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same time 3.778 grains free ammonia, 0.212 grain albuminoid ammonia, and the oxygen absorbed from the potassium permanganate was 2.028 grains per gallon. This liquid is passed upon the filters as has been described and the effluent from these filters contains 1.705 grains free ammonia, 0.078 grain albuminoid ammonia, 0.253 grain mitrogen as nitrites, 0.353 grain nitrogen as nitrates, no suspended matter, and the absorbed oxygen from the potassium permanganate in four hours is only 0.388 grain per gallon.

The great advantage of the septic tank process, if it does what it appears to do, is that so large an amount of suspended matter is removed from the sewage that there will be very much less trouble with the clogging up of the surface of filter-beds in winter, and consequently an area that is large enough for the purification in summer will be more nearly, or possibly quite, sufficient for the work during the winter months.

It is also claimed that a large amount of the organic matter in solution is removed in the septic tank and if this is so, which appears probable from the analyses that have been made, it may not be too much to hope that future developments in this direction taken in connection with the using of the cubical capacity of a bacteria filter, may so reduce the area required for purification, that filter-beds may, without too great expense, be protected from snow and ice.

WORCESTER POLYTECHNIC INSTITUTE. WORCESTER, MASS.

# INVESTIGATION OF THE THEORY OF SOLUBILITY EFFECT IN THE CASE OF TRI-IONIC SALTS.

By ARTHUR A. NOVES AND E. HAROLD WOODWORTH. Received January 20, 1868.

T HE theory of the effect of salts on the solubility of one another has, in the case of di-ionic salts having one ion in comnon, been quite thoroughly tested and confirmed.<sup>1</sup> The solubility of tri-ionic salts in the presence of other salts, however, has been muchless investigated. The theory of the phenomenon has, to be sure, been already developed, and has been partially tested by experiments with lead chloride in the presence of other salts.<sup>2</sup>

<sup>&</sup>lt;sup>1</sup> Compare especially Noyes and Abbot : Zlschr. phys. Chem., 16, 125. <sup>2</sup> Noyes : Ibid. 9, 626.

There was found, however, to be only an approximate agreement between the theory and the facts, probably because the dissociation-values involved are uncertain. Moreover, the theory could not be tested in the case where a salt with a common bivalent ion was added, probably owing to the fact that a double salt was formed. A further investigation of the subject seems therefore to be desirable.

To this end we have determined the solubility of lead iodide in pure water, and in potassium iodide and lead nitrate solutions of varying strengths. We made use of lead iodide because of its slight solubility (one molecular weight in about 600 liters); for, in such dilute solutions, the influence of the two substances on the dissociation of one another is hardly appreciable, and the tendency to the formation of double salts is ordinarily very slight,--two phenomena which often have a disturbing influence in concentrated solutions. In order to determine the solubility. we have measured the electrical conductivity of the saturated solutions, and subtracted from it the conductivity of the water or of the solutions before treating with lead iodide. This method has the advantage over the analytical determination, of greater convenience; and in this case it is especially well adapted, as it furnishes directly a knowledge of the concentration of the ions. so that it is not necessary to consider dissociation-values.

Two samples of each of the three salts were prepared by different methods. These samples were in all cases shown to be exactly alike as far as the conductivity of their solutions was concerned, which indicates that the substances were, in all probability, pure. One sample of the potassium iodide was prepared by treating the commercial, chemically pure salt with alcohol until it was about one-half dissolved, and by subsequent crystallization from this solution by evaporation. The other sample was obtained by crystallizing from water, the residue left undissolved by the alcohol. The lead nitrate was in one case obtained by crystallization of a commercial sample from water; in the other, by precipitation with nitric acid followed by crystallization from water. One sample of lead iodide was prepared by metathesis from lead acetate and potassium iodide; the other, by dissolving a commercial preparation in a strong potassium iodide solution, and then diluting with water. In

