

VII.—ON A DIAGRAM OF FREEZING-POINT DEPRESSIONS FOR  
ELECTROLYTES.—BY PROF. J. G. MACGREGOR, *Dalhousie  
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The object of this paper is to describe a diagrammatic method of taking a bird's-eye view of such knowledge as we possess of the relation of the depression of the freezing-point to the state of ionization in aqueous solutions of electrolytes, and to show that such diagrammatic study gives promise of throwing much light upon the following questions: (1.)\*—Has the depression constant a common value for all electrolytes, and if so, what is it? And (2), What is the state of association, and what the mode of ionization of electrolytes, in solution?

*Construction and Properties of the Diagram.*

If an extremely dilute solution contain an electrolyte whose molecule, as it exists in solution, contains  $p$  equivalents, and dissociates into  $q$  free ions, and if  $a$  is its ionization coefficient and  $k$  its depression constant, the equivalent depression will be:

$$\delta = \frac{k}{p} (1 + a(q-1)).$$

If therefore we plot a diagram of curves with ionization coefficients as ordinates, and equivalent depressions as abscissae, the resulting curves must, at extreme dilution ( $a = 1$ ), be tangential to the straight lines represented by the above equation, provided the proper values of  $k$ ,  $p$ , and  $q$  be employed. These straight lines, which, for shortness, we may call the tangent lines of the curves, can readily be drawn in the diagram, with any assumed value of  $k$ , and on any admissible assumptions as to the values of  $p$  and  $q$ . In the diagram on page 235 the dashed lines are the

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\* On this question, see also a paper recently communicated to the Royal Society of Canada, and to be published in its Transactions for 1900.

tangent lines for the electrolytes examined, on various assumptions as to constitution in solution and mode of ionization, and for  $k=1.85$ . They are indicated by the inscriptions 1—2, 2—3, etc., the first figure in each giving the number of equivalents in the molecule as it is assumed to exist in solution, and the second, the number of free ions into which the molecule is assumed to dissociate. Thus 1—2 is the tangent line for an electrolyte such as NaCl, on the assumption that it exists in solution in single molecules, each of which has therefore 1 equivalent, and dissociates into 2 ions. If assumed to associate in double molecules, with unchanged mode of ionization, its tangent line would be indicated by 2—4, and if the double molecules were assumed to dissociate into Na and NaCl<sub>2</sub>, by 2—2. The line for H<sub>2</sub>SO<sub>4</sub>, on the assumption that its molecules undergo no association, and have thus 2 equivalents, and that they dissociate each into 3 ions, would be 2—3; and 4—6 would be its line if it associated into double molecules, dissociating each into 6 ions.

In a few cases dotted lines have been introduced, to show what the tangent lines would be with other values of  $k$ ,—1.83, 1.84, 1.86, 1.87, the constant used in such cases being indicated.

The curve for any given electrolyte, must start at the intersection of its tangent line with the line:  $a=1$ , to which point we may refer, for shortness, as the intersection of its tangent line. What its form will be, may be anticipated from the following theoretical considerations:—The equivalent depression in dilute solutions of non-electrolytes, is proportional to the osmotic pressure,  $P$ , and the dilution,  $V$ , which corresponds to the product of the pressure,  $p$ , and the specific volume,  $v$ , in the case of a gas. If  $pv$  is plotted against  $v$ , the resulting curve is convex towards the axis of  $v$ , and passes, in general, through a point of minimum value of  $pv$ . Hence, if  $PV$ , and therefore equivalent depression, be plotted against  $V$ , we may expect to get curves of the same general form. And experiment shows, in some cases at least, that we do. As in the case of gases the variation of  $pv$  is ascribed to the mutual action of the molecules and their finite volume, so in the case of solutions, the variation of  $PV$  is attributed to similar disturbing influences.

Owing to ionization, the curve of an electrolyte will differ from that of a non-electrolyte, (1) because of the change thereby produced in the number of molecules (including free ions) in unit of volume, and (2) because of the change produced in the disturbing influences referred to. The former change is doubtless the more important, and I shall assume the latter to be negligible for the present purpose. Now dissociation increases continuously with dilution. If, therefore, association of molecules does not occur, and if the mode of ionization does not change, the equivalent depression must be increased by the dissociation, in a ratio which increases continuously with dilution. The change produced in the curve by dissociation, therefore, will be a shear parallel to the equivalent depression axis, and increasing with dilution. The resulting curve will consequently remain convex towards the axis of dilution, but it will be less likely than the curve of a non-electrolyte, to exhibit the minimum point.

If, now, we plot equivalent depression against ionization coefficient, instead of dilution, the result will be the same as if we shortened the dilution ordinates of the various points of the curve just mentioned, in ratios increasing with the dilution, which process must leave the curve convex towards what was the dilution axis, but is now the ionization coefficient axis.

If, therefore, no change occur in the association of molecules or in the mode of ionization, the curve of an electrolyte on the diagram must start at the intersection of its tangent line, tangentially to that line, and bend away from it, as dilution diminishes, to the right, possibly passing through a point of minimum equivalent depression. We may speak of such a curve as the normal curve for the tangent line, corresponding to the given conditions as to constitution in solution, and mode of ionization.

If, the constitution of the electrolyte in the solution remaining constant, the mode of ionization changes as dilution diminishes, say, in such a way that the molecules dissociate, on the average, into a smaller number of ions, the equivalent depression will diminish more rapidly than it otherwise would. The curvature of the curve will therefore diminish, and may possibly become

zero, and change sign, the curve thus becoming concave towards the ionization coefficient axis, and possibly crossing the tangent line. In such a case, it will at the start coincide with the normal curve of the tangent line determined by the initial conditions as to association and mode of ionization, and at the finish, with the normal curve of the tangent line, determined by the final conditions; and between the start and the finish it will gradually change from the one to the other.

If, as dilution diminishes, association of molecules into double or other multiple molecules occurs, the mode of ionization remaining the same, the equivalent depression will be thereby made to diminish more rapidly than it otherwise would, and the general effect on the form of the curve, will be of the same kind as under the conditions just considered. But the normal curves of the tangent lines determined by the final conditions, will be quite different in the two cases.

