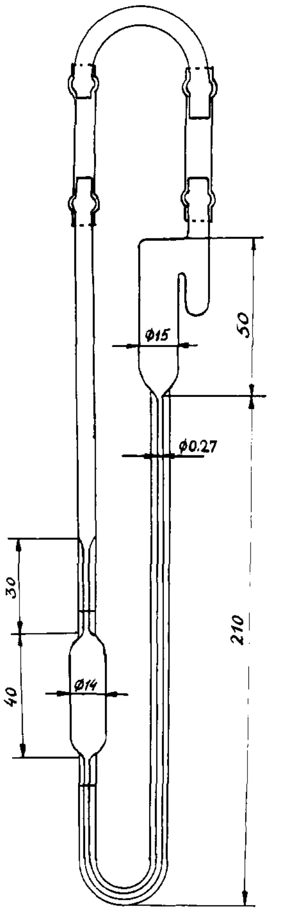

Figure 1. An Ostwald viscosimeter

The viscosity values and the values of ρ/ρ_0 are listed (Tables I and II). The estimated precision is ±0.8%. The greater part of the error comes from values of ρ/ρ_0, which were determined with an estimated accuracy of ±0.5%.

DISCUSSION

The viscosities of heavy water solutions are greater than the viscosities of ordinary water solutions at the same temperature and salt concentration. However, the character of the curves is similar. For instance, both heavy water and ordinary water solutions of KCl, KI, KBr, and $KMnO_4$ exhibit a minimum of viscosity, which disappears with temperature increase. For the other salts, viscosities increase with concentrations for both ordinary and heavy water.

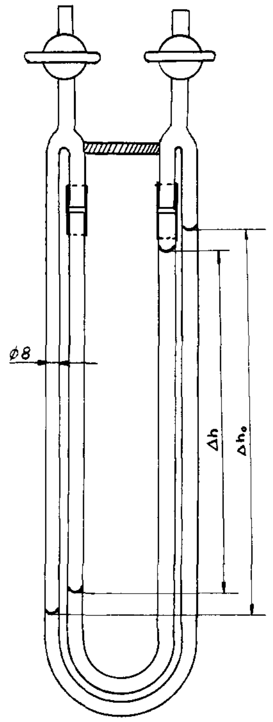

Figure 2. U-tubes for determination of density of solutions

A discussion of structure of electrolyte solutions on the basis of above data would be premature. Such an analysis will be made separately, after more relevant data are available.

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Solubilities and Refractive Indices of Some Inorganic Salts in Heavy Water

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Solubilities and refractive indices were measured for concentrated solutions in heavy water of 14 salts—LiCl, NaF, NaCl, NaBr, NaI, Na_2CO_3, $NaClO_4$, KCl, KSCN, $KMnO_4$, $K_2Cr_2O_7$, $K_4Fe(CN)_6$, CsCl, and Li_2SO_4—at 25°, 35°, 45°, 60°, 75.5°, and 91° C.

DURING an investigation, it was necessary to determine the differences of solubilities of some salts in heavy and light water. Some of the relevant data were available in the literature (*2, 4, 5, 6, 7, 9, 10*), but they were not sufficient. In this work, measurements of solubility were made for 14 salts—LiCl, NaF, NaCl, NaBr, NaI, $NaClO_4$, Na_2CO_3, KCl, KSCN, $KMnO_4$, $K_2Cr_2O_7$, $K_4Fe(CN)_6$, CsCl, and Li_2SO_4—at 25°, 35°, 45°, 60°, 75.5° and 91° C.

