V.—On the Relation of the Surface Tension and Specific Gravity of Certain Aqueous Solutions to their State of Ionization.—By E. H. Archibald, B. Sc., *Dalhousie College, Halifax, N. S.*

In a paper communicated to this Society last winter, Prof. MacGregor[*] pointed out that according to the ionization conception of the constitution of a solution of an electrolyte, in the case of a solution in which the dissociation was not complete, the difference between the physical properties of the solution and those of its solvent, must be compounded of the differences produced by the undissociated molecules and by the free ions. He drew from this that it should be possible to express the numerical values of the various properties of such a solution in terms of the state of ionization of the electrolytes it contained. In sufficiently dilute simple solutions where the molecules dissociated or undissociated might be regarded as being far enough apart to render mutual action between them impossible, such an expression would be of the simple form,

$$S = S_w + k(1-a)n + l\,a\,n \dots\dots\dots\dots\dots\dots\dots(1),$$

where S is the numerical value of any property of a solution (density, surface tension, &c.,) S_w that of the same property of water under the same physical conditions, n the number of equivalent gramme-molecules per unit volume, a the ionization coefficient of the electrolyte in the solution, and l and k constants, called ionization constants, for any given property of any given electrolyte. In the case of mixtures of simple solutions, provided no change of volume occurs on mixing, the expression will be of the form,

$$S = S_w + \left(k_1(1-a_1)n_1 + l_1 a_1 n_1\right)\frac{v_1}{v_1 + v_2 + \&c.}$$

$$+ \left(k_2(1-a_2)n_2 + l_2 a_2 n_2\right)\frac{v_2}{v_1 + v_2 + \&c.} + \&c. \dots\dots\dots(2),$$

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where the n's are the numbers of equivalent gramme-molecules contained in unit volume of the original simple solutions, the a's are the ionization coefficients in the mixture of the respective electrolytes mixed, the v's the respective volumes of the original simple solutions mixed, and the l's and k's the ionization constants found for the simple solutions of the several electrolytes.

Prof. MacGregor applied the above expressions to the calculation of the density, thermal expansion, &c., of some simple solutions and mixtures of Potassium and Sodium Chlorides, and found it possible to calculate the various properties of these solutions within the limits of experimental error.

At his suggestion I have carried out the observations and calculations described in this paper, to see if it is possible to represent by the first of the above expressions the density and surface tension of simple solutions of Sodium, Potassium and Copper Sulphates, salts of more complex molecular structure than those previously examined, and then, by means of the ionization constants thus obtained, to predict the values of the same properties for mixtures of solutions of these salts. I have also thought it well to test the possibility of predicting the specific gravity of solutions containing Potassium Sulphate and Sodium Chloride, and consequently also Sodium Sulphate and Potassium Chloride.

Data for the Calculations.—Experimental Methods.

The methods employed in purifying the water and salts used, and of preparing and mixing solutions and determining their concentration and conductivity, were the same as described in the papers I have read before the Institute during the present session.*

Observations of Surface Tension.

I have made no observations of surface tension myself, but have used those made by Rother.† His measurements were made at 15°C, and are there therefore not strictly comparable with

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* Tran. N S. Inst. Sci., Vol. IX., p. 291, and 307.
† Wied. Ann., 21 (1884), p. 576.

calculated values based on the values of ionization-coefficients for 18° C. I have, however, calculated some of the ionization-coefficients, for the different salts, corresponding to 15°C, by using the conductivity coefficients given by Kohlrausch, and find that the differences between the values for 18° and 15° are not large enough to cause any appreciable error in the calculations Rother seems to regard his measurements as possibly in error by 5 to 8 in the third decimal place. He found the surface. tension of the water he used to be 7.357.

Observations of Specific Gravity.

