LXXXVII.—*The Molecular Refraction of Dissolved Salts and Acids.*

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IN papers on "Refraction Equivalents," published in the *Proc. Roy. Soc.* for 1868, and in the *Phil. Trans.* for 1870, one of us (Gladstone) gave reasons for believing that the law of refraction equivalents holds good in the case of compounds in solution, that is to say, that the refraction equivalent of a solution is the sum of the refraction equivalents of the solvent and of the substance dissolved. If therefore the refraction equivalent, or molecular refraction, of the solvent and its proportionate quantity is known, it is easy to determine the molecular refraction of the salt or other substance in solution. Proceeding on this belief, he determined the molecular refraction of a large number of salts, and deduced from them the atomic refraction of most of the metals. A paper by Janovsky, however, caused some chemists to doubt the correctness of the method, and in 1880 a small committee of the British Association was appointed, "for the purpose of investigating the method of determining the specific refraction of solids from their solutions." The report, drawn up by Professor Phillips Bedson,* detailed various experiments, and arrived at the conclusion that they served to substantiate the law given above.

Professor Kanonnikoff, of Kazan, in 1883, being unaware of what had previously been done, adopted the same method, and, as far as his experiments went, arrived at similar results.

Other researches on dissolved substances brought forth an accumulation of evidence in favour of this law, but, at the same time, it became more and more probable that in certain cases the law was only approximately true. It appeared desirable, therefore to us that the question should be more carefully investigated, especially as the apparent exceptions to a general law are often very fruitful of fresh discovery. We now submit to the Society the results of our own recent experiments, together with those of other observers in the same field.

In the paper in the *Phil. Trans.* already referred to, five reasons are given for confidence in the law. They are essentially as follows.

1. The similarity of the refraction equivalents of certain substances when determined for the solid and from its solution.

2. The close agreement of the refraction equivalent of several organic compounds when dissolved in water with what might be

* All references will be given in Appendix II.

calculated from the values for carbon, hydrogen, and oxygen, as determined by Landolt.

3. That the refraction equivalent, as reckoned from a solution, is not affected by varying the amount of water.

4. The similarity of the refraction equivalent of the salt, whether water or alcohol be the solvent.

5. The constancy of the differences of refraction presented by corresponding series of salts in solution.

We propose in this paper to deal only with Nos. 1 and 3, and that in reference only to salts and acids.

Historical Development.

The instance specially cited in the original paper of 1870, in support of the view that the molecular refraction was constant, was that of sodium chloride. There was a series of observations on solutions of this salt in water, varying in strength from 23.2 to 8.7 per cent. The molecular refraction for the line A varied irregularly about the mean figure 15.42, the extremes being 15.26 on one side, and 15.55 on the other. The same constancy was claimed for other salts, and an examination of the data would seem to warrant the claim in regard to several, but none of these were examined in weak solution, nor indeed through any wide range of strength.

There had been previously published several tables of the refractive indices and densities of solutions of the same salt at different degrees of concentration. From these data, we have calculated the molecular refraction, and the results are given in Appendix I (p. 864, *et seq.*). Thus calculated, Kremer and Beer's tables, published in 1857, indicate for many salts little or no change on dilution.

The figures of Handl and Weiss in 1858, of Landolt in 1862, of Wüllner in 1869, and of Damien in 1881, lead to a similar conclusion. Only those of Schmidt, in 1859, seem to indicate a totally different result.

Subsequent to 1870, Van der Willigen published some elaborate investigations showing little variation, and E. Forster, in 1878, concluded that the specific refractive energy of salt solutions is not so constant as with mixtures of liquids, but that the variations are generally within 1 per cent. of the mean. In Appendix I, the observations of Wüllner, Van der Willigen, and Damien have been reduced by means of their own values for water, in other cases we have used our own.

A second paper by one of the authors (Gladstone), which appears in the *Transactions of the Chemical Society* for 1891, establishes the fact that the value for hydrochloric acid does change with a varying amount of water, that this change is considerable, and that with an

increasing percentage of substance in the solution the refraction becomes smaller. It shows that the same is true of molecular dispersion, the change here being proportionately greater. The same holds good also, though not to the same extent, with other acids, whilst in the case of salts, the evidence is rather in favour of constancy. About the same time, Le Blanc, Wegner, Schütt, and more recently De Muynck, have made determinations on certain groups of acids and salts.

There are other observations, principally by foreign physicists, which would be valuable in this connection, if they had given the density of the solution.

This was the condition of the question when we took it up for re-examination. Since that time, Hallwachs and Kohlrausch, using refined methods for determining the refractive index and the density, have carried the investigation into the region of the most dilute solutions. We have reason also to believe that Nasini has been bringing his great powers of investigation to bear on the same general question.

The Data.

The data employed in this investigation include :

1. Gladstone's old observations (1868—1891) whenever they were considered sufficiently trustworthy and valuable for our present purpose. They have generally been recalculated by means of the value for water which we now employ.

2. The published observations of others. All those mentioned in the introduction are included, unless there was some obvious ground for their omission, and they are calculated out to the molecular refraction.

These two constitute Appendix I.

3. The published observations on such solids and anhydrous liquids as have also been examined in solution.

4. Our own most recent observations ; these were usually made in much the same way as that previously described. But as it was no part of our special object to measure the dispersion ; as the hydrogen and sodium lines can be made use of at any time ; and as most of our Continental fellow-workers have made use of these lines in the spectrum, we have also employed them.

Seeing that the molecular refraction of the salt is the difference between the molecular refraction of the solution and that of the water, it is evident that all experimental errors, as well as all errors arising from impurity of substance, must be accumulated on the very thing we are seeking—the refraction due to the salt itself. We have therefore determined with great care the molecular refraction of the

water employed for the different series of experiments. The figures we have generally found are the following.

Water at 18° C.

	H _α .	D.	H _β .
μ	1·3315	1·3334	1·3375
$(\mu - 1)/d$	0·3318	0·3337	0·3378

It is evident also that the chance of error is greatly increased if the amount of salt is only a small fraction of the solution; so that with all precautions we do not feel justified in placing much reliance on the figures yielded by solutions weaker than 5 per cent., although in a few cases we have placed on record figures obtained from solutions still more dilute.

Table I contains the name of the substance, its formula, the percentage of the substance in the solution, and the molecular refraction for the hydrogen line α or C, the sodium line D, and the hydrogen line β or F.

TABLE I.

Substance.	Formula.	Per-centage.	R _α .	R _D .	R _β .
Hydrochloric acid	HCl	38·93	14·02	14·14	14·46
" "	"	34·30	14·11	14·23	14·55
" "	"	23·00	14·25	14·37	14·72
" "	"	13·18	14·33	14·45	14·80
" "	"	5·23	14·50	14·58	14·94
" " 2nd spec.	"	30·10	—	14·29	
" " "	"	25·70	—	14·31	
" " "	"	20·96	—	14·38	
" " "	"	13·63	—	14·43	
" " "	"	6·87	—	14·50	
" " "	"	3·47	—	14·96	
" " 3rd spec.	"	21·10	14·48	—	14·93
" " "	"	7·60	14·57	—	15·08
Lithium chloride	LiCl	43·40	—	14·47	
" "	"	24·10	—	14·80	
" "	"	13·10	—	14·82	
" "	"	10·59	—	15·02	
" "	"	6·77	—	14·89	
" "	"	5·10	—	15·07	
" " 2nd spec.	"	48·50	14·23	—	14·64
" " "	"	39·80	14·44	—	14·83
" " "	"	39·52	14·46	—	14·87
" " "	"	25·90	14·65	—	15·06
" " "	"	19·09	14·75	—	15·22
" " "	"	12·74	14·89	—	15·26
" " "	"	6·93	14·99	—	15·38
Sodium chloride	NaCl	25·80	—	15·80	
" "	"	4·61	—	15·94	
" " 2nd spec.	"	26·41	15·68	—	16·11
" " "	"	8·32	15·84	—	16·20

TABLE I (*continued*).

Substance.	Formula.	Per-centage.	R _a .	R _D .	R _g .
Potassium chloride	KCl	23·00	18·46	18·58	18·90
" "	"	12·40	18·46	18·62	18·98
" "	"	6·16	18·44	18·48	18·97
Rubidium chloride	RbCl	28·81	—	22·26	
" "	"	15·07	—	22·30	
" "	"	9·20	—	22·04	
" "	"	3·94	—	22·30	
Ammonium chloride	NH ₄ Cl	25·64	22·35	22·47	22·84
" "	"	25·21	22·35	22·48	22·88
" "	"	6·20	22·41	22·50	22·85
" "	"	5·57	22·70	22·51	23·10
Magnesium chloride	MgCl ₂	33·92	—	29·02	
" "	"	13·52	—	29·20	
" "	"	6·89	—	29·24	
Calcium chloride	CaCl ₂	39·55	—	32·35	
" "	"	17·83	—	32·69	
" "	"	9·57	—	32·93	
" "	"	4·96	—	32·93	
Strontium chloride	SrCl ₂	32·06	—	35·02	
" "	"	18·44	—	35·23	
" "	"	9·71	—	35·29	
Barium chloride	BaCl ₂	24·64	—	38·91	
" "	"	12·36	—	39·21	
" "	"	6·38	—	39·24	
Cobalt chloride	CoCl ₂	27·86	32·71	32·97	
" "	"	17·49	32·84	33·12	
" "	"	9·47	32·77	32·99	
" "	"	4·97	32·86	33·53	
Copper chloride	CuCl ₂	36·59	—	33·73	
" "	"	6·85	—	33·18	
" " 2nd spec.	"	42·45	—	33·82	34·99
" " "	"	39·20	—	33·66	34·84
" " "	"	23·30	—	33·60	34·55
" " "	"	11·60	33·17	33·32	34·50
" " "	"	6·08	32·76	33·00	34·44
Ferric chloride	FeCl ₃	40·66	—	53·95	
" "	"	5·19	—	52·31	
" " 2nd spec.	"	44·80	53·32	54·63	
" " "	"	41·30	53·07	54·32	
" " "	"	35·11	52·70	53·17	
" " "	"	20·50	52·08	52·94	
" " "	"	10·95	51·84	52·65	
" " "	"	5·72	51·68	52·55	
Gold chloride	AuCl ₃	61·70	59·27	60·35	
" "	"	7·57	56·97	58·50	
Platinum chloride	PtCl ₄	39·40	78·22	79·81	
" "	"	21·68	77·57	79·03	
" "	"	8·10	77·20	78·39	
Gold sodium chloride	AuCl ₃ .NaCl	52·90	74·33	75·63	
" "	"	33·10	74·36	75·70	
" "	"	11·63	74·90	75·99	79·43
" "	"	6·10	74·29	75·77	79·57
Hydrobromic acid	HBr	44·82	—	20·61	
" "	"	26·60	—	20·78	

TABLE I (continued).

