Temperature dependence of proton spin-lattice relaxation times in some pure liquids

Temperature Dependence of Proton Spin-Lattice Relaxation Times in Some Pure Liquids

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Abstract.

Proton spin-lattice relaxation times T_1 for oxygen-free liquids $CHCl_3$, $CHBr_3$, H_2SO_4, CH_2Cl_2, CH_3Cl and NH_3 have been measured at different temperatures at a resonant frequency of 28 Mc/sec. The results obtained at 20° C were compared with the values calculated by means of the formulae derived for the case of interaction of two different sorts of nuclei in a pure liquid. The experimental values were usually less than the theoretical ones.

A decrease of the expression $T_1 \eta / T$ with increasing temperature was found for several pure liquids containing one, two and three protons per molecule. Theory predicts that this expression should be independent of temperature.

The disagreement with theory is considered to be due to the failure of simplified model of molecular motion.

Résumé.

Le temps de relaxation spin-réseau du proton, T_1, a été mesuré pour les liquides suivants dépourvus d'oxygène: $CHCl_3$, $CHBr_3$, H_2SO_4, CH_2Cl_2, CH_3Cl et NH_3. Les mesures ont été effectuées à différentes températures à une fréquence de résonance de 28 Mc. Les résultats obtenus à 20° C ont été comparés aux valeurs calculées au moyen des formules obtenues dans le cas où l'on a interaction de deux espèces de noyaux différents dans un liquide pur. Les valeurs expérimentales se sont avérées en général plus faibles que les valeurs théoriques.

On a constaté une décroissance de l'expression $T_1 \eta / T$ lors de l'élévation de la température pour plusieurs liquides purs contenant un, deux ou trois protons par molécule.

Nous considérons que le désaccord avec la théorie est implicable à un défaut du modèle simplifié du mouvement moléculaire.

INTRODUCTION.

The comparison with experiment of the Bloembergen, Purcell and Pound [1] * formula for nuclear magnetic spin-lattice relaxation time

* Referred to hereafter as B.P.P.

T_1 in pure liquids seems to be of considerable importance from the point of view of the structure of liquids. This arises because the BPP and all subsequent theories [2, 3, 4] assume the Debye model of liquids, i.e. that the rotational and translational motion of the molecules in liquids is diffusion-like and can be related to the viscosity by means of the well known Stokes law.

The BPP formulas ** for T_1

$$\left(\frac{1}{T_1}\right)_{rot} = \frac{2\pi\hbar^2\gamma^4 a^3 \eta}{b^6 kT} \qquad \cdot \left(\frac{1}{T_1}\right)_{tr} = \frac{3\pi^2\hbar^2\gamma^4 N \eta}{kT}$$

can be compared with experiment in two ways. One is to compare the experimental and theoretical values of T_1 at one temperature; the other is to investigate the function $T_1 \eta/T$ (wherein η is the viscosity of a liquid and T — the absolute temperature) which according to this theory should be independent of the temperature.

Till now, only the temperature dependence measurements of T_1 for water [6, 7, 8], ethyl alcohol [6] and for chloroform [7] have been reported. In all cases the decrease of the function $T_1\eta/T$ is observed. This fact has been discussed by Giulotto et al. [6] who assume a quasi-crystalline structure which gradually vanishes as the temperature is raised. This process affects the frequency spectrum of thermal motions and in consequence T_1.

Very few attempts have been made to compare the theoretical T_1 values with experiment. The difficulty depends on the fact that the BPP T_1 formulae are derived only for liquids containing two equivalent nuclear spins (with $I = 1/2$) in a molecule. Unfortunately there exist very few such liquids. Water is a good example and was used for this purpose in the original BPP paper. The latest measurements of T_1 in water give $T_1 = 3.1$ sec [7] whereas the corrected BPP formulae give 2.5 sec. Further theoretical research has led to T_1 formulae for molecules containing two different nuclei of spin 1/2 [2] and three or four equivalent nuclei of spin 1/2 [3]. But even this progress has not increased the number of liquids suitable to serve as examples.

In this work liquids have been chosen which satisfy approximately the requirements of the theory as applied to molecules containing one, two or three protons. Other nuclei in these molecules have either zero spin or their gyromagnetic ratios are small compared with that of the proton.