It follows that by plotting, so far as experiment allows, the curves of observed equivalent depression against ionization coefficient, and drawing in the tangent lines for different values of the depression constant, and on different assumptions as to association and mode of ionization, we may be able to determine, with a smaller or greater probability, what the state of association and the mode of ionization are, what are the tangent lines to whose intersections the curves would run out if observations at extreme dilution could be made, and what the values of the depression constant are, to which these lines correspond.

#### *Data for the Diagram.*

To draw the experimental curves, we must have corresponding values of the depression, and of the ionization coefficient, at the freezing point, or, what in most cases would be sufficiently near, at  $0^{\circ}\text{C}$ . The former are obtained by direct measurement; but the latter only indirectly, from conductivity observations. It is not, of course, known how closely the ionization coefficients, even during the passage of the current, can thus be determined, or if the state of ionization during the passage of the

current is to be regarded as being the same as when the current is not flowing. But as it has been shown that electrically determined coefficients enable us to predict within the limit of error of observation, not only the conductivity and the results of electrolysis\* of moderately dilute complex solutions, but also their density, viscosity, and other non-electrical properties,† it would appear to be probable that for moderately dilute and very dilute solutions, electrically determined coefficients are approximately exact, not only for a solution through which a current is passing, but generally.

The available data as to ionization coefficients at 0°, are unfortunately few. Whetham† has recently published some most valuable determinations, having measured the conductivity at 0°, of series of solutions down to extreme dilution, with what one may call *appareil de luxe*, and found the ratio of the equivalent conductivity to the maximum equivalent conductivity. For neutral salts, his coefficients must inspire great confidence. But in the case of the acids, they seem to me to be probably too high. For the maximum equivalent conductivity of an acid is probably lower than it would be, were it not for the disturbing influence whatever it is, which makes the equivalent-conductivity-concentration curve not only reach, but pass through a maximum point.

Archibald and Barnes,‡ working in my laboratory, measured the conductivity at 0° and 18° for series of solutions, down to dilutions, at which the ratio of the two conductivities became constant; and assuming that the same ratio would hold at extreme dilution, they calculated the equivalent conductivity at extreme dilution for 0° from Kohlrausch's values for 18°. They used this method only because appliances were not available, with which observations at extreme dilution could be made. If

\* MacGregor: Trans. Roy. Soc. Can. (2), 4, Sec. 3, 117, 1898.

† MacGregor: Trans. N. S. Inst. Sci. 9, 219, 1896-7, and Phil. Mag. (5), 43, 46 and 99, 1897. Also Archibald: Trans. N. S. Inst. Sci. 9, 335, 1897-8, and Barnes: *Ibid.*, 10, 49, and 113, 1899-1900.

‡ Ztschr. f. phys. Chem., 33, 344, 1900.

‡ Archibald: Trans. N. S. Inst. Sci., 10, 33, 1898-9. Barnes: *Ibid.*, 10, 139, 1899-1900, and Trans. Roy. Soc. Canada, (2), 6, —, 1900.

the ratio mentioned really does become constant as dilution increases, the method is likely to give coefficients with too low or too high values, according as the ratio at moderate dilutions diminishes or increases with dilution (it was found to increase with KCl and  $K_2SO_4$ .) For it will probably become constant within the limit of error of observation, before it has really reached constancy. And if it changes with dilution in a slightly wavy manner, even though on the whole tending to constancy, it may be regarded as having become constant, when really passing through a maximum or a minimum point.

Déguisne's\* observations on the variation of conductivity with temperature between  $2^\circ C$  and  $34^\circ$  have enabled me, by the method just mentioned, to make rough determinations of the ionization coefficients at  $0^\circ$  in some cases, on the assumption that his empirical constants might be used down to  $0^\circ$ . According to Déguisne's observations, the ratio of the conductivities at  $0^\circ$  and  $18^\circ$  usually changes gradually down to dilutions of 1,000 litres per gramme-equivalent, and between that and 2,000, undergoes rapid change. As observations at great dilution are attended by considerable difficulty, I have assumed that these sudden changes were probably due to errors of observation. If they were not, my Déguisne coefficients (for which Déguisne himself is of course not to be held responsible) may be considerably out.

In some cases, I have obtained coefficients from the above data by extrapolation, in order to make use of available depression data. In such cases I have plotted, side by side, ionization-coefficient-concentration curves, for both  $0^\circ$  and  $18^\circ$ , using values for  $18^\circ$  based on Kohlrausch's conductivities, and I have then produced the  $0^\circ$  curve beyond the limit of observation, under the guidance of the  $18^\circ$  curve.

I have used all the accessible observations of depression in the case of the electrolytes for which data were available for determining the ionization coefficients at  $0^\circ$ , including observations by

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\* Temperatur-Coefficienten des Leitvermögens sehr verdünnter Lösungen. Dissertation, Strassburg, 1895. See also Kohlrausch u. Holborn: Leitvermögen der Elektrolyte, Leipzig, 1898.

Arrhenius,<sup>1</sup> Raoult,<sup>2</sup> Loomis,<sup>3</sup> Jones,<sup>4</sup> Abegg,<sup>5</sup> Wildermann,<sup>6</sup> Ponsot,<sup>7</sup> Archibald<sup>8</sup> and Barnes<sup>8</sup>. The methods used by these observers are, for the most part, well known. Archibald and Barnes used modified forms of Loomis's method. Arrhenius's observations, and some of Raoult's, were made before important improvements in freezing-point determinations had been recognised as necessary.

In cases in which there was but one series of observations available, I have plotted the actual observations in the diagram, though sometimes smoothing the curves a little. In cases in which two or more series were available, I first plotted the various observations, and then drew mean curves, making them represent all the observations as well as I could, but giving greater weight to recent observations than to those of earlier date, and to long series of consistent observations than to short series, or to series which were more erratic.

The following table gives the data employed in plotting both the curves given in the diagram, and those not so given, which are referred to below. The table includes the concentration in gramme-equivalents per litre, the ionization coefficient at 0°, and the equivalent depression in degrees centigrade per gramme-equivalent in one litre of solution. The interpolated coefficients are indicated by *i*, and those extrapolated by *e*, and the observers from, or by the aid of, whose observations they were obtained, by A, B, D, W, representing Archibald, Barnes, Déguisne and Whetham. Non-significant figures are printed in italics.

