course of our later calculations it will be necessary to estimate the heat capacity of certain other gases, and this estimate will be based upon such data as exist for these gases and upon analogies with the typical gases which have been considered above. These cases may best be considered as they occur in the later calculations.

THE DISSOCIATION OF TERNARY ELECTROLYTES.

By James W. McBain.

Received July 22, 1912.

The last paragraph of Part IV of A. A. Noyes and K. G. Falk's invaluable compilations of the more reliable data for the properties of aqueous electrolytes refers to the divergences in apparent dissociation of ternary electrolytes when the results of conductivity and freezing point measurements are compared without assuming other than the simplest possible ions; that is, assuming $Ba^{\cdot\cdot} + 2Cl'$, but not $BaCl^{\cdot}$ or $BaCl_3'$, etc.

They state:[1] "The most striking discordance between the two sets of ionization values is that presented by the bivalent metal halides, for which the values derived from the freezing point are always much larger than those derived from the conductance ratio. It has already been shown in Part II[2] of this series that the transference numbers of these substances are also abnormal, namely, in the respect that the cation transference decreases markedly with increasing concentration. There appears, however, to be no chemical explanation which would account for both of these anomalies, and it seems therefore probable that physical deviations must enter as a complicating factor."

It is the object of the present note to point out that the two phenomena occur in different ranges of concentration and that they are therefore in all probability due to separate causes. They may be explained in accordance with all other data by assuming intermediate ions (*e. g.*, $BaCl^{\cdot}$) in the more dilute, and complex anions (*e. g.*, $BaCl_3'$) in the more concentrated solutions, the effects of these ions being in opposite directions.

In 1905 the writer was interested in the question as to whether in complicated cases all the data with regard to mode and degree of ionization and the concentration and properties of the various molecular species present in a single aqueous solution could be quantitatively reconciled within the limits of the dissociation theory. To test this the extreme case of cadmium iodide and its potassium iodide derivatives was chosen,[3] since so detailed a comparison of the various methods for such cases did not appear to have been previously attempted. The result was very satisfactory from the standpoint of the dissociation theory, although for

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[1] This Journal, **34**, 489 (1912).

[2] *Ibid.*, **33**, 1454–9 (1911).

[3] McBain, *Z. Elektrochem.*, 11, 222 (1905).

lack of electromotive force data the question of the concentration of the intermediate ion, CdI, could not be fully discussed.

The chief concordances were the determination of the mobility of the CdI_3' ion by three quite independent methods leading to the same numerical value, and furthermore the calculation in agreement with experiment of the conductivity and migration relationships of various solutions containing potassium iodide in addition (*i. e.*, solutions of K_2CdI_4). In view of the nature of these confirmations of theory for so extreme and complicated a case it would seem unfortunate to depart from the simple theory without cogent reason.

While the use of Noyes and Falk's series of compilations of smoothed results is essential to any rational attempt further to develop the dissociation theory, still they must always be used with a full knowledge of the essential disadvantages and uncertainties inherent in such compilations, especially where not supplemented by more detailed studies of all the related data available for particular cases.[1]

A concrete example will make this clear; the only freezing point data quoted by Noyes and Falk for $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2 and $Cd(NO_3)_2$ are those of H. C. Jones, published in 1893 before the theory of the convergence temperature had been developed. On the other hand the results of Jones (also 1893) for $BaCl_2$ and $MgSO_4$ are averaged with those of various later observations with the result that the final values adopted give molar lowerings from 1–2% smaller than those of Jones for $BaCl_2$ (10–100 millinormal solutions) and from 7–8% smaller in the case of $MgSO_4$. Presumably therefore the results for the zinc and cadmium salts are also too high by similar amounts. These are very appreciable uncertainties when comparing the mol numbers obtained in these dilute solutions from freezing point and conductivity measurements, for it is upon the differences so found that Noyes and Falk base their statement quoted above (referring to these limits of concentration). The actual differences between the mol numbers from freezing point and conductivity results were:[2] $BaCl_2$, 0.4–2%; $CaCl_2$ and $MgCl_2$, 2–6%; $CdCl_2$, $CdBr_2$, CdI_2 and $Cd(NO_3)_2$, 4–14%.

Again to take the second sentence of Noyes and Falk's statement above, the migration number of cadmium chloride is *constant* from extreme

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[1] Such as the chlorides of zinc and mercury, K. Drucker, *Ibid.*, **18**, 236 (1912).

