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(1) The absorption-spectra of the three salts examined undergo changes on diluting their solutions.

(2) These changes are of such a nature that the spectra tend to become identical in dilute solutions.

(3) The results of other observers show on the whole that salts of other metals behave in a similar way.

(4) The behaviour of the salts examined leads to the conclusion that, in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light, while in dilute solutions they act independently in doing so.

(5) These results are in substantial agreement with the hypothesis of electrolytic dissociation.

(6) The results cannot be satisfactorily explained on the hypothesis of a hydrolytic dissociation, or on that of molecular aggregates.

In conclusion, I take this opportunity of expressing my thanks to Professor H. B. Dixon, at whose suggestion this investigation was begun, and also to Professor A. Schuster for the kindness with which he placed the Vierordt spectrophotometer and other apparatus at my disposal, and for much valuable advice in carrying out the work.

XXXVI. *On Chemical Equilibrium in Mixed Electrolytes.*

By Dr. G. GORE, *F.R.S.**

IN various researches I have shown that any change occurring in the molecular or chemical constitution of an electrolyte may be easily and quickly detected, and its amount and rate to a certain extent measured, either by the voltaic balance method, or by the simple plan of immersing a suitable voltaic pair of metals in the liquid successively at different periods of time, and noting either the degree of voltaic energy, electromotive force, or strength of current produced; and I have shown that in certain cases, the mixture of electrolytes, especially that of an aqueous solution of a halogen with one of a salt or base (and in some cases a very dilute solution of an acid with one of a salt), the liquid mixture does not at once attain its final or fixed state at 16° C., but attains it rapidly on the application of heat. (See "Method of Examining Rate of Chemical Change in Aqueous Solutions," *Proc. Roy. Soc.* March 14, 1890, p. 440. "On the Molecular Constitution of Isomeric Solutions," *Phil. Mag.* Oct. 1889, p. 289. "Method of Measuring Loss of Energy due to Chemical Union &c.," *Phil. Mag.* Jan. 1892, p. 28.)

* Communicated by the Author.

In a more recent investigation, "On Changes of Electromotive Force, Volume, and Temperature by Mixing Electrolytes" (see *Proc. Birm. Phil. Soc.* vol. viii. p. 28), I have further shown that if, instead of a single mixture of two solutions, a couple of such mixtures, isomeric with each other (for instance $\text{HCl} + \text{NaBr}$, and $\text{HBr} + \text{NaCl}$), was employed, under certain conditions, in all the 25 cases of mixtures of Acids + Salts and of Salts + Salts which were examined, the two mixtures yielded the same amount of electromotive force, and therefore formed the same final product during the act of mixing; in each case the ingredients of the two mixtures started with different total amounts of energy, but arrived at the same final molecular and chemical constitution; each different isomeric couple, however, gave a different final amount. In other researches I found that if the solutions were extremely dilute and the "voltaic balance" method was employed, one of the two mixtures did not at once pass to the same final state, but gave a very different amount of voltaic energy from the other, especially if a free halogen formed part of the mixture. A list of unstable mixtures, as found by the voltaic balance method, has been given in a research on the "Relative Amounts of Available Voltaic Energy of Aqueous Solutions" (*Proc. Birm. Phil. Soc.* vol. vii. 1889, p. 47).

In the present research I have further examined the circumstances which influence the conditions of instability and of chemical and molecular equilibrium of such mixtures. The circumstances examined are:—1st, The influence of a halogen and a salt; 2nd, of a halogen and two salts; 3rd, of time upon the latter; 4th, of heating such a mixture; 5th, of doubling the amount of the halogen; 6th, of halving the amount of the two salts; 7th, of two different halogens and a salt; 8th, of a halogen and an acid; 9th, of two halogens and an acid; 10th, influence of one halogen and two acids; 11th, of halogens and an alkali with aluminium, tin, and zinc, as positive metals; and 12th, of heating the halogens with an alkali.

