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THE RÔLE OF HYDROLYSIS IN GEOLOGICAL CHEMISTRY.¹

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Since geologists can hardly be expected to keep in touch with special questions in chemistry it is natural that they have taken very little notice of the phenomena of hydrolysis, if indeed they realize what is meant by the term. Physical chemistry with its theories of solution and ionization has made such rapid progress that it may be advisable occasionally to translate some of its conclusions into terms which may be understood and applied by geologists.

Hydrolysis concerns aqueous solutions and signifies a reaction of a salt with water so that instead of the salt, *acid* and *base* are produced. Thus, as an extreme illustration,

a reaction produced by evaporating a solution of magnesium chloride. Here the reaction may be carried to practical completion because of the volatility of hydrochloric acid. A hydrolytic reaction may likewise be caused by the removal of one of the possible products as an insoluble precipitate, thus

¹ Published by permission of the director of the U. S. Geological Survey.

although in this case it is necessary to remove the excess of hydrochloric acid by neutralization, or in some other way, at the same time that the ferric hydroxide is precipitated in order to prevent the reverse action.

As thus explained, not much physical chemistry is required for these reactions, but other cases demand a somewhat larger theory of solution and it is necessary to take ionization into account. In accordance with the theory of electrolytic dissociation or ionization of substances in solution a solution of a salt in water contains not only molecules of the undissociated salt but also its simple ions and any other ions capable of being formed from the constituents in the solution including the water itself. The properties of a solution are the properties of its predominating constituents. Thus all solutions of acids are characterized by ionized hydrogen, and bases by hydroxyl ion. No other explanation of acidity and its opposite quality, alkalinity, fits all the facts as well as this one. "Strong" acids and bases are those having chiefly ions and few molecules; "weak" ones those having chiefly molecules and few ions. These various degrees of ionization are counted empirical physical properties of the various acids and bases.

When a salt is dissolved in water and with the water yields a strong acid and a weak base, there are hydrogen ions in plenty but only molecules of the base so that the solution is acid, as with the chlorides of aluminum, copper and zinc. Conversely, if the salt yields a strong base and weak acid the solution will be alkaline, as with potassium or sodium borate, carbonate or cyanide. The acids in order of strength are: hydrochloric, nitric, sulphuric, oxalic, tartaric, acetic, carbonic, hydrosulphuric and boric. Silicic acid is extremely weak, but its exact position in the series has not been determined. For the bases, it has been shown that the hydroxides of the alkali and alkaline earth metals are equally strong, followed by various amines, ammonium hydroxide and aniline.

Mine waters containing metallic salts will, for these reasons, usually "react" acid, but waters containing sodium carbonate

will react alkaline. The hydrolysis is not necessarily accompanied by precipitation.

The degree of hydrolysis of a given salt increases with dilution or with a rise of temperature. The same factors act similarly upon the *rate* of hydrolysis where the reaction proceeds slowly enough to be measurable, as I have shown in the case of ferric sulphate solutions, where the hydrolysis is accompanied by the formation and precipitation of a "basic salt."¹ The rate of hydrolysis in this case was determined by measuring the electrical conductivity of solutions of various dilutions at several temperatures. The increase of conductivity corresponds to the production of sulphuric acid in the solution. The relative rates of change for several cases are shown in the following table:

Dilution, liters containing one gram-equivalent of $\text{Fe}_2(\text{SO}_4)_3$.	Temp. °C.	Initial equivalent conductivity.	Equivalent conductivity after one hour.
300	0°C.	78	86
600	0	96	111
61.1	30	95	102
101	30	110	141
121	30	118	152
151	30	128	180
201	30	142	202
300	30	165	258

The protean shapes taken by iron oxide formations probably illustrate the influence of slight variations in acidity or alkalinity during their deposition. I have not been able to detect any hydrolysis with *ferrous* sulphate solutions occurring slowly enough to follow experimentally.

In most metallic salt solutions showing acid reaction the hydrolysis does not go far before an equilibrium is attained at ordinary temperatures. With sodium carbonate the degree of hydrolysis at 24.1° C. has been determined for several concentrations, the degree expressing the per cent. of total sodium which may be thought of as sodium hydroxide.

Mol. Na_2CO_3 /liter	0.1900	0.0940	0.0477	0.0238
Per cent. hydrolysis	2.12	3.17	4.87	7.10 ²

¹ *Jour. Am. Chem. Soc.*, 31, 1028, 1909.

² Shields, *Z. physik. Chem.*, 12, 167, 1893.

