370. *The Transference of Water. Part II. Its Dependence on Concentration and Temperature in the Electrolysis of Sodium Chloride Solutions.*

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A PREVIOUS investigation (J., 1929, 2095) has shown that in the electrolysis of sodium chloride, transference of water occurs from the anode to the cathode, and the transference per faraday of electricity is greater the lower the concentration of the solution.

In order to obtain further data regarding the effect of concentration and also to observe the effect of temperature, we have now extended our observations to the behaviour of M- and $0.5M$-sodium chloride solutions in the neighbourhood of $0°$.

EXPERIMENTAL.

The migration apparatus has already been described (*loc. cit.*). The thermostat consisted of a large covered tank contained in a sawdust jacket and filled with H_2O containing masses of ice large enough to reach to the lowest part of the migration apparatus. By vigorous stirring, the temp. was kept const. within less than $0.1°$.

To avoid change in concn. of stock solutions, these were stored in containers similar in principle to those described by McInnes and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1119), the air replacing removed solution being drawn in over liquid of the same composition as that in the container.

The flasks for acid and for electrolyte solutions were of Pyrex, and those for alkali of Jena glass.

Materials.—All materials were prepared as described in the first communication (*loc. cit.*).

In August 1930 it was obs. that a stock solution of $0.5M$-NaCl and $0.1M$-urea made up in May of the same year showed slight alkalinity to phenolphthalein, while a similar solution, used in the experiments already described and made up in January 1929, was still neutral. The solution showing alk. reaction was also cloudy, suggesting the presence of an organism. Unlike the first solution, it had been kept and opened in a warm room in which there was traffic. Freshly-made urea and urea–NaCl solutions of about the same urea concn. as those used for electrolysis were inoculated with the cloudy alk. solution, and when kept at room temp. (about $21°$) they became alk. to phenolphthalein in 10 days. Quantities of the same solutions which had not been inoculated remained neutral indefinitely. The gradually increasing alkalinity was therefore undoubtedly due to the presence of an organism which on cultivation on agar produced the typical growth characters of a *penicillium*.

It is necessary to draw attention to these facts since Walden and Werner (*Z. physikal. Chem.*, 1927, **129**, 410), measuring the dielectric const. of $0.2M$-urea aq., observed the onset of alkalinity after 3 days at 20—$22°$. They ascribed the change to slow non-enzymatic hydrolysis hastened by the presence of impurities (" Fremdstoffe "). If their conjecture were correct, urea would be unsuitable as a reference substance in transference experiments.

Once the mould has established itself in a locality, it is difficult to eradicate, and if a solution cannot be used immediately after prepn., we now add 0·5 c.c. of neutral and purified C_7H_8 to about 2 l. of the stock solution, which is tested for neutrality just before it is put into the migration apparatus.

Analytical Method.—This was essentially the same as that already described. McInnes and Dole (*J. Amer. Chem. Soc.*, 1931, **53**, 3261), in the determination of the transport numbers of KCl, observed a tendency to alkalinity at the cathode although there was no trace of gas evolution. This they ascribed to dissolved O acting on the reduced Ag to give AgOH, which further reacted with the NaCl to give AgCl and NaOH. In Expt. 4 we also observed this effect, and a weight titration of a portion of the cathode solution to our standard red tint ($p_H = 5·4$) gave an alkalinity of 0·000042 g.-equiv. per 100 g. of solution.

This would account for the smaller water transport calc. from the composition of the cathode portion as compared with the anode portion in the previous expts. of this series. In Expt. 4, with N-NaCl solutions at 0°, this source of error has been taken into account, with the result that greater concordance between the water transport values as determined from anode and cathode composition has been obtained.

The transference numbers for Na⁺ and Cl′ are not affected in any of the experiments, as the digestion of the solution with HCl for the estimation of urea reconverts any trace of NaOH into its equiv. wt. of NaCl.

Results.

Four experiments were carried out within 0·1° of 0°, two with 0·5M- and two with M-NaCl solutions, the urea being as before 0·1M in each case.

Series A.—Experiments with solutions containing approx. 0·5M-NaCl + 0·1M-urea.

	Expt. 1.	Expt. 2.
E.M.F. applied, volts	80	100
Average current, amp.	0·04	0·072
Duration of run, hours	about 14	about 14

TABLE I.

Accurate weight composition (per 100 g. of solution) before electrolysis :

	Expt. 1.		Expt. 2.	
	NaCl, g.	Urea, g.	NaCl, g.	Urea, g.
As made up	2·5470	0·59321	2·8859	0·60037
By analysis (1)	2·5316	0·59404	2·8858	0·60050
,, (2)	2·5289	0·59401	2·8871	0·60044
Analytical mean	2·5303	0·59402	2·8864	0·60047

In Expt. 1, Table II, no total weights are recorded for the anode- and cathode-middle portions : the close agreement between the composition of these portions and that of the original, as well as the agreement between the composition of the sum of the anode and cathode portions and that of the original solution, renders this omission immaterial.