** The correction made by Kubo and Tomita [5] is introduced.

In consequence the proton spin-lattice relaxation is mainly determined by the proton-proton interactions. Contributions to T_1 from other magnetic nuclei are small and have been included in an approximate way by means of a generalisation of BPP theory. However in the case of $CHCl_3$ and $CHBr_3$ the intramolecular contribution to the spin-lattice relaxation process is merely determined by the interaction between a proton and three nuclei of chlorine and bromine respectively.

An exact T_1 theory for molecules containing symmetrical groups of three or four protons has been developed by Hubbard [3]. The extension of this theory to less simple molecules would be very complicated.

A considerable simplification results from the assumption that the intramolecular neighbours of a given proton each experience independent random motion (due to the motion of the molecule as a whole) in which only the distances between each of them and the given proton are preserved. The theory described below is based on this assumption. This is of course justified for molecules containing not more than two magnetic nuclei as treated by BPP. For molecules which in addition to one or two protons contain other magnetic nuclei, the assumption enables the contributions to T_1 of these other magnetic nuclei to be calculated approximately. This is justified when the interactions between a proton and other nuclei are small.

Although our theory is less justified for three-proton molecules the T_1 values for NH_3 and CH_3Cl are also provided in Table II for comparison with the exact theory of Hubbard and the agreement seems to be quite good.

THEORY.

Let us consider a system of identical molecules (pure liquid) containing nuclei of spin $I_j = 1/2$ and nuclei with arbitrary spin number I_k ($\gamma_j \neq \gamma_k$). We are interested in the interaction of one spin I_i, chosen from the spins I_j, with rest of the system. The Hamiltonian of this interaction $H_i = \hbar G_i$ with $G_i = \sum_j G_{ij} + \sum_k G_{ik}$. The two terms G_{ij} and G_{ik} may be written in the following form

$$G_{il} = -\gamma_i \vec{I_i}\overrightarrow{H_{il}} - J_{il}\vec{I_i}\vec{I_l} = -\frac{1}{2}\gamma_i(I_i^+ H_{il}^- - I_i^- H_{il}^+) - \gamma_i I_{zi}H_{zil} -$$

$$\frac{1}{2}J_{il}(I_i^+ I_l^- + I_i^- I_l^+), \qquad (l = j \ or \ k) \qquad (1)$$

where J_{il} are the coupling constants, $\overrightarrow{H_{il}}$ is the magnetic field produced by spin l at the position of spin i and

$$H_{il}^{\pm} = H_{xil} \pm iH_{yil} \; ; \qquad I_l^{\pm} = I_{xl} \pm iI_{yl} \, .$$

The complete spin-lattice relaxation time T_1 resulting from the interaction of the spin i with the spins j and k is

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{ij} + \left(\frac{1}{T_1}\right)_{ik} \, . \tag{2}$$

Computation of the part $\left(\dfrac{1}{T_1}\right)_{ij}$ is well known as related to the interaction of identical spins of 1/2. The first term $\left(\dfrac{1}{T_1}\right)_{ij}$ is just the result of the application of the BPP theory to the interaction of two identical nuclei.

The second term in Eq. (2) is given by

$$\left(\frac{1}{T_1}\right)_{ik} = 2 \left(|(+|\sum_k G_{ik}|-)|^2\right)_{Av} \, . \tag{3}$$

The matrix element in Eq. (3) is

$$\left(+\Big|\sum_k G_{ik}\Big|-\right) = -\frac{1}{2}\sum_k \left(\gamma_i \, H_{ik}^- + J_{ik}\, I_k^-\right), \tag{4}$$

where

$$H_k^- = (H_k^+)^\star = 2\,\hbar\,\gamma_k \left[f_{ik}^{(0)}\, I_k^+ + f_{ik}^{(1)}\, I_{zk} + f_{ik}^{(2)}\, I_k^-\right]^\star \tag{5}$$

with

$$f_{ik}^{(0)} = \frac{1}{4}\, r_{ik}^{-3}\left[1 - 3\cos^2\theta_{ik}\,(t)\right],$$

$$f_{ik}^{(1)} = \frac{3}{2}\, r_{ik}^{-3}\sin\theta_{ik}\,(t)\,\cos\theta_{ik}\,(t)\,\exp\left[i\,\varphi_{ik}\,(t)\right], \tag{6}$$

$$f_{ik}^{(2)} = \frac{3}{4}\, r_{ik}^{-3}\sin^2\theta_{ik}\,(t)\,\exp\left[2\,i\,\varphi_{ik}\,(t)\right],$$

