

Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapor phase than when the corresponding temperature is low.

4. The relations discussed in Paragraphs 1 and 2 of the summary are just those indicated by the theory that molecules in the surface are oriented, the orientation increasing with increasing dissymmetry, and decreasing with increasing thermal agitation of the molecules. The effect of thermal agitation is illustrated in the case of the alcohols; compounds of the polar-nonpolar type. Fig. 3 indicates that for these compounds the molecular surface energy increases with the temperature. The effect of increased agitation is to overcome the orientation partly, and to throw the more polar groups into the outer surface, thus increasing the surface energy.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

IONIC EQUILIBRIA OF STRONG ELECTROLYTES

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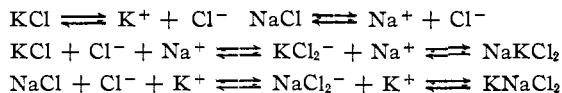
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I

The ionic relationships in relatively concentrated solutions of mixed strong electrolytes have been studied especially by Smith¹ and his students, who have shown that, as the total concentration of a salt mixture of equivalent amounts of two salts increases, the ion fraction of one of the metallic constituents gains on the ion fraction of the other. Recently Kendall² has attacked the problem of "complex formation" between solute and solvent.

II. Conductivity of Concentrated Solutions

When such salts as sodium and potassium chlorides are mixed in solution such equilibria as the following may be set up.



The formation of such molecular or ion complexes in solution, causing the gain of one ion fraction on another³ in a salt mixture, should decrease the conductivity of such a solution of mixed salts. Thus the conductivity of an equimolar solution of sodium and potassium chlorides of a

¹ G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907). Smith and Ball, *THIS JOURNAL*, **39**, 179 (1917). Smith and Braley, *ibid.*, **40**, 1802 (1918). Wells and Smith, *ibid.*, **42**, 185 (1920).

² Kendall, *ibid.*, **39**, 2328 (1917); **43**, 1416 (1921); **43**, 1426 (1921).

³ Noyes and Falk have suggested the existence of SrCl_4 , etc., in solution from the results of transference experiments. *Ibid.*, **33**, 1455 (1911).

total concentration of one equivalent per liter should be less than that calculated from the conductivities of solutions of the pure salts each at the same concentration as the above total concentration. From the isohydric principle we should expect the values obtained in these two ways to be the same. The strongest experimental support of this principle has been derived from conductivity studies although other properties have been studied in connection with it. The writer has studied the heats of dilution⁴ of mixed salt solutions, finding that they deviated from values calculated on the basis of this principle. Bender,⁵ from a study of expansion coefficients, concluded that on mixing salt solutions these coefficients are not the arithmetical mean but that the concentration can be so adjusted as to give this value. Such solutions, having the same expansion coefficients, he termed "corresponding solutions." Doroshevskii and Dvorzhanshik⁶ besides studying the conductivities of dilute mixed salt solutions, found that the refractive indexes of the very dilute solutions of salts of sodium and potassium with the same anion were identical.

For dilute solutions the effect of complex formation on the conductivity may be expected to be very small; in fact for a total concentration of 0.1 N, the upper limit for a majority of conductivity studies, Smith¹ postulates equal ion fractions of Na^+ and K^+ in an equimolar mixture of sodium and potassium chlorides. The effect should vary with varying total concentrations. The value of this effect on conductivity may be expected to be small, however, for such ions as NaCl_2^- , KCl_2^- , Na_2Cl_3^- , K_2Cl_3^- ,⁷ etc., will be highly polar particles and, indeed, may well be of such a nature as to respond easily to the "parting effect" of a weak electrical field,⁸ even though this field alternates in sign periodically.

⁴ Stearn and Smith, *THIS JOURNAL*, **42**, 18 (1920). Smith, Stearn and Schneider, *ibid.*, **42**, 32 (1920).

⁵ Bender, *Wied. Ann.*, **27**, 179 (1884).

⁶ Doroshevskii and Dvorzhanshik, *J. Russ. Phys. Chem. Soc.*, **45**, 1174 (1913).

⁷ We should expect to find sodium the more "noble" metal in the anion according to the usual theory of complex ions, which would mean that, as the total concentration of an equimolar $\text{NaCl} + \text{KCl}$ solution increased, the potassium-ion fraction should gain on the sodium-ion fraction. As a matter of fact, however, Smith [*THIS JOURNAL*, **35**, 39 (1913)] and Smith and Ball [*ibid.*, **39**, 179 (1917)] have shown from a study of the heterogeneous equilibria between aqueous and metallic solutions, that as the total concentration increases, the sodium-ion fraction actually gains on the potassium-ion fraction. No generally satisfactory explanation as to the cause of this seeming anomaly, which indicates a preponderance of complex anions containing potassium instead of sodium, seems to have been offered.

