

SOME IONIZATION EXPERIMENTS.

BY P. N. EVANS.

The proportion existing between the ionized and un-ionized molecules of an electrolyte in (aqueous) solution, is represented by the equation $a \cdot b = k \cdot c$, in which a , b , and c are the concentrations of the anions, kathions and un-ionized molecules of the electrolyte, respectively, and k a constant depending on the nature of the electrolyte and independent of the concentration for moderately or highly dilute solutions.

Supposing this equilibrium to have become established, which is the case in an exceedingly brief time, if not instantaneously, any addition of either kind of ion concerned, the quantity of solvent remaining the same, must result in an increased value for its concentration and produce a corresponding increase in the number and concentration of the un-ionized molecules; for, k being a constant, any increase in the value of a or b will involve an increase of that of c if the equilibrium is to be maintained.

If to a saturated solution of an electrolyte there be added a second soluble electrolyte having an anion or kathion in common with the first, there must result a state of supersaturation with regard to the first electrolyte or a separation of a portion of it in insoluble form.

Many examples of this are familiar to all. For instance, a saturated solution of sodium chloride is instantly precipitated by the addition of concentrated hydrochloric acid, in spite of the water that is added at the same time; on the other hand, the case is complicated and the precipitation assisted, probably by the chemical union taking place between the hydrochloric acid and some of the water, made evident by the evolution of heat, thus increasing all the concentrations by removing (chemically changing) some of the solvent. The same result is obtained and the same reasoning applies when calcium chloride is added to a saturated sodium chloride solution. The precipitation of sodium chloride is brought about without this complication of causes by the addition of crystallized potassium chloride (KCl) or anhydrous sodium sulphate (Na_2SO_4), and even crystallized sodium sulphate ($Na_2SO_4 \cdot 10H_2O$) gives the same result in spite of the water added in the crystals.

Similarly, potassium chloride can be precipitated by hydrochloric acid, sodium chloride ($NaCl$), or potassium sulphate (K_2SO_4); and copper sulphate ($CuSO_4 \cdot 5H_2O$) by cupric chloride ($CuCl_2 \cdot 2H_2O$), copper nitrate ($Cu(NO_3)_2$).

$6\text{H}_2\text{O}$), or sulphuric acid; barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) by hydrochloric acid, or sodium chloride; calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by sulphuric acid, potassium sulphate, calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$); lead chloride (PbCl_2) by hydrochloric acid, sodium chloride, potassium chloride.

In this list we have a very wide range of solubility: 100 parts of water dissolve NaCl 35, KCl 32, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 40, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ 33, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.20, PbCl_2 .74 parts. It is not evident whether easily or difficultly soluble substances should respond more readily in the yielding of a precipitate under these conditions, for the much greater degree of supersaturation attainable with an easily soluble substance may be offset by the greater difficulty in disturbing this state of supersaturation.

The greater the solubility of the electrolyte added to the saturated solution, the more readily a precipitate should be obtained; and the higher the dissociation constant of the second electrolyte, the more probable is a marked result.

In spite of the apparently favorable conditions in this respect, all attempts to precipitate lead chloride from its solution by means of lead nitrate were in vain. A saturated solution is very readily prepared by warming the solution in contact with an excess of the salt, and then cooling, owing to the great difference in solubility in hot and in cold water. The immediate and copious precipitate produced in this solution by the addition of sodium or potassium chloride or hydrochloric acid seemed to indicate that the tendency to remain in the supersaturated condition was very slight in the case of this salt, yet the addition of lead nitrate crystals to the solution (saturated), even in the considerable quantity made possible by the ready solubility of the nitrate (48 parts in 100), failed to cause any precipitation, either immediately or on long standing, or even on adding a crystal of lead chloride to induce crystallization from the solution, supposing it to be supersaturated. Lead nitrate, like most normal salts, has a high dissociation constant, more than half that of the strongest acids in a .1 per cent. solution (calculated by Arrhenius from conductivity experiments by Kohlrausch). This fact, and its high solubility, should be most favorable to the precipitation of the lead chloride, on account of the considerable increase in the concentration of the lead ions made possible thereby.

In harmony with the usual similarity of barium to lead, a saturated solution of barium chloride showed no sign of precipitation with barium nitrate ($\text{Ba}(\text{NO}_3)_2$); as already stated, a precipitate was produced by the

addition of hydrochloric acid, or sodium or potassium chloride to the saturated barium chloride solution.

Similarly, potassium sulphate, though precipitated from its saturated solution by the addition of potassium chloride or sodium sulphate, gave no precipitate with sulphuric acid; and calcium sulphate was not thrown down by either sodium sulphate or ammonium sulphate but did separate slowly on the addition of potassium sulphate and more quickly with sulphuric acid.