Substance.	Formula.	Per-centage.	R _a .	R _D .	R _S .
Hydrobromic acid	HBr	14.72	—	20.89	
" "	"	7.74	—	21.04	
" "	"	3.84	—	21.10	
Potassium bromide	KBr	38.20	—	25.38	
" "	"	8.49	—	25.46	
Gold bromide	AuBr ₃	11.69	82.32		
" "	"	6.14	83.62		
Hydriodic acid	HI	65.30	—	32.15	
" "	"	22.96	—	32.34	
" "	"	12.50	—	32.38	
" "	"	6.56	—	32.48	
" " 2nd spec.	"	55.55	31.68	32.13	
" " " "	"	43.64	31.85	32.04	
" " " "	"	26.00	31.63	32.20	
" " " "	"	14.36	31.88	32.35	
" " " "	"	7.57	31.75	32.35	
Potassium iodide	KI	43.67	—	36.62	
" "	"	7.25	—	36.55	
" "	"	3.74	—	36.19	
" " 2nd spec.	"	57.17	36.02	36.52	37.74
" " " "	"	35.84	36.07	36.54	37.70
Ammonium iodide	NH ₄ I	53.80	—	40.22	
" "	"	8.92	—	40.29	
" "	"	59.50	39.69	40.22	41.63
" "	"	33.95	39.35	40.09	41.53
" "	"	18.86	39.27	39.90	41.27
" "	"	10.00	38.93	39.74	41.09
Nitric acid	HNO ₃	88.00	16.27	16.37	16.67
" "	"	53.60	16.80	17.01	17.36
" "	"	21.37	17.34	17.49	17.94
" "	"	17.80	17.27	17.41	17.83
" "	"	6.30	17.27	17.41	17.91
" " 2nd spec.	"	40.98	17.08	17.24	17.65
" " " "	"	32.08	17.17	17.33	17.76
" " " "	"	24.35	17.39	17.51	17.95
" " " "	"	6.00	17.32	17.51	17.97
Lithium nitrate	LiNO ₃	42.18	17.73	17.91	18.29
" "	"	39.77	17.79	17.91	18.31
" "	"	23.50	17.87	17.99	18.40
" "	"	10.50	17.73	17.81	18.24
" "	"	5.12	17.76	17.72	18.23
" " 2nd spec.	"	60.40	17.77	17.91	18.29
" " " "	"	52.40	17.95	18.07	18.47
" " " "	"	27.53	17.76	17.93	18.43
" " " "	"	14.90	17.72	17.86	18.31
" " " "	"	7.77	17.52	17.61	17.95
Potassium nitrate	KNO ₃	17.55	—	22.26	
" "	"	9.24	—	22.29	
" "	"	4.76	—	22.24	
Silver nitrate	AgNO ₃	44.51	—	27.11	
" "	"	5.88	—	26.60	
" " 2nd spec.	"	62.30	27.113	27.36	28.04
" " " "	"	31.21	26.87	27.07	27.75
" " " "	"	14.80	26.64	26.89	27.55
" " " "	"	7.90	26.38	26.44	27.45

TABLE I (continued).

Substance.	Formula.	Per-centage.	R _a .	R _D .	R _β .
Barium nitrate	Ba(NO ₃) ₂	9·87	44·53	44·78	45·72
" " 	" 	6·77	44·55	44·61	45·33
" " 	" 	4·24	44·45	44·68	45·67
Lead nitrate	Pb(NO ₃) ₂	35·94	—	54·12	
" " 	" 	7·04	—	53·32	
" " 2nd spec....	" 	34·60	53·14	53·67	55·24
" " " 	" 	20·23	52·88	53·50	54·93
" " " 	" 	11·07	52·17	53·12	54·35
Sulphuric acid	H ₂ SO ₄	23·00	22·94	23·06	23·36
" " 	" 	15·98	22·82	22·97	23·22
" " 	" 	10·10	22·79	22·84	23·15
" " 	" 	5·25	22·74	22·76	23·28
" " 	" 	3·25	23·16	23·10	23·64
" " 2nd spec...	" 	97·50	22·34	22·44	22·68
" " " 	" 	85·25	22·42	22·54	22·80
" " " 	" 	83·00	22·53	22·65	22·92
" " " 	" 	37·20	22·73	22·88	23·20
" " " 	" 	21·00	22·86	22·96	23·07
" " " 	" 	11·30	22·96	22·94	23·22
" " " 	" 	5·80	23·00	22·75	22·92
" " 3rd spec...	" 	98·00	22·32	22·47	22·66
" " " 	" 	89·75	22·44	22·55	22·80
" " " 	" 	84·70	22·46	22·59	22·88
" " " 	" 	81·80	22·48	22·62	22·91
" " " 	" 	80·05	22·49	22·61	22·87
" " " 	" 	77·25	22·49	22·60	22·85
" " " 	" 	71·90	22·56	22·66	22·92
" " " 	" 	63·20	22·51	22·65	22·94
Sodium sulphate	Na ₂ SO ₄	30·40	26·54	26·63	26·99
" " 	" 	10·93	26·16	25·93	26·30
" " 	" 	5·75	26·54	25·84	26·04
Potassium sulphate	K ₂ SO ₄	10·44	—	32·41	
" " 	" 	5·43	—	32·55	
Rubidium sulphate	Rb ₂ SO ₄	30·84	38·39	38·58	39·06
" " 	" 	17·53	38·42	38·58	38·98
" " 	" 	9·42	38·53	38·47	39·22
Cæsium sulphate	Cs ₂ SO ₄	58·26	47·53	47·78	48·36
" " 	" 	27·08	47·42	47·93	48·51
" " 	" 	15·24	46·99	47·60	48·47
Magnesium sulphate	MgSO ₄	25·76	24·00	—	24·32
" " 	" 	18·20	24·10	—	24·36
" " 	" 	11·47	24·19	—	24·43
Zinc sulphate.....	ZnSO ₄	32·50	—	26·32	
" " 	" 	8·30	—	27·02	
Potassium zinc sulphate...	K ₂ SO ₄ , ZnSO ₄ , 6H ₂ O	11·94	95·77	95·94	98·08
" " " 	" 	8·41	95·95	96·03	98·01
Ammonium zinc sulphate..	(NH ₄) ₂ SO ₄ , ZnSO ₄ , 6H ₂ O	11·86	102·47	103·10	104·23
" " " 	" 	6·13	102·26	103·46	105·60
Sodium chlorate.....	NaClO ₃	47·10	21·79	22·00	22·15
" " 	" 	27·60	22·33	21·95	22·33
" " 	" 	6·58	22·11	21·87	22·42

ADDENDA.

Substance.	Formula.	Per-centage.	R _A .	R _F .	R _H .
Lithium chloride	LiCl.....	39·52	14·51	15·04	15·49
" "	"	25·87	14·89	15·43	15·96
" "	"	14·53	15·09	15·70	16·20
" "	"	10·03	15·45	16·00	16·50
Hydrobromic acid	HBr.....	44·50	20·07	—	22·19
" "	"	7·80	20·64	—	22·43

Solids and their Saturated Solutions.

As a salt in the solid condition is presumably a more simple body than when it is dissolved in water, and after it may have suffered dissociation or combination with the solvent or its elements, it is most logical to commence by considering whether any change in specific refraction is effected by the act of solution.

Unfortunately there exist very few observations of the refraction of solid salts which are available for our purpose. Nearly all crystallised salts have more than one index of refraction. Again, few observers have given the sp. gr. of the actual specimen of salt from which they have determined its optical properties. Nevertheless we have been able to find determinations of 14 solid substances of simple refraction which answer our purpose, and of 8 other salts which have more than one index of refraction, but so near together that the mean of the two or three indices may be considered as very close to the refraction which the substance would exhibit if it had only one index.

The following table gives these substances in the first column, then the spectrum line observed, after that the molecular refraction of the substance, first as a solid and then in a saturated or nearly saturated solution. The next two columns show the actual difference of the two values and the percentage change respectively, the + sign meaning an increase on solution, the — sign a decrease. In the case of more than one index of refraction, the mean is taken. The final columns give the initials of the observers. Appendix II (p. 867) will explain these and give references.

The list commences with Sir Isaac Newton, whose work included the density as well as the refraction of substances. It will be seen that in drawing up this table, we are greatly indebted to the work of Messrs. Topsoe and Christiansen on crystals. We have also to thank Mons. L. Perrot and Mr. Tutton for supplying us with specimens for solution.

TABLE II.

Salt.	Line.	Molecular refraction.		Change on solution.		Observers.	
		Solid.	Solution.	Actual.	Percentage.	Solid.	Solution.
Sodium chloride	Red	14·88	15·68	+0·8	+5·37	N	H
„	A	14·75	15·56	+0·81	+5·46	Bl	v.d.W.
„	„	14·56	15·4	+0·84	+5·77	G	G
„	a	14·63	15·7	+1·07	+7·31	Bd	Bd
„	D	14·78	15·80	+1·02	+6·97	Gr	H
„	„	14·78	15·76	+0·98	+6·63	Hg	Hl
Potassium chloride	„	18·72	18·58	-0·14	-0·52	Rub	H
Ammonium chloride	a	22·35	22·35	0·0	0·0	Gr	„
Potassium bromide	D	24·85	25·38	+0·53	+2·1	T & C	„
Potassium iodide	a	35·84	36·0	+0·16	+0·44	„	D
„	D	36·29	36·52	+0·23	+0·63	„	H
Ammonium iodide	„	40·81	40·22	-0·59	-1·44	„	„
Sodium chlorate	F	22·52	22·15	-0·37	-1·65	Dus	„
Sodium alum	D	241·0	241·2	+0·2	+0·08	S	G
Ammonium alum	„	255·2	256·8	+1·6	+0·63	S	„
Barium nitrate	„	45·8	44·78	-1·02	-2·22	T & C	H
Lead nitrate	„	57·26	54·12	-3·14	-5·49	„	„
Sodium metaphosphate ..	A*	19·0	19·48	+0·48	+2·53	Bd	Bd
Borax (fused)	A*	42·80	42·83	+0·03	+0·07	„	„
Boric acid	a	15·20	14·77	-0·43	-2·8	„	„
<i>Two indices.</i>							
Silver nitrate	D	{ 28·45 30·76 }	27·11	-2·47	-8·4	Br	H
<i>Three indices.</i>							
Potassium sulphate	a	{ 32·22 32·14 32·39 32·45 }	32·15	-0·1	-0·31	Tut	K
„	D	{ 32·77 32·54 37·83 37·74 37·75 }	32·41	+0·18	+0·55	T & C	H
Rubidium sulphate	a	{ 48·05 47·89 47·50 62·54 66·46 65·78 }	38·39	+0·62	+1·6	Tut	„
Cæsium sulphate	„	{ 65·00 68·82 68·30 65·32 69·16 68·66 }	47·57	-0·24	-0·5	„	„
Magnesium sulphate	„	{ 94·06 95·27 97·84 101·22 102·14 103·41 }	65·87	+0·94	+1·4	T & C	„
Zinc sulphate	„	{ 65·32 69·16 68·66 94·06 95·27 97·84 }	68·8	+1·43	+2·1	„	K
„	D	{ 101·22 102·14 103·41 }	69·1	+1·39	+2·04	„	G
Potassium zinc sulphate ..	„	{ 101·22 102·14 103·41 }	95·94	+0·22	+0·23	Perr	H
Ammonium zinc sulphate	„	{ 101·22 102·14 103·41 }	103·47	+1·21	+1·19	„	„

* This is the A of Cauchy's formula.

