VI. Experimental proof of Van't Hoff's constant, of Arrhenius's generalization, and of Ostwald's law of dilution in very dilute solutions

Dr. Meyer Wildermann

To cite this article: Dr. Meyer Wildermann (1895) VI. Experimental proof of Van't Hoff's constant, of Arrhenius's generalization, and of Ostwald's law of dilution in very dilute solutions , Philosophical Magazine Series 5, 40:242, 119-144, DOI: [10.1080/14786449508620713](https://doi.org/10.1080/14786449508620713)

To link to this article: <http://dx.doi.org/10.1080/14786449508620713>

Published online: 08 May 2009.

Submit your article to this journal [↗](#)

Article views: 2

View related articles [↗](#)

of experiment. These and many other points are receiving consideration, and will be discussed in a subsequent communication. We must, in conclusion, express our great obligations to Mr. D. K. Morris, as well as to Mr. C. Jakeman, for the valuable assistance they have rendered to us in the laborious work of taking and reducing the observations above recorded, as well as in the construction of some of the apparatus used in this research.

VI. *Experimental Proof of Van't Hoff's Constant, of Arrhenius's Generalization, and of Ostwald's Law of Dilution in very Dilute Solutions.* By Dr. MEYER WILDERMANN*.

I. *Proof of Van't Hoff's Constant.*

IT is well known that it was Van't Hoff who first drew attention to the fact that the equations representing the generalizations arrived at by Boyle, Gay-Lussac, and Avogadro in the case of gases are equally applicable to dissolved substances, if the osmotic pressure of the molecules of the dissolved substance be substituted for the pressure of the gas.

Van't Hoff deduced these laws for solution from thermodynamical considerations—a method which gives them increased validity,—and illustrated them from the osmotic experiments of Pfeffer and de Vries.

At the same time Van't Hoff was able to establish a thermodynamical relation between the osmotic pressure of a dissolved substance and the molecular lowering of vapour-pressure; molecular lowering of freezing-point of the solution thereby furnishing a rational basis for the empirical generalizations of Raoult and of Babo and Wüllner, who had previously investigated the same point.

In Van't Hoff's thermodynamical argument the solutions are assumed to be very dilute, and hence their experimental verification is specially important for the case of very dilute solutions.

The determination of the molecular depression of the freezing-point is the safest and most convenient method of testing the validity of these generalizations, and this has been done for moderately dilute solutions by Van't Hoff himself

* Communicated by the Author: read before the British Association on the 13th of August, 1894.

and by Eijkman ; and the equation

$$t = \frac{0.02 T^2}{w},$$

where T = absolute temperature, w = latent heat of fusion of the solvent, has been experimentally verified and confirmed for several solvents.

The method of determining the freezing-point of very dilute solutions *, which was devised by my late friend P. B. Lewis, from 0° to $-0^\circ.2$, and my recent investigations of similar solutions from $-0^\circ.2$ to $-0^\circ.4$ and of the freezing-point of water †, have given us a means of submitting Van't Hoff's equation,

$$t = \frac{0.02 T^2}{w},$$

to a more accurate verification.

The value of t is 1.87 if, with Bunsen and others, we take the latent heat of water to be 80 cal., and is somewhat greater if w is put = 79.6 cal.

First come the experimental data. In the following Tables α is the number of molecules in solution per litre (in pure water this is 0) ; γ is the freezing-point of the water or of the solution, as read on the 1000° thermometer ; δ the number of readings of the temperature made after the freezing-point has been reached ; ϵ the limits within which the readings of the temperature varied ; ϕ is the time over which the readings extended ; b is the amount of over-cooling, or difference between the temperature of the solution before and after the formation of ice, these temperatures being read on the 100° thermometer ; c , the temperature of the ice-bath ; c' , the temperature of the room ; k is the reading of the barometer.

* See 'Transactions of the Chemical Society,' 1894. A fuller account has been given in the *Zeitschrift für phys. Chemie*, xv. p. 358. See also the very valuable work of Jones, *Zeitschr. phys. Chemie*, xi. p. 110. Later investigations of Jones have shown that his method was not brought to the high development we all supposed. It is now a long time ago since Professor Ostwald told me that it is also his opinion that the method used by Jones requires a further development, because the results obtained for non-electrolytes by this method do not agree with the fundamental generalizations of the modern Theory of Solutions. The work of Lewis, which is distinguished by great experimental accuracy, and by the minute and judicious care with which the conditions necessary to secure the best possible results are investigated, enables us now to submit many important questions in very dilute solutions to a more accurate verification.

† See *Zeitschr. phys. Chemie*, xv. p. 365.

TABLE I. (1/1000° thermometer.)

Cane-sugar.								
a.	γ.	δ.	ε.	φ.	b.	c.	c'.	k.
0 *	·4858(9)	5	·4858-·4859	10		-1·8 to -2	18	millim. 756·5
0 *	·4857(8)	7	·4857-·4858	10		-1·8 to -2	18	756·3
0 †	·4873(4)	...		...			...	756·3
0·006535 †	·4758(7)	5	·4758-·4757	8		-1·8 to -2	18	756·5
0·019344 †	·4514(3)	4	·4514-·4513	8		-1·8 to -2	18	757·5
0·03164 †	·4279(8)	7	·4279-·4277	10		-2	18·2	757·5
0·04344 †	·4067(6)	7	·4066-·4068	10		-2	18·3	757·5
0·05477 †	·3848(9)	7	·3847-·3849	10		-2	17·5	760·5
0·06565 †	·3634	9	·3633-·3635	10		-2	17·3	760·5
0·07609 †	·3428(9)	6	·3427-·3429	10		-2	17·1	760·5
0·08612 †	·3233(4)	6	·3233-·3234	10		-2	17	760·5
Urea.								
0 *	·4851(2)	8	·4850-·4852	9		-1·7	20	760·65
0 *	·4852	7	·4852-·4853	8		-1·8 to -2	19	760·5
0 †	·4867(8)	...		...			...	760·5
0·001813 †	·4819	7	·4819-·4820	8		-1·8	18	760·5
0·00905 †	·4694	5	·4694-·4692	5		-2	18·5	760·4
0·02341 †	·4427(8)	6	·4628-·4628	9		-1·8	18·5	760·5
0 *	·4852(3)	6	·4851-·4853	12		-2	19·7	759·5
0·043506 †	·4026(7)	6	·4026-·4027	9		-1·8	19·3	759·5
0·07802 †	·3355(6)	6	·3355-·3358	7		-1·8	19·1	759·5
0·11116 †	·2687(8)	8	·2685-·2688	12		-2	19	759·5
Alcohol, C ₂ H ₅ OH.								
0 *	·4844(5)	7	·4845-·4854	10		-1·8	15·6	754·2
0 †	·4860(1)	...		...			...	754·2
0·00645 †	·4738	7	·4737-·4739	8		-1·8	15	754·2
0·01930 †	·4510(1)	5	·4510-·4512	8		-2	14	754·5
0·04495 †	·4033	9	·4032-·4034	12		-2	13·8	754·8
0·09582 †	·3086	9	·3085-·3087	12		-2	13·5	754·8
0·1459 †	·2152	6	·2152-·2151	10		-2	13·5	754·8
0 *	·4848(7)	6	·4848-·4847	10		-1·8 to -2	15·5	753·7
0·1548 †	·1985	9	·1984-·1986	10		-2	15·5	753·7
0·2039 †	·1064	6	·1063-·1065	12		-1·8 to -2	15·3	753·6
0·2039 †	·1063(4)	6	·1063-·1064	9		-2	15·2	753·7

* Ice-cap on the bulb of the thermometer.