The specific gravity observations were all made at 18°C, and are referred to water at 18°C. Ostwald's form of Sprengel's pyknometer was used in making the measurements. It was filled by dipping one arm in the solution to be measured and connecting the other by means of a rubber tube with an exhaust bottle. When the pyknometer had filled beyond the constant volume mark on the stem, it was placed in a water bath provided with a mechanical stirrer, which was connected with a water wheel driven by the water from a tap. The temperature of the bath was not allowed to vary more than a twentieth of a degree from 18°. When the liquid column in the arm had remained stationary for three or four minutes the meniscus was adjusted to the mark, the pyknometer taken from the bath, dipped in distilled water, then carefully dried with a linen cloth and weighed. From several measurements of the same solution, it would appear that the values of the specific gravity might be in error by about 5 in the fifth decimal place.

The Ionization Coefficients.

For simple solutions, the ionization coefficients, as in former papers, were taken to be the ratios of the specific molecular conductivity to the specific molecular conductivity at infinite dilution. The data for finding them for the simple solutions of Potassium, Sodium, and Copper Sulphates will be found in the above papers. In the case of the chlorides of Potassium and

Sodium, the data are taken from my paper on the "Conductivity of Solutions containing Potassium Sulphate and Sodium Chloride."*

In calculating the ionization coefficients, the values of the specific molecular conductivity at infinite dilution which I used, were those first given by Kohlrausch,† viz., 1280×10^{-8}, 1060×10^{-8}, 1100×10^{-8}, 1220×10^{-8}, and 1030×10^{-8}, in terms of the conductivity of mercury at 0°C, for Potassium, Sodium, and Copper Sulphates, and Potassium, and Sodium Chlorides, respectively. Kohlrausch‡ has since published what he considers closer values for the sulphates, viz., 1270, 1070, 1120, for the Potassium, Sodium, and Copper Sulphates respectively. Having had my attention drawn to these later values. I have recalculated a few of the ionization constants, and find that the difference caused by using the later values is in all cases negligible.

The following table contains the values of the ionization coefficients used in the calculations. They apply to 18°C. Concentrations of solutions are expressed in terms of equivalent gramme-molecules of anhydrous salt, per litre, at 18°C.

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* Trans. Roy. Soc., Can., 2nd Ser., Vol. 3. Sec. 3.

† Wied. Ann., Vol. XXVI, p. 204.

‡ Wied. Ann., 50 (1893), p. 406.

TABLE I.

Concentration.	Ionization Coefficients at 18°C.				
	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}CuSO_4$.	K Cl.	NaCl.
.8416	....	.473	....	....	....
.7500	.545	....	.238	....	....
.7100	....	.492	... .	....	....
.6666	.554	... .	.244	....	....
.6000	....	....	....	.780	.718
.5050	....	.527	....	....	....
.5000	.576	....	.262	.786	.737
.4000	.591	....	.278	.794	.757
.3366	....	.565	....	....	....
.3333	.606	....	.289	....	....
.2525	....	.591	....	....	....
.2500	....	....	....	.811	.786
.2222	.636	....	.318	....	..... .
.2000	....	....	....	.829	.805
.1442	....	.625	....	....	....
.1000	.697	....	.385	.854	.841
.0918	....	.698	....	....	....
.0800	....	....	....	.860	.853
.0750	.721	....	.406	.863	.857
.0666	.727	....	.416	....	....
.0631	....	.730	....	....	....
.0600	....	....	....	.873	.866
.05000	.749	....	.436	.882	.871
.04809	....	.744	....	....	....
.03258	....	.775	....	....	....

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The ionization coefficients of the salts in the mixture were determined by Professor MacGregor's* graphical method. The above table contains all the data required for finding them, as specific gravity measurements showed that even for the strongest solutions the change of volume on mixing was negligible.

Determination of Ionization Constants.

In determining the ionization constants (k and l in expression (1)) for any salt, and for either property, the data for the six weakest solutions examined were in all cases employed; and the values of the constants were found from these data by the method of least squares.