⁸ Cf. Harkins, *Proc. Nat. Acad. Sci.*, **6**, 601 (1920). He suggests that for the degree of dissociation or ionization different measurements, giving different results on the same solution, should be interpreted in different ways. Thus NaIO_3 in solution may be 100% ionized (meaning merely 100% polarized), 85% electrolytically dissociated (*i. e.*, 85% of the molecules have their polar parts far enough apart to respond to an electric field

The effect of complex formation on conductivity may be further decreased by probable ion dehydration. Thus the value of the hydration of the chlorine ion at infinite dilution given by Smith⁹ is 9 and for the potassium ion it is 9.6. At higher concentrations these values will, of course, be smaller, but at any concentration, if m is the number of molecules of water of hydration of the chlorine ion and n the number for the potassium ion, then to obtain the fullest possible effect of complex ion formation on conductivity we should require a hydration of at least $2m + n$ molecules of water for a KCl_2^- ion. This, however, is highly improbable, and thus any dehydration would tend to increase the mobility of the complex and mask the effect of complex formation on the conductivity.

By definition, equivalent conductivity (Λ) is the reciprocal of the resistance of a quantity of solution containing one equivalent of electrolyte, measured between parallel electrodes 1 cm. apart. In practically all the determinations made up to this time the solutions studied have been made up by volume and thus any mass effect of the solvent has been neglected. In the case of dilute solutions the values obtained for volume-normal or weight-normal¹⁰ will not differ appreciably, but in the case of concentrated solutions the mol fraction of one salt in a volume-normal solution will not be the same as that of any other salt at equivalent-volume normality, and any volume change on mixing solutions would interfere with the comparability of results. Previous work on concentrated solutions of mixed electrolytes¹¹ has not taken this into account, and the difference between the observed and calculated values for these solutions has been assumed to be due to experimental error as it has not been consistently of the same sign. For these reasons, in this work the equivalent conductivities of weight-normal solutions were measured and the specific gravities of the same solutions determined by pycnometer. In this way any mass effect of the solvent was constant and any volume changes on mixing solutions have no effect on the comparability of the results.

With such solutions, then, we may look for some effect which, even though, as pointed out above, we may expect to be small, should be consistent in sign, and may be expected to increase with increasing total concentration and become distinctly measurable at higher concentrations. Those up to 4 N were used in this work.

or potential gradient as "free" ions in contradistinction to "bound" ions), while perhaps only 68% is thermodynamically dissociated.

⁹ Smith, *THIS JOURNAL*, **37**, 722 (1915).

¹⁰ *I. e.*, one equivalent of solute per 1000 g. or 55.5 formula weights of H_2O .

¹¹ MacGregor, *Proc. Royal Soc. Canada*, [2] **4**, 117 (1898). MacGregor, Archibald, McIntosh and McKay, *Trans. Nova Scotia Inst. Sci.*, **9** and **10** (1895-99).

Materials

Salts.—The salts used were the chlorides, bromides and iodides of sodium and potassium. *c. p.* salts were recrystallized once, and dried at about 200°. Before using, each was heated until decrepitation ceased.

Solutions.—The chloride solutions could be made up by weighing proper quantities of salts and water. The bromides and iodides were too hygroscopic for this, and so a large quantity of the 4 *N* and of the *N* solutions of the pure salts was made up by weighing the previously heated salt from a stoppered bottle and adding the proper weight of water. The solutions of mixed salts and other concentrations of the pure salts were made by mixing weighed quantities of these solutions with the proper weighed quantities of water.

Conductivity Water.—The most dilute solution studied was 0.1 *N* and its specific conductivity is comparatively high. Nevertheless, conductivity water was prepared by the usual method of distilling the ordinary distilled water from alkaline permanganate and then from very dil. sulfuric acid and condensing by means of block tin or silica condensers. Both kinds were used. All the water used had a specific conductivity between 1×10^{-6} and 2×10^{-6} mhos.

Apparatus and Procedure

The usual conductivity apparatus was employed. It consisted of a Kohlrausch bridge with extension coils, a 5-dial Curtis-coil resistance, a constant-speed high-frequency generator and tunable telephone.¹² Kohlrausch cells were used, varying in constant from about 7 to about 50 for the more concentrated solutions. Some of the work was done with a cell having adjustable electrodes and the same solution thus run in a series of "cells." The cell constants were determined with a normal solution of pure potassium chloride. The capacities of the cells were balanced by variable air condensers across the terminals of the resistance.