We average in a manner similar to [1] by introducing a correlation function and using the relations for average values, namely

$$\left\langle\,|\,f_{ik}^{(1)}\,|\,\right\rangle = \left\langle\,|\,f_{ik}^{(2)}\,|\,\right\rangle = 6\left\langle\,|\,f_{ik}^{(0)}\,|\,\right\rangle = \frac{3}{10}\left\langle\,r_{ik}^{-6}\,\right\rangle \tag{7}$$

and

$$\left\langle\,|\,I_k^+\,|^2\,\right\rangle = \left\langle\,|\,I_k^-\,|^2\,\right\rangle = 2\left\langle\,(I_{zk})^2\,\right\rangle = 2\,I_k\,(I_k+1). \tag{8}$$

With the above calculations we obtain for the rotational part of the second term in Eq. (2)

$$\left(\frac{1}{T_1}\right)_{ik} \mathrm{rot} = \frac{2}{5} \gamma_i^2 \hbar^2 \sum_k \gamma_k I_k (I_k + 1) \left\langle r_{ik}^{-6} \right\rangle \tau_{ck} \left[\frac{1}{3} \frac{1}{1 + (\omega_i - \omega_k)^2 \tau_{ck}^2} + \right.$$

$$\left. + \frac{1}{1 + \omega_i \tau_{ck}^2} + \frac{2}{1 + (\omega_i + \omega_k)^2 \tau_{ck}^2} \right] + \frac{2}{3} \sum_k J_{ik} I_k (I_k + 1)$$

$$\frac{\tau_{ek}}{1 + (\omega_i - \omega_k)^2 \tau_{ek}^2}, \tag{9}$$

where τ_{ck} and τ_{ek} are the nuclear and electronic correlation times, respectively, for spin k.

Assuming that $\omega^2 \tau_c^2 \ll 1$ and adding to Eq. (9) the contribution due to the interaction of spin i with the spins j we find for the rotational part

$$\left(\frac{1}{T_1}\right)_{\mathrm{rot}} = \hbar^2 \gamma_i^2 \tau_c \left[\frac{3}{2} \gamma_i^2 \sum_j \left\langle r_{ij}^{-6} \right\rangle + \frac{4}{3} \sum_k I_k (I_k + 1) \gamma_k^2 \left\langle r_{ik}^{-6} \right\rangle + \right.$$

$$\left. + \frac{2}{3} \sum_k J_{ik} I_k (I_k + 1) \frac{\tau_{ek}}{1 + (\omega_i - \omega_k)^2 \tau_{ek}^2}, \right. \tag{10}$$

where $\tau_c = \tau_{cj} = \tau_{ck} = \frac{4}{3} \frac{\pi \eta a^3}{kT}$ for a rigid molecule of radius a. It is to be noticed that $\left(\frac{1}{T_1}\right)_{\mathrm{rot}}$ calculated from Eq. (10) can depend on the choice of the spin i in the case of molecules containing unsymmetrical groups of magnetic nuclei.

The translational part calculated by a method similar to BPP is of the following form:

$$\left(\frac{1}{T_1}\right)_{tr} = \frac{\pi^2 \hbar^2 \gamma_i^2 N \eta a}{kT} \left[3 \gamma_i^2 \sum_j d_{ij}^{-1} + \frac{8}{3} \sum_k I_k (I_k + 1) \gamma_k^2 d_{ik}^{-1} \right], \tag{11}$$

where N is the number of molecules per cm^3. We assume, like BPP, that the distance of closest approach $d = 2a$.

In the case of two identical spins $I_j = 1/2$ per molecule of liquid the formulas (10) and (11) become of course the same as in the BPP theory [1].