The values thus found were employed in calculating the values of the properties of the various mixtures.

Results of the Caculations.—Simple Solutions.

The following table contains the values of the ionization constants for the various salts and for the two properties investigated, with the values of the properties calculated by means of these constants, and the differences between observed and caluated values. Concentrations of solutions are expressed in terms of the same units as in Table I.

TABLE II.—SURFACE TENSION AT 15°C, (Rother's Observations).

Concentration.	Observed Value.	Calculated Value.	Differences.	Concentration.	Observed Value.	Calculated Value.	Differ ences.
$\frac{1}{2}$ K$_2$SO$_4$.—(k=0.09627; l=0.18001).				$\frac{1}{2}$ Na$_2$SO$_4$.—(k=0.11146; l=0.14223).			
.2341	7.392	7.392	0.000	.2041	7.393	7.394	+0.001
.3881	7.414	7.413	− 1	.4796	7.418	7.418	0
.3946	7.415	7.414	− 1	.7404	7.450	7.450	0
.3966	7.415	7.415	0	1.008	7.481	7.482	+ 1
.3976	7.415	7.415	0	.4773	7.418	7.418	0
.6038	7.442	7.443	+ 1	.4827	7.421	7.418	− 3
.8131	7.473	7.472	− 1	.9995	7.471	7.481	+ 10
1.244	7.537	7.543	+ 6	1.557	7.541	7.552	+ 11

* Trans. N. S. Inst. Science, IX (1896), p. 101.

TABLE III.—SPECIFIC GRAVITY *(at 18°C, referred to water at 18°C).*

Concentration.	Observed Value.	Calculated Value.	Differences.	Concentration.	Observed Value.	Calculated Value.	Differences.
$\frac{1}{2}$ K_2SO_4.—($k=0.05831$; $l=0.07728$).				$\frac{1}{2}$ Na_2SO_4.—($k=0.05429$; $l=0.07207$).			
.0500	1.00360	1.00363	$+0.0_4 3$	.01980	1.00135	1.00136	$+0.0_4 1$
.0666	1.00481	1.00480	$-\quad 1$	.03258	1.00225	1.00222	$-\quad 3$
.0750	1.00535	1.00539	$+\quad 4$	.04809	1.00328	1.00325	$-\quad 3$
.1000	1.00718	1.00715	$-\quad 3$	.06312	1.00423	1.00425	$+\quad 2$
.2222	1.01566	1.01564	$-\quad 2$	.09181	1.00609	1.00612	$+\quad 3$
.3333	1.02323	1.02326	$+\quad 3$	.1442	1.00947	1.00943	$-\quad 4$
.4000	1.02782	1.02781	$-\quad 1$	.2525	1.01635	1.01636	$+\quad 1$
.5000	1.03457	1.03460	$+\quad 3$	.3366	1.02163	1.02165	$+\quad 2$
.6666	1.04572	1.04584	$+0.0_3 1$	.5050	1.03213	1.03214	$+\quad 1$
.7500	1.05130	1.05149	$+0.0_3 2$	.8416	1.05263	1.05276	$+0.0_3 1$
$\frac{1}{2}$ $CuSO_4$.—($k=0.07109$; $l=0.1072$).				$\frac{1}{2}$ $CuSO_4$.—*(Continued.)*			
.0500	1.00433	1.00434	$+0.0_4 1$	.2222	1.01829	1.01833	$+0.0_4 4$
.0666	1.00576	1.00574	$-\quad 2$	.3333	1.02722	1.02718	$-\quad 4$
.0750	1.00640	1.00643	$+\quad 3$	.4000	1.03240	1.03245	$+\quad 5$
.1000	1.00855	1.00851	$-\quad 4$	.5000	1 04016	1.04029	$+0.0_3 1$
K Cl.—($k=0.06676$; $l=0.04556$).				NaCl.—($k=0.03109$; $l=0.04445$).			
.0500	1.00245	1.00241	$-0.0_4 4$	.0500	1.00211	1.00213	$+0.0_4 2$
.0600	1.00289	1.00290	$+\quad 1$	.0600	1.00254	1.00256	$+\quad 2$
.0750	1.00368	1.00364	$-\quad 4$	.0750	1.00320	1.00319	$-\quad 1$
.0800	1.00390	1.00388	$-\quad 2$	.0800	1.00344	1.00340	$-\quad 4$
.1000	1.00482	1.00486	$+\quad 4$	.1000	1.00420	1.00421	$+\quad 1$
.2000	1.00956	1.00958	$+\quad 2$	.2000	1.00836	1.00837	$+\quad 1$
.2500	1.01233	1.01231	$-\quad 2$	.2500	1.01041	1.01039	$-\quad 2$
.4000	1.01970	1.01985	$+0.0_3 2$	.4000	1.01645	1.01648	$+\quad 3$
.5000	1.02401	1.02512	$+0.0_2 1$	.5000	1.02041	1.02047	$+\quad 6$
.6000	1.02860	1.03013	$+0.0_2 2$	.6000	1.02420	1.02440	$+0.0_3 2$