SOLUBILITY DETERMINATION METHOD

A curve of refractive indices of salt solutions against concentration at a constant temperature was plotted. At the saturation point, the curve is broken, and above this point it runs horizontally (Figure 1). The saturation point was determined graphically as the point of intersection of the two parts of the curve. This was checked by determining the solubility curve of NaBr in ordinary water in the temperature range 25° to 70° C. Results are in good agreement with literature data (*3*) (Figure 2). On the basis of observation, this method is considered suitable for determination of solubility on the following conditions. The solubility of a salt must be high enough to plot a curve of refractive indices *vs.* concentration with satisfactory accuracy. The salt must crystallize easily from supersaturated solutions. This is very important at higher temperatures, since during a measurement, some water may evaporate from between the prisms of the refractometer. If the measurement is performed quickly, the evaporation is small. For concentrations above the saturation point, this effect has no influence on the results. In the case of supersaturated solutions, if evaporation is too high, the line dividing dark and light areas in the refractometer becomes indistinct, making the readings difficult. The solutions must not be too dark colored. The temperatures of measurements must lie below 90° C. Above this temperature, thermal stresses may occur in the prisms of the refractometer and damage them.

Measurements of refractive indices were made by means of the RL refractometer, produced by PZO, Warsaw. White light was used. A sharp line dividing dark and light areas was attained by means of Amici prisms. The precision of the refractometer was 0.0002.

CHEMICALS

Heavy water produced in Russia was used. Before the experiments, the isotopic composition of oxygen was normalized by the electrolytic decomposition of water, burning the hydrogen evolved in air. The concentration of deuterium was determined by the picnometric method. Salts were of analytical purity, and were not additionally purified before use.

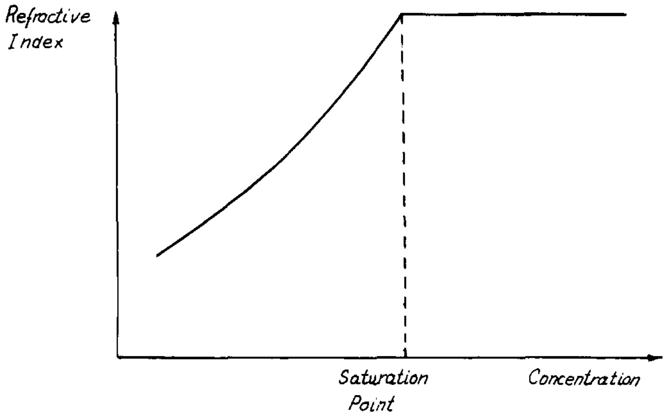

Figure 1. Dependence of refractive index on concentration of salt

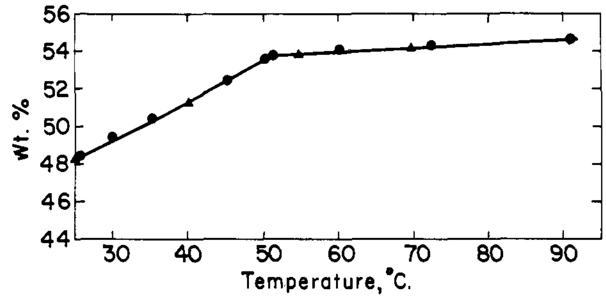

Figure 2. Solubility of NaBr in ordinary water

▲ Points from this work

● Literature data (3)

