Investigations on the FactorsWhich Determine the Reaction of the Soil

I. On the Determination of the Acid and Basic Properties of a Soil
II. On the Reaction of Solutions Saturated With Calcium Carbonate

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SUMMARY

For the purpose of describing the acid and basic properties of a soil various quantities may be employed. Firstly, a statement of the *reaction* may be used. However, it is not sufficient by observing the colour of an indicator to obtain a qualitative statement as to the reaction. The best thing to do is to describe the reaction by stating the hydrogen-ion concentration or the hydrogen-ion exponent (p_H), and these quantities may be determined either in the soil water or in an extract of the soil prepared according to a standardized method. The reaction determined will vary somewhat according to the mode of preparation of the solution used. Secondly, the acid nature of a soil may be described by means of a determination of the *acidity*, i.e. by determining the amount of base required to neutralize the soil. Thirdly, it is possible to obtain a figure describing the basic properties of the soil by means of a corresponding determination of the *basicity*.

It is essential not to confuse the concepts thus defined, namely reaction, acidity and basicity; because determinations of these quantities cannot replace each other, each of them having a separate meaning.

It appears from a summary of the methods which have hitherto been used for the purpose of determining the acid or basic nature of a soil that, when con-

sidered more closely, all the methods aim at a determination of either reaction, acidity or basicity.

The result of a determination of the acidity or basicity of a sample of soil can vary highly according to the method used. Besides several other reasons, it is of great importance that the so-called neutral point to which the soil is brought by addition of base or acid is not characterized by the same reaction in the different methods. In order to obtain a thorough knowledge of a soil, it is a useful procedure to perform the determinations of acidity and basicity according to several different methods, because the various methods will often each supply separate contributions towards the knowledge of the soil. The best thing would be if, for each reaction (p_H), the amount of acid or base, respectively, required to produce this reaction in the soil was determined. By means of electrometric titration it is possible to obtain a series of such results which may be illustrated by means of a *titration curve*.

The exact form of the titration curve is — to an extent which should not be underestimated — dependent on the method of titration used (time, temperature, whether CO_2 has been present or not, the solution used for titration etc.), and it appears from this that a complete picture of the acid and basic properties of a soil is only obtained by means of several titration curves and is consequently of a very complicated nature.

If we could succeed in finding the laws according to which the individual acid and basic constituents of the soil determine the reaction, the amount of these constituents would provide a simple measurement of the acid and basic properties of the soil, because it would then be possible by means of these laws and from the content of such constituents in the soil to calculate all its acid and basic properties. We have therefore set ourselves the task of investigating these laws and have, in the second part of this paper, made a beginning by investigating the influence of calcium carbonate on the reaction.

It follows from the law of mass action that the hydrogen ion concentration ($c_H{}^+$) in an aqueous solution saturated with calcium carbonate is determined according to the following equation by the calcium ion concentration ($C_{Ca}{}^{++}$) and the carbon dioxide pressure (p_{CO_2}):

$$C_H{}^+ = K \cdot \sqrt{C_{Ca}{}^{++}} \cdot \sqrt{p_{CO_2}}$$

Whence, by taking the logarithms, we obtain the following expression for p_H:

$$p_H = - \log K - \tfrac{1}{2} \log C_{Ca}{}^{++} - \tfrac{1}{2} \log p_{CO_2}$$

The above formulae are limiting laws which are exactly valid only for infinitely dilute solutions. For ionic concentrations (C_{ion}) up to 0.2 normal the following formula gives a more exact result:

$$p_{\mathrm{H}} = -\log K - \tfrac{1}{2}\log C_{\mathrm{Ca}^{++}} - \tfrac{1}{2}\log p_{\mathrm{CO_2}} + 0.3\sqrt[3]{C_{\mathrm{ion}}}\,.$$

For ionic concentrations higher than 0.2 normal this formula does not apply either, as the hydration of the calcium ion has a disturbing influence.

The value of K, the reaction constant of calcium carbonate, has been determined according to two different methods.

By electrometrical measurements of p_{H} in solutions of calcium chloride saturated with calcium carbonate at different carbon dioxide pressures we have found $\log K$ at 18° C to be — 5.02.

In these measurements *precipitated* calcium carbonate was employed. By a number of measurements with *Iceland spar* results were obtained which agreed within the experimental error with the above measurements. *Aragonite*, however, gave hydrogen-electrode potentials which on an average were 3.5 millivolts larger, which means a value of $\log K$ increased by 0.06. This higher value of $\log K$ for aragonite is in agreement with available measurements of the relationship between the solubilities of aragonite and Iceland spar.

By combining Schlösing's determinations of the solubility of calcium carbonate in water containing carbon dioxide with Bohr's determinations of the solubility of carbon dioxide in water and with Walker and Cormack's and Kendall's determinations of the conductivity of water containing carbon dioxide, it is possible to calculate the value of $\log K$, and in this way we have obtained a value of — 5.05.

The temperature coefficient of $\log K$ has, according to the same determinations been calculated to be + 0.0045. This value can also be obtained by means of thermo-chemical measurements performed by Julius Thomsen.

In all our calculations we have assumed that the calcium salts were completely dissociated, and we have calculated p_{H} according to the following equation:

$$p_{\mathrm{H}} = (E - E_{\mathrm{o}})/0.0577,$$

where E is the potential of a hydrogen electrode in the solution, and E_{o} the potential of a hydrogen electrode in a solution with an apparent hydrogen ion activity of 1. When the measurement is performed with a $3.5\,M$ potassium chloride calomel electrode as reference half-cell, $E_{\mathrm{o}} = 0.252$, and when using a $0.1\,M$ potassium chloride calomel electrode, $E_{\mathrm{o}} = 0.335$.

According to our formulae it is quite possible for a soil which contains calcium carbonate to have a p_{H} which is less than 7 and consequently to have an acid reaction. The greater the amount of carbon dioxide in the air of the soil and the greater the calcium ion concentration in the soil water, the more acid the reaction of the soil will be.

As the reaction of a saturated solution of calcium carbonate is only dependent on the carbon dioxide pressure and the calcium ion content of the solution, it is natural to detect and to estimate calcium carbonate present in a soil by measuring

the p_H in a solution of calcium chloride saturated with the soil in question at a certain carbon dioxide pressure. Under these circumstances the presence of calcium carbonate in a soil will manifest itself through the maintenance of a constant p_H even after addition of hydrochloric acid and stirring, the value of p_H only decreasing when all the calcium carbonate present has been dissolved by the acid added.