Apparently, then, in these cases, the number of un-ionized molecules of the first is not increased by the addition of the second electrolyte, and the only plausible explanation seems to be that in these cases double salts are formed; e. g., lead-chloride-nitrate (PbClNO_3), barium-chloride-nitrate (BaClNO_3), hydrogen-potassium-sulphate (HKSO_4), calcium-sodium-sulphate ($\text{CaNa}_2(\text{SO}_4)_2$?), and calcium-ammonium-sulphate ($\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2$?).

Taking the case of lead chloride as an example, the addition of the lead nitrate must immediately increase the number of lead ions, but at the same time diminishes both this and the number of the chlorine ions by permitting the formation of lead-chloride-nitrate, so that the value of the product of the concentrations of lead and chlorine ions is not thereby increased, thus causing no rise in value of the concentration of the lead chloride, and, therefore, no separation of this substance as a precipitate. It does not follow that this peculiarity of behavior must accompany the formation of a double salt under similar circumstances, however, for it may be that the increase of the concentration of one kind of ion concerned may more than counterbalance the simultaneous decrease in this and that of the other kind of ion involved; this is simply a question of the value of the dissociation constants of the electrolytes present.

It seems probable that double salts exist in solutions whenever there is a polyvalent acid in presence of two or more bases or a polyvalent base in presence of two or more acids, though other evidence of the existence of most of these compounds is at present lacking. Since, however, we know and recognize the existence of only those double salts which separate out from solutions of their constituents rather than these constituents in distinct crystals, the evidence so far accepted for the existence of such compounds is of a very limited kind, namely, only their solubility relative to that of their constituents. In other words, if these separate in preference to the double compound, the latter does not exist so far as this kind of evidence is concerned.

Now, supposing that in a solution of equivalent quantities of the constituents the dissociation constants of these and the double salt are such that approximately equal numbers of molecules of the three kinds exist un-ionized, and the solution be concentrated, the double salt will separate if its molecular solubility (solubility divided by molecular weight) is less than that of either constituent, but not otherwise. Of course, it is not probable that the constants are such as to even approximately produce a condition like that imagined in the example just described, but inasmuch as normal salts do not differ very widely in their dissociation constants, the facts may be nearly enough in harmony with the supposition to make a study of these molecular solubilities not without interest in this connection, though the data available are not so numerous as might be desired.

An examination of the solubilities of twelve double salts selected at random showed the facts to be in accordance with this theory without a single exception. The figures are given in the following table, the formulas selected being those of the substances separating out as crystals from their solutions.

<i>Formula.</i>	<i>a. Molecular weight.</i>	<i>b. Solubility in 100 parts water.</i>	<i>b ÷ a × 100</i>
K_2SO_4	174	12.5	7.2
$Al_2(SO_4)_3 \cdot 18H_2O$	665	85	12.8
$KAl(SO_4)_2 \cdot 12H_2O$	474	9.5	2.0
$(NH_4)_2SO_4$	132	77	57.6
$Al_2(SO_4)_3 \cdot 18H_2O$	665	85	12.8
$(NH_4)Al(SO_4)_2 \cdot 12H_2O$	452	9	2.0
K_2SO_4	174	12.5	7.2
$Cr_2(SO_4)_3 \cdot 18H_2O$	717	120	16.7
$KCr(SO_4)_2 \cdot 12H_2O$	500	20	4.0
$(NH_4)_2SO_4$	132	77	57.6
$Cr_2(SO_4)_3 \cdot 18H_2O$	717	120	16.7
$(NH_4)Cr(SO_4)_2 \cdot 12H_2O$	478	over 12	over 2.5
K_2SO_4	174	12.5	7.2
$Fe_2(SO_4)_3 \cdot 9H_2O$	562	over 80	over 14.1
$KFe(SO_4)_2 \cdot 12H_2O$	503	20	4.0

<i>Formula.</i>	<i>a. Molecular weight.</i>	<i>b. Solubility in 100 parts water.</i>	<i>b ÷ a × 100</i>
$(\text{NH}_4)_2\text{SO}_4$	132	77	57.6
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	60	21.6
$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	392	17	4.3
NH_4Cl	53.4	33	61.8
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	350	over 1900	over 543
$(\text{NH}_4)_2\text{SnCl}_6$	366	33	9.0
K_2SO_4	174	12.5	7.2
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	172	0.205	0.12
$\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	328	0.25	0.08
K_2SO_4	174	12.5	7.2
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	280	58	20.7
$\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	437	19	4.3
K_2SO_4	174	12.5	7.2
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	281	67	23.9
$\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	437	5.3	1.21
KCl	75	32	42.6
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	203	130	64.0
$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$	278	64.5	23.2
K_2CO_3	138	110	80.0
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	286	21	7.34
$\text{KNaCO}_3 \cdot 6\text{H}_2\text{O}$	230	13	5.6