[2] Only the data quoted in their table (*loc. cit.*, p. 475) are here cited. In glancing through the papers referred to in this note the following arithmetical errors happened to attract notice: THIS JOURNAL, 34, 475 (1912), CdI_2 in 0.001 N solution 87.0% ionized, instead of 86.3%; *Ibid.*, **32**, 1024, 1027 (1910), molar lowering of CdI_2 in 0.2 N solution 2.266, instead of 2.287, and mol number 1.200, instead of 1.229, mol. number of $SrCl_2$ in 0.2 N solution 2.611, instead of 2.603; *Z. Elektrochem.*, **11**, 220 (1905), CdI_2 in 0.1 N solution (Jones) 0.126 ionized, instead of 0.116.

dilution up to 125 millinormal, that of cadmium bromide up to 200 millinormal, and even that of cadmium iodide up to 25 millinormal.

The case of barium chloride is particularly interesting, since the careful measurements of Bukschnewski indicate that the migration number *falls* from 0.55 in 7 millinormal to 0.54 in 33 millinormal solution. The precision measurements of Noyes on barium chloride refer to only two concentrations, giving 0.558 at 40 millinormal and 0.585 at 200 millinormal, and therefore they cannot be adduced as evidence for or against the existence of this minimum in 33 millinormal solution, although they of course helped to produce Noyes and Falk's smoothed curve of results rising regularly with the concentration. Fortunately I can cite Drucker[1] as also regarding the experimental existence of a minimum as plausible (also for $CdBr_2$).

In the following table the data of Noyes and Falk for the percentage ionization values of cadmium iodide from freezing point and conductivity[2] are tabulated in full (those marked with an asterisk are omitted by them in their table of comparison) together with the differences between these, and also the migration ratios (Redlich and Bukschnewski). Concentration is expressed in milli-equivalents per liter.

TABLE I.—CADMIUM IODIDE.

Concentration.	0.	10.	20.	50.	100.	200.	750.
Per cent ionization, freezing pt.	..	59.3	54.0	40.0	22.5	10.0	..
" " " conductivity	..	57.3	46.9	34.5*	26.1*	20.6*	..
" " " difference	..	+2.0	+7.1	+5.5	—3.6	—10.6	..
Migration ratio	0.557	0.557	0.554	0.61	0.68	0.85	1.20

The conductivity results may be substantiated by comparison with those of Zelinsky and Krapiwin. The chief point to be noted is that the differences between freezing point and conductivity change sign in the higher concentrations where the migration ratio has commenced rapidly to rise.

McBain[1] has pointed out that according to the mass law the concentration of a complex ion like CdI_3' should vary with the cube of the concentration of the iodine ion; that is, these anions should disappear with extreme rapidity through dilution. On the other hand, as Drucker[2] remarks, intermediate ions like $CdI^{\cdot}$ should change quite slowly with the concentration. It may be pointed out here that owing to increase in the normal dissociation and to divergence from the mass law intermediate ions may persist into very dilute solutions, and indeed when complex ions like CdI_3' are formed in strong solutions the relative concentration (per-

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[1] *Loc. cit.*

[2] It is interesting to note that Noyes and Falk take 113.0 for the conductivity of cadmium iodide at infinite dilution; Wershoven himself used 120.4, Drucker 120, and McBain 119.5; this divergence corresponds to an uncertainty of about 14% in the value for the mobility of the cadmium ion.

centage of total salt) of the intermediate ion might even increase on dilution. The explanation here advanced is in agreement with the essential constancy of the migration ratios of other related salts, such as cadmium bromide, to much higher concentration, since cadmium iodide is recognized as furnishing an extreme typical case of complex formation.

To sum up, the behavior of ternary salts can be explained within the experimental error of the available data as being due to the pressure of intermediate ions, and also of complex ions in the more concentrated solutions.

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CERTAIN PHYSICAL PROPERTIES OF THE ALKALI NITRATES AND CHLORIDES.

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Received July 15, 1912.

The elements belonging to any group in the periodic classification exhibit, as is well known, chemical and physical properties which, in a general way, are simple functions of the atomic weights. Thus, if the numerical values for a given property be taken, they will show, as a rule, a more or less regular increase—or decrease, as the case may be—with increasing atomic weights of the elements. The same general statement may be said to apply to a series of compounds of the elements in such a group. This relation may be easily represented graphically by plotting the atomic weights as abscissas and the given properties as ordinates. When this is done it will at once be clear that the above generalization is only a rough approximation, since the points so plotted will seldom, if ever, lie exactly in a straight line or on a regular curve.

The present investigation is a study of several physical properties of two salts of the entire series of alkali metals, including lithium, sodium, potassium, rubidium, cesium and the radical ammonium, the object in view being the determination of the exact quantitative relations which exist between the properties considered and the atomic weights of the metals. For this purpose the nitrates and chlorides have been chosen. The following physical properties have been considered:

1. Specific gravity of solids.
2. Melting points.
3. Heat of solution.
4. Solubility.
5. Specific gravity of solutions.
6. Expansion of solutions.
7. Index of refraction of solutions.

For the more common salts these properties have all been quite thor-