† Ditto, corrected by +0°·0016.

‡ No ice-cap is formed on the Hg bulb of the thermometer.

From these experimental data are deduced the following Tables, in which are given :—

α , the number of molecules of the substance dissolved, p. litre.

a , the lowering of the freezing-point which is observed.

b , the number of degrees of over-cooling read on the smaller thermometer.

c , the amount of the solvent which separated as ice, expressed in percentages.

d , the factor by which the number of molecules given under α must be multiplied in order to obtain

α corrected; *i. e.* the concentration of the solution after the separation of the ice. (It is better to correct the density than the lowering of the freezing-point, on account of dissociation.)

$\frac{a}{\alpha \text{ corrected}}$ gives the molecular lowering of the freezing-point, which, according to Van't Hoff, is represented by

$$t = \frac{0.02T^2}{w} = 1.878 \text{ (if } w = 79.6),$$

$$\text{or} \quad = 1.87 \text{ (if } w = 80).$$

TABLE II.

Cane-sugar.						
α mol. norm.	a .	b .	c .	d .	α corr.	$\beta = \frac{a}{\alpha \text{ corr.}} \times 100$
(1.) 0.006535	[0.0100(1)] 0.016(7)	0.888	per cent. 1.06	$\frac{100}{98.94}$	0.006602	[151.5] 175.7 (177.2)
(2.) 0.019344	[0.0344(5)] 0.0360(1)	0.855	1.03	$\frac{100}{98.97}$	0.019546	[176 (176.5)] 184.5 (184.7)
(3.) 0.03164	[0.0579(80)] 0.0595(6)	0.731	0.88	$\frac{100}{99.12}$	0.03192	[181.4 (181.7)] 186.4 (186.7)
(4.) 0.04344	[0.0792(1)] 0.0808(9)	0.789	0.95	$\frac{100}{99.05}$	0.04386	[180.6 (180.3)] 184.3 (184.5)
(5.) 0.05477	[0.1010(1)] 0.1026(7)	0.755	0.91	$\frac{100}{99.09}$	0.05527	[182.7 (1.2.9)] 185.6 (185.8)
(6.) 0.06565	[0.1224] 0.1240(1)	0.673	0.81	$\frac{100}{99.19}$	0.06619	[184.9] 187.3 (187.5)
(7.) 0.07609	[0.1430(1)] 0.1446(7.8)	0.751	0.90	$\frac{100}{99.1}$	0.07678	[186.2 (186.4)] 188.3 (188.5)
(8.) 0.08612	[0.1624(5)] 0.1640(1)	0.643	0.77	$\frac{100}{99.25}$	0.08679	[187.1 (187.3)] 189.0 (189.1)

Urea.						
<i>a</i> mol. norm.	<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>a</i> corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100$
(1.) 0.001813 *	0.0034(3)	0.862	per cent. 1.03	$\frac{100}{98.97}$	0.001832	185.6 (181.2)
(2.) 0.00905	[0.0158] 0.0174(3)	0.850	1.02	$\frac{100}{98.98}$	0.009142	[172.8] 195.8 (189.2)
(3.) 0.02341	[0.0424(5)] 0.0440(1)	0.804	0.96	$\frac{100}{99.04}$	0.02364	[179.4 (179.8)] 186.1 (186.6)
(4.) 0.04351	[0.0826] 0.0842	0.68	0.82	$\frac{100}{99.18}$	0.04387	[188.3] 191.8
(5.) 0.07803	[0.1497] 0.1513	0.67	0.81	$\frac{100}{99.19}$	0.07866	[190.3] 192.4
(6.) 0.1112	[0.2165] 0.2181	0.585	0.70	$\frac{100}{99.3}$	0.1120	[193.3] 194.7
Alcohol, C ₂ H ₅ OH.						
(1.) 0.00645	[0.0106(7)] 0.0122(3)	0.94	per cent. 1.18	$\frac{100}{98.82}$	0.006527	[162.4 (163.9)] 186.9 (183.4)
(2.) 0.01930	[0.0337] 0.0353	0.975	1.22	$\frac{100}{98.78}$	0.01953	[172.6] 180.8
(3.) 0.04495	[0.0811(2)] 0.0827(8)	0.933	1.166	$\frac{100}{98.83}$	0.04548	[178.3 (178.5)] (182.1) 181.8
(4.) 0.09582	[0.1758(9)] 0.1774(5)	0.87	1.09	$\frac{100}{98.91}$	0.09688	[181.5 (181.6)] (183.3) 183.1
(5.) 0.1459	[0.2692(3)] 0.2708(9)	0.739	0.92	$\frac{100}{99.08}$	0.1472	[182.9 (183)] 184
(6.) 0.1548	[0.2862(3)] 0.2878(9)	0.70	0.88	$\frac{100}{99.12}$	0.1562	[183.2] 184.3
(7.) 0.2039	[0.3783(4)] 0.3799(800)	0.62	0.785	$\frac{100}{99.22}$	0.2055	[184.1] 184.9
(7') 0.2039	[0.3784] 0.3800	0.665	0.83	$\frac{100}{99.17}$	0.2056	[184.1] 184.9

* Ice-cap on the bulb of the thermometer.

In the above tables under α and β two values are given. In the case of cane-sugar, alcohol, and urea (with the exception of the solution of urea which contains 0.001813 molecules per litre) there were, with all concentrations, fine needles of ice in the solution, but no ice-cap on the thermometer. In square brackets there are given under α and β the values which have been obtained when the freezing-point of water, as read off when there was a well-closed ice-cap round the bulb of the big (and the little) thermometer, is taken as the true zero; the other figures (without brackets) under α and β are obtained when the freezing-point of water, as read off when there is no ice-cap round the bulb, is taken as the true zero.

In the latter case (of a well-closed ice-cap) the freezing-point of water has been found to be under my experimental conditions on an average $0^{\circ}.0016$ higher*, and may err, like all determinations in very dilute solutions, by about 1, 2, or less often 3 ten-thousandths of a degree. In the above tables the figures and results are given exactly as they were obtained from the observations. In these tables, in the cases of cane-sugar and urea, Van't Hoff's constant appears very clearly if the completely closed ice-cap be avoided in the determination of the freezing-point of water, and would appear still more clearly if one were to make the allowable correction of from 1 to 2 or 3 ten-thousandths of a degree: in short, so far as the degree of exactitude of the method itself allows, Van't Hoff's constant appears very clearly. In the cases of alcohol and cane-sugar the values of β fall in the more dilute solutions short of 1.87 by about $1\frac{1}{2}$ per cent.