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both cases the salt was purified by crystallizing twice from water. The solubility determinations were carried out as follows : Small forty-cc. glass-stoppered bottles were charged with an excess of the solid lead iodide and with pure water or with solutions of lead nitrate or potassium iodide; the stoppers were coated with paraffin, and the bottles rotated for five hours in a thermostat by means of a previously described apparatus.<sup>1</sup> The solutions were then allowed to settle for a short time, and blown out by means of a wash-bottle arrangement into a resistance cell of the Arrhenius type; and the conductivity was measured in the usual way.<sup>2</sup> All the solubility determinations and conductivity measurements were carried out at 25°. In all cases, duplicate determinations of the solubility were made in such a way that the condition of saturation was approached from both sides-that of supersaturation and that of undersaturation. Moreover, in order to make certain of the purity of the lead iodide, not only were the two different samples used, but each sample was also treated with successive amounts of water, and the conductivity of the corresponding solutions determined. A complete agreement was found to exist.

The following tables contain the specific conductivities (multiplied by  $10^{-7}$ ) expressed in Siemens' units. In all cases the conductivity of the water used (which was equal to  $9 \times 10^{-7}$ ) has been subtracted.

CONDUCTIVITY OF WATER SATURATED WITH LEAD IODIDE.

	1.	11.	111.	1V.	Mean.
$Undersaturated \dots$	4016	4016	4023	4030	4021
Supersaturated	4039	4041	4042	4041	4041

CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS SATURATED WITH LEAD IODIDE.

Ur	idersaturated.	Supersaturated.	Undersaturated.	Supersaturated.

I 6174	6184	5316	5343
II 6172	6200	5310	5335
Mean 6173	6192	5313	5339
1 Ztschr. phys. Chem., 9, 606.			

<sup>2</sup> Ostwald : Zischr. phys. Chem., 2. 561.

CONDUCTIVITY OF LEAD NITRATE SOLUTIONS SATURATED WITH LEAD IODIDE.

the lead nitrat	e =0.003077 equi	=0.003077 equivalent per liter.		0.002000 equivalent per liter.	
	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.	
I	· · · · · 6807	6783	5798	5800	
II	6791	6799	5796	5784	
III · · · · ·	6799	6802	••••	• • • •	
Mean	6799	6795	5797	5792	

A consideration of the results in the tables shows that the comparable values agree closely with one another, although the determinations were carried out with different salts and at different times. The supersaturated solutions were, to be sure, about a half per cent. higher than the undersaturated, except in those experiments where lead nitrate was used, in which case they were practically equal. In the calculations described below, of the corresponding concentrations of the ions, the mean of the supersaturated and of the undersaturated values is always used.

In the following tables, the specific conductivities of the pure potassium iodide and lead nitrate solutions are given. In the upper half are the conductivities of the freshly-made solutions, and in the lower half those of the same solutions, after they had been rotated for the same time and under the same conditions as prevailed in the solubility experiments.

Conductivity of the Potassium Iodide and Lead Nitrate Solution before Treatment with Lead Iodide.

Potassium io	Potassium iodide solution.		Lead nitrate solution.	
Equivalents per liter = 0.003077	0,002000	0.003077	0.002000	
First solution 4247	2809	3782	2498	
Second solution · · · 4257	2807	3785	2497	
Mean 4252	2808	3784	2498	
First solution 4288	2836	3771	2487	
Second solution 4288	2849	3774	2487	
Mean 4288	2843	3773	2487	