From the above table we may at once draw the following conclusions.

1. That in every instance the molecular refraction of the salt is not very different in the solid and dissolved conditions.

2. That in the majority of cases there is a difference which can scarcely be attributed to errors of observation. The greatest difference occurs in the case of sodium chloride, and of lead and silver nitrate, whilst in the case of the alums, potassium iodide, and perhaps one or two other substances, the difference is so small that it may be purely accidental.

3. That the change of refraction of a salt when dissolved is sometimes in the direction of increase, and at other times in the direction of decrease. Thus nearly all the haloid salts of the metals give an increase on solution; whilst the three nitrates show the opposite effect.

4. As to the salts which exhibit three indices of refraction, the data are scarcely sufficient to allow of our drawing any deductions beyond the general one, that there is no great departure from the mean of these indices when the crystals are dissolved.

5. Six of the salts examined contain water of crystallisation. As they give nearly the same molecular refraction in the solid and dissolved condition, it is evident that there can be little or no difference produced by the liquefaction of the water of crystallisation.

Other deductions from this table must be reserved till after we have considered the effect of diluting the saturated solutions.

Anhydrous Liquids and their Solutions.

Besides the solids, we have eight substances of which the refraction is known when they are in a liquid condition. They are all acids. There are the three halogen acids, HCl, HBr, and HI, all of which exist as a gas at ordinary temperatures; but they can be liquefied by pressure and cold, and the refraction of the liquids so produced has been determined by Bleekrode. There is HCN, which is a liquid at ordinary temperatures; and there are nitric, sulphuric, formic, acetic, and propionic acids; these last five are miscible with water in all proportions.

The following table is on the lines of Table II, with the addition of another column for the gas in the case of the halogen acids. It must also be explained that whereas the refraction equivalent for the solution in the case of the first three entries represents the effect of the minimum amount of water required to convert the anhydrous acid into a solution, in the subsequent cases, where the acid is perfectly miscible with water, the point of comparison is taken more arbitrarily.

TABLE III.

Substance.	Line.	Liquid.	Gas.	Solution.	Actual change.	Observer.		
		R.	R.	R.		Liquid.	Gas.	Solution.
Hydrochloric acid . . .	D	10·98	9·959	14·14	+4·16	Blk	Mas	H
Hydrobromic acid . . .	"	16·15	12·745	20·77	+4·62	"	"	G
Hydriodic acid	"	26·28	20·25	32·15	+5·87	"	"	H
Hydrocyanic acid . . .	"	10·19	9·732	9·85	-0·34	B & B	"	B & B
Nitric acid	A	16·22*	—	16·39	+0·17	G	—	G
Sulphuric acid	a	22·34†	—	22·53	+0·19	H	—	H
Formic acid	"	13·91	—	14·07	+0·16	Lan	—	Lan
Acetic acid	"	21·13	—	21·30	+0·17	"	—	"
Propionic acid	"	28·62	—	28·79	+0·17	"	—	"

* 98·7 per cent.

† 97·5 per cent.

A glance at this table is sufficient to show that, in the case of hydrogen chloride, hydrogen bromide, and hydrogen iodide, we have a very great increase on solution, far greater, in fact, than in any of the cases where solids were dissolved; it amounts to some 26 per cent. if we compare it with the liquid, and very much more if compared with the gas. On the other hand, in the case of hydrogen cyanide, nitric acid, and sulphuric acid, and especially in the case of the three organic acids, we have no sudden transition from the liquid to the dissolved condition.

Varying Strengths of Solution.

We now come to consider the effect of increasing the amount of water in which the salt or acid is dissolved. For this we have the very large amount of evidence contained in Appendix I and Table I. To bring this into one general view, we have drawn up the following table. The whole evidence cannot be tabulated, so we have included only that derived from the weakest and strongest solutions of the same salt, and for this purpose few solutions of less than 5 per cent. have been admitted, for reasons already explained, except in the case of Kohlrausch and Hallwach's determinations.

As the comparison on which we are now entering deals with figures whose variations are always near to the limits of experimental error, we think it well to indicate what we believe to be the accuracy of our more recent figures. The index may be considered correct to one in the fourth decimal place, so taking $\mu = 1·4000$, the error in the determination of $\mu - 1$, may be somewhere about 1 in 4000. The density was generally determined with a possible

error of 1 in 8000, or including a possible want of coincidence between the temperatures at which the index and the density were determined, 1 in 6000. Errors in the determination of the strength of solution will depend very much on the nature of the salt itself and the methods of its analysis; but we consider that it is usually not more than 0.1 per cent. This is unimportant where the specific refraction of the salt is very nearly the same as that of water, but tells where the specific refraction varies greatly in either direction. The value taken for water also affects the result most when the specific refraction is very different. It must be remembered, too, that these different sources of error may either be added together, or may tend to neutralise one another, in any given observation. The aggregate error, of course, falls entirely upon the determination of the salt itself, and when that constitutes only 5 per cent. of the solution, it may be taken at possibly somewhat less than 1 in 100 in the more recent work marked H. In strong solutions, the total error is, of course, less. But in many cases this possible error is diminished by our having taken more than one series of observations on the same substance, and often with different apparatus.

The table is constructed in the following manner. Column 1 contains the name of the substance. Column 2, the formula. Column 3, the line of the spectrum observed. Column 4 gives the highest and lowest percentages of salt or acid, p_1 and p_2 , contained in the solutions that have been employed. Column 5 gives the corresponding molecular refractions R_1 and R_2 . Column 6 gives the average change in molecular refraction for 1 per cent. change in strength of solution, $\frac{R_2 - R_1}{p_1 - p_2}$. The signs + or - indicate whether the change on dilution is in the direction of increase or decrease respectively. It was thought undesirable to extend these figures beyond the third decimal place, and when the number is less than 0.005, and thus clearly within the limits of experimental error, we have not entered it, but simply indicated the tendency. In judging also of their value, it must be remembered that no account is taken of any intermediate observations; and that the range of strength employed by different observers, or by the same observer at different times, often varies greatly. This is especially the case with the observations of Kohlrausch and Hallwachs on very weak solutions. These really show scarcely any change, but on account of the short percentage-range in strength, appear to show more change than stronger solutions do. We have therefore put the sign only. The last column gives the initials of the observer.

TABLE IV.

Substance.	Formula.	Line.	Change in strength, p_1 to p_2 .	Change in molecular refraction, R_1 to R_2 .	Average rate of change, $\frac{R_2 - R_1}{p_1 - p_2}$.	Observer.
Hydrochloric acid...	HCl.....	F	36.09—5.13	14.54—15.12	+0.019	G
" " "	" " " "	"	21.1—7.6	14.93—15.08	+0.011	H
" " "	" " " "	D	30.1—6.87	14.29—14.55	+0.011	"
" " "	" " " "	"	38.93—5.23	14.14—14.58	+0.013	"
" " "	" " " "	"	1.20—0.025	14.44—14.57	+	Kl & Hl
" " "	" " " "	"	24.36—7.45	13.95—14.47	-0.03	Le Bl
Lithium chloride...	LiCl.....	Red	40.0—24.5	14.42—14.76	+0.022	Kr & Br
" " "	" " " "	C	48.5—6.93	14.23—14.99	+0.018	H
" " "	" " " "	D	43.4—5.1	14.47—15.07	+0.016	"
" " "	" " " "	a	11.72—5.84	14.83—14.82	—	Weg
Sodium chloride...	NaCl.....	A	23.2—8.7	15.33—15.30	—	G
" " "	" " " "	"	26.58—8.65	15.56—15.47	-0.005	v.d.W.
" " "	" " " "	C	26.41—8.32	15.68—15.84	+0.0088	H
" " "	" " " "	D	25.80—4.61	15.80—15.94	+0.0066	"
" " "	" " " "	"	14.0—0.72	15.76—15.84	+0.006	Kl & Hl
" " "	" " " "	"	1.44—0.03	15.79—15.79	0	"
" " "	" " " "	a	25.0—1.0	15.70—15.82	+0.005	Sch
" " "	" " " "	D	24.13—4.79	15.72—15.80	+	Le Bl
" " "	" " " "	a	24.73—7.99	15.70—15.76	+	Weg
Potassium chloride...	KCl.....	A	24.1—12.1	18.70—18.60	-0.008	G
" " "	" " " "	D	23.0—6.16	18.58—18.48	-0.006	H
" " "	" " " "	a	9.92—4.99	18.97—18.95	—	Weg
Rubidium " "	RbCl.....	D	28.81—3.94	22.26—22.30	+0.0016	H
Ammonium chloride	NH ₄ Cl....	A	24.83—11.79	22.19—22.14	—	v.d.W.
" " "	" " " "	"	25.64—5.57	22.35—22.70	+0.017	H
Magnesium " "	MgCl ₂	D	33.92—6.89	29.02—29.24	+0.008	"
Calcium chloride...	CaCl ₂	Red	40.4—24.75	31.51—32.01	+0.032	Kr & Br
" " "	" " " "	A	40.64—16.75	31.89—32.06	+0.007	v.d.W.
" " "	" " " "	D	39.55—4.96	32.35—32.93	+0.017	H
Strontium chloride...	SrCl ₂	Red	32.00—19.93	34.49—34.46	+0.0025	Kr & Br
" " "	" " " "	D	32.06—9.71	35.02—35.29	+0.012	H
Barium chloride...	BaCl ₂	"	24.64—6.38	38.91—39.24	+0.017	"
Cobalt " "	CoCl ₂	a	29.86—4.97	32.71—32.86	+0.006	"
Copper " "	CuCl ₂	D	36.59—6.85	33.73—33.18	-0.018	"
" " "	" " " "	"	42.45—6.08	33.82—33.00	-0.022	"
Zinc chloride...	ZnCl ₂	a	71.8—35.9	31.32—31.56	+0.007	Wüll
" " "	" " " "	A	38.98—23.0	30.59—31.03	+0.028	v.d.W.
" " "	" " " "	"	46.1—35.3	30.52—30.63	+0.010	G
Cadmium chloride...	CdCl ₂	"	57.52—14.76	36.09—36.14	+	de M
Ferric chloride...	FeCl ₃	a	40.66—5.19	53.95—52.31	-0.049	H
" " "	" " " "	a	44.80—5.72	53.32—51.68	-0.042	"
Gold chloride...	AuCl ₃	D	61.7—7.57	60.35—58.5	-0.034	"
Platinum chloride...	PtCl ₄	"	39.4—8.1	79.81—78.39	-0.045	"
Gold sodium chloride	AuCl ₃ , NaCl	"	52.9—6.1	75.63—75.77	+	"
Hydrobromic acid...	HBr.....	F	65.59—15.47	20.80—21.83	+0.020	G
" " "	" " " "	D	44.82—7.74	20.61—21.04	+0.012	H
" " "	" " " "	A	44.5—7.85	20.10—20.64	+0.0146	G
Lithium bromide...	LiBr.....	a	9.28—4.02	21.05—20.9	-0.03	Weg
Sodium " "	NaBr.....	Red	45.2—28.87	22.09—22.27	+0.011	Kr & Br
" " "	" " " "	a	31.02—4.95	21.83—21.89	+	Weg
Potassium bromide...	KBr.....	"	37.7—23.2	25.6—25.53	-0.005	Kr & Br

TABLE IV (continued).