The importance of the question on which we are engaged induces me to point out that Van't Hoff's constant can also be demonstrated most distinctly, independently of the freezing-point of water. Since cane-sugar, urea, and alcohol can only be very little dissociated, we can determine the several depressions and concentrations, starting from a given solution which does not cause the formation of an ice-cap round the bulb of the thermometer (instead of taking water as the starting-point), and state the results in relation to this; by this means any error which attaches to the determination of the freezing-point of water is eliminated. Starting, then, from the most dilute solution, in which no ice-cap was observed, the following results are obtained:—

* The convergence temperature was here above the freezing-point temperature.

TABLE III.

Cane-sugar.				Urea.				Alcohol, C ₂ H ₅ OH.			
	<i>a.</i>	<i>a</i> corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100$		<i>a.</i>	<i>a</i> corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100$		<i>a.</i>	<i>a</i> corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100$
8-1.	0.1624(5) - 0.0100(1) = 0.1524	0.086790 - 0.006602 = 0.08019	190.1	6-2.	0.2007	0.10285	191.5	7-2.	0.3450	0.1860	185.5
				5-2.	0.1339	0.06952	193.5	7-2.	0.3449(50)	0.1860	185.4 (185.5)
7-1.	0.1330	0.07018	189.5	4-2.	0.0668	0.03473	192.3	6-2.	0.2530	0.1367	185
6-1.	0.1124(3)	0.05959	188.6	3-2.	0.0269(70)	0.01450	186.2	5-2.	0.2358(9)	0.1277	184.7 (184.8)
5-1.	0.0910	0.04867	187		(Corr. + 0°-0003)			4-2.	0.1424(5)	0.07735	184.1 (184.2)
4-1.	0.0692	0.03726	185.7					3-2.	0.0477(8)	0.02595	183.8 (184.2)
3-1.	0.0479	0.02532	189.2								
2-1.	0.0244	0.01295	188.4								

Thus, by this plan, the constant 1·87 or 1·88 appears very satisfactorily in the case of sugar and urea, and in the case of alcohol the constant is only about $1\frac{1}{2}$ per cent. too small. The general run of the values of β in the cases of cane-sugar, urea, and alcohol, shows that in the more concentrated solutions the values obtained for the molecular lowering of the freezing-point are greater than 1·87, and that it is only as the solutions become more dilute that the constant 1·87 becomes apparent. Now Van't Hoff's laws were only deduced for very dilute solutions, for "ideal" solutions.

This year I repeated the investigations of cane-sugar, alcohol, &c. under more favourable conditions, where no closed ice-cap but ice-bands or network of ice are formed round the Hg bulb of the $\frac{1}{1000}^{\circ}$ thermometer, and the convergence temperature was under the freezing-point temperature. The difference in the capsules is conditioned by the differing of the ice-crystal, which is brought into the over-cold liquid to crystallize it. When the convergence temperature is under the freezing-temperature, the correct freezing-point of water, as well as of solutions, is directly obtained with the ice-cap. [A consideration of the processes which take place at the freezing-temperature, when the convergence temperature is above and under the freezing-temperature, is of great interest and will form the subject of a separate communication.] Thus I have shown by this third method, that Van't Hoff's constant holds good in dilute solutions. Table I'. gives the experimental data obtained with the $\frac{1}{1000}^{\circ}$ and $\frac{1}{100}^{\circ}$ thermometer for cane-sugar, alcohol, and from these data Table II'. is deduced. The Van't Hoff constant appears very clearly, and is in the most dilute solution only about $1\frac{1}{2}$ per cent. less than 1·87. Table III'. gives the molecular depressions, starting from the most dilute solutions, for cane-sugar &c.

TABLE III'.

	α corr.	1/1000° Thermometer.		1/100° Thermometer.	
		α .	β .	α .	β .
2-1.	0·003985	0·0073	183·2	0·0069	173·1
3-1.	0·011687	0·0221	189·1	(59) 0 0218	(148·1) 186·5
4-1.	0·018727	0·0346	184·7	0 0339	181
5-1.	0·028437	0·0521	183·2	0·0519	182·5 &c.

Cane-sugar. (1/1000° thermometer.)									
<i>a.</i>	<i>γ.</i>	<i>δ.</i>	<i>ε.</i>	<i>φ.</i>	<i>δ.</i>	<i>c.</i>	<i>c'.</i>	<i>k.</i>	
0	°4870(1)	7	·4870-4871	10		-0·75	13	millim. 752 (13·5)	With ice-cap. Without ice-cap.
"	"	"	"	"		"	"	"	"
0·004114	·4793(2)	7	·4792-4793	10	1·339	-1·87	12	751·5 (12)	"
0·005068	·4716(7)	8	·4716-4718	11	0·980(1)	-1·92	11·5	750·5 (11)	"
0·015656	·4566(7)	9	·4567-4567	10	1·082	-1·87	11·5	750·2 (13·5)	"
0·022632	·4442(1)	8	·4441-4443	10	0·963	-1·9	12	750 (13·5)	"
0·032255	·4266(7)	8	·4266-4267	10	0·887	-1·9	12·7	750	"
Alcohol. (1/1000° thermometer.)									
0	·4898(9)	5	·4838-4839	8		-1·8	9·5	744·3 (9·3)	With ice-cap. Without ice-cap.
0	"	"	"	"		"	"	"	"
0·005463	·4753(4)	6	·4733-4734	8	0·915	-1·8	9·5	743·1 (9·5)	"
0·01086	·4622	6	·4622-4621	8	0·887	-2	9·5	742·1 (9·5)	"
0·02414	·4390	6	·4390-4392	8	0·800	-1·9	9·5	741·8 (9·5)	"
0·03688	·4149	6	·4149-4150	8	0·897	-1·9	9·5	740·8 (9·5)	"
0·06088	·3691(2)	6	·3691-3692	8	0·861	-2·05	9·5	740·4 (9·5)	"
0·09472	·3042(3)	6	·3042-3043	8	0·727	-1·9	9·5	740 (9·5)	"

TABLE II'.

Cane-sugar. (1/1000° thermometer.)							
a.	a.	$k_1 - k_2$	a corr.	b.	c.	d.	$\beta = \frac{a \text{ corr.}}{a \text{ corr.}} \times 100.$
1. 0·004114	0·00780	millin. -0·5	0·0077	1·339	1·674	$\frac{100}{98 \cdot 33}$	184·1
2. 0·008068	0·0054	-1·5	0·0150	0·980 (1)	1·225	$\frac{100}{98 \cdot 775}$	183·7
3. 0·015656	0·0304	-1·8	0·0298	1·082	1·353	$\frac{100}{98 \cdot 647}$	187·8
4. 0·022632	0·0429	-2	0·0423	0·963	1·204	$\frac{100}{98 \cdot 796}$	184·6
5. 0·032255	0·0604	-2	0·0598	0·887	1·101	$\frac{100}{98 \cdot 899}$	183·5
Cane-sugar. (1/100° thermometer.)							
	0·008	-0·5	0·0079				188·8
	0·015(4)	-1·5	0·0148 (0·0138)				181·2 (169)
	0·030	-1·8	0·0298				187·8
	0·042	-2	0·0418				182·5
	0·060	-2	0·0598				183·5

Table II'. (*continued*)