Since CO_2 escapes from a sodium carbonate solution upon boiling the hydrolysis may be carried further, as follows, starting with a normal solution.¹

Time of boiling	1.25	3.5	6.0	8.5	23.3	38	hours.
NaOH formed	3.3	5.4	7.3	8.6	13.0	17.2	per cent.

The geologic application of these facts is that solutions are not always what they seem. A sodium carbonate solution really contains sodium hydroxide and may be expected to have the geologic action of sodium hydroxide, as in dissolving silica or precipitating hydroxides where the hydroxides are more insoluble than carbonates.

Solutions of all carbonates are more or less hydrolyzed, not excepting solutions of the insoluble carbonates.

Considering only ions the reactions for hydrolysis would be

The first reaction occurs chiefly with normal carbonates, the second to a slight extent both with normal and acid carbonates. In accordance with these views a sodium bicarbonate solution contains (1) ionized sodium Na' , (2) bicarbonate ion, HCO_3' , (3) NaHCO_3 molecules, (4) hydroxyl ion, OH' , (5) carbonic acid, H_2CO_3 , (6) free carbon dioxide, CO_2 , (7) a vanishingly small quantity of hydrogen ion, H' , to correspond with the dissociation of the water. Other salt solutions may be worked out similarly. These cases show that the simple equations often given by geologists to account for observed occurrences do well if they explain the principal mechanism of the changes considered.

In the ionization of univalent-bivalent acids and bases the primary ionization is into two univalent ions.

¹ Küster u. Grütters, *Ber.*, 36, 748, 1903.

It is only in the ionization of *salts* that the simpler bivalent or polivalent radicles occur to a large extent.

If hydroxide ion is the chief agent in attacking a rock it is evident that sodium carbonate would act more vigorously than sodium bicarbonate, the latter more vigorously than water and the last more vigorously than acid solutions. Similar deductions would follow from a consideration of the hydrolysis of silicates and borates.

Since all the hydrolytic reactions with which we are acquainted proceed further at higher temperatures than at ordinary, it is obvious that in geologic reactions where water is present at any considerable elevation of temperature hydrolysis plays a very important rôle. Water attains its critical temperature at 365°C . and its critical pressure at 195 atmospheres, which corresponds to about 2,500 feet in depth in a rock as dense as 2.5.

High temperatures correspond to certain general chemical conditions. In the first place substances tend to exist in simpler compounds than at lower temperatures. Many gases are partially dissociated. Fused substances often exist as mere mixtures of their constituents in indefinite proportion. Complex molecules are broken down. Hydrates or solvates, solid at lower temperatures, are decomposed above their "transition temperature" into water or solvent and lower hydrates or anhydrous salts, the water of course forming saturated solutions of the salts present.

The phenomena of ionization and hydrolysis change somewhat as the temperature rises.

Concerning the extent of ionization in aqueous salt solutions, the researches of A. A. Noyes and his co-workers have proved

that ionization in dilute solutions decreases steadily in all cases with rising temperature, the decrease being more rapid the higher the temperature and the greater the valence-product of the ions of the salt.¹ But the decrease in the reactivity which might be expected on this account is more than made up for by the higher rates of diffusion and the chemical activity of water at higher temperatures.

In contrast to the decrease of ionization of salts with rising temperature water itself increases its ionization and becomes at high temperatures a very active chemical agent. The increase in its ionization is shown in the following table:²

Temp.	Ionization $C_H \times 10^7$.
0°	0.30
18	* 0.68
25	0.91
100	6.9
156	14.9
218	21.5
306	13.0

It is seen that the ionization increases rapidly from ordinary temperatures up to about 250° attaining a maximum somewhere between 250° and 275°. If the water were pure and the ionization of hydroxyl into O" and H' is neglected the above concentrations of hydrogen-ion would also be those of hydroxyl-ion. In salt solutions, however, as has been stated, the hydroxides and acids are rarely of equal "strength," the hydrogen-ion-concentration exceeds or is less than the hydroxyl-ion-concentration, as the case may be, giving alkaline or acid reaction. When it is remembered that the ionization of weak acids and bases decreases with rise of temperature and that this acts in the same direction in increasing the hydrolysis of salts as the ionization of water shown above it will be evident that salts must hydrolyze much further at high temperatures. The result would appear to be in general a marked tendency towards the separation of the

¹ *J. Am. Chem. Soc.*, 31, 1009.

² Noyes, Carnegie Inst., Pub. 63, 346.

oxides of the metals, particularly if there were at the same time any chance for the escape of volatile products. At these temperatures very slight changes in acidity and alkalinity would undoubtedly condition important changes in crystallization and so on. This may be the key to the action of traces of water as a "mineralizer."