XXIII.—*On the Reaction of Natural Waters with Soluble Lead Salts.* By ARTHUR CONNELL, Esq., F.R.S.E., *Professor of Chemistry in the University of St Andrews.*

(Read 19th January 1846.)

In a former communication to the Society, I noticed a reaction presented by all spring, well, and river waters which I had examined, that, even after being boiled, they yielded, with acetate of lead, a precipitate readily soluble, in whole or in great part, in acetic acid. This easy solubility in acetic acid shewed that the precipitate was neither a sulphate nor a phosphate, and the comparatively slight action of nitrate of silver proved that it was not a chloride. There seemed, therefore, to remain only the conclusion that it was either a carbonate, or was due to organic matter. The former alternative, of course, depended on whether the solution in acetic acid was attended with effervescence or not; and as this seemed usually not to be the case, and as, on decomposing some of the precipitate by sulphuretted hydrogen, some organic matter in solution was obtained, the conclusion seemed to be, that the appearance was caused by organic matter, probably of the nature of the crenic and apocrenic acids of BERZELIUS. I have since, however, found that by very careful observation, effervescence may be noticed during the solution of the precipitate more frequently than I at first supposed. It is not so easy as might be imagined to determine this point. If acetic acid is added before the precipitate has subsided, no effervescence can be noticed, in almost any case, from the water dissolving the carbonic acid evolved and diffused through the whole liquid. And even when allowed to subside, and the greater part of the liquid is decanted, the addition of acetic acid not unfrequently causes solution without apparent effervescence. The cautious addition, however, of a heavier acid, such as the nitric or even the muriatic, after allowing the lead precipitate to collect at the bottom, and decanting the greater part of the liquid, seldom fails to shew the effervescence where a carbonate is really present.

In so far, then, as the precipitate is dissolved by acids with effervescence, we may conclude that it has been caused by some carbonate remaining dissolved after boiling the water; and in so far as the solution may not exhibit effervescence, we may conclude that it is due to organic matter, provided silver salts do not indicate the presence of a sufficient quantity of chlorides, and provided acetic acid instantly causes solution in whole or great part. In some instances I have found that acetate of lead does not yield a precipitate, *unless* the water has been previously boiled, a circumstance obviously due to excess of carbonic acid retaining the carbonate of lead in solution. In regard to chlorides, I have never met

with any spring, well, or river water, not coming under the denomination of a mineral water, which contained so much of any chloride as to be indicated by a lead salt. The chloride of lead is too soluble to become visible, unless where the contamination is considerable. The portion of the precipitate not soluble in acetic acid is usually due to the presence of some sulphate.

Taking the fact as I have now ascertained it to be, that natural waters which have passed through the strata or soils of the earth, *i. e.*, well, spring, and river waters, very commonly or invariably yield, even after boiling, and filtering, if necessary, a greater or less amount of precipitate with acetate of lead, readily dissolved, in whole or in part, by acetic acid with effervescence; in other words, that such natural waters contain frequently or invariably, even after boiling, one or more dissolved carbonates, the question arises, What is the nature of such carbonate? As these waters, when they have been much concentrated after being boiled and filtered, and have then been made up to their former bulk by distilled water, are found to have lost their power of shewing the same phenomena as before with lead salts, and to have deposited carbonate of lime during concentration, the effect must have been due to this carbonate of lime whilst held in solution. The farther question, therefore, arises, how this carbonate of lime came to be dissolved?

I tried to ascertain whether water would dissolve carbonate of lime in its nascent state as precipitated by boiling a solution in excess of carbonic acid. A current of carbonic acid was passed through lime water prepared with distilled water, until the precipitate at first formed was redissolved. The solution was then boiled for a similar short time as in the original experiments, and filtered. It was then found to be affected only very feebly either by oxalate of ammonia or by acetate of lead; the action being not at all equal to that produced on boiled natural waters by these reagents. The carbonate of lime in the act of precipitation by boiling, had evidently not been dissolved except in very insignificant quantity by the water. I then, before boiling the solution, exposed it for a day to the air in an evaporating basin, after keeping it for some days in a close vessel; but did not find that the quantity of carbonate retained after ebullition, short subsidence, and filtration, was increased.

As it was possible that some of those saline matters contained in natural waters might promote the solubility of carbonate of lime, minute quantities of solutions of muriate of lime, sulphate of lime, muriate of magnesia, and chloride of potassium were added to lime water prepared with distilled water. A current of carbonic acid was then conducted through the liquid so as to redissolve the precipitate which it at first caused. The liquid, after ebullition, short subsidence, and filtration, was found scarcely to be affected by acetate of lead; and any feeble deposit formed was not soluble in acetic acid, being sulphate of lead due to the sulphates which had been added.

It thus seemed evident that by the aid of carbonic acid no sufficient quantity

of carbonate of lime can be dissolved, independently of the continued presence of the free acid, to cause the appearances referred to.

I next tried the solvent action of water alone on finely divided carbonate of lime. Distilled water, which had been boiled and cooled, was left in contact with marble in impalpable powder for several days in a close vessel. It was then found by the action both of acetate of lead and of oxalate of ammonia, that rather more carbonate of lime had been taken up by the pure water than was left in solution after boiling the carbonated water, but still that the amount was considerably less than the reactions which have been referred to, indicate in ordinary natural waters ; and it is remarkable that the effect of the lead salt is usually more decided than that of the oxalate.