Furthermore, when a molecule contains a pair of unlike spins of value $1/2$, Eq. (10) is identical with Solomon's formula [2] for $\left(\frac{1}{T_1}\right)_{\mathrm{rot}}$.

Finally by substituting $I_k = \frac{1}{2}$ $(\gamma_j \neq \gamma_k)$ Eqs. (10) and (11) reduce to formulae given by Gutowsky and Woessner [4].

NUMERICAL EVALUATION OF PROTON T_1 AT 20° C.

The pure dipole-dipole interaction is the only relaxation mechanism for H_2SO_4 and NH_3, whereas for liquids CH_3Cl, CH_2Cl_2, $CHCl_3$ and $CHBr_3$ an electron-coupled exchange interaction must be introduced in calculation of $\left(\frac{1}{T_1}\right)_{rot}$ from Eq. (10). This exchange interaction was not taken into account because the coupling constants J_{HCl} and J_{HBr} and corresponding electronic correlation times τ_{ek} have not been known. However, as a rough estimation shows, the contributions to $1/T_1$ caused by the exchange interaction seem to be rather small for these liquids.

The translational parts of T_1 for $CHCl_3$, $CHBr_3$, CH_2Cl_2 and CH_3Cl were calculated by introducing in Eq. (11) the natural abundance of chlorine and bromine isotopes.

In the rotational parts for $CHCl_3$, CH_2Cl_2 and CH_3Cl the isotope ^{35}Cl was taken into account. In the case of bromoform $\left(\frac{1}{T_1}\right)_{rot}$ was evaluated for configuration $CH^{81}Br_2{}^{79}Br$ (the most abundant in the mixture of molecules).

TABLE I.

Liquid	$2a$ (Å)	b_{ij} (Å)	b_{ik} (Å)	Literature values * of viscosity at 20° C (cp)
$CHCl_3$	5.47		2.34	0.571 (α)
$CHBr_3$	5.80		2.224	2.015 (β)
CH_2Cl_2	5.00	1.771	1.756	0.401 (γ)
H_2SO_4	4.93	3.0		37.0 (δ) (100% conc.)
CH_3Cl	4.65	1.817		0.244 (ε)
NH_3	3.76	1.628		0.1365 (γ)

* References for literature values in Table I:
(α) Kaye, C.W.G. and T.H. Laby, Tables of Physical and Chemical Constants, Longmans, Green & Co., London 1956.
(β) Landolt-Börnstein, Physikalisch-Chemische Tabellen.
(γ) Hennel, J.W. and K. Krynicki (to be published).
(δ) Varlamov, M.I.M.I., Zhur. Prikl. Khim. (U.S.S.R.), *25*, 553 (1952).
(ε) Wilson, K.S., et al., Chem. Eng. News, *21*, 1254 (1943).

The values of three important parameters, e.i. molecular diameters $2a$, internuclear distances b_{ij} and b_{ik} and viscosities at 20° C are given in Table I. Molecular diameters were calculated from the maximum densities

of liquids assuming the filling factor 0.71 for spherical molecules. Internuclear distances were taken either from Raman and infrared spectra (NH_3, CH_3Cl) or from recent data of microwave spectra (CH_2Cl_2, $CHCl_3$, $CHBr_3$). In the case of H_2SO_4 the H-H distance was assumed 3Å.

The theoretical values of proton T_1 for the above mentioned liquids are given in Table II.

TABLE II.

Liquid at 20° C	Hubbard's theory $\left(\frac{1}{T_1}\right)^*$ rot (sec^{-1})	Authors' theory $\left(\frac{1}{T_1}\right)$ rot (sec^{-1})	$\left(\frac{1}{T_1}\right)$ tr (sec^{-1})	T_1 calc (sec)	Authors' measurements T_1 exp (sec)
$CHCl_3$		6.00×10^{-3}	9.73×10^{-3}	63.6	90 [7]
$CHBr_3$		0.238	4.85×10^{-2}	3.50	16.8
H_2SO_4 100%		0.676	1.736	0.41	1.23
CH_2Cl_2		0.192	1.62×10^{-2}	4.80	28.6
NH_3	8.650×10^{-2}	8.616×10^{-2}	1.844×10^{-2}	9.6	22.4
CH_3Cl	0.150	0.150	1.70×10^{-2}	6.0	18.6

* These (T_1) rot values refer to considerably larger abundance.