Alcohol. (1/1000° thermometer.)							
<i>a.</i>	<i>a.</i>	<i>k₁ - k₂</i>	<i>a</i> corr.	<i>b.</i>	<i>c.</i>	<i>d.</i>	$\beta = \frac{a \text{ corr.} \times 100}{a \text{ corr.}}$
0.005463	0.0105	millim. -1.2	0.0102	0.915	1.144	100 98.56	184.6
0.01086	0.0216 cor. - 0.0003	-2.2	0.0209 cor. 0.0206	0.887	1.109	100 98.89	190.2 cor. 187.5
0.02414	0.0449(50) cor. + 0.0003	-2.5	0.0442 cor. 0.0445	0.800	1.00	100 99.00	181.3 cor. 182.6
0.03688	0.0689(90)	-3.5	0.0681	0.897	1.121	100 98.88	182.6
0.06088	0.1147	-3.9	0.1135	0.861	1.076	100 98.92	184.5
0.09472	0.1796	-4.3	0.1783	0.727	0.9088	100 99.09	186.5
Alcohol. (1/100° thermometer.)							
	0.0110	-1.2	0.0108				185.2
	0.020	-2.2	0.0197				179.3
	0.046	-2.5	0.0456				187
	0.069(70)	-3.5	0.0685 0.0695				183.6 186.3
	0.115(6)	-3.9	0.1144 0.1154				186.7 187.5
	0.179	-4.3	0.1783				186.6

In any case, what has still to be said is, that there are present subsidiary causes which might in part affect the equation and the constant 1.87: such as dilution-heat put forward by Van't Hoff himself, by Nernst, and recently by Dieterici and by Evans; or as the formation of higher molecules, which I believe to be present in greater or lesser number in all solutions. But the influence of such causes could only be slight, and the only relations here quite certainly expressed are those given by Van't Hoff in the equation $t = \frac{0.02 \cdot T^2}{w}$. Besides this I regard it for various

reasons as very probable that the absolute value of the scale of my thermometer is, between $0^\circ.4900$ and $0^\circ.3900$ or $0^\circ.3600$, 1-2 per cent. too small. My further investigations will decide this question. In every case Van't Hoff's thermodynamical equation has found excellent confirmation in dilute solutions, much better even than most generalizations established on the thermodynamical basis.

The results of Loomis (Wied. *Ann.* li.) obtained with the $\frac{1}{100}^\circ$ thermometer, which show a continuous decrease of the values of β , may now be calculated, starting from the most dilute solutions ($\frac{1}{100}$ mol. normal) (Table IV.).

The observations of Loomis (made with a $\frac{1}{100}^\circ$ thermometer) extend to $\frac{1}{100}$ molecule-normal. The lowering of the freezing-point for a $\frac{1}{100}$ molecule-normal solution of a "non-conductor" is about $0^\circ.0187$; with such a fall of the freezing-point no formation of an ice-cap round the bulb of the thermometer is possible. Here we have taken the $\frac{1}{100}$ molecule-normal solution as starting-point, and the result is that Loomis's investigations point indubitably to Van't Hoff's constant. In the case of cane-sugar the figure obtained with almost all the more dilute solutions is 187; in the case of urea and alcohol we obtain constants which are too small by 2 or 3 per cent. But the fact that these constants are almost the same at all concentrations shows most clearly that Mr. Loomis has not correctly determined the strength of his original solutions—a mistake which does not depend on the method itself. The low values of the molecular lowering of the freezing-point obtained by Loomis, values which for a $\frac{1}{100}$ normal solution are already too small by 10 and more per cent., may be therefore here attributed in the first place to incorrect determination of the freezing-point of water. But the not unimportant fluctuations in the value of b in the cases of alcohol and urea (after the elimination of the error which may depend on the freezing-point of water), which will be noticed in the above tables, shows this, that results obtained with a $\frac{1}{100}^\circ$ thermometer, in spite of the exactitude which

TABLE IV.

Cane-sugar.				Urea.				Alcohol, C ₂ H ₅ OH.			
$\beta = \frac{a}{a'}$	a	α corr.	$\beta = \frac{a}{a' \text{ corr.}} \times 100.$	$\beta = \frac{a}{a'}$	a	α corr.	$\beta = \frac{a}{a' \text{ corr.}} \times 100.$	$\beta = \frac{a}{a'}$	a	α corr.	$\beta = \frac{a}{a' \text{ corr.}} \times 100.$
$\frac{(2-1)a}{(2-1)a}$	(0.01840)	(0.01)	(18.4)	$\frac{(2-1)a}{(2-1)a}$	(0.08557)	(0.02)	(177.9)	$\frac{(2-1)a}{(2-1)a}$	0.01790	0.01	179
$\frac{(3-1)a}{(3-1)a}$	0.03750	0.02	187.5	$\frac{(3-1)a}{(3-1)a}$	0.07345	0.04	183.6	$\frac{(3-1)a}{(3-1)a}$	0.03586	0.02	179.3
$\frac{(4-1)a}{(4-1)a}$	0.05584	0.03	186.1	$\frac{(4-1)a}{(4-1)a}$	0.16513	0.09	183.5	$\frac{(4-1)a}{(4-1)a}$	0.05568	0.03	185.6
$\frac{(5-1)a}{(5-1)a}$	0.07505	0.04	187.6	$\frac{(5-1)a}{(5-1)a}$	0.34969	0.19	184	$\frac{(5-1)a}{(5-1)a}$	0.07216	0.04	180.4
$\frac{(6-1)a}{(6-1)a}$	0.09442	0.05	188.8					$\frac{(6-1)a}{(6-1)a}$	0.09072	0.05	181.4
$\frac{(7-1)a}{(7-1)a}$	0.11350	0.06	189.1					$\frac{(7-1)a}{(7-1)a}$	0.12804	0.07	182.9
$\frac{(8-1)a}{(8-1)a}$	0.17266	0.09	191.8					$\frac{(8-1)a}{(8-1)a}$	0.16533	0.09	183.7
$\frac{(9-1)a}{(9-1)a}$	0.27141	0.14	195.9					$\frac{(9-1)a}{(9-1)a}$	0.20199	0.11	183.6
$\frac{(10-1)a}{(10-1)a}$	0.37464	0.19	197.2					$\frac{(10-1)a}{(10-1)a}$	0.23926	0.13	184
								$\frac{(11-1)a}{(11-1)a}$	0.27549	0.15	183.6

distinguishes Loomis's method in a great many points, are affected with greater experimental errors than Mr. Loomis supposes to be possible. The results which I have obtained with my $\frac{1}{100}^{\circ}$ thermometer by a method which by far surpasses Loomis's method in precision, are more or less of the same character (see Table II'). At the same time with the observations recorded above and made with a $\frac{1}{1000}^{\circ}$ thermometer on cane-sugar, urea, and alcohol, similar observations were made with a $\frac{1}{100}^{\circ}$ thermometer. The results obtained are affected by experimental errors of from $0^{\circ}001$ – $0^{\circ}002^{\circ}$, and even occasionally greater; and that means that we cannot use the $\frac{1}{100}^{\circ}$ thermometer for minute readings in very dilute solutions. For with the $\frac{1}{100}^{\circ}$ thermometer we have to deal with experimental errors which cannot easily be removed or eliminated. In the first place it is not easy to avoid errors of from 1 to 2 thousandths degree in making the readings, even with the use of a microscope and a micrometer-scale, although with the method mentioned above we are able to observe the obtained freezing-point during the 10 to 15 minutes occupied making several readings; the more must that be the case with other methods, where the obtained freezing-point can be observed only a short time. Now even in solutions which are only diluted to $\frac{1}{25}$ or $\frac{1}{50}$ molecule-normal, an experimental error of $0^{\circ}002$ makes a difference of about 3 to 5 per cent. (in the case of non-conductors) in the lowering observed, and therefore also in the calculated molecular lowering of the freezing-point. The $\frac{1}{100}^{\circ}$ thermometer can therefore in very dilute solutions only give us qualitative data.