I incline, therefore, to think, that the carbonate of lime present, in such circumstances as have been described, has a different origin, viz., Double Decomposition, between a lime-salt and a carbonated alkali ; as it would seem that the carbonate of lime formed is, in this kind of nascent state, dissolved more readily than when precipitated by boiling from a carbonic solution. The following experiments illustrate this origin of the reaction. To half an ounce of distilled water, a few drops of a solution of sulphate of lime in water were added. A single drop of solution of chloride of calcium, and a single drop of solution of carbonate of potash were then added. The liquid remained quite transparent, and did not affect turmeric or cabbage paper. When boiled it still remained transparent. When a drop of solution of acetate of lead was added to a portion of this liquid, either before or after boiling, a considerable white cloud was formed, which disappeared on the addition of a drop of acetic acid. Thus was the reaction of the spring waters exactly imitated. I at first inclined to think that in such cases no actual double decomposition ensued until the liquid was concentrated by heat, and that the action on the lead-salt was due to the carbonated alkali present. But farther experiments lead me to believe that the carbonate of lime is actually formed, at least to a considerable extent, and then dissolved by the water ; for, if a couple of drops of solution of chloride of calcium and a drop of solution of carbonate of potash be added to a few drops of distilled water, muddiness will be produced ; and this will disappear when half an ounce of distilled water is shaken with the mixture, without any deposit being formed by rest. The solution, however, of the carbonate of lime is dependent on the action of the water taking place either on the nascent salt, or at least immediately after its formation ; for I found that when carbonate of lime, precipitated by double decomposition, was collected on a filter, washed, and allowed to stand some minutes, and then left in contact all night with boiled and cooled distilled water, acetate of lead had only a very feeble effect on the liquid.

It was, of course, necessary, in order to establish this view, to ascertain that those natural waters which exhibit the reaction referred to, actually contain

alkaline matters. This was, accordingly, done in numerous instances by ordinary methods. Although the potash or soda present may have been originally dissolved as a carbonate; yet we, of course, ultimately obtain it on evaporation, as a chloride or sulphate, through double decomposition with the lime or magnesian salts present; or through the stronger affinity of the acids of these salts, if their earths have been previously removed by chemical means. In no instance of a natural water which gave the reaction with lead salts, did I fail to detect either potash or soda, or both; and it ought to be recollected that a very minute quantity of either is sufficient. It will be found that one drop each of solutions of carbonate of potash, of sulphate of magnesia, and of chloride of calcium, added to several ounces of distilled water, will produce the reactions referred to with lead salts and acetic acid.

If these views are well-founded, it is evident that lead salts become a probable indication, at least where their effect is considerable, of the presence of alkalis in natural waters. And, in general, we may conclude, that if after boiling, and filtration if necessary, any water yields a considerable cloud with acetate of lead, readily soluble by adding a drop or two of acetic acid, the cause will be either carbonate of lime, probably due to double decomposition, or it will be organic matter, if any such matter precipitable by lead salts is present in sufficient quantity.* In so far as it is dissolved by an acid, after subsidence, with effervescence, it will be due to the former cause; in so far as, without effervescence, to the latter.

It seems, at all events, evident from the experiments which have been detailed, that the carbonate of lime present has not owed its presence to the solvent agency of carbonic acid, even when first taken up.

It is plain, that the carbonate of lime thus held dissolved by spring waters, from whatever source it may be obtained, must be of considerable importance in the economy of nature in furnishing a supply, through the intervention of these waters, of that lime which is so essential a constituent, in its various states of combination, of the inorganic portion of plants. This will hold whether such waters are applied to the land in the way of irrigation, or by the more slow processes of natural infiltration.

* Dr CHRISTISON informs me that moss-water is not precipitated by acetate of lead. This, I have no doubt is a correct observation; but still other states of organic matter may occasion a precipitate. The crenic and apocrenic acids are both known to precipitate lead salts.

Although fluorine is now known to be occasionally present in ordinary natural waters, and although fluoride of lead is sparingly soluble in water, yet I am not aware that fluorine is ever present in such quantity in such waters as to affect lead salts; and, if it were, acetic acid might very likely not dissolve the precipitate. Dr WILSON mentions that fluoride of barium is less soluble in acids than carbonate or phosphate of barytes.

POSTSCRIPT.

Since this paper went to press, I have ascertained that the town water of St Andrews, which is one of those which gives the reaction referred to with lead salts, yields by evaporation, after having been boiled and filtered, $\frac{1}{31323}$ of its weight of carbonate of lime. Other waters may of course contain more. I also observe, that FRESSENIUS found, that when distilled water was boiled a long time (probably, from the context, several hours) with freshly precipitated carbonate of lime, so as to form a saturated hot solution, and this solution was then kept for four weeks at common temperatures, in contact with undissolved carbonate of lime, under frequent agitation, it yielded by evaporation $\frac{1}{10601}$ of its weight of carbonate of lime.—*Liebig's Annalen*, July 1846. In so far as regards spring waters, it is unnecessary to say, that Nature does not take such pains to charge them with lime. The method suggested above seems a more simple one, and may often be as effectual, possibly even more so; when the still more simple means of free carbonic acid are not brought into play. From the experiments of FRESSENIUS, it appears, that carbonate of lead is much less soluble in water than carbonate of lime, viz., in 50,551 parts, which is quite conformable to the results above stated.