, 427 [1931]; Z. Phys. **32**, 569 [1931].

[3] F. Wagner jr., ANL-4490, 5 [1950].

[4] J. Tobailem, J. Phys. Radium **16**, 235 [1955].

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