Table I. Solubility of Salts in Heavy Water, Mole %

Salt	Temp., ° C. 25	35	45	60	75	90	Concn. of D_2O in Water, Mole %
LiCl	27.0 ± 0.1	27.8 ± 0.1	28.6 ± 0.2	30.5 ± 0.3	32.0 ± 0.2	33.6 ± 0.2	99.8
Li_2SO_4	5.15 ± 0.05	5.05 ± 0.05	4.96 ± 0.05	4.89 ± 0.05	4.83 ± 0.05	4.78 ± 0.05	98.5
NaF	1.62 ± 0.02	1.64 ± 0.02	1.66 ± 0.02	1.69 ± 0.02	1.88 ± 0.05	1.96 ± 0.05	99.8
NaCl	9.6 ± 0.1	9.6 ± 0.1	9.72 ± 0.09	9.89 ± 0.09	9.98 ± 0.09	10.13 ± 0.09	99.8
NaBr	14.1 ± 0.1	15.0 ± 0.1	16.0 ± 0.1	16.1 ± 0.1	16.1 ± 0.1	16.2 ± 0.1	99.8
NaI	18.3 ± 0.2	19.5 ± 0.2	21.0 ± 0.2	24.0 ± 0.2	25.9 ± 0.2	26.5 ± 0.3	99.8
$NaClO_4$	23.38 ± 0.04	25.1 ± 0.1	27.2 ± 0.2	29.4 ± 0.2	30.1 ± 0.3	30.8 ± 0.2	99.8
Na_2CO_3	4.21 ± 0.05	7.88 ± 0.06	7.42 ± 0.06	7.26 ± 0.06	7.02 ± 0.06	6.99 ± 0.06	98.5
KCl	7.42 ± 0.07	8.05 ± 0.05	8.58 ± 0.05	9.02 ± 0.07	9.68 ± 0.07	9.9 ± 0.1	98.5
KSCN	30.0 ± 0.1	32.6 ± 0.1	35.2 ± 0.1	39.8 ± 0.1	44.4 ± 0.1	48.7 ± 0.1	99.8
$KMnO_4$	0.67 ± 0.02	1.02 ± 0.01	1.37 ± 0.01	2.05 ± 0.03	2.97 ± 0.04	. . .	99.8
$K_2Cr_2O_7$	0.66 ± 0.02	1.02 ± 0.02	1.46 ± 0.02	2.25 ± 0.03	3.07 ± 0.03	3.91 ± 0.03	99.8
$K_4Fe(CN)_6$	1.25 ± 0.02	1.56 ± 0.02	1.88 ± 0.01	2.36 ± 0.01	2.82 ± 0.02	3.23 ± 0.03	99.8
CsCl	16.12 ± 0.08	16.82 ± 0.08	17.53 ± 0.07	18.31 ± 0.07	18.93 ± 0.07	19.52 ± 0.07	99.8
$K_2Cr_2O_7$	0.91 ± 0.02	1.32 ± 0.02	1.81 ± 0.02	2.67 ± 0.03	3.55 ± 0.03	4.41 ± 0.03	natural water