Comments on above Tables.

Surface Tension.—The differences between observed and calculated values are well within the limits of error, through the whole range of the observations used in determining the ionization constants; and in the case of the K_2SO_4 somewhat beyond this. The alternation of sign is also satisfactory.

Specific Gravity.—For all the salts examined, and through a somewhat greater range of concentration than that of the observations used in determining the constants, the differences are within the limits of error. Change of sign is also quite satisfactory.

It thus appears that for both properties of all the salts examined, the expression under consideration represents the observed values well throughout the range to which it has been applied.

Mixtures.

Tables IV and V contain the results of the endeavor to predict the values of the surface tension and specific gravity for mixtures by means of the above expression (2) of page 335, employing the values of the ionization constants obtained as above from observations on simple solutions. All the mixtures whose specific gravity I determined, were mixtures of equal volumes of the constituent solutions. Rother's mixtures were mixtures of equal weights, which renders the calculations much more tedious. His paper, however, furnishes the requisite data for determining the volumes of the solutions which he mixed; and these are given in the table below. As I had equi-molecular solutions of the Copper and Potassium Sulphates prepared for the purpose of finding their electrical conductivity, these solutions were used in preparing the mixtures for specific gravity measurements.

The following tables also contain the ionization coefficients in the mixtures, as determined by the graphical method referred to above. Concentrations of solutions are expressed in terms of equivalent gramme-molecules of anhydrous salt per litre at 18°C. The specific gravities are those at 18°C, referred to water at 18°C.

TABLE IV.—SURFACE TENSION *(Rother's Observations).*

Concentration.		Volumes (litres).		Ionization Coefficients in the Mixture.		Observed Value.	Calculated Value.	Difference.
$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.			
.2341	.2041	.14770	.14738	.631	.587	7.394	7.393	$- 0.0_21$
.3881	.4796	.14622	.14575	.588	.540	7.416	7.413	$-$ 3
.3946	.7404	.14616	.14355	.573	.509	7.433	7.432	$-$ 1
.3966	1.008	.14614	.14143	.560	.487	7.451	7.455	$+$ 4
.3976	.4773	.14613	.14577	.587	.538	7.420	7.417	$-$ 3
.6038	.4827	.14422	.14572	.574	.512	7.432	7.432	0
.8131	.9995	.14229	.14151	.540	.450	7.470	7.476	$+$ 6
1.244	1.557	.13878	.13742	.508	.389	7.539	7.549	$+$ 0.01

TABLE V.—SPECIFIC GRAVITY.

Sodium and Potassium Sulphate Mixtures.

