	I			II			III
Kern	A_{kk} (gemessen) [MHz]			Anisotr. Hfs für Mittelwert [MHz]			isotr. Hfs [MHz]
	A_{xx}	A_{yy}	A_{zz}	B_{xx}	B_{yy}	B_{zz}	$a=\frac{1}{3}\sum A_{kk}$
α-Protonen							
1. Dublett-Komponente	−22,47	−6,33	−15,77	−7,66 **	+8,57 **	+0,91 **	−14,96 *
2. Dublett-Komponente	−22,77	−6,46	−15,98				
Aufspaltung [kHz]	300	130	210				
β-Protonen							
1. Dublett-Komponente	−4,1	−7,24	−6,44	+1,86 **	−1,31 **	−0,54 **	−5,96 *
2. Dublett-Komponente		−7,31	−6,56				
Aufspaltung [kHz]	breite Linie	70	120				
α-Deuteronen							
1. Dublett-Komponente	(−3,48) ***	(−0,98) ***	−2,48	−1,18 **	+1,32 **	−0,14 **	−2,30 *
2. Dublett-Komponente			−2,51				
Aufspaltung [kHz]	—		30				

* Mit der Forderung Sp $\tilde{B}=0$ aus Spalte I berechnet, d. h. $a=\frac{1}{3}(A_{xx}+A_{yy}+A_{zz})$.
** Mit Meßwerten aus Spalte I und der Konstante a aus Spalte III berechnet.
*** Mit dem Verhältnis $A_{zz}^{\alpha}/A_{zz}^{\beta}$ berechnet.

Tab. 1. Hyperfeinstruktur-Daten des Naphthalin-Moleküls im Triplett-Zustand.

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Self-Diffusion in Molten Thallous Chloride. A Re-Determination

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The self-diffusion coefficient of the Tl^+-ion in molten TlCl has been remeasured with the porous-frit technique [1, 2]. The result can be described by the following Arrhenius equation:

$$D=2.2\times10^{-3}\exp(-6000/R\,T) \qquad (450-556\ ^\circ\mathrm{C})$$

where D is expressed in $\mathrm{cm}^2\,\mathrm{s}^{-1}$, R in $\mathrm{cal\,mole}^{-1}$, and T in degrees Kelvin. This result is within experimental error equal to the results by Berne and Klemm [3] and by Angell and Tomlinson [4] who used the conventional capillary technique [5].

Among the different experimental techniques developed for measuring self-diffusion coefficients in molten salts (see ref. [4], p. 2315) the porous-frit method has been recognized as particularly well suited for difficult experimental conditions. This fact has been established by Sjöblom and Andersson [6]. There have been some doubts about the reliability of the method due to the discrepancy between the TlCl results by Berne and Klemm [3] and by Angell and Tomlinson [4] (who both used the conventional capillary technique) on one side and the results by Sjöblom and Lundén [2] (who used the porous-frit technique) on the other. The activation energies differed by a factor of two while the magnitudes of the diffusion coefficients agreed reasonably well. It was difficult to pinpoint any reason for this difference but it came to our knowledge that similar problems had been encountered by Laity [7] in his measurements of external transport numbers in molten TlCl. He found that the (apparent) activation energy of the conductivity increased from 3.4 kcal mole^{-1} to 10.1 kcal mole^{-1} when the melt had been standing in air at 500 °C for 48 hours. (An appreciable fraction of the salt had been transformed into Tl_2O during this period.) He was, however, able to obtain good results by keeping the experimental time very short. (The agreement between his results and later, more accurate, external transport number values by Fischer and Klemm [8] is quite satisfactory if a correction is made for the temperature increase inside the cell used by Laity.)

We thus decided to re-determine the self-diffusion coefficient of the Tl^+-ion in molten TlCl in order to in-

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vestigate if the previously obtained difference was a property of the porous-frit method as such or rather due to unexpectedly rapid decomposition of the melt. The latest version of the porous-frit method is particularly suitable for this purpose since the diffusion times can be decreased to less than 100 seconds for salts with diffusion coefficients of the order of 5×10^{-5} cm^2 s^{-1}. This means of course also that errors both of immersion and time measurement become more serious, but this fact has to be weighed against the necessity to keep the time of contact between the melt and the atmosphere to a minimum.

The experimental technique has been described elsewhere [2, 6]. Commercially available thallous chloride (Schuchardt, München) was dried and used without further purification (total metallic impurities less than 200 ppm). Radio-active $Tl^{204}NO_3$ was obtained from NEN, Boston, Massachusetts, and converted into TlCl. Conventional liquid β-counting techniques were employed. The whole experimental series was performed without cooling and reheating the furnace (which was carefully blanketed with dry argon gas in order to exclude atmospheric moisture and oxygen from the melt).

The experimental results can be described by an Arrhenius equation (obtained by least squares fitting):

$$D_{\mathrm{Tl}} = 2.2 \times 10^{-3} \exp(-6000/R\,T) \quad (450-556\ ^\circ\mathrm{C}) \quad (1)$$

where D is expressed in cm^2 s^{-1}, R in cal mole^{-1}, and T in degrees Kelvin. The standard deviation [9] in the activation energy is 1.4 kcal mole^{-1} and the standard error of estimate [10] in D is 10%. Equation (1) agrees within experimental error [11] with the results obtained by BERNE and KLEMM [3] and by ANGELL and TOMLINSON [4]. Their reproducibilities are better, though, which is to be expected since the porous-frit technique in its present form is not well suited for measurements of comparatively high self-diffusion coefficients (as noted above) [12]. It can nevertheless be safely concluded that the previously obtained discrepancy in the results by the porous-frit method [2, 4] is due to chemical reasons and that the porous-frit technique as such is not affected by any systematic errors.

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[11] The experimentally obtained "activation energy" is somewhat higher in the present investigation (but still within experimental error equal to the previous values).

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