Substance.	Formula.	Line.	Change in strength, p_1 to p_2 .	Change in molecular refraction, R_1 to R_2 .	Average rate of change, $\frac{R_2 - R_1}{p_1 - p_2}$	Observer.
Potassium bromide ..	KBr.....	D	38·2 — 8·49	25·38—25·46	+	H
" " " "	" " " "	a	19·82— 5·01	25·17—25·21	+	Weg
Calcium bromide....	CaBr ₂	Red	55·9 —38·9	44·01—44·78	+0·045	Kr & Br
Strontium bromide..	SrBr ₂	"	48·56—32·2	47·29—47·21	-0·005	"
Barium bromide	BaBr ₂	"	50·50—33·60	53·07—53·04	-	"
Cadmium bromide....	CdBr ₂	D	33·29—11·98	49·37—49·75	+0·018	de M
Gold bromide.....	AuBr ₃	a	11·69— 6·14	82·32—83·62	+0·240	H
Hydriodic acid.....	HI.....	D	65·3 — 6·56	32·15—32·48	+0·006	"
" " " "	" " " "	"	55·55— 7·57	32·13—32·35	+0·005	"
Lithium iodide.....	LiI.....	a	10·54— 3·08	31·90—31·88	-	Weg
Potassium iodide....	KI.....	Red	55·05—37·90	36·26—36·48	+0·013	Kr & Br
" " " "	" " " "	a	55·12—18·70	36·06—35·61	-0·010	Dam
" " " "	" " " "	D	43·67— 7·25	36·62—36·55	-	H
" " " "	" " " "	"	57·17—35·84	36·52—36·54	+	"
" " " "	" " " "	a	20·04— 5·01	36·17—36·29	+0·008	Weg
Ammonium " " "	NH ₄ I.....	D	53·81— 8·92	40·22—40·29	+	H
" " " "	" " " "	"	59·5 —10·0	40·22—39·74	-0·01	"
Cadmium iodide	CdI ₂	"	31·12— 9·56	72·03—70·47	-0·07	de M
Sodium iodide	NaI.....	a	14·70— 6·25	32·85—32·93	+0·01	Weg
Sulphuric acid.....	H ₂ SO ₄	C	94·3 —17·05	22·97—23·80	+0·011	Hd & Ws
" " " "	" " " "	"	94·72—23·29	22·36—22·52	+	v.d.W.
" " " "	" " " "	a	23·0 — 5·25	22·94—22·74	-0·011	H
" " " "	" " " "	"	97·5 — 5·8	22·34—23·0	+0·007	"
" " " "	" " " "	"	98·0 —63·2	22·32—22·51	+0·005	"
" " " "	" " " "	D	94·11— 4·78	22·23—22·82	+0·006	Le Bl
" " " "	" " " "	"	2·35— 0·050	22·9 —23·2	+	Kl & Hl
Sodium sulphate	Na ₂ SO ₄	A	10·51— 6·8	26·20—26·14	-0·016	v.d.W.
" " " "	" " " "	"	14·10— 7·19	24·32—23·88	-0·064	F
" " " "	" " " "	a	30·4 — 5·75	26·54—25·54	-0·040	H
" " " "	" " " "	D	25·51— 4·76	26·30—26·23	-	Le Bl
Potassium sulphate..	K ₂ SO ₄	"	10·44— 5·43	32·41—32·55	+0·024	H
Magnesium " " "	MgSO ₄	a	25·76—11·47	24·00—24·19	+0·013	"
" " " "	" " " "	D	1·47— 0·03	24·14—24·26	+	Kl & Hl
Zinc sulphate	ZnSO ₄	"	32·5 — 8·3	26·32—27·02	+0·029	H
" " " "	" " " "	"	1·58— 0·033	27·10—27·08	-	Kl & Hl
Sodium chlorate.....	NaClO ₃	a	47·10— 6·58	21·79—22·11	+0·008	H
Nitric acid	HNO ₃	A	98·7 —43·1	16·22—16·81	+0·011	G
" " " "	" " " "	a	88·0 — 6·3	16·27—17·27	+0·012	H
" " " "	" " " "	"	41·0 — 6·0	17·08—17·32	+0·007	"
" " " "	" " " "	D	69·18—14·09	16·64—17·55	+0·015	Le Bl
Lithium nitrate.....	LiNO ₃	a	42·18— 5·12	17·73—17·76	+	H
" " " "	" " " "	"	60·4 — 7·77	17·77—17·52	-0·005	"
Sodium " " "	NaNO ₃	A	44·35—16·86	18·53—18·53	0	v.d.W.
" " " "	" " " "	"	42·9 —21·23	18·78—18·74	-	F
Potassium nitrate...	KNO ₃	D	17·55— 4·76	22·26—22·24	-	H
Cadmium " " "	Cd(NO ₃) ₂ ...	"	54·03— 8·68	30·86—32·03	+0·026	de M
Silver nitrate	AgNO ₃	a	62·3 — 7·9	27·11—26·38	-0·013	H
" " " "	" " " "	D	44·5 — 5·88	27·11—26·6	-0·013	"
" " " "	" " " "	A	57·87—15·82	27·47—26·32	-0·028	F
" " " "	" " " "	a	21·3 —13·51	27·23—27·06	-0·021	Kan

TABLE IV (continued).

Substance.	Formula.	Line.	Change in strength, p_1 to p_2 .	Change in molecular refraction, R_1 to R_2 .	Average rate of change, $\frac{R_2 - R_1}{p_1 - p_2}$.	Observer.
Barium nitrate.....	Ba(NO ₃) ₂ ..	α	9·87—4·24	44·53—44·45	-0·017	H
Lead nitrate.....	Pb(NO ₃) ₂ ..	A	31·65—14·27	52·43—51·21	-0·070	F
" "	"	D	35·94—7·04	54·12—53·32	-0·027	H
" "	"	"	34·6—11·07	53·67—53·12	-0·023	"
Mercurous nitrate..	HgNO ₃	α	21·22—13·86	35·87—36·11	+0·033	Ghira
Phosphorous acid....	H ₃ PO ₃	D	73·69—30·66	21·29—22·09	+0·019	Zec
Sodium hydrate.....	NaHO	A	34·74—11·45	9·34—9·31	-	v.d.W.
Ammonia	NH ₃	"	34·80—13·40	8·76—9·03	+0·012	G
Sodium carbonate...	Na ₂ CO ₃	"	16·30—9·32	21·33—21·95	+0·089	"
" "	"	α	14·25—5·93	21·84—22·22	+0·046	H
" "	"	D	2·25—0·095	22·56—22·72	+	Kl & Hl
Hydrocyanic acid ...	HCN	"	100·0—33·33	10·19—10·21	+	B & B
Pot. selenocyanate...	KSeCN	B	43·5—32·8	41·83—42·31	+0·045	Zp.
Selenic acid	H ₂ SeO ₄	"	41·8—27·3	29·79—29·39	-0·027	"
Selenious acid	H ₂ SeO ₃	"	30·6—23·0	26·98—26·84	-0·018	"
Formic acid	H ₂ CO ₂	α	83·64—63·01	13·97—14·07	+0·005	Lan
" "	"	D	29·06—18·69	14·02—14·00	-	Le Bl
Acetic "	H ₄ C ₂ O ₂	"	100·0—20·65	21·13—21·33	+	Lan
" "	"	"	100·0—10·81	21·14—21·39	+	Dam
" "	"	"	5·2—0·057	21·45—21·45	0	Kl & Hl
" "	"	"	100·0—18·19	21·26—21·43	+	Le Bl
Propionic acid	H ₆ C ₃ O ₂	α	89·16—67·27	28·71—28·79	+	Lan
Butyric acid	H ₈ C ₄ O ₂	"	100·0—47·85	36·22—36·40	+	"
Trichloroacetic acid ..	HCl ₃ C ₂ O ₂ ..	D	30·11—14·13	47·66—47·72	+	Le Bl
Sodium formate.....	NaHCO ₂	A	44·99—41·39	16·60—16·63	+0·008	G
" "	"	D	8·72—5·58	17·07—17·09	+0·006	Le Bl
" acetate	NaH ₃ C ₂ O ₂ ..	"	45·89—5·41	24·48—24·71	+0·005	"

What are the conclusions to be drawn from this table?

1. It clearly and fully substantiates the old conclusion of one of the authors (Gladstone), that the molecular refraction of a dissolved salt or acid is the same, or nearly the same, whatever be the proportion of water.

2. It shows that differences unquestionably do exist in many instances, but to a smaller extent than between solids and their solutions. To illustrate this, we may take the first three substances in the list. Of hydrochloric acid, we have an experiment showing the change of molecular refraction from 14·54 to 15·12, or 4 per cent.; which is certainly far beyond the limits of experimental error. But this does not stand alone. It is supported by four experiments, made by two other observers with different apparatus, which give nearly the same ratio of refraction change, and always in the same direction, namely, that of increase. Moreover, an examination of the

whole data in Appendix I and Table I (p. 835) will make it evident that there is a gradual and fairly even progress from the lower to the higher figures as the strength of the solution is reduced. A similar deduction may be made from the observations on lithium chloride. With sodium chloride it is somewhat different; no series shows any very marked change, but the cumulative evidence leads distinctly to the conclusion that the sodium chloride is affected by dilution, in the same way as hydrogen and lithium chlorides, though not to the same extent.

3. The table shows not merely that in some cases at least there is a change on dilution, but that it has a chemical significance. This will be shown more fully in a subsequent section.

On comparing the conclusions in the two previous sections, it will be seen at once that there is a close coincidence, and that the effect of additional amounts of water is merely a continuation of the effect of water in first dissolving the salt or acid.

In both cases, we find that certain salts or acids exhibit a decided change, while the majority of them are not very clearly affected; those that show a marked increase in the one table, show a marked increase in the other, and *vice versâ*, and they appear in the same order.