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<sup>1</sup> Ztschr. f. phys. Chemie. 2, 491, 1888.

<sup>2</sup> *Ibid.*, 2, 501, 1888, and 27, 617, 1898.

<sup>3</sup> Phys. Review, 1, 199 and 274, 1893-4; 3, 270, 1896, and 4, 273, 1897.

<sup>4</sup> Ztschr. f. phys. Chem., 11, 110 and 529, 1893; and 12, 623, 1893.

<sup>5</sup> *Ibid.* 20, 207, 1896.

<sup>6</sup> *Ibid.* 19, 233, 1896.

<sup>7</sup> Recherches sur la Congélation des Solutions Aqueuses: Paris, Gauthier-Villars, 1896.

<sup>8</sup> *Loc. cit.*

Gramme-equivalent per litre.	Ionization Coefficient at 0°C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0°C.	Equivalent Depression.
KCl. (Barnes.)			KCl. (Abegg.)		
.0001	.989	.....	.00488	.976 i. W.	3.70
.0002	.986	.....	.00972	.962 "	3.63
.0005	.977	.....	.0118	.958 "	3.64
.001	.971	.....	.0145	.953 "	3.63
.005	.944	.....	.0193	.944 "	3.53
.010	.930	.....	.0237	.917 i. B.	3.51
.03	.910	3.533	.0240	.917 "	3.49
.05	.892	3.504	.0286	.912 "	3.51
.08	.871	3.470	.0354	.904 "	3.50
.10	.862	3.458	.0469	.895 "	3.47
.20	.832	3.398	.0583	.887 "	3.45
.30	.819	3.390	.0697	.878 "	3.43
.40	.804	3.372			
KCl. (Loomis.)			KCl. (Wildermann.)		
.01	.943 i. B.	3.60	.009818	.943 i. B.	3.538
.02	.923 "	3.55	.009822	.943 "	3.583
.03	.910 "	3.52	.01954	.924 "	3.542
.035	.905 "	3.53	.03883	.900 "	3.515
.05	.892 "	3.50	.07884	.900 "	3.532
.1	.862 "	3.445	.07652	.873 "	3.491
.2	.832 "	3.404	.07668	.873 "	3.487
.4	.804 "	3.353			
KCl. (Jones.)			KCl. (Ponsot)		
.001	.992 i. W.	3.80	.0234	.915 i. B.	3.419
.00299	.983 "	3.6789	.0439	.896 "	3.417
.00499	.976 "	3.7074	.1465	.846 "	3.413
.00698	.970 "	3.6246	.1688	.840 "	3.406
.00897	.965 "	3.6120	.2344	.827 "	3.392
.01095	.960 "	3.5982	.2456	.825 "	3.375
.02	.944 "	3.5750	.2472	.825 "	3.378
.04	.897 i. B.	3.5325	.2544	.824 "	3.377
.0592	.885 "	3.5067			
.078	.873 "	3.4923	NaCl. (Barnes.)		
.09646	.863 "	3.4688	.0001	.996	.....
.2	.832 "	3.4300	.0002	.991	.....
.28	.821 "	3.41074	.0005	.982	.....
KCl. (Raoult.)			.001	.974	.....
.01445	.953 i. W.	3.523	.005	.955	.....
.02895	.933 "	3.561	.010	.936	.....
.05825	.904 e. W.	3.478	.03	.896	3.573
.1168	.878 "	3.431	.05	.877	3.536
			.08	.860	3.530
			.10	.850	3.515
			.20	.815	3.443
			.30	.787	3.431
			.40	.765	3.412



Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.
NaCl. (Loomis.)			NaCl. (Abegg.)		
.01	.936 i. B.	3.674	.00241	.965 i. B.	3.91
.02	.916 "	3.597	.00478	.956 "	3.91
.03	.896 "	3.560	.00714	.945 "	3.84
.04	.886 "	3.541	.00948	.937 "	3.82
.05	.878 "	3.531	.01180	.931 "	3.70
.06	.870 "	3.529	.01410	.925 "	3.66
.07	.864 "	3.510	.0221	.906 "	3.56
.08	.860 "	3.501	.0439	.882 "	3.57
.09	.855 "	3.494	.0653	.867 "	3.55
.10	.850 "	3.484	.0871	.856 "	3.50
.20	.815 "	3.439	.1083	.847 "	3.47
NaCl. (Jones.)			NaCl. (Arrhenius.)		
.001	.974 i. B.	3.7500	.0467	.879 i. B.	3.79
.002	.967 "	3.7500	.117	.843 "	3.64
.02999	.963 "	3.683	.194	.816 "	3.54
.004	.959 "	3.650	.324	.781 "	3.51
.004998	.955 "	3.681	NaCl. (Ponsot.)		
.005995	.950 "	3.678	.1318	.836 i. B.	3.445
.006995	.947 "	3.631	.1808	.821 "	3.418
.007985	.942 "	3.628	.2016	.814 "	3.413
.008985	.939 "	3.628	.2248	.808 "	3.403
.01	.936 "	3.605	.2288	.806 "	3.405
.02	.915 "	3.578	.3136	.784 "	3.402
.0298	.896 "	3.544	HCl. (Barnes.)		
.0395	.887 "	3.538	.001	.996	.....
.04955	.878 "	3.519	.002	.995	.....
.05975	.870 "	3.507	.005	.989	.....
.0697	.865 "	3.500	.010	.984	.....
.0790	.861 "	3.492	.0207	.971	3.638
.0882	.856 "	3.483	.0518	.955	3.595
.0973	.851 "	3.477	.0829	.941	3.569
.1063	.848 "	3.469	.104	.932	3.556
.15	.831 "	3.447	.207	.909	3.585
.1925	.818 "	3.418	.305	.897	3.633
.2329	.805 "	3.414	.40	.884	3.638
.300	.787 "	3.410	NaCl. (Raoult.)		
NaCl. (Raoult.)			NaCl. (Raoult.)		
.0300	.896 i. B.	3.656	.0300	.896 i. B.	3.656
.0584	.870 "	3.550	.0584	.870 "	3.550
.1174	.843 "	3.473	.1174	.843 "	3.473
.2370	.804 "	3.465	.2370	.804 "	3.465

Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.
HCl. (Loomis.)			HNO <sub>3</sub> . (Loomis.)		
.01	.982 i. B.	3.61	.01	.977 i. D.	3.50
.02	.972 "	3.60	.02	.967 e. D.	3.56
.05	.955 "	3.59	.03	.959 "	3.53
.1	.933 "	3.546	.05	.950 "	3.51
.2	.910 "	2.565			
.3	.897 "	3.612			
HCl. (Jones.)			HNO <sub>3</sub> . (Jones.)		
.001222	.996 i. B.	3.7643	.001054	.994 i. D.	3.7951
.003662	.991 "	3.7411	.003158	.989 "	3.7682
.006112	.987 "	3.7467	.005253	.982 "	3.7693
.008538	.984 "	3.7033	.007378	.981 "	2.7409
.01222	.979 "	3.6743	.009456	.978 "	3.7331
.03619	.962 "	3.6750	.01153	.975 e. D.	3.7294
.05919	.951 "	3.6611	.03119	.958 "	3.7179
.08127	.940 "	3.5856	.05103	.949 "	3.7076
.1025	.933 "	3.5609			
.1228	.928 "	3.5692			
NH <sub>4</sub> Cl. (Loomis.)			KOH. (Loomis.)		
.01	.951 i. D.	3.56	.01	.965 i. D.	3.43
.02	.931 "	3.56	.02	.956 e. D.	3.45
.035	.914 "	3.50	.05	.943 "	3.44
.05	.900 "	3.48	.1	.932 "	3.43
NH <sub>4</sub> Cl. (Jones.)			KOH. (Jones.)		
.001	.987 i. D.	3.8	.001069	.983 i. D.	3.7418
.00599	.963 "	3.7062	.003202	.973 "	3.7477
.00997	.951 "	3.6108	.005327	.969 "	3.7169
.0595	.892 e. D.	3.5143	.007443	.967 "	3.6947
			.009550	.965 "	3.6859
			.01069	.964 e. D.	3.6296
			.03163	.950 "	3.6263
			.05174	.942 "	3.5756
			.07481	.935 "	3.6142
KNO <sub>3</sub> . (Loomis.)			BaCl <sub>2</sub> . (Loomis.)		
.01	.938 i. D.	3.46	.02	.860 i. W.	2.495
.02	.915 "	3.52	.04	.820 e. W.	2.475
.025	.899 "	3.46	.1	.768 "	2.385
.05	.876 "	3.41	.2	.724 "	2.345
.1	.832 e. D.	3.314	.4	.658 "	2.3275
.2	.789 "	3.194			

Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.
Ba Cl <sub>2</sub> . (Jones.) *			K <sub>2</sub> SO <sub>4</sub> . (Archibald.)—Continued.		
.002	.953 i. W.	2.7500	.002	.925	.....
.003996	.932 "	2.7027	.004	.904	.....
.005988	.917 "	2.6720	.005	.895	.....
.008	.906 "	2.6250	.008	.871	.....
.009984	.896 "	2.6142	.010	.859	.....
.011964	.889 "	2.5828	.050	.755	2.370
.01394	.880 "	2.5753	.055	.748	2.356
.01592	.872 "	2.5754	.060	.743	2.345
.01788	.866 "	2.5560	.070	.732	2.327
.02	.860 "	2.5500	.080	.722	2.314
Ba Cl <sub>2</sub> . (Ponsot.)			.100	.705	2.285
.00926	.900 i. W.	2.484	.200	.645	2.161
.00994	.897 "	2.515	.250	.629	2.118
.01030	.895 "	2.524	.300	.616	2.080
.01290	.887 "	2.481	.350	.606	2.056
.01304	.883 "	2.531	.400	.598	2.032
.02500	.845 "	2.480	.450	.591	2.014
.02740	.839 "	2.482	.500	.588	1.990
.03310	.827 e. W.	2.477	.600	.583	1.950
.03588	.822 "	2.481	.700	.580	1.916
.03676	.820 "	4.475	K <sub>2</sub> SO <sub>4</sub> . (Loomis.)		
.03824	.818 "	2.458	.02	.821 i. A.	2.46
.04810	.803 "	2.453	.04	.772 "	2.38
.05112	.802 "	2.445	.1	.705 "	2.271
.05520	.796 "	2.446	.2	.645 "	2.1585
.0620	.790 "	2.436	.4	.598 "	2.0335
.0680	.785 "	2.426	.6	.583 "	1.9455
.0774	.771 "	2.416	K <sub>2</sub> SO <sub>4</sub> . (Jones.)		
.2060	.717 "	2.316	.002	.925 i. A.	2.725
.2095	.716 "	2.320	.003992	.904 "	2.693
.2235	.710 "	2.309	.005990	.886 "	2.663
.3100	.685 "	2.297	.007970	.871 "	2.641
.3280	.682 "	2.308	.009930	.859 "	2.613
.3470	.679 "	2.317	.012	.850 "	2.613
K <sub>2</sub> SO <sub>4</sub> . (Archibald)			.01396	.842 "	2.593
.0001	.983	.....	.01590	.836 "	2.582
.0002	.976	.....	.01784	.829 "	2.545
.0004	.969	.....	.01976	.823 "	2.525
.0005	.964	.....	.03949	.771 "	2.469
.0006	.960	.....	.0579	.745 "	2.413
.0008	.953	.....	.07556	.727 "	2.372
.001	.946	.....	.10	.705 "	2.307

\* I have by oversight used one of Jones' two sets of observations, instead of the mean of his two sets; but the curve of mean values would not differ appreciably from the curve of single values.