The method employed of measuring the electromotive force was that of opposition with a thermopile of iron and german silver and an astatic galvanometer, as in several of the previous researches (see more particularly "A Method of Measuring Loss of Energy due to Chemical Union, &c.," *Phil. Mag.* Jan. 1892, p. 28). The positive metal of the voltaic couple used in the experiments of Tables I. to X. and XIII. to XV. was of zinc, and in Table XI. of aluminium, and XII., of tin; the negative metal in all cases was platinum.

Distilled water was used in making all the solutions. In making them the following rules were observed:—In each Table, Nos. I. to X. and XIII. to XV., under the head of “Ingredients,” each ingredient—halogen, acid, or salt, as the case might be—was dissolved in the proportion of one equivalent weight in grains of the absolute substance in one unit quantity or 511,500 grains of water; in Tables XI. and XII. the proportion of water was 1800 grains. Under the head of “Mixtures,” an equivalent quantity in grains of *each* of the two or more substances forming the mixtures was *collectively* dissolved in a single unit quantity of water; but in Table V. two unit quantities in grains of one of the ingredients was included, as shown by the formulæ given. The substances employed were of a high degree of purity.

The experiments are divided into three chief sections, viz., Section A, Halogens + Salts; B, Halogens + Acids; and C, Halogens + Bases.

Section A.—HALOGENS + SALTS. Positive metal, Zinc.

TABLE I.—*Influence of a Halogen + a Salt.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br.	1·8706	Br + KCl.	1·7276	1·5450	Gain	·1826 = 11·81
KCl.	1·1927					
Cl.	1·9250					
KBr.	1·1556	Cl + KBr.	„	1·3323	„	·3953 29·67
I.	1·4410	I + KCl.	1·40156	1·3501	Gain	·05146 = 3·81
KI.	1·1470	Cl + KI.	„	1·2840	„	·11756 9·15
		I + KBr.	1·3844	1·3029	Gain	·0815 = 6·25
		Br + KI.	„	1·3823	„	·0021 ·15

In each of these three cases of isomeric couples, each of the two mixtures gave the same amount of electromotive force, and had therefore acquired the same chemical and molecular composition at once on mixing.

TABLE II.—*Influence of a Halogen + two Salts.*

Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl + (KBr + KI).	1·5274	1·2376	Gain	·2898 = 23·41
Br + (KCl + KI).	1·4702	1·3101	„	·1601 12·22
I + (KCl + KBr).	1·3787	1·2806	„	·0981 7·65

The additional salt in each of these three cases of isomeric mixture prevented the mixture from at once attaining a fixed or final chemical and molecular constitution.

N.B. Compare the results with those of Tables III. and IV.

TABLE III.—*Influence of Time.*

	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
After standing 24 hours.	Cl+(KBr+KI).	1·37868	1·2376	Gain ·14108 =	11·37
" " "	Br+(KCl+KI).	"	1·3101	" ·0685	5·22
" " "	I+(KCl+KBr).	"	1·2806	" ·0980	7·65

By standing a sufficient period of time at ordinary atmospheric temperature, the first two solutions of Table II. lost energy, and acquired the same chemical and molecular composition as the third one, *i. e.*, the one having the smallest electromotive force; these two mixtures therefore were in an unstable condition.

TABLE IV.—*Influence of Heating.*

	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
After heating.	Cl+(KBr+KI).	1·3701	1·2376	Gain ·1325 =	10·70
" "	Br+(KCl+KI).	1·3844	1·3101	" ·0743	5·67
" "	I+(KCl+KBr).	1·35294	1·2806	" ·0723	5·65

Each mixture, newly made, was heated to 90° C. during 15 minutes in a stoppered glass flask and then cooled. In each case the percentage of gain of electromotive force which had occurred during the mixing was largely reduced, but least so with the last liquid. These results indicate that all three of these mixtures were more or less unstable, the first one the most and the last one the least so, that neither of them had completely attained the most fixed chemical and molecular condition, and that heating caused a rapid change in each to a fixed state. The chemical change and the final state arrived at evidently depend upon the temperature; even at 16° C. a slow change occurs, see Table III.