This will become evident on a detailed examination of the tables, but will be better shown by the following diagrammatic arrangement. As, however, the molecular refraction in these previous tables involves the molecular weight, and as that is not of advantage for our present purpose, we have drawn out the results graphically upon the basis of the specific refractive energy of the salts instead of their molecular refraction, that is $\frac{\mu - 1}{d}$ instead of $\frac{\mu - 1}{d}P$. This has also the additional advantage that it is possible to bring our results together within more reasonable limits.

Another important change has also been made. Instead of plotting the percentage of salt in solution, we have transformed this into the weight of water for one part of the salt in each solution, and thus, the amount of salt being preserved uniform, we can see more clearly what is the actual effect on it of varying amounts of water.

In the diagrams, the ordinates represent the specific refractive energy of the salts or acids whether solid, liquid, or in saturated or weaker solutions. The abscissæ represent the proportionate amount of water, and the first that is plotted after zero indicates the specific refractive energy of the substance in saturated or nearly saturated solution. This is joined to the refractive energy of the anhydrous compound, but it must be borne in mind that the dotted lines are not intended to represent any continuous change in refrac-

DIAGRAM I.

tion, but merely to connect the specific refractive energy of the solid salt with that of the same salt when it is dissolved in a minimum of water; from the nature of the case, there is no intermediate term. The continuous lines afterwards do represent the action of more and more water in modifying the refraction as revealed by the experiments.

The whole of the results might have been put on one very long diagram, but they would have interfered with each other, and it was thought more convenient and more instructive to break it up into four shorter and simpler diagrams, according to the nature of the compounds.

Diagram I gives chlorides.

Diagram II gives bromides and iodides.

Diagram III gives nitric acid and nitrates, to which have been added two other salts of analogous composition.

Diagram IV gives a series of sulphates, single and double.

A few substances are omitted from these tables, generally on account of shortness of range.

These four diagrams agree in showing clearly that the greater portion of a refractive change takes place in the passage from the solid or liquid to the dissolved condition. Where, however, this is

DIAGRAM II.

DIAGRAM III.

considerable the change is continued, as more and more water is added, in the same direction, but decreasing in amount, until in very dilute solutions it approximates to uniformity, and appears in the diagram simply as a straight line. In the majority of cases, however, this change on passing from the saturated to the weak solution is small, and in many cases it is scarcely perceptible. In that case it may be considered within the limits of experimental error. In another aspect, however, the curves exhibit a remarkable contrast. Generally speaking, the diagrams of the halogen compounds show a series of refraction changes by water, in the direction of increase; very large in the upper part of the diagram, but very small in the lower part. The diagram of the nitrates shows a moderate increase in the acid itself, but a striking decrease with the salts of the heavy metals, whilst the diagram of the sulphates is notable for an almost entire absence of any marked refraction change all along the scale.

DIAGRAM IV.

If we study the diagrams more in detail, we observe the following facts.

Diagram I. *The Chlorides*—By far the greatest refraction change is with the hydrogen compound, and we are able to observe that superiority, both in the difference between the anhydrous compound and the dissolved acid, and in the subsequent effect of different amounts of water. With the lithium salt, we have not the means of observing the change between the solid and the dissolved condition, but we may note the sharp curvature produced by successive dilutions. With the sodium salt, on the contrary, what we see is

the great change on first dissolving, which of course cannot reveal itself as a curve, and which seems to have nearly exhausted the power of the salt to change in refraction through the further action of water. The potassium salt shows a very slight decrease, the rubidium is nearly constant. If we turn to the diatomic metals, the magnesium, calcium, strontium, and barium salts all show an increase on dilution, and so does cobalt. When, however, we turn to those salts in which more than two atoms of chlorine are joined with a metal, namely iron, gold and platinum, we have, on the contrary, a remarkable decrease of refraction on dilution.

Diagram II. *Bromides and Iodides*. These show a close analogy with the chlorides. The two hydrogen compounds show an action of water similar to that of hydrogen chloride, although not to so great an extent. The two potassium salts show an increase of specific refractive energy on passing from the solid to the dissolved condition, with no very perceptible change afterwards.

Diagram III. *Nitrates*.—Here again we find that the anhydrous acid when gradually mixed with water increases its refraction till it has combined with about four times its weight of water, after which it looks as though there were a slight decrease.

The lithium compound exhibits a similar kind of action, though to a much smaller extent. The sodium and potassium salts show little or no change through the continued action of water. The barium salt shows a decided decrease, and so do the lead and silver salts to a still greater extent.

Diagram IV. *The Sulphates*.—Hydrogen sulphate shows a close analogy to hydrogen nitrate, though to a smaller extent; a sudden rise when a little water is added to the anhydrous acid, a gradual curve upwards, and after that a slow decrease. The other sulphates generally show little, if any, change of refraction attributable to water, beyond the bringing of three indices of refraction into one, which is sometimes a little above and sometimes a little below the mean value of the three.

We have hitherto not referred to two striking exceptions, the cadmium and the ammonium salts. According to de Muijnck's experiments, both the chloride and bromide of cadmium show at first a decrease of refraction, and afterwards a rather rapid increase. The two curves are very similar in form, and unlike any other on the halogen diagrams. The cadmium nitrate and sulphate show a rapid increase in refraction on dilution, in opposition to other salts of the same acid radicles. As the ammonium chloride heads Diagram I with practically a horizontal line, it is in striking contrast with its neighbour, hydrogen chloride, which shows the greatest amount of change. Ammonium iodide is also at the top of Diagram II, followed

by hydrogen bromide and hydrogen iodide, and exhibiting a greater contrast, for it absolutely shows a decrease from both the initial and the subsequent action of water.

The following diagram, V, enables us to study the refraction change of acids in solution far better than we can in the separate diagrams, and to introduce observations on other acids.

DIAGRAM V.

From this diagram, we see clearly the enormous change of refraction due to the action of water on the halogen acids, hydrogen chloride being far the most affected, followed by hydrogen bromide and hydrogen iodide. The next in order is unquestionably nitric acid; sulphuric acid is much lower. At a considerable distance come the organic acids. The difference in these is strikingly shown in the diagram by the horizontal line for acetic acid, which crosses the rising curve of hydrogen chloride. Yet there is a certain resemblance in the form of these curves. They show a quick rise at the commencement, then a rather sharp bend, and finally a horizontal line. The difference is mainly in proportion; the rise in the case of acetic acid is only about one twenty-fifth part of what it is in hydrogen chloride. The acetic acid has attained its maximum when it has mixed with about 1 mol. of water; the inorganic acids require very much more.

Formic acid shows a curve quite similar to that of acetic acid, and the short curve of propionic acid indicates a close resemblance. The short line of trichloroacetic acid, is, as far as it extends, of the same form as that of acetic acid itself.

In the case of nitric, sulphuric, and acetic acids, there is, perhaps, a maximum, and then a slight descent.

Hydrofluoric acid has a specific refractive energy of only about 0.115, so that it could not be included in the present diagram. The portion of the curve hitherto examined does not show either rise or fall.

Effect of Change of Temperature.

We have already stated that any slight differences in the temperature of the solutions in Appendices I and II produces so small an effect that it may be taken as negligible.* Our principal experiments on this point were as follows. The figures in the last two columns are for the line α ; MR and $\overline{MR}$ give respectively the molecular refractions by the old and by the Lorentz formulæ.

The different values for the molecular refraction of water at the different temperatures were taken into account in calculating out the results. It is evident that there is not much difference in refraction produced by the rise of 55° , or thereabouts, of temperature, especially with the stronger solutions. What small change there is seems generally to be in the direction of a fall at the higher temperatures. It must also be borne in mind that the difficulty of determining the refractive index at a particular temperature is greatly increased when that temperature is so much above that of the room.

* Wüllner, long ago, practically showed this in his experiments on solutions of zinc chloride. Van d. Willigen also gives many observations on solutions at different temperatures.

Salt.	Per cent.	Temp.	M.R.	M.R.
Hydrochloric acid	21·1	23°·0	14·48	—
„ „	—	77°·0	14·29	—
„ „	7·6	22°·0	14·57	—
„ „	—	77°·0	14·22	—
Lithium chloride	48·5	48°·0	14·23	8·298
„ „	—	80°·0	14·25	8·261
„ „	39·8	28°·5	14·45	8·352
„ „	—	74°·2	14·48	8·376
„ „	26·8	20°·5	14·81	8·557
„ „	—	82°·5	14·84	8·572
„ „	19·09	20°·0	14·75	8·600
„ „	—	75°·0	14·65	8·545
„ „	12·74	21°·0	14·90	8·689
„ „	—	77°·6	14·76	8·619
„ „	6·93	24°·0	14·99	8·747
„ „	—	75°·5	14·76	8·594
Sodium chloride	26·41	21°·5	15·68	9·126
„ „	—	77°·0	15·72	9·198
„ „	8·32	22°·0	15·84	9·250
„ „	—	78°·0	15·47	9·067
Magnesium sulphate	21·85	22°·0	24·05	13·607
„ „	—	79°·0	23·98	13·587
„ „	7·9	23°·0	24·13	13·590
„ „	—	80°·5	24·05	13·535
Cobalt chloride	26·35	21°·0	33·20	18·989
„ „	—	60°·0	33·20	19·074
„ „	10·59	18°·0	32·29	18·398
„ „	—	73°·5	32·01	18·310

In connection with a possible change of refraction by change of temperature, the following experiment on solutions of sodium chloride at very low temperatures will be interesting. The columns speak for themselves. In determining the molecular refraction of the salt at the different temperatures, Damien's values for the refraction of water at those temperatures were taken.

Salt.	Per cent.	Temp.	M.R.
Sodium chloride	24·3	-6°·0	15·63
„ „	—	-5°·0	15·70
„ „	—	-2°·5	15·72
„ „	—	-0°·6	15·70
„ „	—	+8°·3	15·53
„ „	9·1	-3°·3	15·63
„ „	—	-2°·5	15·60
„ „	—	-0°·7	15·50
„ „	—	+0°·8	15·58
„ „	—	+2°·4	15·62
„ „	—	+5°·6	15·74
„ „	—	+9°·5	15·71

From these observations, it will be impossible to affirm that there is any variation in the refraction, either in the two different strengths or at the varying temperatures. There is also no indication of any particular change about zero or $+4^{\circ}$, the temperatures which have a special significance in the case of pure water.

Alternative Formulæ.

It may naturally occur to the reader that the small differences recorded in this paper may be due to the formula employed in the reduction of the experimental data, namely, $\frac{\mu - 1}{d}$; and that if the Lorenz formula $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ had been used instead, these differences might have become smaller or disappeared entirely.

Now, in cases where the refractive indices of the compounds compared differ widely, as in the comparison of gas with liquid, the two formulæ give very different relative results. But where the indices are nearly the same, as in the cases here examined, the two formulæ, though giving different absolute values, furnish very nearly the same relative results. We have occasionally thought it worth while to calculate out some of our data by the Lorenz formula, but have found that it did not affect the general conclusions. Instances of this are given in the preceding section on the effect of change of temperature.