Gramme-equivalent per litre.	Ionization coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization coefficient at 0° C.	Equivalent Depression.
$K_2 SO_4$ . (Jones.)— <i>Continued.</i>			$Na_2 SO_4$ . Archibald.— <i>(Continued.)</i>		
.116	.692 i. A.	2.289	.250	.690	2.120
.1357	.677 "	2.231	.300	.578	2.084
.152	.668 "	2.208	.350	.561	2.045
.16765	.661 "	2.197	.400	.546	2.025
.1826	.624 "	2.178	.450	.535	1.993
.19685	.647 "	2.160	.500	.525	1.975
			.600	.511	1.925
			.700	.501	1.890
$K_2 SO_4$ . (Abegg)			$Na_2 SO_4$ . (Loomis.)		
.00876	.865 i. A.	2.79	.02	.821 i. A.	2.545
.01306	.846 "	2.60	.04	.771 "	2.435
.01734	.829 "	2.47	.10	.694 "	2.295
.0216	.815 "	2.43	.20	.624 "	2.170
.0258	.803 "	2.40	.40	.546 "	2.036
.0299	.794 "	2.385	.60	.511 "	1.938
$K_2 SO_4$ . (Arrhenius.)			$Na_2 SO_4$ . (Raoult.)		
.0728	.729 i. A.	2.53	.1174	.678 i. A.	2.39
.182	.654 "	2.225	.2866	.584 "	2.18
.454	.590 "	2.09	.426	.540 "	2.68
$K_2 SO_4$ . (Ponsot.)			$Na_2 SO_4$ . (Arrhenius.)		
.0724	.731 i. A.	2.307	.056	.741 i. A.	2.515
.0752	.726 "	2.301	.1402	.661 "	2.325
.2295	.635 "	2.113	.234	.607 "	2.205
.2360	.633 "	2.110	.390	.549 "	2.095
.4140	.596 "	2.012			
.4280	.594 "	2.002			
$Na_2 SO_4$ . (Archibald.)			$H_2 SO_4$ . (Barnes.)		
.005	.893	.....	.002	.883	.....
.008	.870	.....	.004	.831	.....
.010	.859	.....	.010	.783	.....
.050	.752	2.382	.020	.734	.....
.055	.743	2.371	.0406	.720	2.224
.060	.736	2.360	.1016	.644	2.084
.070	.722	2.340	.1622	.609	2.017
.080	.712	2.320	.204	.596	1.979
.100	.694	2.286	.406	.569	1.940
.200	.624	2.165	.608	.553	1.918

Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.
$H_2SO_4$ . (Loomis.)			$H_2SO_4$ . (Wildermann.)— <i>Continued.</i>		
.02	.770 i. B.	2.247	.06244	.688 i. B.	2.098
.04	.721 "	2.155	.09216	.653 "	2.049
.10	.645 "	2.065	.1358	.622 "	2.004
.20	.598 "	1.984	.1930	.599 "	1.970
.40	.570 "	1.925			
$H_2SO_4$ . (Jones.)			$Na_2CO_3$ . (Loomis.)		
.002696	.962 i. W.	2.7077	.02	.735 i. D.	2.535
.007182	.906 "	2.5620	.04	.684 "	2.465
.011650	.870 "	2.5150	.10	.611 e. D.	2.32
.016106	.844 "	2.4091			
.02054	.823 "	2.3710	$Na_2CO_3$ . (Jones.)		
.02696	.796 "	2.3108	.003030	.859 i. D.	2.805
.07100	.678 i. B.	2.2183	.008068	.803 "	2.764
.11358	.633 "	2.0514	.013090	.770 "	2.753
.15472	.612 "	1.9952	.018096	.743 "	2.741
.19450	.598 "	1.9732	.02120	.730 "	2.722
.2330	.586 "	1.9498	.04802	.670 "	2.676
			.07736	.632 e. D.	2.494
			.09588	.613 "	2.335
$H_2SO_4$ . (Ponsot.)			$MgSO_4$ (Loomis.)		
.0149	.790 e. B.	2.282	.02	.594 i. D.	1.331
.0181	.770 "	2.265	.04	.522 "	1.277
.0365	.726 "	2.192	.06	.485 "	1.237
.0395	.720 i. B.	2.203			
.0503	.706 "	2.147	$MgSO_4$ (Jones.)		
.0669	.681 "	2.108	.002	.817 i. D.	1.7000
.0727	.674 "	2.091	.003996	.773 "	1.6767
.0876	.658 "	2.043	.005998	.728 "	1.6533
.2570	.587 "	1.895	.007976	.694 "	1.6174
.2580	.587 "	1.899	.009960	.669 "	1.6064
.4476	.565 "	1.850	.011994	.651 "	1.5913
.4516	.565 "	1.849	.01400	.634 "	1.5785
.8872	.535 "	1.859	.015972	.614 "	1.5590
			.017940	.608 "	1.5496
			.019904	.596 "	1.5323
			.03950	.521 "	1.4912
			.05872	.502 "	1.4391
$H_2SO_4$ . (Wildermann.)					
.009208	.889 i. W.	2.422			
.009216	.889 "	2.388			
.016808	.842 "	2.297			
.016834	.842 "	2.293			
.01690	.840 "	2.325			
.03206	.776 "	2.190			
.03212	.735 i. B.	2.183			
.06238	.688 "	2.10			

Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.	Gramme-equivalent per litre.	Ionization Coefficient at 0° C.	Equivalent Depression.
H <sub>3</sub> PO <sub>4</sub> (Loomis.)			H <sub>3</sub> PO <sub>4</sub> (Jones.)		
.03	.614 i. D.	0.94	.003279	.881 i. D.	1.1894
.06	.513 "	0.893	.009843	.771 "	1.1515
			.019605	.669 "	1.0967
			.027705	.627 "	1.0721
			.03279	.602 "	1.0522

The curves of the diagram are so labelled with the initial letters of observers' names, (Ab for Abegg), as to show both the depression observations, on which they are based, and the ionization coefficients used in plotting them. Thus the inscription KCl (J—W), means that Jones' depressions and Whetham's coefficients were used; H<sub>2</sub>SO<sub>2</sub> (J L B—B), that the curve is a mean curve based, mainly at least, on depression observations by Jones, Loomis, and Barnes, and plotted with Barnes' coefficients. The limits of concentration for the curves, are indicated also, in gramme-equivalents per litre.

Some of the curves are entered on an inset, drawn on four times the scale of the main diagram.