II. *Proof of Arrhenius's Generalization.*

We proceed to the generalization of Arrhenius. Van't Hoff showed by four different methods, that a law analogous to that of Avogadro was valid for solutions of non-electrolytes like cane-sugar; it then became of importance to account for exceptional cases in which the depression of freezing-point was abnormal, and in particular the cases of salts, acids, and bases in aqueous solution. The explanation was given when Arrhenius showed that by two independent quite different methods, the observation of lowering of freezing-point and of the electrical conductivity of a solution, the same value would be obtained for the factor i , which denotes the ratio of the pressure actually exerted by the substance to the pressure which the substance would exert if it consisted entirely of undissociated molecules.

Arrhenius made determinations on about 40 bodies in moderately dilute solutions of various concentrations and verified

the law more accurately. From the intimate connexion which exists between Van't Hoff's laws and the dissociation theory, it follows also that the generalization of Arrhenius may find a more exact experimental confirmation in dilute solutions. Therefore a more exact confirmation of the generalization of Arrhenius in very dilute solutions is not only important on account of the great light which the theory of dissociation has thrown upon the two provinces of chemistry and physics, but it is also important inasmuch as thereby the laws of Van't Hoff will find in every point their more exact confirmation.

We found above the normal value of the molecular lowering of the freezing-point in the cases of cane-sugar, urea, and alcohol—substances belonging to the class of bad conductors of electricity. In the following Tables are given the results obtained with sulphuric acid, potassium chloride, dichloroacetic acid, trichloroacetic acid, and orthonitrobenzoic acid. First come the experimental data. (The meanings of α , γ , δ , ϵ , ϕ , b , c , c' , k , have already been given with Table I.)

TABLE V.

Trichloroacetic Acid.								
α .	γ .	δ .	ϵ .	ϕ .	b .	c .	c' .	k .
0 *	4842 ^o	7	4842 ^o	8	0.950	-2 ^o	20.3	millim. 758
0 †	4858(9)	9	4858-4859	10	0.768	-1.8	20.6	758
0.005132 †	4666(7)	7	4666-4667	10	0.70	-1.7	20	758
0.010182 †	4487	5	4487	10	0.978	-2	19.5	757.9
0.017636 †	4232(1)	6	4232-4233	10	0.852	-1.9	19	758
0.029761 †	3798(9)	9	3797-3799	12	0.987	-2	18	758
0.0414 †	3397(8)	6	3397-3399	10	0.827	-2	18	758
0 *	4841	5	4840-4841	10	0.748	-1.8	17.5	757
0 †	4857	...		...				757
0.04443 †	3304	5	3304	10	0.67	-1.8	17.8	757
Dichloroacetic Acid.								
0 *	4852	...		...	0.82			
0 †	4867	...		...	0.80			
0.002573 *	4758	...		...	0.795			
0.005125 *	4669(70)	...		...	0.785			
0.010230 †	4515	...		...	0.766			
0.015294 †	4366(5)	...		...	0.730			
0.02032 †	4220(1)	...		...	0.615			
0 *	4834(5)	...		...	0.685			
0.027551 †	3933	...		...	0.680			

* Ice-cap round the bulb of thermometer.

† The ice-cap is avoided in a manner described in *Zeitschr. phys. Chemie*, xv.

‡ No ice-cap on the Hg bulb of the thermometer.

Table V. (continued).

Orthonitrobenzoic Acid.								
a.	γ .	δ .	e.	ϕ .	b.	c.	c'.	k.
0†	·4855	9	·4855-·4856	6	0·8	-1·8	21	762·7
0†	·4855(6)	5	·4855-·4856	6	0·78	-1·8	22	762·7
0·006169†	·4667	8	·4866-·4867	9	0·78	-1·8	22	762·2
0·008318†	·4607	8	·4606-·4608	10	0·734	-1·8	22·5	762·2
0·01197†	·4518(9)	8	·4517-·4519	10	0·766	-1·8	23	762
0·015037†	·4447(6)	8	·4446-·4447	8	0·778	-1·8	23·5	761·2
0·017083†	·4385(6)	10	·4385-·4387	8	0·72	-1·8	23	760·5
0·02046†	·4308	10	·4306-·4310	7	0·81	-1·8	23	760·4
Sulphuric Acid, SO ₄ H ₂ .								
0†	·4841(2)	9	·4841-·4842	10	...	-2	18	752·3
0*	·4824(5)	5	·4824-·4825	10	...	-2	18	752·3
0·0007611†	·4809	6	·4808-·4810	10	...	-2	18	752·3
0·008329†	·4455	5	·4455	10	...	-2	18	752·3
0·015875†	·4139	7	·4139	9	...	-2	18	752·3
0*	·4814	10	·4813-·4815	8	...	-2	17	749·2
0†	·4829	5	·4829	8	...	-2	17	749·5
0†	·4829(30)	7	·4829-·4830	7	...	-2	17	749·5
0·00456†	·4609	4	·4606-·4609	10	...	-2	17	749·5
0·00456†	·4609	11	·4608-·4609	10	...	-2	17	749·5
0†	·4842(3)	8	·4842-·4843	8	...	-1·8bisto-2	19	752·7
0·00456†	·4620(19)	8	·4619-·4620	12	...	-1·9	19	752·9
0·00456†	·4620(19)	6	·4619-·4620	8	...	-1·9	19	753·5
0·008329†	·4457(6)	7	·4456-·4457	9	...	-2	19	754·7
0†	·4849	5	·4849	8	...	-2	18	755·8
0†	·4849(50)	11	·4849-·4850	10	...	-2	18	755·8
0·008367†	·4466(7)	6	·4466-·4468	10	...	-1·8bisto-2	18·5	755·6
0·008367†	·4465(6)	8	·4465-·4466	10	...	-1·8	19	755·6
0·015912†	·4148	9	·4147-·4150	10	...	-1·8	19	755·5
0·03092†	·3539(40)	6	·3539-·3540	10	...	-1·8	19	755·3
0·03092†	·3540(39)	10	·3539-·3540	10	...	-2	19	755·3
0†	·4839(40)	9	·4830-·4830	10	...	-1·8	18·5	753·3
0·04567†	·2951(2)	10	·2951-·2955	11	...	-2	18·7	753·3
0·06740†	·2118(9)	8	·2116-·2121	8	...	-1·8	19	753·2
0·09569†	·1038(9)	9	·1038-·1039	8	...	-1·9	20	753·2
0†	6·147	(Small thermometer.)		...	...	-2	18	
0·1436†	5·590	7	5·589-5·591	8	...	-2	18	
0·18645†	5·429(30)	8	5·428-5·430	8	...	-2	18	

* Ice-cap round the bulb of thermometer.