The same remarks will apply to such modifications of this formula as have been suggested by Ketteler and others.

Analogies between Refraction Change and other Phenomena.

a. Refraction Change and Specific Refractive Energy.—The general relation is quite evident on a glance at the diagrams. In the upper part of the diagrams, where the specific refractive energy is greatest, there is the greatest increase on dilution. In the middle part, there is not much change, and in the lower part, the refraction decreases on dilution. There are exceptions to this, some of which will be afterwards considered.

The neutral zone between rising and falling change seems to be in about the same place with the chlorides, nitrates, and sulphates, say 20 to 24 on the scale of ordinates.

b. Refraction Change and Combining Proportion.—In 1870, it was pointed out that if those metals which form soluble salts be arranged in the order of their refractive energies, it will be seen that, with few exceptions, they are in the inverse order of their combining proportions—not their atomic weights, and that this “clearly points to

some connection between the power of a metallic element to saturate the affinities of other elements, and its power to retard the rays of light," *Phil. Trans.*, p. 27.

In a lecture at the Royal Institution in 1877, this observation was somewhat extended, and it was shown that in regard to the univalent metals hydrogen, lithium, sodium, potassium, rubidium, silver, cesium, and thallium, the specific refractive energy is, roughly speaking, inversely proportional to the square root of the combining proportion. The figures are not very exact, the specific refractive energy of sodium being too small.

Turning to the refraction change, we find it far the greatest with hydrogen, and in descending order come lithium, sodium, rubidium, potassium, and silver or cesium, nearly the same as that given above. These belong to the first column in Mendeléeff's arrangement.

If we turn to the second column, we find its members giving a refraction change which is considerable in calcium and in strontium and less in barium. In Mendeléeff's column 8, we have iron, gold, and platinum, each of which shows a decided fall.

In column 7 are contained the three halogens, chlorine, bromine, and iodine, while in our diagrams chlorine compounds show the greatest change, bromides showing somewhat more than the iodides.

Hence it appears that members of the same natural family of elements have special resemblances in regard to the property we are considering as well as in other respects.

This is further shown by the exceptional behaviour of ammonium chloride, which, although it stands at the top of Diagram I, and above hydrochloric acid, shows no change in refraction either on solution or dilution. It therefore is quite out of order with the chlorides of the univalent metals. But it must be remembered that ammonium is not a metal, although it plays the part of one.

c. Dispersion of Light.—It has been shown that variations in dispersion accompany variations in refraction, and it would seem not unreasonable to expect that if water should so modify a salt as to produce an increase or decrease in the refraction of one particular ray, it would produce a corresponding increase or decrease in the refraction of any other ray. If so, the change in specific dispersion,

$\frac{\mu_H - \mu_A}{d}$, should be proportional to the change in the specific refrac-

tive energy of A or H, or any other line in the spectrum. It was observed, however, as far back as 1887, that the dispersion equivalents of the chlorides, bromides, and iodides of potassium and sodium in solution were greater than what the dispersion of other salts of the same bases would seem to warrant; and in 1891 very

rapid advance in dispersion was clearly shown in regard to the halogen acids and nitric acid.

Our additional data afford some means of testing this, both on solid and liquid compounds as compared with the same substances in solution, as well as between different strengths of solution. It is evident, however, that to measure this change will require the best experiments and the widest range of lines observed in the spectrum. On the other hand, it may be remarked that the experimental errors are practically reduced to those which occur in measuring the two lines, as changes in strength of solution, density, or temperature are excluded.

In the following table, we give the molecular refraction and dispersion of two salts in the solid and the dissolved condition; sodium chloride, which shows the greatest rise on solution, and lead nitrate, which shows the greatest fall. In the case of sodium chloride, the molecular dispersion is reckoned for the A and H lines— $P \frac{\mu_H - \mu_A}{d}$; in the other case, we have only the data for the shorter range $P \frac{\mu_\beta - \mu_\alpha}{d}$.

	Sodium chloride.		Lead nitrate.	
	Mol. ref.	Mol. disp.	Mol. ref.	Mol. disp.
Solid	14·6	0·86	56·60	2·45
Saturated solution.....	15·6	1·13	53·14	2·10

In the case of sodium chloride, the increase in molecular dispersion between the solid salt and the salt in saturated solution is as much as 31 per cent., instead of the bare 7 per cent. shown by refraction.

In the case of lead nitrate, the decrease in the molecular dispersion is 14 per cent. instead of 6.

Our tables give little opportunity of judging of the change of dis-

Per cent. in solution.	Lithium chloride.		
	Mol. ref.	Mol. disp.	Ratio.
39·52	14·51	0·98	0·067
25·87	14·89	1·07	0·071
14·53	15·09	1·11	0·073
10·03	15·45	1·05	0·068

persion, as compared with the refraction change, at different degrees of dilution. The best instance is that series of lithium chloride in which the lines A and H are measured.

In this case, the dispersion seems to increase about *pari passu* with the refraction.

d. Magnetic Rotation.—It is well known that there is an analogy between the molecular refraction of a substance and its power of rotating the plane of polarized light. Now, as Dr. Perkin has determined the rotation of several acids and salts in aqueous solution at different strengths, we are able to test the question whether the analogy also holds good in this case.

In making this comparison, it must be borne in mind that Perkin gives his results for different percentages of the compound in solution, and it is for the molecular refraction that they are calculated out; hence his observations are comparable with our series as given in Table I, and Appendix I. The changes in molecular rotation have hitherto been found almost always larger in amount than the corresponding changes in refraction.

As to the halogen acids, Perkin shows that in the cases of hydrochloric, hydrobromic, and hydriodic acids, the molecular rotations found for the pure acids, first rise as the solution is diluted and then become practically stationary. It would appear, also, that the change is proportionally much greater with hydrochloric than with hydriodic acid, hydrobromic taking an intermediate position. All this agrees with what we find in the case of the molecular refraction of these acids in solution.

As to lithium chloride, Perkin remarks that aqueous solutions of this salt behave in a manner analogous to solutions of hydrochloric acid, and a comparison of the numbers given shows that the change is comparatively quite as great. Here, again, we have a close agreement.

In regard to sodium chloride, Perkin states that "in the presence of water, it does not increase in rotation to nearly the same extent as hydrochloric acid does." He shows, moreover, that the rotation of the salt when dissolved in water is much higher than when it is in the solid condition as rock salt. In both these respects, the refraction changes are of the same kind.

In the case of nitrates, on the contrary, there is an apparent discrepancy between the two phenomena. Nitric acid shows a very distinct decrease in rotation on the successive additions of water, whereas there is an increase in refraction, at all events till the strength is reduced to somewhere about 25 per cent. After this, the rotation is fairly constant.

With lithium nitrate, there is, at first, a decrease in rotation

against the slight increase in refraction, but, afterwards, a slight decrease in both.

In the case of sulphuric acid, there is a steady, though small, decrease in rotation on the continued addition of water; whereas, in the refraction, there is a moderate increase at first, and, afterwards, a tendency to decrease. Both properties remain much more uniform on continued dilution of the acid than in the case of the halogen compounds.

Formic, acetic, and propionic acids in solution show no change by the further addition of water, either in molecular rotation or refraction. Here, again, therefore, we have a remarkable similarity.

Taking a broad view of the above summary, it will be seen that there is some correspondence, both when a change does occur and when it is absent.

Bearing on the General Question of Refraction Equivalents.

The results arrived at during this investigation explain to a considerable extent the difficulties experienced by one of the authors (Gladstone) in deducing the refraction equivalents of metals and other elementary substances from solutions of salts containing them. At the same time they point out improvements in the method of arriving at such equivalents. In the 1869 paper, it is said of the tabulated differences between long series of salts, they "are sufficiently near to show that we are dealing with a reality, but they are sufficiently wide apart to show that we must rely upon the average of the numbers, and not on any single experiment, if we wish to get a refraction equivalent true to the first place of decimals. Unfortunately all experimental errors fall upon this residuary number." The refraction equivalents arrived at independently by Kanonnikoff for many of the same elements by means of solutions do not exhibit a very satisfactory agreement with those just referred to.

This is not to be wondered at when we find that the refraction equivalents of many dissolved salts vary somewhat according to the strength of the solution, and may vary still more from that of the anhydrous salt, whilst at the same time other salts containing the same metal will not vary to a perceptible extent.

Attention was especially drawn in early days to the case of hydrogen in the halogen acids, which was stated to have an equivalent somewhere about 2.2 greater than in the organic acids, and intermediate values in nitric and sulphuric acids.

Again, in determining the actual value for potassium, which was the starting point for the metals in general, deductions from the chloride, bromide, and iodide were omitted, from the conviction that

they gave values which were too high. Kanonnikoff went further, and, making no use of the haloïd salts, he drew his conclusions solely from the nitrates, sulphates, and organic compounds of the metals. This difficulty is perfectly explained by the great influence which water exerts on these acids, and, to a minor degree, on most of their salts.

Now we are in a position to lay down the following principles which should guide in any future revision of these refraction equivalents where derived from salts. 1st, The anhydrous salt itself (or its hydrated crystal), when it can be obtained free from the influence of double refraction, should be taken in preference to its aqueous solution; 2nd, if deductions are made from aqueous solutions, it should be ascertained whether there is any appreciable difference in refraction according to the amount of water. If not, it may be assumed that the dissolved salt has practically the same refraction as the anhydrous salt. If, however, there be a change, the calculation should be made from the strongest solution, and the direction and nature of the dilution curve will give a good idea as to whether the true value should be in excess or deficiency, and also some idea of how much.

In this way, no doubt, we shall arrive at much greater accuracy than has been hitherto attainable.

Bearing on Theories of Solution.

The course of this investigation has led us more and more to the conviction that we were not dealing with salts or acids merely liquefied by the solvent and diffused through it. The many forms assumed by this refraction change, their evident dependence on the chemical and electrolytic nature of the substances dissolved, and the fact that different parts of the spectrum are unequally affected in solutions of different strengths, can scarcely be explained on any other supposition than that we are dealing more or less with new substances, produced by the interaction of the salt and its solvent. We have been observing, in fact, a mixture, not of two, but of several compounds, varying in their relative amount according to the proportion of water added.

Under these circumstances, there is no improbability that the changing chemical composition of the solution should reveal itself by alteration in its effect on the velocity of light. No argument can be drawn from these phenomena against the correctness of the law that the specific refractive energy $\frac{\mu - 1}{d}$ of a substance remains the same notwithstanding great changes of physical condition, and that "the

specific refractive energy of a mixture is the mean of the specific refractive energies of its constituents" (*Phil. Trans.*, 1870). On the other hand, the results afford abundant indications of the general correctness of the law.