Table II. Refractive Indices for Salt Solutions in Heavy and Light Water

Concn., Wt. %	Temp., ° C.						Concn. of D_2O in Water, Mole %
	25	35	45	60	75.5	91	
LiCl							
39.95	1.4237	1.4225	1.4213	1.4192	1.4171	1.4149	99.8
42.97	1.4305	1.4292	1.4279	1.4259	1.4237	1.4215	99.8
47.46	...	...	...	1.4373	1.4353	1.4331	99.8
49.41	...	...	...	...	1.4407	1.4383	99.8
Sat.	1.4328	1.4340	1.4353	1.4393	1.4424	1.4460	99.8
NaF							
1.61	1.3298	1.3287	1.3273	1.3248	1.3219	1.3185	99.8
2.01	1.3304	1.3292	1.3280	1.3253	1.3225	1.3190	99.8
2.95	1.3317	1.3305	1.3290	1.3265	1.3235	1.3200	99.8
3.58	...	...	...	...	1.3240	1.3206	99.8
3.83	...	...	...	...	1.3242	1.3209	99.8
Sat.	1.3323	1.3311	1.3296	1.3272	1.3244	1.3211	99.8
NaCl							
22.15	1.3706	1.3690	1.3672	1.3643	1.3612	1.3581	99.8
23.14	1.3729	1.3712	1.3693	1.3665	1.3635	1.3603	99.8
23.55	1.3740	1.3722	1.3703	1.3676	1.3645	1.3614	99.8
24.19	...	...	...	1.3695	1.3663	1.3630	99.8
Sat.	1.3792	1.3727	1.3715	1.3699	1.3673	1.3650	99.8
NaBr							
42.51	1.4113	1.4093	1.4070	1.4037	1.4005	1.3972	99.8
44.97	1.4173	1.4151	1.4130	1.4101	1.4063	1.4027	99.8
46.70	1.4197	1.4200	1.4179	1.4144	1.4106	1.4074	99.8
Sat.	1.4197	1.4228	1.4281	1.4251	1.4210	1.4179	99.8
NaI							
55.75	1.4691	1.4665	1.4639	1.4597	1.4559	1.4515	99.8
59.01	1.4820	1.4795	1.4770	1.4726	1.4686	1.4636	99.8
65.00	...	...	1.5026	1.4990	1.4953	1.4915	99.8
71.87	...	...	...	...	1.5303	1.5247	99.8
Sat.	1.4977	1.5033	1.5104	1.5260	1.5331	1.5305	99.8
$NaClO_4$							
62.16	1.3855	1.3831	1.3806	1.3768	1.3730	1.3690	99.8
63.85	1.3874	1.3851	1.3825	1.3788	1.3751	1.3712	99.8
67.36	...	...	1.3873	1.3837	1.3801	1.3763	99.8
70.35	...	...	...	1.3875	1.3840	1.3805	99.8
72.41	...	...	...	...	1.3881	1.3844	99.8
Sat.	1.3892	1.3896	1.3903	1.3903	1.3883	1.3862	99.8
KSCN							
61.56	1.4719	1.4696	1.4672	1.4635	1.4597	1.4555	99.8
63.93	1.4780	1.4756	1.4733	1.4696	1.4655	1.4616	99.8
67.52	1.4874	1.4850	1.4826	1.4790	1.4753	1.4715	99.8
71.84	...	...	1.4953	1.4917	1.4880	1.4836	99.8
74.80	...	...	...	1.5004	1.4966	1.4926	99.8
78.50	...	...	...	...	1.5077	1.5034	99.8
82.09	...	...	...	...	...	1.5184	99.8
Sat.	1.4876	1.4926	1.4973	1.5049	1.5121	1.5190	99.8
$KMnO_4$							
2.08	1.3320	1.3305	1.3290	1.3260	1.3215	...	99.8
5.08	...	1.3377	1.3360	1.3323	1.3382	...	99.8
13.36	...	...	...	1.3520	1.3480	...	99.8
Sat.	1.3390	1.3435	1.3475	1.3540	1.3630	...	99.8
$K_2Cr_2O_7$							
4.02	1.3360	1.3347	1.3333	1.3305	1.3270	1.3231	99.8
6.87	1.3419	1.3405	1.3391	1.3365	1.3331	1.3294	99.8
12.16	...	1.3519	1.3506	1.3479	1.3446	1.3406	99.8
17.21	...	...	1.3620	1.3593	1.3569	1.3530	99.8
25.08	...	...	...	1.3785	1.3753	1.3715	99.8
31.88	...	...	...	...	1.3961	1.3925	99.8
Sat.	1.3463	1.3540	1.3634	1.3790	1.3957	1.4116	99.8
$K_4Fe(CN)_6$							
17.11	1.3673	1.3657	1.3642	1.3616	1.3583	1.3545	99.8
19.17	...	1.3710	1.3696	1.3668	1.3635	1.3597	99.8
20.18	...	1.3735	1.3719	1.3695	1.3658	1.3625	99.8
25.50	...	...	1.3869	1.3840	1.3805	1.3777	99.8
32.62	...	...	...	...	1.3997	1.3966	99.8

Table II. Refractive Indices for Salt Solutions in Heavy and Light Water (*Continued*)