TABLE V.—*Influence of Doubling the Amount of the Halogen.*

Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
2Cl+(KBr+KI).	1·62178	1·3113	Gain ·31048 =	23·67
2Br+(KCl+KI).	"	1·5634	" ·05338	3·40

Doubling the amount of the halogen caused each of the two mixtures to assume the same chemical and molecular composition immediately on mixing. It appears from a comparison of these results and those of Table I. with those of Table II., that the condition of chemical and molecular equilibrium depends upon the proportion of free halogen to that of the salts. If the proportion of the halogen to the total of the salt was 1 eqt. to 1 eqt. as in Table I., or 2 eqts. to 2 eqts. as in Table V., each mixture at once suffered a change and attained a fixed state; but if it was 1 eqt. of halogen to 2 eqts. of the salt, as in Table II., each mixture was in a condition of instability, and was prevented from assuming at once the fixed state, but it was not prevented from undergoing a gradual change at atmospheric temperature (see Table III.); the additional proportion of salt therefore only *hindered* the change.

The degree of solubility of iodine in water was too small to enable a double proportion of it to be used.

TABLE VI.—*Influence of Halving the Amount of the Salts.*

Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
I + .5(KCl + KBr).	1.41014	1.3203	Gain .0898	= 6.8

The proportion of gain of mean amount of electromotive force is somewhat less than in the comparison case in Table II., as if diminishing the proportion of salt to halogen increased the amount of chemical and molecular change and assisted the mixture to attain a fixed state, similar to the effect of doubling the amount of the halogen, as shown in Table V.

TABLE VII.—*Influence of Two Halogens + a Salt.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl + Br.	1.8992	(Cl + Br) + KI.	1.63036	1.4556	Gain .17476	= 12.00
Cl + I.	1.7133	(Cl + I) + KBr.	1.62178	1.4775	„ .14428	9.76
Br + I.	1.69338	(Br + I) + KCl.	„	1.5615	„ .06028	3.80

The amounts of electromotive force obtained by means of experiment in the three instances are so nearly alike that they may be regarded as identical. On comparing the results

with those of Table I., we find that whether the mixtures contained a single halogen or two different ones, each of the mixtures which were isomeric to each other at once attained the same final state; and on comparing them with those of Tables I. and II., it appears that whilst an additional salt hindered the chemical and molecular change, the addition of a second halogen did not impede the change, probably because the halogen was free and had greater chemical energy.

In a previous research (Phil. Mag. Jan. 1892, p. 49) I have examined the influence upon the electromotive force of a cadmium platinum couple of heating aqueous solutions of chlorine, bromine, and iodine alone, during successive periods of time, until a state of equilibrium was attained, and have shown the amounts of change thereby produced; the strength of solution then employed was one equivalent weight of the halogen in grains in 449,500 grains of water. These experiments with the three halogens showed the limits of the amount of chemical and molecular change produced in their aqueous solutions by means of heat.

Section B.—HALOGENS + ACIDS. Positive metal, Zinc.

TABLE VIII.—*Influence of a Halogen + an Acid.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl.	1·9250	Cl + HBr.	1·73332	1·4954	Gain ·2379	= 15·9
HBr.	1·30718					
Br.	1·8706	Br + HCl.	1·73904	1·7102	„ ·0288	1·68
HCl.	1·35866					
HI.	1·18134	Cl + HI.	1·41014	1·3428	Gain ·06734	= 5·01
I.	1·4410	I + HCl.	„	1·4226	Loss ·0125	·87
		Br + HI.	1·40156	1·4464	Loss ·0448	= 3·09
		I + HBr.	„	1·3888	Gain ·01276	·91

With the two mixtures of the first isomeric couple the electromotive forces were unsteady, and the amounts obtained by means of experiment are so nearly alike that they may be regarded as identical. In all three cases the two isomeric mixtures of each couple appear to have at once attained the same final chemical and molecular composition and state of equilibrium.