It may therefore be fairly expected that the phenomena described will throw some light on the controversies of the day as to the condition of salts in solution. As to the nature of the changes which we have been watching, we have not been able to satisfy ourselves, and we feel that there are several questions which require fuller investigation. These questions include—

1. How far is this refraction change dependent on the solvent used?
2. How far is it an additive effect as between acid and basic radicles?
3. What is the meaning of the positive and negative change? Does it indicate opposing properties or is it differential?
4. Why does not dispersion change *pari passu* with refraction?
5. Is this refraction change confined to electrolytes?

There are, however, some points on which we are prepared to give an opinion.

The Hydrate Theory.—We have little doubt of the existence of hydrates in solution, but our experiments do not give any clear evidence of them. In hydrated crystals, the salt and the water of crystallisation have the same specific refractive energy as though they were not combined, and though we have looked for coincidences between probable hydrates in solution and changes of curvature in our diagrams, we have not found any that we could distinctly recognise.

Decomposition into Base and Acid.—It has been suggested that NaCl, for instance, is converted by H₂O into HCl and NaHO, more or less. Our results are opposed to this, for it is evident that such a reaction cannot take place with HCl itself. Yet the refraction change on dilution is evidently the same phenomenon in the case of NaCl, LiCl, and HCl, the acid, in fact, showing it most strongly.

Gaseous Properties.—Whatever may be the evidence from other sources that a substance extended through a large amount of solvent gradually assumes the properties of a gas, our experiments show that this is not the case with its influence on light. Our having employed the $\frac{\mu - 1}{d}$ formula, enables us to form some opinion on this subject.

The specific refractive energy of a vapour or gas is appreciably less than that of the same substance in the solid or liquid condition. The values obtained for dissolved salts in no case show diminutions com-

parable with what would be obtained with vapours, while in most cases they are of an opposite order; that is, they increase instead of decreasing.

Electrolytic Dissociation.—There is no doubt that whether the views which have been advanced by van't Hoff, Arrhenius, Ostwald, and others are correct or not, they have served as a connection between many different physical and chemical properties of electrolytes. To this group of properties must now be added the refraction change here described, for hydrochloric, hydrobromic, hydriodic, nitric, sulphuric, formic, acetic, and propionic acids follow one another in the same order, and are of about the same relative magnitude as when we are dealing with electric conductivity or chemical affinity (Diagram V).

There is also a qualitative resemblance between the curves of specific refraction and of electric conductivity in the case of nitric and sulphuric acids, when they are plotted according to the percentage composition, but this matter requires more detailed observation, and we propose to return shortly to the subject.

We therefore reserve final judgment on the cause of this refraction change till our investigations have been extended.

Summary.

The general conclusion is that when a salt or acid dissolves in water, the law of permanency of specific refractive energy, notwithstanding change of physical condition, does hold good; but that in many, if not most, cases there is some circumstance which causes a slight departure from it, while with the "strong acids" the departure is very considerable. This change takes place principally in the initial stage of solution of the solid or liquid compound, but in many cases a small further change is discernible as more and more water is added, but this becomes inappreciable as a balance is arrived at. This change in some cases is in the direction of an increased refraction, especially in the haloid salts and the acids; in other cases, especially the nitrates and salts of low refractive energy, the change is in the opposite direction.

In either case, the dilution effect is in the same direction as that due to solution. In a few cases, where the dispersion was capable of being estimated, the change in it was proportionally greater than the change in the refraction itself.

The origin of this refraction change is at present obscure; but it probably arises from some gradual change of arrangement in the constituents of the salt or acid under the influence of water; and there are clear indications of some connection between the amount of this

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change and the amount of the specific refractive energy of the salts themselves, and also their combining proportions. It stands also in some relation to the phenomena of electric conductivity, and especially to those of the magnetic rotation of polarised light.

APPENDIX I.—*Molecular Refraction of Salts in Solution, previously published, or calculated from the Refractive Indices of Solutions given by various observers.*

Salt.	%.	Line.	R.	Obs.	Salt.	%.	Line.	R.	Obs.
HCl	36·09	F	14·54	G*	NaCl	24·73	α	15·70	Weg
"	31·26	"	14·63	"	"	23·63	"	15·71	"
"	28·73	"	14·69	"	"	22·40	"	15·73	"
"	25·40	"	14·77	"	"	21·37	"	15·73	"
"	20·32	"	14·82	"	"	16·57	"	15·76	"
"	16·71	"	14·94	"	"	7·99	"	15·76	"
"	10·42	"	15·13	"	"	25·0	α	15·70	Schütt
"	8·67	"	15·20	"	"	10·0	"	15·74	"
"	5·13	"	15·12	"	"	5·0	α	15·76	"
"	24·36	D	13·95	Le Bl	"	3·0	"	15·78	"
"	7·45	"	14·47	"	"	2·0	"	15·78	"
"	1·2	"	14·44	Kl & Hl	"	1·0	"	15·82	"
"	0·601	"	14·44	"	"	14·0	D	15·76	Hl
"	0·05	"	14·49	"	"	2·8	"	15·79	"
"	0·025	"	14·57	"	"	0·72	"	15·84	"
"					"	1·4	"	15·85	Kl & Hl
LiCl	40·0	red	14·42	Kr & Br	"	0·72	"	15·85	"
"	24·5	"	14·76	"	"	0·06	"	15·795	"
"	11·72	α	14·83	Weg	"				
"	9·11	"	14·38	"	KCl	24·15	A	18·70	G*
"	5·84	"	14·82	"	"	21·62	"	18·77	"
NaCl	26·14	red	15·66	Kr & Br	"	17·15	"	18·60	"
"	15·04	"	15·63	"	"	12·12	"	18·60	"
"	23·23	A	15·33	G	"	9·92	α	18·97	Weg
"	21·31	"	15·48	"	"	7·40	"	19·07	"
"	18·84	"	15·26	"	"	4·99	"	18·95	"
"	16·88	"	15·32	"	CaCl ₂	40·4	red	31·51	Kr & Br
"	15·29	"	15·47	"	"	24·75	"	32·01	"
"	13·98	"	15·43	"	"	40·64	A	31·89	v d W
"	12·87	"	15·55	"	"	31·79	"	32·02	"
"	11·93	"	15·51	"	"	24·38	"	32·00	"
"	11·11	"	15·37	"	"	16·75	"	32·06	"
"	8·73	"	15·30	"	"				
"	26·58	"	15·56	v d W	SrCl ₂	32·00	red	34·49	Kr & Br
"	22·78	"	15·56	"	"	19·93	"	34·46	"
"	21·69	"	15·56	"	"				
"	20·73	"	15·57	"	ZnCl ₂	71·81	α	31·32	Wüll
"	16·68	"	15·63	"	"	57·40	"	31·27	"
"	15·85	"	15·55	"	"	47·87	"	31·56	"
"	8·65	"	15·47	"	"	35·90	"	31·56	"
"	14·14	α	15·7	Bed	"	46·08	A	30·52	G
"	24·13	D	15·72	Le Bl	"	41·43	"	30·69	"
"	5·31	"	15·88	"	"	35·25	"	30·63	"

* Series marked by an asterisk have been curtailed.

APPENDIX I—continued.

Salt.	%.	Line.	R.	Obs.	Salt.	%.	Line.	R.	Obs.
ZnCl ₂	38·98	A	30·59	v d W	LiI	10·54	<i>a</i>	31·90	Weg
"	31·50	"	30·68	"	"	5·90	"	31·85	"
"	23·0	"	31·03	"	"	3·08	"	31·88	"
CdCl ₂	57·52	D	36·09	de M	NaI	14·70	<i>a</i>	32·85	"
"	41·55	"	35·92	"	"	9·28	"	32·93	"
"	29·98	"	35·93	"	"	6·25	"	32·93	"
"	14·78	"	36·14	"	KI	55·05	red	36·26	Kr & Br
NH ₄ Cl	24·83	A	22·19	v d W	"	37·09	"	36·48	"
"	19·68	"	22·18	"	"	55·12	<i>a</i>	36·06	Dam
"	14·51	"	22·20	"	"	44·22	"	36·31	"
"	11·79	"	22·14	"	"	39·70	"	36·22	"
HBr	65·59	F	20·80	G	"	23·44	"	35·54	"
"	56·00	"	21·03	"	"	18·70	"	35·61	"
"	39·71	"	21·17	"	"	20·04	"	36·17	Weg
"	24·60	"	21·52	"	"	15·12	"	36·14	"
"	15·47	"	21·83	"	"	10·27	"	36·26	"
LiBr	9·28	<i>a</i>	21·05	Weg	"	5·01	"	36·29	"
"	5·81	"	21·01	"	HNO ₃	98·70	A	16·22	G
"	4·02	"	20·90	"	"	69·60	"	16·38	"
NaBr	45·2	red	22·09	Kr & Br	"	43·10	"	16·81	"
"	28·87	"	22·27	"	"	69·18	D	16·64	Le Bl
"	31·02	<i>a</i>	21·83	Weg	"	40·52	"	17·19	"
"	20·44	"	21·88	"	"	28·66	"	17·42	"
"	11·96	"	21·88	"	"	14·09	"	17·55	"
"	4·95	"	21·89	"	NaNO ₃	44·35	A	18·53	v d W
KBr	37·7	red	25·60	Kr & Br	"	39·19	"	18·52	"
"	23·2	"	25·53	"	"	33·89	"	18·56	"
"	19·82	<i>a</i>	25·17	Weg	"	26·28	"	18·52	"
"	8·57	"	25·21	"	"	16·86	"	18·53	"
"	5·01	"	25·21	"	"	42·9	"	18·78	For
CaBr ₂	55·9	red	44·01	Kr & Br	"	21·23	"	18·74	"
"	38·9	"	44·78	"	AgNO ₃	57·87	"	27·47	"
SrBr ₂	48·56	"	47·29	"	"	29·01	"	26·89	"
"	32·20	"	47·21	"	"	15·82	"	26·32	"
BaBr ₂	50·50	red	53·07	"	"	21·3	<i>a</i>	27·23	Kan
"	33·60	"	53·04	"	"	13·51	"	27·06	"
CdBr ₂	33·29	D	49·37	de M	HgNO ₃ † ...	21·22	"	35·87	Ghira
"	23·97	"	48·78	"	"	13·86	"	36·11	"
"	20·55	"	48·93	"	Pb(NO ₃) ₂ ..	31·65	A	52·43	For
"	11·98	"	49·75	"	"	14·27	"	51·21	"
					Cd(NO ₃) ₂ ..	54·03	D	30·86	de M
					"	43·72	"	30·99	"
					"	30·90	"	31·06	"

† Dissolved in very dilute nitric acid.

APPENDIX I—continued.