PREPARATION OF SAMPLES

As the atmospheric oxygen dissolved in liquids affects T_1 considerably, it was necessary to prepare samples of air-free liquids. In almost every case a special technique was required for careful purification and degassing.

a) *Bromoform.* C.P. bromoform was used as starting material. To purify, it was fractionally distilled several times and twice recrystallised. It was melted and refrozen while being pumped by a rotary oil vacuum pump. Subsequently a sample tube was rinsed with condensate and filled up with air-free bromoform by vacuum distillation (5×10^{-3} mm Hg).

b) *Liquid ammonia.* Gaseous ammonia obtained in a synthetic way was used. The gas from a cylinder was made to pass through very pure KOH and roasted CaO and then was liquified in a glass container cooled by solid CO_2. It was then twice distilled. Freezing and melting were

repeated several times and the air above the solid NH_3 was evacuated (10^{-2} mm Hg). Together with the sample tube a closed type Ostwald viscometer was filled.

c) *Methyl chloride.* Schering Adlershof Company's A.R. grade methyl chloride was the starting material. It was made to boil and to freeze alternately several times in a closed system connected with a pump. The sample tube was filled up by vacuum distillation (6×10^{-3} mm Hg).

d) *Methylene chloride.* A.R. grade methylene chloride was used. It was purified by fractional distillation repeated four times and then was dried with very pure Na. Degassing (8×10^{-3} mm Hg) and filling of the sample tube and the viscometer were similar to the case of bromoform.

e) *Sulphuric acid.* Riedel de Haën Company's A.R. grade fuming sulphuric acid ($25\% SO_3$) was used as starting material. SO_3 was removed by strong heating for a few minutes. In a closed system the air was removed with the pump and H_2SO_4 once again was heated. After freezing and remelting the acid several times, the system was sealed off to fill up the sample tube by vacuum distillation (6×10^{-3} mm Hg).

Although care was taken to remove the moisture, the presence of small amounts of moisture is still possible except methylene chloride. The glass apparatus was carefully cleaned to eliminate the possibility of contamination of the samples by paramagnetic materials which previous work [9] has shown to affect T_1 considerably.

EXPERIMENTAL.

The method of T_1 measurements and some details of the experimental arrangement have been described elsewhere [10]. All measurements of proton T_1 were carried out at a resonant frequency of 28 Mc/sec using a high frequency bridge of the double-T type [11]. The bridge circuit was mounted in a box made from a brass block, which was kept at the constant temperature required by means of a thermostat.

The temperature was measured with a glass-mercury thermometer mounted in the outlet tube of the block, through which water flowed back into the thermostat. The readings of this thermometer were calibrated by comparison with an exact resistance thermometer situated in place

of the sample. The corrections obtained amounted to $(0 + 0.1)°$ C for 20° C and $(1.5 + 0.3)°$ C for 90° C. The reproducibility of these corrections was satisfactory.

The measurement of temperature was then improved by mounting a copper resistance thermometer within the brass block. It was calibrated in the way mentioned above.

The samples used were of 12 mm outer diameter and about 24 mm long.

RESULTS AND DISCUSSION.