Series B.—Experiments with solutions containing approx. 1·0M-NaCl + 0·1M-urea.

In both expts. (3 & 4) in this series, *E.M.F.* applied = 210 volts; average current = 0·074—0·076 amp.; duration of run = about 14 hrs.

TABLE II.

Composition and Total Weight of Portions (Series A).

Portion.	Wt. of NaCl. (G./100 g. of soln.)	Wt. of Urea.	Total weight of		
			Soln., g.	NaCl, g.	Urea, g.
Experiment 1.					
Original	2·5303	0·59402	—	—	—
Anode	2·2062	0·59845	146·031	3·2217	0·87393
Anode middle	2·5319	0·59418	—	—	—
Cathode middle	2·5269	0·59412	—	—	—
Cathode	3·1134	0·58631	82·473	2·5677	0·48355
Total weight of anode and cathode portions			228·504	5·7894	1·35748
As calc. from original compn.,					
		228·504 g. of soln. contain		5·7818	1·35736
Experiment 2.					
Original	2·8864	0·60047	—	—	—
Anode	2·4247	0·60685	151·012	3·6616	0·91642
Anode middle	2·8865	0·60004	199·130	5·7479	1·19486
Middle	2·8852	0·60019	63·196	1·8233	0·37930
Cathode middle	2·8848	0·59986	176·029	5·0781	1·05594
Cathode	3·7500	0·58827	80·288	3·0108	0·47231
		Total	669·655	19·321₇	4·0188₃
As calc. from original compn..					
		669·655 g. of soln. contain		19·3294	4·0211

TABLE III.

Accurate weight composition (per 100 g. of solution) before electrolysis :

		Expt. 3.		Expt. 4.	
		NaCl, g.	Urea, g.	NaCl, g.	Urea, g.
As made up	....	5·4954	0·56511	5·8664	0·54594
By analysis	....	5·4997	0·56413	(1) 5·8703	
				(2) 5·8712	0·54549
				(3) 5·8699	0·54539
				(4) 5·8704	0·54544
			Analytical mean	5·8705	0·54544

Table V gives for Expts. 1 and 2 (Series A), the wts. of NaCl and H_2O associated with a const. quantity of urea, and also the wt. of NaCl associated with a const. quantity of H_2O in the two electrode portions before and after electrolysis; the wts. of Ag deposited in the coulomb-meters are also given.

Table VI gives the same values for Expts. 3 and 4 (Series B).

Tables VII and VIII record for $0.5M$- and $1.0M$-solutions, respectively, at $0°$, the equivs. of H_2O, n_w, and of NaCl, n_s, transported, the true transport numbers, T_{Na} and T_{Cl}, and the Hittorf transference numbers, T_{Na}^H, T_{Cl}^H, the number N_w^F of g.-mols. of H_2O transported per faraday, and the number n_w/n_s of g.-mols. of H_2O transported per g.-mol. of NaCl.

In the case of each concn. at $0°$, the solutions of the second expt. were subjected to more skilled analysis than those of the first. The closer concordance of anode and cathode values in the results of Expts. A2 and B4 is a measure of their greater reliability. Consequently, in Table IX, the mean values for the transport of H_2O and of Na· at $0°$ are derived from these two expts., while the values at $25°$ are the result of previous work (J., 1929, 2103) and of Wash-

burn's expts. (*J. Amer. Chem. Soc.*, 1909, **31**, 322). These numbers show that at 0°, as well as at 25°, the transference of H_2O to the cathode is greater the more dil. the solution, and also that for a given concn. it is greater the lower the temp.

TABLE IV.

Composition and Total Weight of Portions (Series B).

Portion.	Wt. of NaCl. (G./100 g. of soln.)	Wt. of Urea.	Total weight of Soln., g.	NaCl, g.	Urea, g.
Experiment 3.					
Original	5·4997	0·56413	—	—	—
Anode	4·9768	0·57045	144·629	7·1979	0·82504
Anode middle	5·4987	0·56302	118·447	6·5130	0·66688
Middle	5·4994	0·56411	91·273	5·0195	0·51488
Cathode middle	5·4993	0·56390	88·823	4·8846	0·50087
Cathode	6·3384	0·55559	88·798	5·6284	0·49335
		Total	531·970	29·243$_4$	3·0010$_2$