Concn., Wt. %	Temp., °C.						Concn. of D_2O in Water, Mole %
	25	35	45	60	75.5	91	
$K_4Fe(CN)_6$							
33.94	...	...	...	...	1.4032	1.4001	99.8
Sat.	1.3720	1.3802	1.3881	1.3980	1.4055	1.4120	99.8
CsCl							
57.79	1.4037	1.4021	1.4003	1.3976	1.3945	1.3918	99.8
59.78	1.4081	1.4067	1.4045	1.4016	1.3989	1.3962	99.8
61.55	1.4117	1.4100	1.4083	1.4054	1.4029	1.4003	99.8
63.95	...	...	1.4146	1.4121	1.4097	1.4072	99.8
66.22	...	...	...	...	1.4177	1.4152	99.8
Sat.	1.4125	1.4142	1.4154	1.4170	1.4178	1.4186	99.8
$K_2Cr_2O_7$							
12.55	1.3556	1.3541	1.3524	1.3493	1.3461	1.3429	natural water
22.65	...	...	1.3740	1.3704	1.3676	1.3641	natural water
29.69	...	...	...	1.3869	1.3877	1.3802	natural water
33.27	...	...	...	...	1.3941	1.3907	natural water
41.90	...	...	...	...	...	1.4175	natural water
Sat.	1.3565	1.3655	1.3750	1.3910	1.4068	1.4222	natural water
	25°	35°	45°	60°	75°	90°	
KCl							
9.43	1.3440	1.3428	1.3410	1.3379	1.3949	1.3320	98.5
16.65	1.3557	1.3539	1.3523	1.3500	1.3466	1.3446	98.5
21.05	1.3616	1.3605	1.3590	1.3574	1.3542	1.3507	98.5
23.02	...	1.3635	1.3622	1.3605	1.3577	1.3542	98.5
25.61	...	...	...	1.3650	1.3620	1.3585	98.5
Sat.	1.3651	1.3660	1.3665	1.3670	1.3669	1.3640	98.5
Li_2SO_4							
9.55	1.3474	1.3462	1.3451	1.3420	1.3382	1.3354	98.5
13.98	1.3551	1.3538	1.3529	1.3500	1.3464	1.3436	98.5
18.11	1.3641	1.3632	1.3621	1.3595	1.3574	1.3545	98.5
19.83	1.3678	1.3670	1.3659	1.3634	1.3612	1.3588	98.5
20.89	1.3694	1.3685	1.3677	1.3660	1.3636	1.3613	98.5
21.94	1.3718	1.3709	...	...	...	...	98.5
Sat.	1.3739	1.3719	1.3701	1.3677	1.3652	1.3628	98.5
Na_2CO_3							
4.88	1.3400	1.3391	1.3375	1.3349	1.3319	1.3292	98.5
9.21	1.3501	1.3486	1.3470	1.3445	1.3417	1.3385	98.5
13.35	1.3588	1.3578	1.3563	1.3538	1.3509	1.3476	98.5
18.28	1.3696	1.3683	1.3670	1.3649	1.3619	1.3591	98.5
21.62	1.3710	1.3759	1.3742	1.3716	1.3685	1.3660	98.5
23.01	...	1.3795	1.3777	1.3751	1.3719	1.3693	98.5
27.82	...	1.3902	1.3882	1.3857	1.3828	1.3793	98.5
Sat.	1.3707	1.3975	1.3920	1.3894	1.3842	1.3805	98.5

RESULTS

The results of solubility measurements are presented in Table I. A comparison of data from Table I with corresponding data for ordinary water shows that solubility in heavy water is, in general, lower. Only LiCl (below 87° C.), NaI (below 66.5° C.), and, according to published data (*1, 4, 5, 8*), LiF, NaD_2PO_4, and $SrCl_2$ (below 60° C.) are more soluble in heavy water. The results of the present measurements for KCl agree with the data obtained by Sherman and Menzies (*7*) only in temperature range 35° to 45° C. Above this range, solubility in the present experiments is lower, about 10% at 90° C., and about 1% higher at 25° C. This work confirms earlier findings that the transition point temperatures for salts forming hydrates are lower in heavy water solutions than in natural water solutions. The differences are 5.9° C. for NaBr, 2.5° C. for NaI, and 1.3° C. for $NaClO_4$.

When the temperature increases, the relative difference of solubility

$$r = \frac{s_{H_2O} - s_{D_2O}}{s_{H_2O}}$$

where *s* is the solubility in mole %, changes in various ways. For the salts for which solubility increases strongly with increase of temperature, such as $K_2Cr_2O_7$ and $K_4Fe(CN)_6$, *r* decreases with the temperature increase. For NaBr, NaCl, CsCl, and KSCN, a small increase in *r* was observed with increasing temperature in range 25° to 90° C. For $NaClO_4$, LiCl, and $KMnO_4$, there is a minimum and for NaF a maximum value of *r*.