† The ice-cap is avoided in a manner described in *Zeitschr. phys. Chemie*, xv.

‡ No ice-cap on the Hg bulb of the thermometer.

From these experimental data are deduced the following
Tables (Tables VI. 1-3).

In these Tables are given under α'_1 the degrees of dissociation as deduced from the freezing-point, when the value of Van't Hoff's constant is taken to be 1.87; α_2 gives the degrees of dissociation as determined by electric conductivity by a careful interpolation. The result is that the agreement between the values α'_1 and α_2 is excellent. I think, therefore, that the latent heat of ice is more correctly estimated at 80 than at 79 cal. It appears that the degrees of dissociation deduced from the freezing-point under α'_1 are somewhat smaller than those deduced from electric conductivity. Now the values of α , α'_1 , and α_2 have been determined at various temperatures (from about 0° and 18° or 25°), and in view of the investigations of Kohlrausch and Ostwald (on acetic acid, &c.), we have good ground for presuming that the degree of dissociation deduced from electric conductivity would be somewhat smaller for the same concentration at lower temperatures. I also think—being, till lately, singular in this opinion—that we may assume that in the solutions there are always present, in greater or lesser number, still higher undissociated and dissociated molecules which cause greater or lesser deviations from the strict agreement of the degrees of dissociation as deduced from the freezing-point and from electric conductivity. But the most probable reason is, that the absolute value of the graduated scale of the $\frac{1}{1000}^\circ$ thermometer is, between 0.49 and 0.36, 1–2 per cent. too small. From various causes I regard this as very probable. My further investigations will decide this question. In every case we ought, no doubt, in our calculations of the degrees of dissociation to use in all our given concentrations, or in concentrations measured by the scale 0.49 to 0.36, the value 1.84 or 1.85 instead of the theoretical 1.87, since we have practically found in the case of non-electrolytes under similar conditions in the more dilute solutions the value 1.85 or 1.84. If we do so, the law of Arrhenius finds in the observations given above the most wonderful, unexpected confirmation. See in the table above, α_1 and α_2 . In any case, look at the above results how we may, there is no doubt that the law of Arrhenius has found remarkable confirmation in the cases of the non-conductors cane-sugar, urea, and alcohol, and of the conductors potassium chloride, sulphuric acid, dichloroacetic acid, trichloroacetic acid, orthonitrobenzoic acid.

TABLE VI. (1).

Sulphuric Acid, SO_4H_2 . (1/1000° thermometer.)											
α .	a .	b .	c .	d .	a corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100$.	$i = \frac{\beta}{1.84}$.	$i' = \frac{\beta}{1.87}$.	Generalization of Arrhenius.		
									α_1^* fr. p.	$\alpha_1'^*$ fr. p.	$\alpha_2^\dagger$ elect. cond.
									($\ln$	fluence of NH_3 .)	
0.0007611	0.0032(1)	0.765	0.92	$\frac{100}{99.08}$	0.0007687	429.3		229.5	$\left. \begin{array}{l} 74.8 \\ 75.2 \end{array} \right\}$	$\left. \begin{array}{l} 72.8 \text{ (73.2)} \\ 67.1 \end{array} \right\}$	$\left. \begin{array}{l} 77.2 \\ 72.7 \end{array} \right\}$
0.0008329	0.0386(7)	0.775	0.93	$\frac{100}{99.7}$	0.008404	459.3 (460.6)	249.6 (250.3)	245.6 (246.3)			
0.015875	0.0702	0.785	0.94	$\frac{100}{99.06}$	0.01803	437.9	238	234.2	69		
"	[0.0685]	"	"	"	"	[4273]					
0.000456	0.0220(1)	0.871	1.05	$\frac{100}{98.95}$	0.004608	477.5 (479.6)	259.5 (260.65)	255.4 (256.5)	$\left. \begin{array}{l} 79.75 \\ 80.33 \end{array} \right\}$	$\left. \begin{array}{l} 77.7 \text{ (78.25)} \\ 81.3 \end{array} \right\}$	$\left. \begin{array}{l} 81.3 \\ 81.3 \end{array} \right\}$
0.000456	0.0220(1)	0.876	1.05	$\frac{100}{98.95}$	0.004608	477.5 (479.6)	259.5 (260.65)	255.4 (256.5)	$\left. \begin{array}{l} 79.75 \\ 80.33 \end{array} \right\}$	$\left. \begin{array}{l} 77.7 \text{ (78.25)} \\ 81.3 \end{array} \right\}$	$\left. \begin{array}{l} 81.3 \\ 81.3 \end{array} \right\}$
"	[0.0205]	"	"	"	"	[444.9]					
0.000456	0.0223	0.806	0.97	$\frac{100}{99.03}$	0.004604	484.4	263.3	259	81.65	79.5	81.3
0.000456	0.0223	0.826	0.99	$\frac{100}{99.01}$	0.004604	484.4	263.3	259	81.65	79.5	81.3
0.0008329	0.0386	0.879	1.06	$\frac{100}{95.97}$	0.008417	458.6	249.2	245.3	74.6	72.65	77.2

0.008367	0.0384	0.808	0.97	$\frac{100}{99.03}$	0.00845	465	252.8	248.7	76.4	74.35	77.25
0.008367	0.0384	0.779	0.93	$\frac{100}{99.07}$	0.008449	465.2	253.2	249	76.6	74.5	77.25
0.015912.	0.0701(2.)	0.767	0.92	$\frac{100}{99.08}$	0.01606	436.5	237.2	233.4	68.6	66.7	72.7
0.03092	0.1310	0.717	0.86	$\frac{100}{99.14}$	0.03119	420	228.3	224.6	64.15	62.3	66.1
0.03092	0.1310	0.822	0.98	$\frac{100}{99.02}$	0.03122	419.6	228	224.4	64	62.2	66.1
0.04567	0.1888	0.758	0.89	$\frac{100}{99.11}$	0.04608	409.7	[222.7]	219.1	[61.35]	59.55	63.1
0.06740	0.2721	0.602(3)	0.72	$\frac{100}{99.28}$	0.0679	400.7	[217.8]	214.3	[58.91]	57.15	58.91
0.09569	0.3801	0.698	0.84	$\frac{100}{99.16}$	0.0965	393.9	[214.1]	210.6	[56.55]	55.3	56.55
(1/100° thermometer.)											
0.1436	0.557	0.405	0.49	$\frac{100}{99.51}$	0.1443	386		206.4		53.2	53.34
0.18645	0.718(7)	0.659	0.79	$\frac{100}{99.21}$	0.1880	381.9 (381.4)		204.2 (203.9)		52.1 (51.95)	51.82

* $a_1 = \frac{i-1}{2}, a_1' = \frac{i'-1}{2}.$

† $\mu_\infty = 374 \left(10^{\frac{k}{m}} \right).$

TABLE VI. (2).