In order to ascertain the conductivity of the dissolved lead iodide in the presence of the other two salts, we have subtracted the mean values in the lower half of this table from those of the saturated solutions in the two previous tables, it being assumed that the conductivity at these dilutions is an additive property. That this assumption is approximately correct may be concluded from the fact that the lead nitrate and the potassium iodide at a dilution of 500 liters are 93.6 and 98.5 per cent. respectively dissociated, while at a dilution of 325 liters they are 92.0 and 96.9 per cent. respectively dissociated ; in other words, the degree of dissociation is so great, and changes so little with increasing concentration, that it cannot be appreciably affected by the presence of the relatively small amount of lead iodide ions. In order now to derive the corresponding concentrations of the ions from the conductivity values, it is only necessary to divide the latter by the molecular conductivities of the respective salts at infinite dilution. We take as the values of the rates of migration, those calculated by Bredig, namely K = 70.6, I = 72.0, and  $NO_{4} = 65.1$  The value for the lead ion has, so far as we know, not as vet been derived. Franke' has, to be sure, measured the conductivity of lead nitrate in dilute solution, from which the rate of migration can be calculated. Since, however, this value is for our purpose of fundamental importance, we thought it advisable to confirm the accuracy of his determinations by measurements of our own. We have therefore determined the conductivity of both of our samples of lead nitrate at different dilutions. Our values (represented by  $\mu_{i}$  and  $\mu_{i}$ , the mean value by  $\mu$ ), together with those of Franke  $(\mu_{\rm Fr})_{\rm i}$ , are given in the following tables.

# EQUIVALENT CONDUCTIVITY OF LEAD NITRATE.

$\nu$ .	$\mu_{1}$	$\mu_{2}$ .	μ.	$\mu_{Fr.}$
256	120.8	120.9	120.9	122.2
325	122.6	122.8	122.7	
500	124.9	124.8	1 <b>2</b> 4.9	
512	125.2	125.3	125.3	125.9
1024	128.2	127.7	128.0	127.1

As is seen, the conductivities of our two samples agree almost completely with each other, and also fairly well with those of Franke. To obtain the value at infinite dilution, we make use of Bredig's<sup>2</sup> extrapolation-values, which have been derived from a consideration of a large number of salts. The values, extrapolated in this manner from our measurements, are, for the three dilutions, 256, 512, and 1024 liters, 132.9, 133.3, and 134.0, re-

1 Ztschr. phys. Chem., 16, 471. 2 Ibid. 13, 198. spectively. We therefore take the mean, 133.4, as the value of the conductivity of the lead nitrate at infinite dilution.

Since the rate of migration of the NO, ions is equal to 65.1, that of the lead ion must be 68.3, from which it follows that lead iodide has for its value at infinite dilution 140.3. Finally, the value derived for potassium iodide at infinite dilution from the above given rates of migration is 142.6. Now, if the corresponding specific conductivities are divided by these limiting values, we obtain the concentrations of the ions which correspond to the conductivity measurements given above. The results of these divisions are presented in the following table, those in the case of the lead iodide being placed under the heading "Found."

CONCENTRATION OF THE IONS IN THE SATURATED SOLUTIONS.

Potassium	Lead iodide ions.		Lead nitrate	Lead iodide ions.	
iodide ions.	Found.	Calculated.	ions.	Found.	Calculated.
0.00	0.002873	• • • • • •	0.00	0.002873	• • • • • •
0.001969	0.001770	0.001731	0.001872	0.002358	0.002369
0.002982	0.001351	0.001296	0.002837	0.002155	0.002175

It is readily seen from these numbers that the solubility in the potassium iodide solutions as well as in those of the lead nitrate, is considerably less than in pure water, and further that the diminution caused by equivalent amounts of the two salts is quite different. We will now compare quantitatively the experimental results with the requirements of the principle of solubility effect.

The laws of mass action require that in the case of a saturated solution of a tri-ionic salt, the product of the concentration of the bivalent ion into the square of the concentration of the univalent ion shall be a constant quantity, whatever other salts may be present at the same time.<sup>1</sup> In this case the equation,

$$Pb \times (I)^2 = a \text{ constant},$$

should hold, where the chemical symbols denote the concentrations of the respective ions.