TABLE IX.—*Influence of Two Halogens and One Acid.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl+Br.	1·8992	HI+(Cl+Br).	1·6847	1·5249	Gain ·1598 =	10·48
Cl+I.	1·7133	HBr+(Cl+I).	1·7076	1·5814	„ ·1262	7·98
Br+I.	1·69338	HCl+(Br+I).	1·6847	1·6464	„ ·0383	2·33

The additional halogen did not prevent the three mixtures attaining nearly the same final state.

TABLE X.—*Influence of One Halogen and Two Acids.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HBr+HI.	1·27858	Cl+(HBr+HI).	1·5274	1·3751	Gain ·1523 =	11·11
HCl+HI.	1·3329	Br+(HCl+HI).	1·4702	1·5119	Loss ·0417	2·76
HCl+HBr.	1·3529	I+(HCl+HBr).	1·4072	1·4015	Gain ·0057	·40

The additional acid retarded the attainment of a state of stable chemical equilibrium similar to the effect of an additional salt (see Table II.).

Section C.—HALOGENS + BASES.

Strength of solution = 1 equivalent weight in grains in 1800 grains of water.

TABLE XI.—*With Al as Positive Metal.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water.	1·5816	Br+KHO.	1·5244	1·4991	Gain ·0253 =	1·68
KHO solution.	1·3814					
After heating 1 min. to 90° C.						
		„ „	1·5101	„	„ ·0110	·73

TABLE XII.—*With Sn as Positive Metal.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water.	1·2213	Br+KHO.	·9496	1·0976	Loss ·1480 =	13·49
KHO solution.	·9210					
After heating 1 min. to 90° C.						
		„ „	·9067	„	„ ·1909	17·40

The bromine solution used in Tables XI. and XII. was not rendered colourless by the alkali; the resulting mixture gave with test-paper an alkaline reaction followed by a bleaching effect; its colour was not visibly altered by heating, nor by the addition of a second equivalent of the alkali. Both by means of an aluminium positive metal and a tin one a loss of electromotive force caused by heating the mixture was detected, and it was shown that the most stable condition of chemical equilibrium was not attained during the act of mixing.

With Zn as Positive Metal.

Strength of Solution = 1 equivalent weight in grains in 511,500 grains of water.

TABLE XIII.—*Chlorine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
H ₂ O.	1.1270					
KHO solution.	1.0755					
Cl water.	1.9250	Cl + KHO.	1.8420	1.4055	Gain .4365 =	31.06
After heating 1 min. to 98° C.		" "	1.6990	"	" .2935	20.88
" " 1 " "		" "	1.5274	"	" .1219	8.67
" " 5 " "		" "	1.3129	"	Loss .0926	6.59
" " 30 " "		" "	1.17216	"	" .2334	16.61
" " 30 " "		" "	1.13270	"	" .2728	19.40

The solution of Cl + KHO in these experiments required much more prolonged heating than one of Cl alone, in order to reduce the electromotive force to the smallest amount and to complete the chemical and molecular change. Whilst also with the mixture of Cl + KHO the electromotive force was finally reduced nearly to that given by water alone; with a solution of Cl alone it finally remained constant at a number nearly double that given by water (*ibid.*).

TABLE XIV.—*Bromine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water	1.8706	Br + KHO.	1.69614	1.4696	Gain .22654 =	15.41
After heating 1 min. to 98° C.		" "	1.61320	"	" .1436	9.77
" " 1 " "		" "	"	"	" .04922	3.35
" " 5 " "		" "	1.51882	"	Loss .2754	18.70
" " 30 " "		" "	1.19420	"	" .3426	23.31
" " 30 " "		" "	1.1270	"		

The electromotive force was finally reduced to that of water, and the chemical and molecular change appeared to be nearly complete.