The specific conductivities of the solutions were measured at 25° ± 0.02°, and from the determined specific gravities the volumes containing one gram-equivalent of solute were calculated and the equivalent conductivity thus obtained.

The solutions used were those of sodium and potassium chlorides and mixed chlorides in the molecular proportions 2NaCl : KCl, NaCl : KCl, and NaCl : 2KCl, with total equivalent concentrations of 0.1 *N*, 0.25 *N*, 0.5 *N*, 1 *N*, 2 *N*, and 4 *N*. The same concentrations of bromides and iodides were also run, except that 3 *N* solutions were also included.

Results

Table I gives the equivalent conductivities, Λ , for the chlorides, bromides and iodides, respectively. For the mixed salts the calculated and observed values are both given and also their difference. With the formation of complexes the observed value should be less than that calculated on the basis of the isohydric principle and the differences in this direction are called positive, in the other direction are called negative. They are termed $\Delta\Lambda$.

Table II gives the values of the specific gravities of the various solutions employed. They are referred to water at 4° and corrected for the buoyancy of air.

¹² All furnished by the Leeds and Northrup Company.

TABLE I
EQUIVALENT CONDUCTIVITIES
Chlorides

Conc. N	Λ NaX	Λ KX	Λ 2NaX:KX		$\Delta\Lambda$	Λ NaX:KX		$\Delta\Lambda$	Λ NaX:2KX		$\Delta\Lambda$
			Calc.	Obs.		Calc.	Obs.		Calc.	Obs.	
0.10	106.82	128.34	113.99	114.12	-0.13	117.58	117.46	0.12	121.16	120.97	0.19
0.25	100.11	121.98	107.40	107.02	0.38	111.05	110.69	0.36	114.69	114.58	0.11
0.50	93.92	117.06	101.63	101.51	0.12	105.50	105.16	0.35	109.35	109.10	0.25
1.00	86.36	111.60	94.77	94.14	0.63	98.98	98.75	0.23	103.19	102.82	0.37
2.00	75.90	105.70	85.83	85.17	0.66	90.80	90.12	0.68	95.77	95.20	0.57
3.00
4.00	60.11	96.25	72.16	71.21	0.95	78.18	77.06	1.12	84.20	83.31	0.89
Bromides											
0.10	110.60	130.95	117.70	117.82	-0.12	120.78	120.84	-0.06	124.00	124.20	-0.20
0.25	103.42	126.55	111.13	110.83	0.30	115.09	114.68	0.32	118.85	118.70	0.15
0.50	97.86	120.90	105.53	104.91	0.62	109.38	108.90	0.48	113.22	113.10	0.12
1.00	90.60	117.20	99.57	99.04	0.53	103.90	103.30	0.60	108.30	107.88	0.42
2.00	80.50	111.10	90.70	90.28	0.42	95.80	95.26	0.54	100.90	100.52	0.38
3.00	72.39	105.96	83.58	82.67	0.91	89.17	88.30	0.87	94.77	94.03	0.74
4.00	64.85	101.09	76.93	75.52	1.41	82.50	81.63	0.97	89.01	87.95	1.06
Iodides											
0.10	109.40	130.56	116.50	116.60	-0.10	120.00	120.15	-0.15	123.50	123.50	0.00
0.25	104.10	127.00	111.75	111.43	0.32	115.50	114.96	0.54	119.40	119.30	0.10
0.50	98.83	122.20	106.62	106.20	0.42	110.50	110.12	0.38	114.40	114.11	0.29
1.00	92.53	118.58	101.21	100.68	0.53	105.55	104.90	0.65	109.89	109.55	0.34
2.00	83.66	113.69	93.67	93.02	0.65	98.67	98.10	0.57	103.68	103.15	0.53
3.00	75.76	109.08	86.87	86.00	0.87	92.42	91.70	0.72	97.97	97.30	0.67
4.00	68.36	103.74	80.15	79.36	0.79	86.05	85.20	0.85	91.95	90.70	1.25