Concentrations of Constituent Solutions.		Ionization Coefficients in Mixture		Specific Gravity of Mixture.		
$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$.	Observed Value.	Calculated Value.	Difference.
.02500	.0505	.771	.750	1.00256	1.00261	$+ 0.0_45$
.0500	.0505	.748	.737	1.00354	1.00351	$-$ 3
.1000	.0673	.718	.709	1.00577	1.00582	$+$ 5
.1000	.1010	.701	.691	1.00690	1.00693	$+$ 3
.2500	.2525	.636	.593	1.01694	1.01698	$+$ 4
.2500	.5050	.598	.551	1.02484	1.02489	$+$ 5
.3333	.5050	.592	.544	1.02777	1.02774	$-$ 3
.4166	.5050	.586	.534	1.0306C	1.03056	$-$ 4
.4957	.4996	.578	.523	1.03300	1.03305	$+$ 5
.5000	.5050	.577	.522	1.03331	1.03337	$+$ 6
.4957	.6658	.570	.507	1.03809	1.03820	$+ 0.0_31$

TABLE V. *(Continued)* — SPECIFIC GRAVITY.

Copper and Potassium Sulphate Mixtures.

Concentrations of Constituent Solutions.		Ionization Coefficients in Mixture.		Specific Gravity of Mixture.		
$\frac{1}{2}K_2SO_4.$	$\frac{1}{2}CuSO_4.$	$\frac{1}{2}K_2SO_4.$	$\frac{1}{2}CuSO_4.$	Observed Value.	Calculated Value.	Difference.
.04000	.04000	.783	.427	1.00322	1.00319	$-\ 0.0_43$
.05000	.05000	.766	.410	1.00395	1.00397	$+\quad 2$
.06666	.06666	.749	.386	1.00527	1.00525	$-\quad 2$
.07500	.07500	.743	.376	1.00591	1.00589	$-\quad 2$
.0909	.0909	.729	.359	1.00707	1.00710	$+\quad 3$
.1000	.1000	.722	.349	1.00783	1.00780	$-\quad 3$
.1666	.1666	.679	.300	1.01271	1.01275	$+\quad 4$
.2222	.2222	.658	.283	1.01694	1.01690	$-\quad 4$
.3333	.3333	.635	.253	1.02503	1.02510	$+\quad 7$
.4000	.4000	.625	.239	1.03000	1.03006	$+\quad 6$
.5000	.5000	.603	.226	1.03720	1.03734	$+\ 0.0_31$

It appears from the above Tables IV and V that the differences between calculated and observed values are within the limits of error, throughout nearly the same range of concentration as that of the observations on simple solutions used in determining the constants. This range is somewhat greater for the Sodium and Potassium Sulphate mixtures than for the Copper and Potassium Sulphate mixtures, which would seem to support the view taken of these mixtures in my previous paper, viz., as to the existence of a double salt in the solution. It might also be mentioned here, in support of this view, that for mixtures of stronger solutions of the Copper and Potassium Sulphates than are here given, I have observed a quite noticeable change of volume on mixing which is not the case for mixtures of solutions of the Sodium and Potassium Sulphates for a like concentration.

As the ionization constants used in the calculations were not determined from the observations of these tables, such alternation

of sign is not to be expected in the differences as was observed in the differences between observed and calculated values for the simple solutions. In any case in which variation of sign might be expected, as in the case of mixtures of the Copper and Potassium Sulphates where the solutions mixed were equimolecular, alternation of sign in the differences is quite satisfactory.

The results of the above tables would seem to warrant the conclusion that it is posssible by aid of the dissociation theory of electrolysis, to predict the surface tension and specific gravity of mixtures of moderately dilute solutions of Sodium Sulphate with Potassium Sulphate and Potassium Sulphate with Copper Sulphate within the limits of the error of observation, by means of data obtained by observations on simple solutions of these salts.

Observations on the Specific Gravity of Solutions containing Potassium Sulphate and Sodium Chloride.