TABLE XV.—*Iodine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Iodine water	1.4416	I+KHO.	1.3844	1.3295	Gain .0549 =	4.136
min.						
After heating 1 to 98° C.		" "	1.3272	"	Loss .0023	.1730
" " 1 " "		" "	1.2843	"	" .0452	3.400
" " 5 " "		" "	1.1942	"	" .1353	10.17
" " 30 " "		" "	1.1270	"	" .2025	15.23

Similar remarks may be made respecting the results of this Table as about those of Table XIV.

In each of these three tables the process of heating caused a gradual loss, and at a diminishing rate of electromotive force; and each of the liquids appeared to finally acquire a fixed chemical and molecular state. The total percentage losses of mean amount of electromotive force with the three mixtures were as follows:—with Cl+KHO, 50.4; with Br+KHO, 38.7; and with I+KHO, 19.30.

General Remarks and Conclusions.

1. The mixtures employed in this research may be divided into two classes, viz., those which spontaneously change with such rapidity that they at once attain on mixing a comparatively fixed state of chemical and molecular equilibrium, and those which only slowly change and attain such a state.

2. The results of the present research and of previous ones show, that with mixtures of acids+salts, and of salts+salts, a fixed state of equilibrium was in nearly all cases immediately attained; but with halogens+salts, halogens+acids, and halogens+bases, a greater or less degree of retardation of attainment of such a state frequently happened.

3. According to the results given in Tables V. and VI. compared with those of Table I., doubling the degree of concentration of the solution did not produce any conspicuous effect upon the state of chemical equilibrium.

4. The results of Table III. indicate that with the particular mixtures there employed, a gradual change by lapse of time occurred, and each liquid attained a state of comparative equilibrium in 24 hours.

5. The great influence of temperature is shown in a number of cases in Tables IV., XI., XII., XIII., XIV., and XV.; in all cases it acted so as to promote chemical and molecular

change, and enabled the mixtures to arrive at a fixed state. The results of previous experiments (Phil. Mag. Jan. 1892, p. 49) show that the action of the higher temperature was upon the halogen present. In all cases of heating aqueous solutions, either of Cl, Br, or iodine alone (*ibid.*), or of Cl + (KBr + KI), Br + (KCl + KI), or I + (KCl + KBr), Table IV. ; Br + KHO, with a positive metal of aluminium or of tin, Tables XI. and XII. ; Cl + KHO, Br + KHO, or I + KHO, with zinc as a positive metal—a relative *loss* of electromotive force took place, and a more fixed state of chemical equilibrium was attained.

6. The results of Table I. show that if the ingredients of a mixture of a halogen and a salt in water were in the proportion of their chemical equivalents, the complete change and attainment of a fixed condition of equilibrium was promoted. If, however, as in Table II., the saline ingredient was in excess, the change to a fixed state of chemical equilibrium was retarded. But if, as in Tables V. and VI., the electro-negative one was in excess, the changes were not retarded.

7. Mixtures of halogens and acids in chemically equivalent proportions, as in Table VIII., acted much like those of halogens and salts in Table I., *i. e.*, their solutions at once attained a fixed or final state of chemical equilibrium on mixing; but an additional acid, like an additional salt, retarded the chemical change (see Table X.).

8. Comparison of the results given in Tables I. and II. with those in Tables VII. and IX., shows that whilst doubling the proportion of salt to halogen retarded the change, doubling that of the halogen had no such effect.

9. Comparison also of the results given in Tables XIII., XIV., and XV. with those obtained with solutions of the halogens alone (Phil. Mag. Jan. 1892, p. 49) shows that the addition of a caustic alkali to a solution of a halogen considerably retarded the rate of change which occurred on heating. An inspection of the results in Tables XIII., XIV., and XV., further shows that the greatest retardation occurred with chlorine and the least with iodine; probably because the chlorine had the largest amount of molecular motion to be retarded.

10. The leading idea in all these cases is *the degree of freedom of molecular motion*, and the most general conclusion is, that the smaller the degree of freedom of such motion of the halogen molecules, the greater the retardation of chemical change; heat therefore increases, and the presence of dissolved alkalies, salts, or acids decreases the rate of change and retards the attainment of a fixed state of chemical equilibrium.