TABLE II
 SPECIFIC GRAVITIES

Conc. N	Solutions of pure sodium halide		
	Chloride	Bromide	Iodide
4.00	1.1357	1.2707	1.3856
3.00	1.2084	1.3012
2.00	1.0710	1.1424	1.2058
1.00	1.0363	1.0724	1.1061
0.50	1.0172	1.0350	1.0520
0.25	1.0073	1.0160	1.0243
0.10	1.0012	1.0042	1.0105
	Solutions of pure potassium halide		
4.00	1.1513	1.2792	1.3890
3.00	1.2191	1.3063
2.00	1.0806	1.1497	1.2107
1.00	1.0410	1.0764	1.1092
0.50	1.0197	1.0375	1.0540
0.25	1.0087	1.0172	1.0254
0.10	1.0017	1.0054	1.0108
	Solutions containing two mols of sodium to one mol of potassium halide		
4.00	1.1413	1.2722	1.3857
3.00	1.2107	1.3012
2.00	1.0747	1.1443	1.2059
1.00	1.0378	1.0731	1.1054
0.50	1.0180	1.0353	1.0523
0.25	1.0079	1.0161	1.0244
0.10	1.0015	1.0045	1.0105
	Solutions containing one mol of sodium to one mol of potassium halide		
4.00	1.1437	1.2743	1.3864
3.00	1.2144	1.3029
2.00	1.0767	1.1461	1.2083
1.00	1.0384	1.0740	1.1072
0.50	1.0185	1.0358	1.0526
0.25	1.0081	1.0165	1.0248
0.10	1.0014	1.0048	1.0106
	Solutions containing one mol of sodium to two mols of potassium halide		
4.00	1.1459	1.2770	1.3889
3.00	1.2167	1.3058
2.00	1.0780	1.1476	1.2103
1.00	1.0394	1.0754	1.1084
0.50	1.0188	1.0370	1.0535
0.25	1.0082	1.0168	1.0253
0.10	1.0015	1.0048	1.0106

Table III gives values of $\Delta\Lambda$ per 100 mhos conductivity at the different concentrations.

The 3 curves are plotted from data taken from Table V. The effect is small, even at the higher concentrations, but with the exception of the more dilute solutions its sign is consistently positive and it increases fairly consistently with the concentration. If the totals in the above table

TABLE III

Conc. <i>N</i>	$\Delta\Delta$ Chlorides			$\Delta\Delta$ Bromides			$\Delta\Delta$ Iodides		
	2Na:K	Na:K	Na:2K	2Na:K	Na:K	Na:2K	2Na:K	Na:K	Na:2K
0.10	-0.11	0.10	0.16	-0.10	-0.05	-0.16	-0.08	-0.12	0.00
0.25	0.35	0.33	0.10	0.27	0.28	0.13	0.29	0.47	0.08
0.50	0.12	0.33	0.23	0.60	0.45	0.11	0.40	0.35	0.25
1.00	0.66	0.24	0.36	0.53	0.60	0.40	0.53	0.63	0.31
2.00	0.78	0.76	0.60	0.47	0.57	0.38	0.70	0.58	0.52
3.00	1.10	0.99	0.79	1.01	0.79	0.68
4.00	1.33	1.45	1.07	1.87	1.18	1.20	1.00	1.00	1.38
Totals	3.13	3.21	2.52	4.74	4.02	2.85	3.85	3.70	3.22

be taken to represent the tendency toward complex formation, Table IV shows the evident tendency toward complex formation for the different metal ratios and also for the different halides.

TABLE IV

2Na:K	Na:K	Na:2K	Chlorides	Bromides	Iodides ^a
11.72	10.93	8.59	8.86	8.73	8.29

^a The values for the 3.00 *N* solutions of the bromides and iodides are omitted from these last three totals in order to compare them with the chlorides.

The first three figures in this table are easily explained on the basis of the results obtained by Smith and his students who have found that it is the potassium which has the greater tendency to go into the anion.

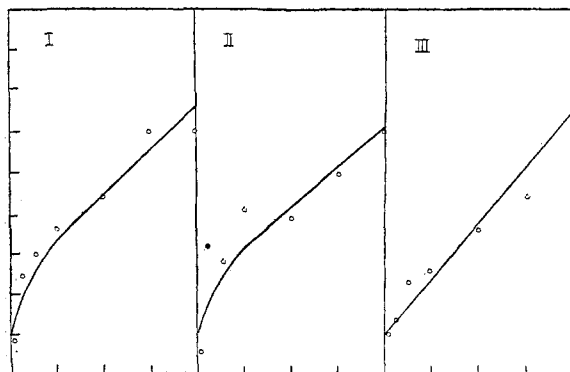


Fig. 1.—Concentrations plotted as abscissas and values of $\Delta\Delta$ plotted as ordinates. These curves are plotted from data in Table IV for the iodides. Curve I represents the molecular mixture 2NaI:KI; Curve II, NaI:KI; and Curve III, NaI:2KI.