Accuracy of measurement is difficult to estimate, because it is difficult to determine the error produced by evaporation of solvent from between the prisms of the refractometer. The scatter of results, expressed as the maximum deviation from the arithmetic mean, is shown in Table I.

In the course of the work, a number of refractive indices for concentrated solutions of different salts in heavy water were measured. These data are listed in Table II. The scatter of the results of the refractive indices measurements was about ±0.0003 in lower temperatures, and about ±0.0004 in higher temperatures.

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Kinetics of Reaction between Isopropyl Methylphosphonofluoridate and Hydrogen Chloride

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Rate constants have been determined at 25°, 81.5°, and 100° C. for the reaction of isopropyl methylphosphonofluoridate (Sarin) with anhydrous hydrogen chloride. The reaction rates were measured using proton magnetic resonance spectroscopy. The reaction appears to follow third-order kinetics. An Arrhenius plot for the reaction is linear, with an activation energy of 17.8 kcal. per mole.

ISOPROPYL methylphosphonofluoridate (Sarin) is a highly toxic phosphorus ester. It belongs to a class of compounds that act as inhibitors of cholinesterase, an enzyme in nerve tissue that catalyzes the hydrolysis of acetylcholine. Since this reaction is essential to the proper functioning of the nerves, these compounds are powerful nerve poisons. For intramuscular and oral administration, Askew (*1*) determined the LD_{50} for rats to be 0.17 and 0.6 mg. per kg., respectively, and Grob and Harvey (*2*) estimated the lethal dose in man to be 0.03 and 0.14 mg. per kg., respectively.

Sarin may be prepared by the reaction of 2-propanol with an equimolar mixture of methylphosphonic dichloride and methylphosphonic difluoride (*5*).

$$CH_3P(O)Cl_2 + CH_3P(O)F_2 + 2\,(CH_3)_2CHOH \rightarrow 2\,CH_3P(O)(F)OCH(CH_3)_2 + 2\,HCl \tag{1}$$

Further reaction between the products can occur according to the reaction

$$CH_3P(O)(F)OCH(CH_3)_2 + HCl \rightarrow CH_3P(O)(F)OH + (CH_3)_2CHCl \tag{2}$$

As part of an investigation into the stability of crude Sarin when stored for long periods of time under varying climatic conditions, a knowledge of the kinetics of Reaction 2 seemed desirable. However, very little work has been carried out on this reaction from the standpoint of reaction kinetics. The only available publication is that of Sass *et al.* (*4*), who investigated the reaction for short periods of time over limited concentration and temperature ranges without attempting to determine the rate equation. The purpose of this study was to provide the data necessary to determine a reliable rate equation for Reaction 2.

EXPERIMENTAL

Freshly distilled Sarin was obtained from the Organic Chemistry Section of this laboratory. No impurities were detected in the NMR spectrum of the liquid. Depending on the amount of HCl desired, various amounts of Matheson's tank HCl of 99% purity were passed through an H_2SO_4 drying train into a known weight of Sarin contained in a flask immersed in a dry ice–acetone bath. The amount of HCl added was determined from the increase in weight. Using small funnels with long capillary stems, 1-ml. aliquots of each solution were introduced into each of several 5-mm.-i.d. NMR tubes and flame-sealed. Continued quenching of the reaction was accomplished in all cases by placing each tube in a dry ice–acetone bath immediately after sealing until all tubes were sealed. One of the samples was then warmed to room temperature, and its NMR spectrum obtained to determine the initial concentrations of the reactants. The samples studied at elevated temperatures were transferred together from the cold bath to an oil bath regulated at the desired temperature to ±0.1° C. After various time intervals, the samples were successively withdrawn, and the reaction was quenched by immersion in the cold bath. For the 25° C. measurements, the samples were merely stored in the air-conditioned laboratory maintained at 25° ± 2° C. All spectra, regardless of experimental temperature, were recorded at room temperature using a Varian Associates Model A-60 NMR

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