If  $m_0$  is the solubility of lead iodide in pure water, *m* its solubility in a potassium iodide or lead nitrate solution whose concentration is *n* (all expressed in equivalents), and  $a_0$ , *a*, and  $a_1$ , the corresponding dissociation values, the following equation applies in the case where lead nitrate is present:

1 Zischr. phys. Chem., 9, 627.

$$(ma + na_{0}) m^{2}a^{2} = m_{0}^{3}a_{0}^{3},$$

and where potassium iodide is present this equation:

$$ma (ma + na_1)^2 = m_0^3 a_0^3.$$

The value  $m_0 a_0$ , the concentration of the ions in the saturated solution in pure water, is found to be 0.002873; and the values of  $na_1$ , the concentrations of the ions in the lead nitrate and potassium iodide solutions in the four solubility experiments, are given in the first and fourth columns of the last table. From these we have calculated the values of ma (the concentration of the lead iodide ions) by the two formulas given above. This cubic equation is easily solved by substituting an estimated value of ma, and calculating the value of the left member of the equations, repeating this process until the value thus found becomes equal to  $m_0^3 a_0^3$ . The theoretical values obtained in this way are found in the last table under the headings " calculated."

The agreement between the experimental and the theoretical values, although not complete, is however entirely sufficient to prove the essential correctness of the solubility principle. The deviations are, in the case of the lead nitrate, 0.9 and 0.3 per cent., and in that of the potassium iodide, 4.1 and 2.2 per cent. It is however to be considered that the values of ma were not directly measured, but were obtained as the differences of two larger experimentally determined values, whereby the percentage error is greatly increased. In order to give an idea of the existing error relations, it may be mentioned that an error of one-half per cent. in the conductivity of the lead nitrate solution saturated with lead iodide, and an equal error in the subtracted conductivity of the pure lead nitrate solution, would cause in the value ma an error which would probably amount to 1.3 per cent. in the 0.003077 normal solution and 0.9 per cent. in the 0.002000 normal solution. Equal errors in the potassium iodide experiments would cause errors of 2.0 and 1.0 per cent. respectively in ma. It is therefore seen that the method cannot furnish very accurate results, and that the differences between the actual and the calculated values are not improbably due to experimental errors.

It has therefore been established by this investigation within

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the (somewhat wide) limits of experimental errors, that the solubility of lead iodide is diminished both by potassium iodide and by lead nitrate in such a way that the product of the concentration of the lead ions into the square of the concentration of the iodine ions remains constant.

Massachusetts Institute of Technology. January, 1898.

#### GLUCOSE IN BUTTER.<sup>1</sup>

By C. A. CRAMPTON. Received January 22, 1898.

I have been unable to find, in the literature of food products or of food adulteration, any reference to the use of glucose or other form of sweetening material in butter. The nearest approach to it is the mention of starch by some of the German authorities as among the possible adulterants. In domestic practice, however, the addition of sugar to butter for purposes of preservation is doubtless almost as old as the art of buttermaking itself, sugar and salt being the standard household preservatives for food products from time immemorial. But the use of sugar in this way is comparatively rare, salt being universally preferred as a preservative for this food product as it is for most products of animal origin. Sugar appears in several of the various U. S. Patents for so-called " improving" or renovating processes for butter, being added to it along with salt, saltpeter, and, in some cases, sodium carbonate. The sugar is usually in small quantity in these formulas, perhaps an ounce to eight pounds.

Within the past few years glucose has been used in butter specially prepared for export to tropical countries, as the West Indies or South America. The hot climate of these countries renders its preservation very difficult. It is usually put up in tins and various means are resorted to by the dealers in different nations who export to them for preventing the decomposition of their goods before they reach the consumer. Very large quantities of salt are used by the French exporters. I give below the figures obtained from the analysis of two samples of French butter, as exported, the one to Brazil, the other to the Antilles:

<sup>1</sup> Read at the Washington meeting, December 30, 1897.