In interpreting the curves, we must not only bear in mind what has been said above about the probable accuracy of the ionization coefficients, but must in addition note the tendency exhibited by the curves of the various observers, as dilution increases, to run off at great dilution in directions characteristic of the observers, to the left or right relatively to the course pursued by them at moderate dilution. Thus Abegg's curves (see NaCl, KCl, K<sub>2</sub>SO<sub>4</sub>), and Jones's (see NaCl, KCl, NH<sub>4</sub>Cl, HCl) run off to the right. So do Arrhenius's in a marked manner. Raoult's tendency is also to the right, (see NaCl; his K<sub>2</sub>SO<sub>4</sub>, not plotted, shows it also; his most dilute KCl observation, he himself clearly regards as accidentally out.) On the other hand, Loomis's curves (see HCl, KNO<sub>3</sub>, NH<sub>4</sub>Cl, BaCl<sub>2</sub>) go to the left.

So do Ponsot's, and probably Wildermann's (not plotted), and I gather from Ponsot's diagrams of Pickering's observations, to which I have not access, that Pickering's also have the leftward tendency. Archibald's and Barnes' curves show less tendency to diverge than those of any other observers. And although this may be partially, it is not wholly, due to their having worked at moderate dilutions only. For in several cases, pointed out below, the curves of other observers start on a divergent course within their limit of dilution. But the fact that their curves usually agree with Loomis's, would lead one to suspect them of a leftward tendency.

The divergence, as shown on the diagram, is most marked in the case of highly dissociated electrolytes ( $\text{NaCl}$ ,  $\text{HCl}$ , etc.) in which, at great dilution, the rate of increase of ionization with dilution is small, the curves being crushed up, therefore, into a small space. But it is obvious also, in the  $\text{K}_2\text{SO}_4$  curves (especially Abegg's) and the  $\text{BaCl}_2$  curves (including Ponsot's, not shown). And although for  $\text{MgSO}_4$  and  $\text{H}_3\text{PO}_4$ , whose ionization increases rapidly with dilution, the single curves do not reveal it, the relative positions of the two curves in each case are what they might be expected to be, if they were tending unduly, Jones's to the right, and Loomis's to the left.

This tendency is explicable at once, when we reflect that as it is equivalent depression that is plotted, the errors of the observations are brought into greater and greater prominence as dilution increases. According, therefore, as the characteristic error of an observer's method of measuring total depression is positive or negative, will his curves of equivalent depression diverge at great dilution to the right or left of their true course. And they must diverge even if the error is very small.

The equivalent depression curves of single observers are therefore open to grave suspicion at high dilutions; and since one can never be sure that the errors of different methods will even approximately neutralise one another, mean curves are, at high

dilution, not much more trustworthy than their components.\* It is much safer, therefore, to base conclusions as to depression constant on moderate dilution curves, although the conclusions they admit of may not be so exact as we might wish.

#### *Discussion of the Curves.*

Electrolytes such as NaCl, HNO<sub>3</sub>, KOH, have 1 equivalent in the single molecule, and 2 ions. If, therefore, they exist in solution in single molecules, their curves should be normal 1—2 curves. If the molecules are all double or triple, the curves should be 2—4 or 3—6 curves, provided the association does not involve change in the mode of ionization. If it does, they may be 2—2, or 3—4, 3—3, 3—2 curves respectively, according to the change that may occur. If the molecules are single at extreme dilution, but become double or triple as dilution diminishes, the curves should start as 1—2 curves, and undergo the appropriate transformation.

The electrolyte for which we have the most complete and trustworthy data, is KCl. The LB—B curve is based on two series of observations in close agreement and by a method exhibiting less divergence than the others. Jones's runs a little to the right of it; Abegg's a little to the left. Both Raoult's and Wildermann's cross it, the latter being somewhat steeper, the former less steep. Ponsot's

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\* It follows that it is inadmissible to proceed as Raoult has done in determining depression constants, (*loc. cit.* p. 658), viz., by selecting high dilution curves which are in agreement, and applying extrapolation to a mean curve derived from them; for such procedure may mean the selection of observations made by methods which have characteristic errors of the same sign. In fact, a mean curve based on observations which agree well at low dilution, but disagree markedly at high dilution, would be likely to give a better result, as more probably combining observations with small characteristic errors of opposite sign. Raoult's procedure is open to other objections. For (1) his curves of equivalent depression against total depression, make series of observations appear to be in greater disagreement than they really are, and are thus not helpful in making a judicious selection of observations to be used; and (2.) extrapolation of such curves not only gives a result affected by the average of the characteristic errors of the observations used, but also neglects the possibility, in some cases the probability, that owing to change in association and mode of ionization, the law of the change of curvature may be very different beyond the limits of observation, from what it is within these limits.



coincides with the lower part, but in the upper part diverges to the left. In form the curve is thus probably trustworthy. But being plotted with Barnes' coefficients it may be too high or too low. The R—W and J—W curves (see inset) are not open to this suspicion, but at the dilutions to which even their lower and more trustworthy parts apply, they may have begun to diverge unduly rightwards. If the L B—B curve (see inset) be raised about 2.5 per cent., as is shown to be necessary by a comparison of Whetham's and Barnes' coefficients, it comes into a position to the left of the R—W and J—W curves, the usual relative position of the curves of these observers. Loomis's own curve for somewhat greater dilutions than those of the L B—B curve, when plotted with Whetham's coefficients, coincides very nearly with the boundary line of the inset; Wildermann's is a little to the left of Loomis's, and somewhat steeper. Both exhibit a slight rightward bending, as do all the others.

It would be difficult to draw a mean curve with any confidence; but any such curve would run about midway between the 1—2 and 2—4 (1.85) lines, would have a slight rightward bending at its upper end, and if produced with diminishing curvature, would run out to a point a little to the right of the 1—2 (1.85) intersection.

If this intersection were the starting point of the curve, and if there were no association, the curve should lie wholly to the right of the 1—2 (1.85) line. If, as dilution diminished, sufficient doubling of molecules with unchanged mode of ionization should occur, the curve, after first bending away from that line to the right, would change its curvature, bend towards the line and cross it, and then run towards, and finally away from, the 2—4 line, as the mean curve appears to do.

As the 2—2 line is far to the left, the mean curve might be accounted for also, on the assumption of a very slight formation of double molecules dissociating into two ions; and a slight formation of such molecules would probably involve no greater variation of the migration numbers with concentration than has been observed.