As calc. from original compn.,

531·970 g. of soln. contain 29·257$_3$ 3·0010$_0$

Portion.	Wt. of NaCl.	Wt. of Urea.	Soln., g.	NaCl, g.	Urea, g.
Experiment 4.					
Original	5·8705	0·54544	—	—	—
Anode	5·3347	0·55160	149·851	7·9941	0·82657
Anode middle	5·8727	0·54537	114·547	6·7270	0·62470
Middle	5·8709	0·54547	175·260	10·2894	0·95599
Cathode middle	5·8735	0·54542	90·946	5·3417	0·49604
Cathode	6·8037	0·53478	87·207	5·9333	0·46637*
		Total	617·811	36·285$_5$	3·3696$_7$

As calc. from original compn.,

617·811 g. of soln. contain 36·268$_4$ 3·3697$_8$

* Corrected for alkalinity of cathode solution (see p. 2498).

TABLE V.

	Anode solution.			Cathode solution.		
	Initially, g.	Finally, g.	Diff., g.	Initially, g.	Finally, g.	Diff., g.
Experiment 1.						
Calculated to constant urea.						
Urea	0·87393	0·87393	—	0·48355	0·48355	—
NaCl	3·7225	3·2217	−0·5008	2·0597	2·5677	+0·5080
H_2O	142·524	141·935	−0·589	78·859	79·422	+0·563
Calculated to constant water.						
H_2O	141·935	141·935	—	79·422	79·422	—
NaCl	3·7072	3·2217	−0·4855	2·0744	2·5677	+0·4933
Experiment 2.						
Calculated to constant urea.						
Urea	0·91642	0·91642	—	0·47231	0·47231	—
NaCl	4·4051	3·6616	−0·7435	2·2704	3·0108	+0·7404
H_2O	147·295	146·434	−0·861	75·914	76·805	+0·891
Calculated to constant water.						
H_2O	146·434	146·434	—	76·805	76·805	—
NaCl	4·3794	3·6616	−0·7178	2·2970	3·0108	+0·7138

Weight of silver deposited in coulomb-meters.

	Expt. 1.	Expt. 2.
Anode	2·4939 g.	3·6251 g.
Cathode ...	2·4943 g.	3·6257 g.
Mean	2·4941 g. = 0·023119 equiv.	3·6254 g. = 0·033606 equiv.

TABLE VI.

	Anode solution.			Cathode solution.		
	Initially, g.	Finally, g.	Diff., g.	Initially, g.	Finally, g.	Diff., g.
			Experiment 3.			
Calculated to constant urea.						
Urea	0·82504	0·82504	—	0·49335	0·49335	—
NaCl	8·0433	7·1979	−0·8454	4·8097	5·6284	+0·8187
H_2O	137·382	136·606	−0·776	82·150	82·676	+0·526
Calculated to constant water.						
H_2O	136·606	136·606	—	82·676	82·676	—
NaCl	7·9981	7·1979	−0·8002	4·8405	5·6284	+0·7879
			Experiment 4.			
Calculated to constant urea.						
Urea	0·82757	0·82757	—	0·46637	0·46637	—
NaCl	8·8963	7·9941	−0·9022	5·0194	5·9333	+0·9139
H_2O	141·820	141·030	−0·790	80·017	80·807	+0·790
Calculated to constant water.						
H_2O	141·030	141·030	—	80·807	80·807	—
NaCl	8·8467	7·9940	−0·8527	5·0690	5·9333	+0·8643

Weight of silver deposited in coulomb-meters.

	Expt. 3.	Expt. 4.
Anode	4·0487 g.	4·4496₅ g.
Cathode ...	4·0486 g.	4·4487₅ g.
Mean	4·04865 g. = 0·037530 equiv.	4·4492 g. = 0·041242 equiv.

TABLE VII.

Series A (0·5M-NaCl solution).

	Expt. 1 (Temp. = 0·07° ± 0·06°).			Expt. 2 (Temp. = 0·09° ± 0·04°).			Mean of Expts. 1 and 2.
	Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.	
n_w	0·03269	0·03123	0·03196	0·04779	0·04946	0·04863	—
n_s	0·008568	0·008629	0·008629	0·01272	0·01267	0·01270	—
T_{Na}	0·3706	0·3759	0·3733	0·3785	0·3769	0·3777	0·3755
T_{Cl}	0·6294	0·6241	0·6268	0·6215	0·6231	0·6223	0·6245
T_{Na}^H	0·3592	0·3650	0·3621	0·3654	0·3633	0·3643	0·3632
T_{Cl}^H	0·6408	0·6350	0·6379	0·6346	0·6367	0·6357	0·6368
n_w/n_s	3·816	3·594	3·705	3·757	3·904	3·831	3·768
n_w^F	−1·414	+1·351	1·383	−1·422	+1·471	1·446	1·415

TABLE VIII.