Dichloroacetic Acid. (1/1000° thermometer.)											
a.	a.	b.	c.	d.	α corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100.$	$i = \frac{\beta}{1.84}.$	$i' = \frac{\beta}{1.87}.$	Generalization of Arrhenius.		
									α_1^* fr. p.	α_1^* fr. p.	α_2^+ elect. cond.
0.002573	0.009	0.795	0.99	$\frac{100}{99.01}$	0.002599	361.7	196.6	193.4	96.6	93.4	95.6
0.005125	0.0182(3)	0.785	0.98	$\frac{100}{99.02}$	0.005177	351.6 353.5	191.1 (192.1)	1.88 (1.89)	91.1 (92.1)	88 (89)	91.3
0.010230	[0.0337]	0.766	0.96	$\frac{100}{99.04}$	0.01033	[326.2]					
"	0.0352	"	"	"	"	340.8	185.2	1.823	85.2	82.3	84.3
0.015294	[0.0486(7)]	0.730	0.91	$\frac{100}{99.09}$	0.015447	[314.6 (315.2)]					
"	0.0501(3)	"	"	"	"	324.3 (325.6)	176.3 (177.0)	1.737 (1.747)	76.3 (77.0)	73.7 (74.1)	80.6
0.02032	[0.0632]	0.615	0.77	$\frac{100}{99.23}$	0.02048	[308.6]					
"	0.0647(8)	"	"	"	"	315.9 (316.4)	171.7 (172)	1.692	71.7 (72)	69.2	73.1
0.027551	[0.0849]	0.680	0.82	$\frac{100}{99.18}$	0.02778	[305.6]					
"	0.0864	"	"	"	"	311.0 (311.4)	169 (169.2)	1.663	69(69.2)	66.3	70.3

Table VI. (2) (continued).

Orthonitrobenzoic Acid. (1/1000° thermometer.)											
a.	a.	b.	c.	d.	a corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100.$	$i = \frac{\beta}{1.84}.$	$i' = \frac{\beta}{1.87}.$	Generalization of Arrhenius.		
									α_1^* fr. p.	$\alpha_1'^*$ fr. p.	$\alpha_2^\dagger$ elect. cond.
0.006169	0.0188(9)	0.780	0.94	$\frac{100}{99.06}$	0.006227	301.9 (303.5)	164.1 (164.9)	1.614 (1.623)	64 (64.9)	$\left. \begin{array}{l} 61.4 \\ (62.3) \end{array} \right\}$	62.8
0.008318	0.0248(9)	0.734	0.88	$\frac{100}{99.12}$	0.008391	295.6 (296.8)	160.6	1.581 1.587	60.6	$\left. \begin{array}{l} 58.1 \\ (58.7) \end{array} \right\}$	56.3
0.01197	0.0337	0.766	0.92	$\frac{100}{99.08}$	0.01208	279	151.65	1.492	51.65	49.2	"
0.015037	0.0408(9)	0.778	0.94	$\frac{100}{99.06}$	0.01518	268.8 (269.4)	146.1 (146.4)	1.437 (1.441)	46.1 (46.4)	$\left. \begin{array}{l} 43.7 \\ (44.1) \end{array} \right\}$	"
0.017083	0.0470	0.721	0.87	$\frac{100}{99.13}$	0.01723	272.6	148.1	1.458	48.1	45.8	"
0.02046	0.0547(8)	0.812	0.97	$\frac{100}{99.03}$	0.02066	264.7 (265.5)	143.85 144.3	1.415 (1.42)	43.85 44.3	$\left. \begin{array}{l} 41.5 \\ (42) \end{array} \right\}$	"

* In the case of orthonitrobenzoic acid, trichloroacetic acid, dichloroacetic acid, potassium chloride, $\alpha_1 = i - 1$, $\alpha_2' = i' - 1$.
† In the case of orthonitrobenzoic acid, trichloroacetic acid, dichloroacetic acid, measurements of W. Ostwald (25°), in the case of ClK measurements of Kohlrausch (18°). μ_{∞} for ClK is = 123 (Kohlrausch).

Table VI. (2) (continued).

Trichloroacetic Acid. (1/1000° thermometer).											
a.	a.	b.	c.	d.	a corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100.$	$i = \frac{\beta}{1.84}.$	$i' = \frac{\beta}{1.87}.$	Generalization of Arrhenius.		
									α_1^* fr. p.	α_1^* fr. p.	α_2^+ elect. cond.
0.005132	[0.017516]	0.70	0.84	$\frac{100}{99.16}$	0.005176	[340]					
"	0.0191(2) corr. + 0.0003	"	"	"	"	369 (371)	(200.5)	1.973	(100.5)	97.3	96.9
0.010182	[0.0355]	0.978	1.17	$\frac{100}{98.83}$	0.0103	[344.7]	corr. 198.8		corr. 98.8		
"	0.0371(2)	"	"	"	"	360.2 (361.2)	195.75 (196.3)	1.926 (1.932)	95.75 (96.3)	92.6 (93.2)	94.1
0.017636	[0.0611]	0.852	1.03	$\frac{100}{98.97}$	0.01782	[342.8]					
"	0.0627(8)	"	"	"	"	351.8 (352.4)	191.2 (191.5)	1.879 (1.884)	91.2 (91.5)	87.9 (88.4)	92.1
0.029761	[0.1043(4)]	0.987	1.18	$\frac{100}{98.82}$	0.03012	[346.3]					
"	0.1059(60)	"	"	"	"	352	191.3	1.882	91.3	88.2	90.2
0.0414	0.1444(5)	0.827	0.99	$\frac{100}{99.01}$	0.04182	[345.3]					
"	0.1461	"	"	"	"	349.4	[189.9]	1.868	[89.9]	86.8	"
0.0443	0.1537	0.669	0.80	$\frac{100}{99.2}$	0.04479	[343.2]					
"	0.155300	"	"	"	"	346.5	[188.3]	1.853	[88.3]	85.3	"

* For footnote, see above.

† For footnote, see above.

TABLE VI. (3).

Potassium Chloride, CLK. (1/1000° thermometer.)											
a.	a.	b.	c.	d.	a corr.	$\beta = \frac{a}{a \text{ corr.}} \times 100.$	$i = \frac{\beta}{184}.$	$i' = \frac{\beta}{187}.$	Generalization of Arrhenius.		
									a_1^* fr. p.	a_1^* fr. p.	$a_2^\dagger$ elect. cond.
0.009711	0.0352	0.87	1.08	$\frac{100}{98.92}$	0.009818	358.8	194.8	191.7	94.8	91.7	93.4
0.009711	0.0379	0.91	1.14	$\frac{100}{98.86}$	0.009822	358.3	194.7	190	94.7	90	
0.01934	[0.0677]	0.89	1.11	$\frac{100}{88.89}$	0.01956	[347.2]	192.55	189.5	92.55	89.5	91.6
"	0.0693	"	"	"	"	354.3					
0.01934	[0.0676]	0.82	1.03	$\frac{100}{98.97}$	0.01954	[345.9]	192.4	189.4	92.4		89.1
"	0.0692	"	"	"	"	354.1			92.1	88.9	
0.03845	[0.1356]	0.811	1.01	$\frac{100}{98.99}$	0.03884	[349.5]	192.1	188.9	92.1		87.5
"	0.1372	"	"	"	"	353.4			91.1	88	
0.03845	[0.1349]	0.792	0.99	$\frac{100}{99.01}$	0.03883	[347.6]	[189.8]	186.7	[89.8]	86.7	86.5
"	0.1365	"	"	"	"	351.7			[89.7]	86.5	
0.07606	[0.2655]	0.481	0.60	$\frac{100}{99.4}$	0.07652	[347.0]					
"	0.2671	"	"	"	"	349.2					
0.07606	[0.2658]	0.651	0.81	$\frac{100}{99.19}$	0.07668	[346.7]					
"	0.2674	"	"	"	"	348.8					

* For footnote, see above.