Figures 1, 2, 3 and 4 show the plots of proton T_1 and the function $T_1\eta/T$ versus temperature. In all cases reported here a decrease of this function with increasing temperature was obtained. Neither the decrease
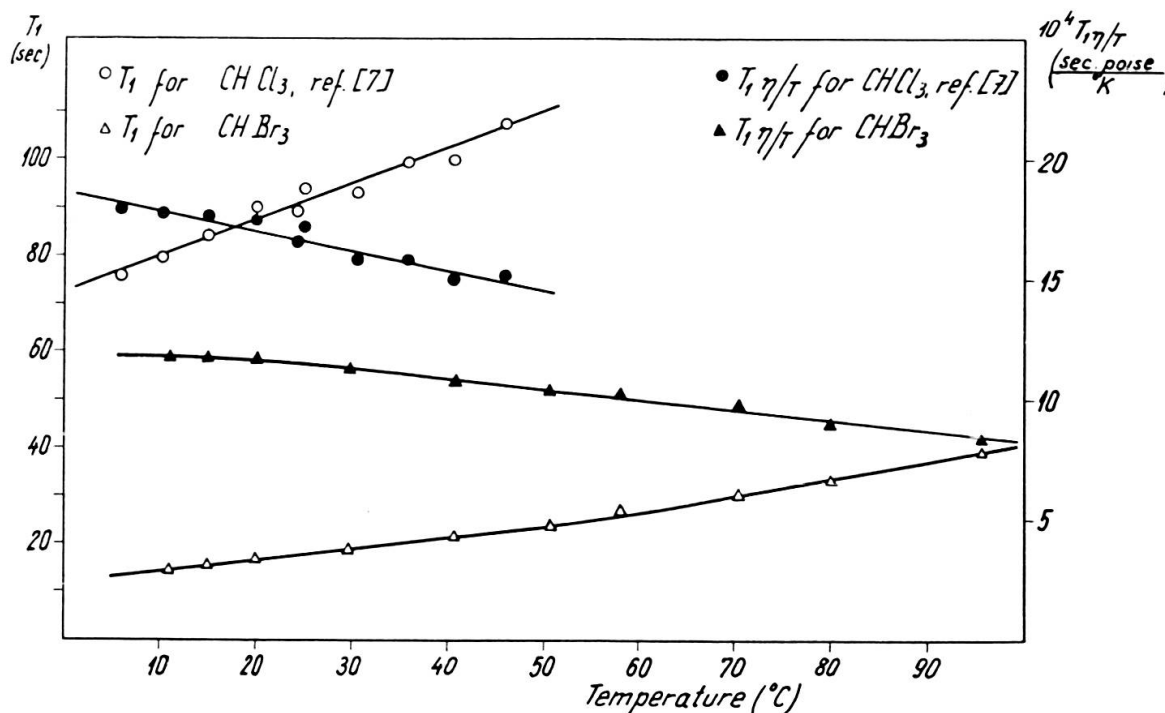

Fig. 1.