Series B (1·0M-NaCl solution).

	Expt. 3 (Temp. = 0·04° ± 0·03°).			Expt. 4 (Temp. = 0·04° ± 0·03°).			Mean of Expts. 3 and 4.
	Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.	
n_w	0·04307	0·02920	0·0361	0·04385	0·04385	0·0439	—
n_s	0·01447	0·01401	0·0142	0·01543	0·01563	0·0155	—
T_{Na}	0·3854	0·3732	0·379₃	0·3742	0·3790	0·376₆	0·378
T_C	0·6146	0·6268	0·620₇	0·6258	0·6210	0·623₄	0·622
T_{Na}^H	0·3647	0·3591	0·361₉	0·3537	0·3585	0·356₁	0·359
T_{Cl}^H	0·6353	0·6409	0·638₁	0·6463	0·6415	0·643₉	0·641
n_w/n_s	2·977	2·085	2·531	2·842	2·804	2·823	2·677
n_w^F	1·148	0·778	0·963	1·063	1·063	1·063	1·014

TABLE IX.

Concn.	1·0M.		0·5M.	
Temp.	0°.	25°.	0°.	25°.
T_{Na}	0·377	0·379	0·378	0·382
T_{Na}^H	0·356	0·362	0·364	0·372
n_w/n_s	2·82	2·2	3·83	2·83
n_w^F	1·063	0·83	1·446	1·08

Discussion.

The calculation from these numbers of the absolute hydration of each ion in N- and $0\cdot5N$-sodium chloride solution on the assumption that the hydration is independent of the concentration, and that the decrease in water transport with concentration depends on the change in transport number (J., 1929, 2105), gives the impossible values of 240 and 145 for the hydration of the sodium and chlorine ions respectively.

The inclusion of all the values obtained in Series A and B in calculating the mean transport numbers of the sodium ion at 0° merely emphasises the above impossible result. In short, the water transport at 0° increases with dilution at a rate which is altogether too great to be accounted for by mere increase in the transport number of the more highly hydrated ion. Similarly, it is impossible that the cause of the increase in water transport with fall in temperature can be due to change in the relative mobility of ion hydrates whose composition is independent of the temperature, since the true transport number of the sodium increases with rise in temperature while the transference of water to the cathode shows marked decrease. We must therefore conclude, either that the extent of hydration of each ion is appreciably sensitive to moderate changes of temperature and concentration, or that the ions during migration transport water with which they are not chemically combined. The results of the determination of activity coefficients of salt solutions appear to indicate a total ionic hydration which, at a given temperature and apart from very high concentrations, is independent of concentration.

Bjerrum (*Z. anorg. Chem.*, 1920, **109**, 275) has suggested that the relationship between the observed activity coefficient F_a and the molar concentration c of a uni-univalent electrolyte might be represented by the equation

$$\ln F_a = \ln f_a + (2m - 2)c/55\cdot5$$

where f_a represents the activity coefficient of the hydrated ions and m the total number of water molecules attached to the two ions.

Harned (*J. Amer. Chem. Soc.*, 1922, **44**, 252) pointed out that an empirical equation of similar form to the above, in which the co-efficient of c is constant for a given temperature, expresses with considerable accuracy the relationship between the observed activity

coefficient and the concentration. Recent determinations by Harned and Nims (*ibid.*, 1932, **54**, 423) of the activity coefficients of sodium chloride solutions within wide ranges of temperature and concentration are in accord with this expression, thus indicating that m is independent of concentration. Apart from considerations entailing any specific interpretation of the observed values of the activity coefficients of salt solutions, Bjerrum (*loc. cit.*), depending solely on the law of mass action, has pointed out that the fall in activity of the solvent due to increase in concentration of an electrolyte is insufficient to produce a measurable change in the degree of hydration of the ions even up to a concentration as high as $4M$. The conclusion is therefore justified that, while the ions in aqueous solution may combine chemically with the solvent, they must also transport during migration a considerable quantity of water with which they are not so combined.

Summary.

Migration experiments have been carried out with M- and $0.5M$-aqueous sodium chloride solutions at $0°$, urea being used as non-electrolytic reference substance, to enable the water transport to be estimated.

The results confirm the conclusion of previous experiments (J., 1929, 2095) that the transference of water to the cathode increases with increasing dilution at a rate altogether too great to be accounted for by change in the transport numbers of the ions.

They also show that transport of water to the cathode increases with decrease in temperature, an effect which again cannot be referred to change in transport number of the kation, which decreases with fall in temperature.

It is concluded that, since activity considerations point to a total ionic hydration which is independent of concentration, the results here obtained must be interpreted as indicating that the ions during migration transport a considerable quantity of water with which they are not chemically combined.