† For footnote, see above.

III. *The Law of Dilution as deduced from the Freezing-Point.*

We proceed to illustrate one of the most important, if not the most important, of the foundations of the theory of dissociation, namely, Ostwald's law of dilution based upon the freezing-point. (Planck's name also should be mentioned here.) It was notably Ostwald who first showed the relation between the numbers of dissociated and undissociated molecules to depend upon the action of mass, and who took the pains to verify the same experimentally in the case of two hundred acids by means of their electric conductivity. From the above-mentioned generalization of Arrhenius it follows that the law of dilution ought also to be deducible from the freezing-point, since the freezing-point as well as the electric conductivity enables one to know the degree of dissociation, and it may be at the same time interesting, inasmuch as we have not here to do with velocity of ions or with the theory of the electric conductivity. On the other hand, from the intimate connexion which exists between Van't Hoff's laws and the dissociation theory, it follows that the law of dilution must find its experimental confirmation in dilute solutions. This has not been possible before now, because the constant deduced from the law of dilution is greatly affected by the experimental error, and the freezing methods were till now far from being sufficiently exact for this purpose. But we have now made a sufficient advance in the freezing methods to be able to undertake this proof under favourable circumstances. Here we have to take into account two conditions : first, the degree of dissociation must not be small, especially because, in consequence of the nature of the calculation, the experimental error affects not the whole value observed, but only that part of it which gives the degree of dissociation; secondly, the degree of dissociation must very considerably change with the degree of dilution, or else the influence of dilution is difficult to ascertain. The law of dilution can therefore only be proved in the case of a few substances which fulfil these conditions. Dichloroacetic acid and ortho-nitrobenzoic acid are suitable for this purpose.

Below are given the constants calculated according to the law of dilution in the cases of dichloroacetic acid and ortho-nitrobenzoic acid. In the last Table are given under "*a* corrected" the concentrations of the solutions, and under Δ the degree of dissociation, when $t=1.87$. The constant K given by the law of dilution appears indubitably, but is smaller

TABLE VII.

Dichloroacetic Acid. (1/1000° therm.)						
α corr.	Δ'	Δ''	$1 - \Delta$	$\frac{\Delta'' \cdot \alpha}{1 - \Delta} = K'$ The law of Dilution.	Δ	Δ^2
0.005177	91.1 (92.1)	8300 (8410)	8.9 (7.9)	4.823 (5.516)	88 (89)	7743 (7920)
0.01033	85.2	7259	14.8	5.066	82.3	6773
0.015447	76.3 (77)	5822 (5929)	23.7 (23)	3.794 (3.989)	73.7 (74.1)	75439 (5498)
0.02048	71.7 (72)	5141 (5183)	28.3 (28)	3.791 (3.792)	69.2	4789
0.02778	69 (69.2)	4761 (4788)	31 (30.8)	4.266 (4.319)	66.3	4396
						3.341 (3.727) 3.952 3.199 (3.284) 3.184 3.623
Orthonitrobenzoic Acid. (1/1000° therm.)						
0.006227	64.1 (64.9)	4109 (4212)	35.9 (35.1)	7.123 (7.471)	61.4 (62.3)	3774 (3882)
0.008391	60.6	3672	39.4	7.821	58.1 (58.7)	3376 (3446)
0.01208	51.65	2668	48.35	6.669	49.2	2421
(0.01518)	[46.1 (46.4)]	[2125 (2153)]	[53.9 (53.6)]	5.985	[43.7 (44.1)]	(1945)
0.01723	48.1	2314	51.9	(6.098)	45.8	(55.9)
0.02066	43.85 (44.3)	192.3 (196.2)	56.15 (55.7)	7.687 7.075 (7.238)	41.5 (42)	2098 172.3 (176.4)
						54.2 58.5 (58)
						6093 (6411) 676 (700) 5757 (5281) 6664 6083 (6283)
Trichloroacetic Acid. (1/1000° therm.)						
0.0103	95.75 (96.3)	9168 (9273)	4.25 (3.7)	(22.22) 25.81		
(0.01782)	[91.2 (91.5)]	[8318 (8371)]	[8.8 (8.5)]	[16.85 (17.55)]		
0.03012	91.8	8385	8.7	28.75		
0.04182	89.9	8081	10.1	33.45		
0.04479	88.3	7796	11.7	29.84		

than that deduced from electric conductivity (25° Ostwald) Much better is the agreement between the constant from freezing-point and the constant from electric conductivity, if the practically found $t=1.84$ is used ; the constant is well obtained then also in the case of trichloroacetic acid. See Δ' and K' in Table VII.

I may be permitted to express my heartiest thanks to the authorities of Christ Church and to Mr. A. G. Vernon Harcourt for kindly placing the resources of their laboratory at my disposal.

Christ Church, Oxford.

VII. *Notices respecting New Books.*

Annals of British Geology, 1893. By J. F. BLAKE, M.A., F.G.S. 8vo., xxiv and 365 pages, with 90 illustrations, February 1895. Dulau & Co., London.

THIS digest of Books and Papers published during the year (1893), with an Introductory Review, is a welcome continuation of three former volumes, already noticed in the 'Philosophical Magazine.' The subjects taken in order from page 1 to page 301 are:— 1. General Geology; 2. Stratigraphical Geology; 3. Palæontology; 4. Palæobotany; 5. Mineralogy; 6. Petrology; 7. Economical products; 8. Maps and Sections relating to England and Scotland. Notices of notes and memoirs on Foreign Geology, published in Britain, taken in much the same order as the above, occupy pages 302–353. Three good Indexes are found at pages 355–365.

The aim of this work is to provide annually for students of Geology a condensed account of all that has been done in the science so far as the British Islands are concerned. For this purpose the various papers and other publications are classified under larger and smaller subdivisions, so that the whole work is a kind of subject-index.

The several papers are either merely recorded, or more or less fully abstracted. The "Introductory Review" aims at giving a succinct account of the general progress in Geological Science, and treatment of disputed questions, during the year concerned, based on the information afforded by the said publications. Where desirable and convenient, especially with new species of fossils, figures (copied by "process") are given in the text. In the abstracts of the papers the ideas advanced or supported by the several authors are represented from their own points of view; in the "Introductory Review" the reviewer (he objects to be regarded as a "compiler" of this most careful and laborious work) writes critically on his own responsibility.

The number of publications dealt with each year has varied