As it appears from the above results to be possible to predict the specific gravity of a mixture of two solutions of sulphates, and from Prof. MacGregor's results in the case of mixtures of two chlorides also, I thought it would be interesting to see if a similar prediction was possible in the case of a mixture of a sulphate solution with that of a chloride of a different metal In such a case there will be four electrolytes present in the solution. Hence the formula for calculating, expression (2) on page 335, will involve four each of the quantities k, l, α, n, v, and the calculation is thus extremely difficult. Prof. MacGregor has found it practically impossible to calculate even the conductivity in the case of mixtures of any two solutions taken at haphazard. I therefore did not attempt to do so in the case of the specific gravity. The plan adopted was that of my paper on the conductivity of solutions containing Potassium Sulphate and Sodium Chloride,* viz., to prepare simple solutions of the four salts having the same concentration of ions and to mix

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* *Loc. cit.*

these in the proportions as to volume requisite to prevent change of ionization on mixing, and then to measure and calculate the specific gravity of the mixture. For the exact mode of determining the ionization coefficients, concentrations and volumes of the four simple solutions to be mixed, I may refer to my paper cited above. All the data required for the calculations are given in Table VI, together with the calculated and observed values. The concentrations of solutions and specific gravities are expressed in terms of the same units as in previous tables. The column headed "volumes" contains the volumes in c. c. of the Potassium and Sodium Chloride solutions mixed with 25 c. c. each of the sulphate solutions.

TABLE VI.

CONSTITUENT SOLUTIONS.						SPECIFIC GRAVITY $\frac{18°}{18°}$		
Concentration.				Volumes in c.c. of K Cl and Na Cl. Solutions.	Concentration of ions.	Observ'd.	Calculated.	Difference.
K Cl.	NaCl.	$\frac{1}{2}K_2SO_4$.	$\frac{1}{2}Na_2SO_4$					
.0500	.0512	.0607	.0611	30 53	.0445	1.00325	1.00319	-0.0_46
.0527	.0536	.0640	.0644	30.57	.0467	1.00339	1.00334	— 5
.0648	.0659	.0791	.0800	30.88	.0568	1.00403	1.00410	+ 7
.0787	.0800	.0969	.0984	31.25	.0683	1.00492	1.00500	+ 8
.1032	.1063	.1287	.1419	34.37	.0887	1.00664	1.00668	+ 4
.1219	.1265	.1552	.1700	34.85	.103	1.00795	1.00789	— 6
.1310	.1349	.1674	.1834	34.99	.112	1.00849	1.00847	— 2
.1675	.1736	.2201	.2374	35.42	.141	1.01084	1.01092	+ 8
.2008	.2083	.2702	.2902	36.14	.167	1.01310	1.01317	+ 7
.2380	.2500	.3225	.3478	36.56	.196	1.01556	1.01568	$+0.0_31$

The above table shows that in all except the last solution examined the differences between the observed and calculated values are either within or but little beyond (in three cases within and in six a little beyond) what I consider my possible error of observation. They are also about equally divided as to sign. Considering the large number of sources of error involved

in the preparation of the solutions, and in the calculations, the agreement between observed and calculated values seems to me to be exceedingly satisfactory, and to justify the conclusion that even in this very complex case it is possible by aid of the dissociation theory to predict the specific gravity within the limits of experimental error.

Summary of Conclusions.

(1.)   Expression (1) represents observed values of the surface tension and specific gravity of the solutions examined through a range of concentration extending from 0.05 to about 0.4 or 0.5 equivalent gramme-molecules per litre.

(2.)   It is possible by aid of the dissociation theory of electrolysis to predict the surface tension and specific gravity of mixtures of Potassium and Sodium Sulphate solutions and the specific gravity of mixtures of solutions of Potassium and Copper sulphates throughout nearly the same range as above, within the limits of the error of observation.

(3.)   It is possible by aid of the above theory to predict the specific gravity of mixtures of solutions of Potassium Sulphate and Sodium Chloride within the limits of experimental error.

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