If the 1—2 (1.86) intersection, were assumed as the starting point of the curve, the mean curve would cut the 2—4 (1.86) line. If, therefore, association in molecules with unchanged mode of ionization were assumed, some formation of triple molecules would be indicated, and if the associated molecules were assumed to dissociate into two free ions, a greater extent of such association would be indicated. Thus, with this starting point, less probable assumptions as to association must be made, to account for the observations.

If the 1—2 (1.84) or even the 1—2 (1.845) intersection were taken as the starting point, the curve must bend considerably to the left before running out,—of which bending none of the experimental curves give any indication whatever.

The most probable conclusion, then, that we can draw from the observations, is that the depression constant is 1.85, with a limit of error of .01, or perhaps .005, that the electrolyte has single molecules at great dilution, and that as dilution diminishes, either double molecules with unchanged mode of ionization form to a considerable extent, or double molecules dissociating into two ions, to a small extent.

Loomis's and Barnes' observations, on which the NaCl (L B—B) curve is based, are also in close agreement; but as Loomis's curve for slightly greater dilution bends slightly to the right, the upper part of the L B—B curve should probably have greater curvature. Jones' curve for moderately dilute solutions runs a little to the left of it, and at higher dilutions diverges markedly to the right, as separately shown. Abegg's observations are on both sides of it, but at higher dilutions his curve also goes to the right. Raoult's touches it, but goes off to the right. Arrhenius's is considerably to the right, and goes widely rightward at greater dilutions. Ponsot's is a little to the left. As the L B—B curve is plotted with Barnes' coefficients, it is probably too low. If it be raised about as much as was found necessary in the case of the KCl curve, it will lie along the 1—2 line, or a little above or below it, with its upper end, as drawn, so directed, as to run out probably at a point nearer the

1—2 (1.85) intersection, than either the 1—2 (1.83) or the 1—2 (1.87) intersection. Thus the defective data as to ionization prevent our drawing a more definite conclusion than that the association indicated, if any, is less than in the case of KCl, and that the depression constant is 1.85, with a limit of error of perhaps .02.

The HCl curve is interesting as exhibiting a point of minimum equivalent depression. The observations on which the L B—B curve is based, are in good agreement. Jones' curve almost coincides with it in the lower part, but goes off to the right in the upper part and at higher dilutions, as shown separately. Loomis's curve at higher dilutions (also separately shown) goes to the left, but in a less marked manner. As drawn, the upper part of the mean curve lies between the 1—2 and 2—4 (1.85) lines, and it is running out to a point a little beyond the 1—2 (1.86) intersection (see inset). But as it is plotted with Barnes' co-efficients it is perhaps too low. If raised 1 or 2 per cent. it would appear to run out at some point between the 1—2 (1.84) and 1—2 (1.86) intersections. The data are of course very defective; but they are consistent with a depression constant of about 1.85, and they seem to indicate a greater extent of association than in the case of KCl.

The L—D and J—D curves for  $\text{NH}_4\text{Cl}$  are not in agreement, having the usual relative position of Loomis's and Jones' curves. A mean curve based on their lower parts would be slightly to the left of the 1—2 (1.85) line, and directed to a point considerably to the right of the 1—2 (1.86) intersection. It might thus indicate anything between a high value of the depression constant accompanied by very considerable association of molecules, and a constant of about 1.85, with no association in dilute solutions, and only a slowly increasing association in stronger solutions.

The  $\text{HNO}_3$  curve (see inset) is a mean curve based on Loomis's and Jones's. Both are beyond the bounds of the inset, the former to the left, the latter to the right. Neither this curve nor that of  $\text{KNO}_3$  is sufficiently trustworthy to warrant any

close inspection, but both are clearly consistent with the 1.85 value of the depression constant. If the leftward bending of the  $\text{KNO}_3$  curve in its lower part were actual, as well as the position of the curve, the formation of triple molecules might be indicated. But being a Loomis curve, it is open to the suspicion of being as a whole, too far to the left; and it is plotted with doubtful coefficients.

The KOH curves, Loomis's on the main diagram and Jones's on the inset, are useful only to illustrate the difficulty of making concordant observations by different methods. As usual, Loomis's is to the left, and Jones's to the right.

Electrolytes such as  $\text{BaCl}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ , have 2 equivalents in the single molecule, which may dissociate into 3 or into 2 ions. If there is no association, they will therefore have 2—3 or 2—2 curves, according to the mode of ionization. If there is complete doubling of molecules, the curves will be 4—6 or 4—4 curves, provided the doubling does not involve change in mode of ionization. Otherwise they might be 4—5, 4—3 or 4—2 curves. (The corresponding tangent lines are so far to the left of the experimental curves that they are not entered on the diagram.) If the molecules are associated in threes, the curves will be 6—9 or 6—6 curves, with the above proviso.

Both Loomis's and Jones' curves for  $\text{BaCl}_2$  are shown on the diagram, plotted with Whetham's coefficients (rough extrapolated values, however, in the case of the former). Ponsot's curve agrees very closely with Loomis's. Bearing in mind the rightward and leftward tendencies of Jones's and Loomis's curves, respectively, we may conclude from the curves of the diagram that the actual curve runs down to the right of the 2—3 line, bending away from it to the right, and that it would intersect the  $a=1$  line at a point between the 2—3 (1.85) and 2—3 (1.87) intersections, probably nearer the former than the latter. The curve is thus, so far as we can judge, a normal 2—3 ( $1.85 \pm .01$ ) curve, running, however, very close to the 2—3 line. The diagram, therefore, indicates that  $\text{BaCl}_2$  exists in solution in single molecules, dissociating into 3 ions, at least for the most part, and that it has a depression constant nearer 1.85 than 1.87.