itself not its slope can be related simply to any of such features as the number of protons in a molecule, the ratio of the rotational and the translational parts of T_1, viscosity, or degree of association. As was mentioned before, water and ethyl alcohol show similar behaviour.
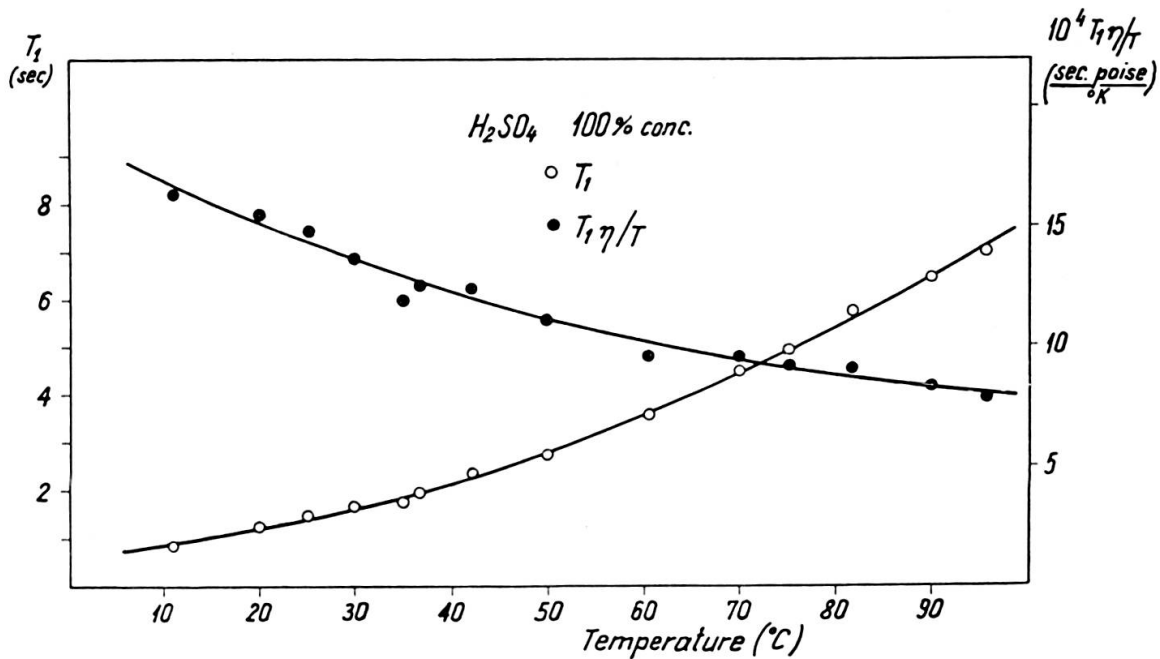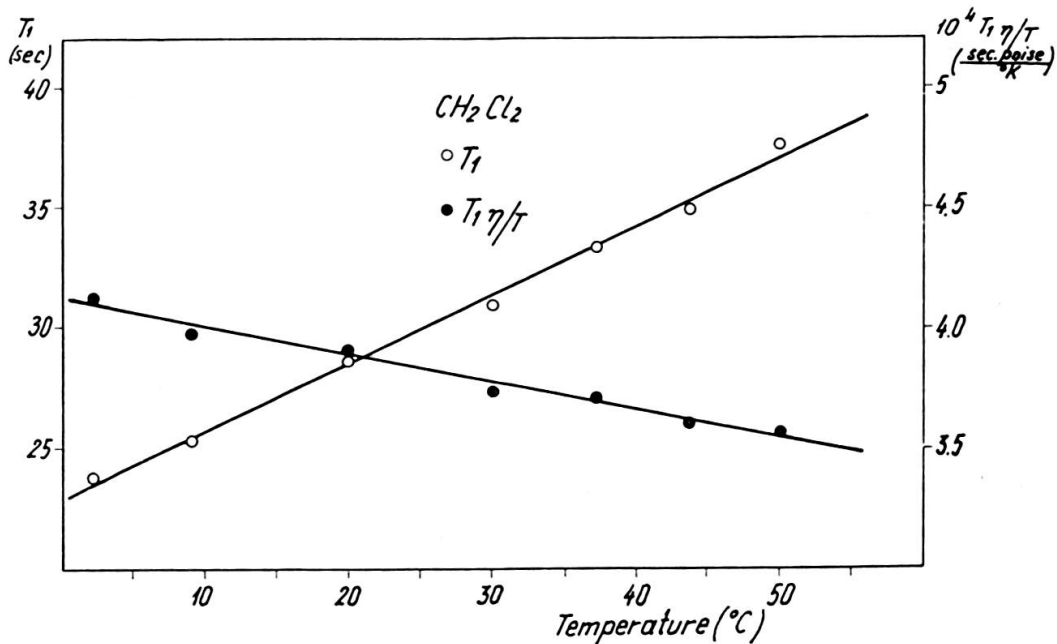
Fig. 2.

Fig. 3.

The temperature dependence of T_1 of methyl chloride is of special
interest. It remains practically constant within a range of temperature
from 10° C to at least 70° C as shown in figure 4. The theory based on the