Salt.	%.	Line.	R.	Obs.	Salt.	%.	Line.	R.	Obs.
Cd(NO ₃) ₂ ...	21·35	D	31·44	de M	MgSO ₄	1·47	D	24·14	Kl & Hl
".....	14·90	"	31·81	"	".....	0·75	"	24·12	"
".....	8·68	"	32·03	"	".....	0·63	"	24·32	"
H ₃ PO ₃	73·69	"	21·29	Zec	".....	0·31	"	24·26	"
".....	30·66	"	22·09	"	ZnSO ₄	1·58	"	27·10	"
H ₂ SO ₄	94·72	A	22·36	v d W*	".....	0·79	"	26·98	"
".....	91·43	"	22·19	"	".....	0·066	"	27·12	"
".....	85·93	"	22·27	"	".....	0·033	"	27·08	"
".....	71·97	"	22·31	"	Soda alum..	21·39	"	241·2	G
".....	63·69	"	22·54	"	Amm. alum.	8·83	"	256·8	G
".....	56·25	"	22·35	"	NaHO.....	34·74	A	9·34	v d W
".....	47·22	"	22·48	"	".....	18·5	"	9·36	"
".....	38·78	"	22·58	"	".....	11·45	"	9·31	"
".....	23·29	"	22·52	"	Na ₂ CO ₃	16·30	"	21·66	G
".....	15·82	"	22·33	"	".....	13·77	"	22·02	"
".....	94·33	"	22·97	Hd & Ws	".....	10·50	"	22·18	"
".....	88·10	"	23·11	"	".....	9·32	"	22·46	"
".....	81·19	"	23·25	"	".....	2·25	D	22·56	Kl & Hl
".....	73·51	"	23·06	"	".....	1·13	"	22·68	"
".....	64·91	α	23·08	"	".....	0·57	"	22·52	"
".....	55·22	"	23·17	"	".....	0·095	"	22·72	"
".....	44·22	"	23·43	"	NH ₃	34·80	A	8·76	G
".....	31·62	"	23·50	"	".....	33·40	"	8·95	"
".....	17·05	"	23·80	"	".....	21·40	"	9·06	"
".....	94·11	D	22·23	Le Bl	".....	19·92	"	8·88	"
".....	79·68	"	22·42	"	".....	13·40	"	9·03	"
".....	60·98	"	22·50	"	KSeCN....	43·55	D	41·83	Zp
".....	35·77	"	22·62	"	".....	32·77	"	42·31	"
".....	21·68	"	22·74	"	H ₂ SeO ₄	41·8	"	29·79	"
".....	10·10	"	22·88	"	".....	27·3	"	29·39	"
".....	4·78	"	22·82	"	H ₂ SeO ₃	30·6	"	26·98	"
".....	2·35	"	22·90	Kl & Hl	".....	23·0	"	26·84	"
".....	1·77	"	22·86	"	CH ₂ O ₂	100·0	α	13·92	Lan
".....	1·195	"	22·76	"	".....	83·64	"	13·97	"
".....	0·60	"	23·00	"	".....	71·88	"	13·96	"
".....	0·075	"	23·39	"	".....	63·01	"	14·07	"
".....	0·050	"	23·28	"	".....	29·06	D	14·02	Le Bl
".....	0·025	"	23·0	"	".....	18·69	"	14·00	"
Na ₂ SO ₄	10·51	A	26·20	v d W	NaHCO ₂ ...	44·99	A	16·60	G
".....	9·55	"	26·28	"	".....	41·39	"	16·63	"
".....	8·8	"	26·08	"					
".....	6·8	"	26·14	"					
".....	14·10	"	24·32	For					
".....	7·19	"	23·88	"					
".....	25·51	D	26·30	Le Bl					
".....	6·46	"	26·45	"					
".....	4·76	"	26·23	"					

* Series marked by an asterisk have been curtailed.

APPENDIX I—continued.

Salt.	%.	Line.	R.	Obs.	Salt.	%.	Line.	R.	Obs.
NaHCO_2	37·28	A	16·58	G	$\text{C}_2\text{H}_4\text{O}_2$	18·70	D	21·39	Le Bl
".....	8·72	D	17·07	Le Bl	".....	18·19	"	21·43	"
".....	5·58	"	17·09	"	".....	5·2	"	21·45	Kl & Hl
$\text{C}_2\text{H}_4\text{O}_2$	100·0	a	21·13	Lan*	".....	2·7	"	21·43	"
".....	99·87	"	21·14	"	".....	1·37	"	21·44	"
".....	99·5	"	21·16	"	".....	0·22	"	21·47	"
".....	98·2	"	21·20	"	".....	0·114	"	21·46	"
".....	93·02	"	21·27	"	".....	0·057	"	21·45	"
".....	86·96	"	21·29	"	$\text{NaH}_3\text{C}_2\text{O}_2$..	45·89	D	24·48	Le Bl
".....	81·63	"	21·32	"	".....	21·81	"	24·53	"
".....	76·92	"	21·29	"	".....	9·70	"	24·58	"
".....	70·39	"	21·30	"	".....	5·41	"	24·71	"
".....	60·66	"	21·28	"	$\text{C}_3\text{H}_5\text{O}_2$	100·0	a	28·62	Lan
".....	50·82	"	21·30	"	".....	89·16	"	28·71	"
".....	30·82	"	21·33	"	".....	80·44	"	28·74	"
".....	20·65	"	21·33	"	".....	73·27	"	28·78	"
".....	10·38	"	21·24	"	".....	67·27	"	28·79	"
".....	100·0	"	21·14	Dam*	$\text{C}_4\text{H}_5\text{O}_2$	100·0	a	36·22	"
".....	93·02	"	21·24	"	".....	90·72	"	35·77	"
".....	86·96	"	21·34	"	".....	83·02	"	35·76	"
".....	72·73	"	21·33	"	".....	76·52	"	35·76	"
".....	62·50	"	21·29	"	".....	47·85	"	36·40	"
".....	51·81	"	21·23	"	$\text{C}_2\text{HCl}_3\text{O}_2$..	30·11	D	47·66	Le Bl
".....	30·77	"	21·33	"	".....	14·13	"	47·72	"
".....	20·72	"	21·27	"					
".....	10·81	"	21·39	"					
".....	100·0	D	21·26	Le Bl					
".....	40·38	"	21·45	"					

* Series marked by an asterisk have been curtailed.

APPENDIX II.—List of Authorities referred to, with the Abbreviations used in the Tables.

Bd & W....	Bedson and Carleton Williams, <i>Brit. Assn. Report</i> , 1881, 155 (salts, solid and dissolved).
Bl.....	Bleekrode, <i>Proc. Roy. Soc.</i> , 37 , 339 (liquefied gases).
Br.....	Brewster, <i>Ency. Britt.</i> , Optics (silver nitrate).
B & B.....	Bussy and Buignet, <i>Ann. Chim. Phys.</i> , 1864, [4], 3 , 231 (hydrocyanic acid).
Dam.....	Damien, <i>Ann. École Norm.</i> , 1881, [2], 10 , 233 (acetic acid and potassium iodide).
Dus.....	Dussaud, <i>Arch. Sc. Genève</i> , 1892 (sodium chlorate).
F.....	Forster, <i>Arch. Sc. Genève</i> , 1878 (salts).
Ghira.....	Ghira, <i>Gazzetta</i> , 1894, 24 , i (mercurous nitrate).
G.....	Gladstone, <i>J. Chem. Soc.</i> , 1865, 18 , 108 (rock salt, &c.); <i>Proc. Roy. Soc.</i> , 1868, 16 , 439 (salts, acids, &c.); <i>Phil. Trans.</i> , 1870, 160 , 9 (salts and acids, &c.); <i>Phil. Mag.</i> , 1885 (alums); <i>J. Chem. Soc.</i> , 1891, 59 , 589 (acids and salts).
	Gladstone and Dale, <i>Brit. Assn. Report</i> , 1863, 12 (solutions).

APPENDIX II—continued.

G.....	Gladstone and Perkin, <i>J. Chem. Soc.</i> , 1889, 55 , 750 (correspondence with magnetic rotation).
Hg	Haagen, <i>Ann. Phys. Chem.</i> , 1867, 131 (rock salt).
Hl	Hallwachs, <i>Ann. Phys. Chem.</i> , 1894, 53 , 1 (acids and salts).
Hd & W....	Handl and Weiss, <i>Wien. Ber.</i> , 1858, 30 (sulphuric acid).
H	Hibbert. Janovsky, <i>Wien. Ber.</i> , 1880, 82 , 148.
K.....	Kanonnikoff, <i>J. pr. Chem.</i> , 1885, [2], 31 , 321 (potassium sulphate, &c.).
Kl & Hl....	Kohlrausch and Hallwachs, <i>Ann. Phys. Chem.</i> , 1894, [2], 53 , 14 (density of solutions, &c.).
Kr & Br	Kremers and Beer, <i>Ann. Phys. Chem.</i> , 1857 (various salts).
Lan	Landolt, <i>Ann. Phys. Chem.</i> , 1862, 117 , 353 (organic acids).
Le Bl	Le Blanc, <i>Zeit. physikal. Chem.</i> , 1889, 4 , 553 (acids and their soda salts).
Mas	Mascart, <i>Compt. rend.</i> , 1878 (gaseous halogen acids).
de M.....	de Muynck, <i>Ann. Phys. Chem.</i> , 1894, [2], 53 , 559 (cadmium salts).
N.....	Newton, <i>Opticks</i> , 2nd Book, Part 3, Prop. 10 (rock salt). Perkin, <i>J. Chem. Soc.</i> , 1886, 49 , 777; 1889, 55 , 680; 1893, 63 , 57; 1894, 65 , 20 (magnetic rotation).
Perr.....	Perrot, <i>Arch. Sc. Genève</i> , 1890 (double zinc sulphates).
R.....	Rubens, <i>Ann. Phys. Chem.</i> , 1894, [2], 53 (sylvin). Schmidt, <i>Ann. Phys. Chem.</i> , 1859, 107 , 539 (salts).
Sch	Schütt, <i>Zeit. physikal. Chem.</i> , 1890, 5 , 4 , 349 (sodium chloride).
S	Soret, <i>Arch. Sc. Genève</i> , 1884, 12 , 553; 1885, 13 , 5; 1888, 20 , 517 (alums).
T & C	Topsoe and Christiansen, <i>Vidensk. Selsk</i> , 1873, 9 , 9, 625 (crystals).
Tut	Tutton, <i>J. Chem. Soc.</i> , 1894, 65 , 628 (sulphates of alkalis).
Weg.....	Wegner, Berlin, 1889 (haloid salts).
v. d. W.....	v. d. Willigen, <i>Arch. Mus. Teyler</i> , 1868, 1 , 74 and 161 (sulphuric acid and other solutions); <i>Arch. Mus. Teyler</i> , 1869, 2 , 238 (acids).
Wüll.....	Wüllner, <i>Ann. Phys. Chem.</i> , 1868, 133 , 1 (zinc chloride).
Zec	Zecchini, <i>Real Acad. Lincei</i> , 1893, 31 (phosphorous acid).
Zp	Zoppellari, <i>Gazzetta</i> , 1894, 24 , ii, 396 (selenium compounds).