The  $\text{H}_2\text{SO}_4$  (J—W) curve for high dilutions, being a Jones curve, is probably too far to the right, and being plotted with Whetham's coefficients, is probably too high. Wildermann's curve for high dilutions runs parallel to it, considerably to the left. The J L B—B curve, for lower dilutions, is very nearly coincident with Barnes' curve, and in its lower part with Jones's and Loomis's as well. But in the upper part, Jones' curve goes off markedly to the right, and Loomis's markedly to the left. Wildermann's is slightly to the left at the lower end, and diverges somewhat leftwards in the upper part. Ponsot's runs nearly parallel to it, somewhat to the left, and diverging to the left at higher dilutions. The J L B—B curve is thus trustworthy as to form; but being plotted with Barnes' coefficients, it is probably too low. The actual curve would thus appear to cross the 2—3 (1.85) line not far from its starting point, bend towards the 4—6 line, and run down below that line, finally bending slightly towards it. Its course is therefore what it would be if it started as a 2—3 curve, for  $k=1.85$  or thereabout, changed its curvature at a somewhat early stage, and tended to be transformed slowly into either a double molecule curve or a 2—2 curve, or perhaps both. The diagram would therefore indicate that at extreme dilution  $\text{H}_2\text{SO}_4$  exists in solution in single molecules, dissociating into three ions, that at an early stage and in a somewhat marked manner, either doubling of molecules sets in, or partial dissociation into two ions, or perhaps both, that the change increases slowly and steadily as dilution diminishes, and that at a concentration of about 0.6, if the coefficients at this concentration are to be trusted, the change is increasing in rate; also that the depression constant may quite readily be about 1.85.

The  $\text{K}_2\text{SO}_4$  (L J A—A) curve, is based on series of observations which in the main are in good agreement. It very nearly coincides with the Loomis and Archibald curves, and Ponsot's runs down slightly to the left. In its lower part it coincides with the Jones curve, but in its upper part the Jones curve, which is separately represented for great dilutions, runs off to the right. Abegg's curve for higher dilutions runs even more

markedly to the right, although it is farther to the left at its lower end. Arrhenius's is considerably to the right, and diverges widely rightwards. The  $\text{Na}_2\text{SO}_4$  (L A—A) curve is also almost coincident with both the Loomis and the Archibald curves. Both Raoult's and Arrhenius's are considerably to the right, and diverge slowly rightwards. Such of these curves as are entered on the diagram, being plotted with Archibald's coefficients, are probably somewhat too high or too low, as the case may be. Those for great dilutions are too discordant to admit of discussion. The mean curves for both salts have the same general form, and run down, as drawn, a little below the 2—3 line. Their upper ends are so directed as to suggest their running out at the 2—3 (1.85) intersection, or thereabout. At their lower ends they turn sharply to the left and cross the 2—3 line, going towards the region of the double molecule curves, or of the 2—2 curve. The turns are too sharp, and the 4—6 and 6—9 lines too near, to make their transformation into double or triple molecule curves, with unchanged ionization, probable. The diagram suggests rather their transformation into 4—5, 4, or 2 or 2—2 curves. If this be accepted, it means that at extreme dilution these sulphates exist in solution in single molecules, dissociating into three ions, that partial dissociation into two ions or doubling of molecules sets in, apparently at an early stage, but increases more slowly than in the case of  $\text{H}_2\text{SO}_4$ , until the dilution has been considerably diminished, when it undergoes a rapid increase. A close determination of the depression constant cannot be made; but even if the curves have to be either raised or lowered a little, and if, Loomis's tendency being leftward, their upper parts have to be shifted somewhat to the right, they will be consistent with its being about 1.85.

The  $\text{Na}_2\text{CO}_3$  curves are too discordant to form a basis for discussion. But either Loomis's curve or a mean curve, or even Jones's curve itself, is quite consistent with a depression constant of about 1.85; and both curves indicate the occurrence of rapid association or of rapid change of ionization after considerable diminution of dilution. The fact that

Loomis's curves bend towards the left, suggests that the actual curve after starting at the 2—3 intersection, may bend considerably to the right before association or change of mode of ionization has advanced sufficiently to change the direction of its curvature.

An electrolyte such as  $\text{MgSO}_4$ , according as it may exist in solution in single, double or triple molecules, and according to its mode of ionization in associated molecules, may have a 2—2, 4—4 or 2, or 6—6, 4, 3 or 2 curve. Jones' curve lies to the right of the 2—2 (1.85) line, bending towards it, and may quite readily be a 2—2 (1.85) curve, changing to a 4—4 or 4—2 curve. Loomis's lies between the 2—2 and 4—4 lines. A mean curve would already, at a concentration .02, have crossed the 2—2 line. The data, such as they are, are consistent with the depression constant having a value of about 1.85, and would indicate single molecules in dilute solutions, doubling of molecules at a very early stage, and a steady increase in association throughout.

According as  $\text{H}_3\text{PO}_4$ , if it exist in solution in single molecules, may dissociate into 4, 3 or 2 ions, will it have a 3—4, 3—3, or 3—2 curve. If it have double molecules, its curve may be a 6—8, 6—7, etc., to 6—2 curve, according to the mode of ionization. Jones' curve runs down to the right of the 3—2 (1.85) line, bending towards the line. Loomis's lies between the 3—2 and 6—4 lines. A mean curve would be just to the right of the 3—2 line, and might readily run out at the 3—2 (1.85) intersection. This would indicate single molecules in dilute solutions dissociating into two ions, an early occurrence of doubling of molecules, and steady increase in the extent of association as dilution diminished, the double molecules formed dissociating into 4, 3, or 2 ions, but not into more. Although the coefficients with which the curve is plotted are doubtful, the curve is so nearly parallel to the axis of ionization coefficients, that even a considerable error in their values would not affect the above conclusions.

*General Conclusions.*

Although the observations on which the above discussion is based are defective, and the particular conclusions drawn are consequently tentative, I think it may be held with some confidence (1) that the curves of equivalent depression against ionization coefficient, have positions, forms, and slopes, such as they might be expected to have, on reasonable assumptions as to mode of ionization and constitution in solution, according to the Van 't Hoff-Arrhenius theory of the depression of the freezing-point in solutions of electrolytes, (2) that for all the electrolytes examined, they are consistent with the depression constant having a common value of about 1.85, and that in the case of the electrolyte for which we have the best data, the curve is not consistent with a greater limit of error in this value than about .01, unless improbable assumptions are made with respect to the constitution of the electrolyte in solution, and (3) that the diagram enables us to reach in some cases, conclusions of considerable probability with respect to the constitution of the electrolyte in solution, and its mode of ionization.