diffusion model of liquids gives $T_1/D =$ const. So in the case of methyl chloride either the self diffusion coefficient D is constant, **or the diffusion** model is inadequate. It is worth mentioning that in water the function T_1/D decreases with temperature whereas the function $D\eta/T$ remains constant as found by Simpson and Carr [8].
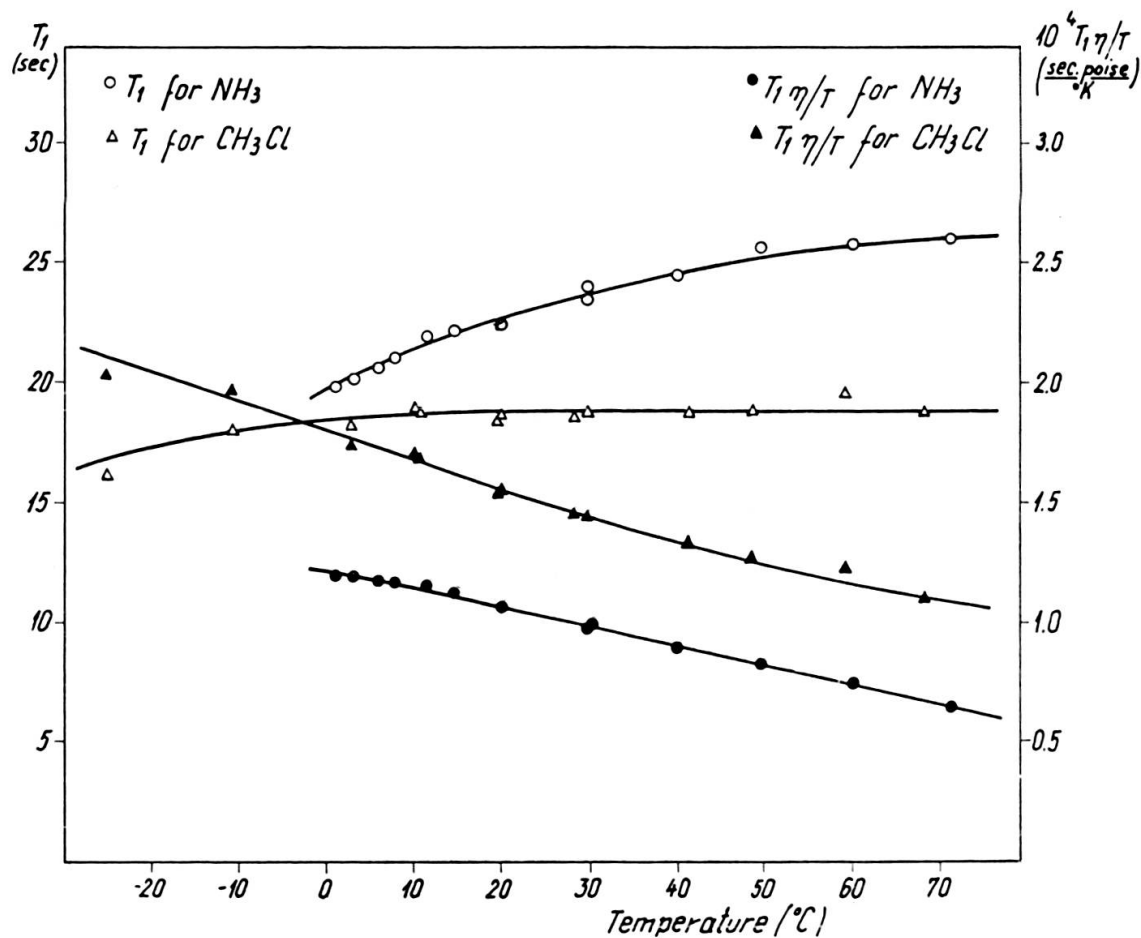

Fig. 4.

Table II shows the calculated (on the basis of formulae (10) and (11)) and experimental values of T_1 at 20° C. It is to be noticed that for all the liquids investigated the theoretical values are smaller than experimental values. All T_1 measurements in the present work are accurate to about 3%.

The theoretical values of T_1 are highly dependent on the assumed molecular radius a because $\left(\frac{1}{T_1}\right)$rot is proportional to a^3. The T_1 data

in the Table II are calculated assuming a^3 values obtained from the density of liquid at the freezing points.

In order to test the reliability of the molecular radii a used in the calculations, values for ammonia have been obtained in four different ways: **

from the viscosity of the gas . . . . $a^3 = 8.74$ Å^3
from the thermal conductivity of the gas . . . . $a^3 = 8.88$ Å^3
from the Van der Vaals constant b . . . . $a^3 = 3.67$ Å^3
from the density of the liquid . . . . $a^3 = 6.66$ Å^3

The consistency of these values suggests that the discrepancies between the experimental and theoretical values are not due to incorrect molecular radii.

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** Kaye, C. W. G. and T. H. Laby, Tables of Physical and Chemical Constants, Longmans, Green & Co., London 1956, formulae on page 39.