Thus we should expect the mass effect of the sodium to be significant and this indeed seems to be the case. The last three figures, however, indicate a decreasing tendency toward complex formation as we go from chlorides to iodides, whereas the opposite tendency has been shown to

hold.¹³ In an attempt to account for this seeming anomaly the viscosities of some of the more concentrated solutions of the chlorides and iodides were measured. The relative viscosities of these solutions are given in Table VII. They were run at 25°, and compared to water at the same temperature. A Washburn viscosimeter was used, but as the total time of flow was only from 28 seconds to as low as 17 seconds for certain of the heavier solutions of low viscosity, the values are only approximate. They do indicate, however, that the positive values of $\Delta\Delta$ obtained are not due merely to an increase in viscosity on mixing salt solutions, as in most cases there is an actual decrease. This decrease, however, seems greater for chlorides than for iodides, though of course the actual viscosities are much greater in case of the former. And this difference, instead of explaining the above mentioned anomaly, tends quantitatively to augment it.

TABLE V
VISCOSITIES

Solution	4.00 N	2.00 N	1.00 N
NaCl.....	1.443	1.142	1.050
2NaCl:KCl.....	1.257	1.088	1.023
NaCl:KCl.....	1.219	1.061	1.014
NaCl:2KCl.....	1.140	1.034	0.997
KCl.....	1.063	0.988	0.971
NaI.....	1.244	1.071	1.022
2NaI:KI.....	1.147	1.020	0.998
NaI:KI.....	1.097	0.999	0.984
NaI:2KI.....	1.058	0.979	0.985
KI.....	0.987	0.937	0.944

There seems to be "some other tendency superimposed upon complex-ion formation to make this progression go the wrong way," and at present this is unexplained, though it is hoped that the results of some work now in progress at the University of Illinois on transference in mixed salt solutions may throw some light on the matter. The atomic volumes of the three halogens are not far apart and relatively larger velocities of iodide complexes may result from relatively greater dehydration tendency than with the bromides or iodides.

Summary

1. Equivalent conductivities of solutions of the halides of sodium and potassium of varying weight normal concentrations were determined at 25°.
2. The observed values for the mixed salt solutions were compared with those calculated from the values for the pure salt solutions at equivalent total concentrations on the basis of the isohydric principle.
3. The difference between the calculated and the observed values

¹³ Wells and Smith, *THIS JOURNAL*, **42**, 185 (1920).

were found to be positive and to increase with total salt concentration, with the numerical value of the ratio of sodium to potassium salt in the mixture, but to decrease generally as one goes from chlorides to iodides.

4. In general the results can be explained on the basis of complex formation, though at present no explanation is offered for the seeming decrease in complex formation proceeding from chlorides to iodides.

5. Tables of specific gravities of the solutions studied, and the relative viscosities of certain of these solutions are given.

It is a pleasure to acknowledge my thanks to Dr. George Shannon Forbes for helpful comments on certain of the results.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE EFFECT OF CHANGING HYDROGEN-ION CONCENTRATION ON THE POTENTIAL OF THE ZINC ELECTRODE

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When a metal of weak basic character (such as gallium) is studied with regard to its single electrode potential, the salt solutions in which the metal is immersed must be acidified to prevent hydrolysis. The possible effect on the potential of such acidification has not been adequately ascertained.¹ Accordingly, this paper recounts a brief study of the effect of adding acid to the salt solution around a typical easily and exactly reproducible metal electrode, in order to demonstrate experimentally the sign and magnitude of the potential difference thus caused. Zinc was chosen for the purpose. The results were merely preliminary, and were inevitably not very conclusive. Nevertheless, when, as here, theory is incomplete, even tentative experimental results may be of value.

Earlier papers on this subject are as follows. Broughton² studied the decomposition voltage of zinc sulfate solutions in the presence of acid, but since he made his measurements with a flowing current, the *fall* of potential which he observed was due (as he saw) to the decrease of resistance of the solution. For the present purpose these results have no significance. A. Siemens³ measured the potential of zinc in an acid solution, but not in pure zinc sulfate. Details are lacking, moreover, as to salt-bridges and other particulars, so that these results also have little signifi-

¹ Since the completion of our experimental work a general but rather vague theoretical discussion of this matter by A. Smits has been published in "Die Theorie der Allotropie," (Barth, Leipzig, 1921), especially on pp. 176 and 399. Apparently our results are not inconsistent with his conclusions.

² Broughton, *Met. Chem. Eng.*, **20**, 155 (1919).

³ Siemens, *Z. anorg. Chem.*, **41**, 249 (1904).