# XII.—*Action of Organic Acids on Minerals.*

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CHEMISTS have long employed the commoner organic acids, especially acetic, oxalic, tartaric, and citric acids in mineral analysis, but with few exceptions they have overlooked the application of these acids to the decomposition of minerals. Acetic acid has been used to separate minerals from their matrix of calcite; Karsten (*Archiv. of Min.* XXII, 572) and Sterry Hunt have used it in the proximate analyses of mixtures of calcite, dolomite, and magnesite; calamine and willemite are sometimes distinguished by the gelatinization of the former with the same acid; Dr. J. Lawrence Smith (*Am. J. Sci.*, [2] XX, 244) has noticed the solubility of anglesite in ammonium citrate; W. B. and R. E. Rogers (*Am. J. Sci.*, 1848) have made experiments on the solubility of minerals in water containing carbonic anhydride; but there is no record of any systematic investigation of the action of organic acids on minerals with a view to the determination of species.

The following research was suggested by the difficulty of transporting liquid mineral acids on mineralogical journeys, and the need of a substitute in solid form. A few preliminary tests showed that tartaric and citric acids possess far greater power to decompose minerals than is commonly imagined, and demonstrated the desirability of extended study. Accordingly we selected and prepared for treatment, by the methods to be described, 225 specimens of minerals of whose purity and authenticity there was no doubt; these represent 200 species, their names are given in the accompanying table. For convenience these minerals may be divided into five groups, viz. :—I, *Carbonate;* II, *Sulphides, Arsenides,* &c.; III, *Oxides;* IV, *Silicates;* V, *Sundry Minerals,*—including phosphates, sulphates, arseniates, native metals, &c.

## *Reagents Employed.*

The organic acids employed in this research were chiefly citric, tartaric, and oxalic; a few tests were also made with malic, formic, acetic, benzoic, pyrogallic, and picric acids. Of the solid acids the solutions used were saturated in the cold; citric acid being the strongest in its action was more exhaustively studied than the others.

The behaviour of the minerals with these acids was studied in a simple manner; the finely pulverized specimens, freed from gangue, were treated in test-tubes with the reagents both cold and boiling. In certain cases the gases disengaged were examined by test papers; and the filtrates with appropriate reagents, whenever decomposition was not otherwise evident.

Having observed that a strong solution of citric acid decomposes (*a*) sodium nitrate, (*b*) potassium iodide, and (*c*) ammonium fluoride,—setting free nitric acid, hydriodic acid, and hydrofluoric acid respectively, we applied these reactions to the decomposition of those minerals which resist the action of citric acid alone. We will briefly describe these reactions.

(*a*) When solid sodium,—potassium—or ammonium nitrate is added to a boiling solution of citric acid (also tartaric and oxalic acids), on reaching a certain degree of concentration nitric acid is set free, which immediately reacts upon the organic acid, liberating carbonic anhydride and nitric oxide. If we admit the formation of oxalic acid, the reaction may possibly proceed thus:—

$$11\,H_3C_6H_5O_7+16\,KNO_3=8\,K_2HC_6H_5O_7+3\,H_2C_2O_4+17\,H_2O+$$
$$12\,CO_2+8\,N_2O_3$$

This mixture of reagents, which for convenience we shall designate the "nitrocitric mixture," proved to be a very powerful oxidizing solvent, as is shown in column I of the accompanying table.

Potassium nitrite decomposes citric acid in a similar manner,—the action beginning in the cold, and proceeding with energy.

(*b*) The well known facility with which even the weakest acids decompose potassium iodide, and the instability of hydriodic acid, makes the mixture of the solid salt with citric acid a very strong solvent of several classes of minerals. We call it for convenience the "iodo-citric mixture."

(*c*). When ammonium-fluoride is added in solid form to a concentrated solution of citric acid, and heated, a mixture is obtained which attacks silicates with considerable power. The tests are of course made in platinum vessels. Partial decomposition is ascertained by testing for fluoride of silicon with a moistened rod. Since, however, we have carried on this research largely with a view to *field-work,* we have examined only a few minerals with this mixture, and we omit these reactions in the table.

### *Behaviour of Carbonates.*

All the natural carbonates examined dissolve with effervescence in cold or hot solutions of the organic acids named above.

Citrates being in general more soluble than tartrates and oxalates, citric acid attacks the minerals more strongly. Oxalic acid, however, yields precipitates, some of which are characteristic of the bases contained in the minerals; thus calcite is decomposed with formation of white pulverulent calcium oxalate, which appears amorphous under the microscope; witherite yields beautifully feathered crystals of barium oxalate; siderite gives a pale yellow granular ferrous-oxalate, appearing under the microscope in the form of minute prisms, having a basal termination; and cerussite yields a heavy white precipitate of lead oxalate.

Acetic acid acts energetically; in fact glacial acetic acid does not attack calcium carbonate even on boiling; but decomposition begins at once on adding one fourth part of water. Formic acid acts similarly, and yields with cerussite a white, lustrous, crystalline deposit of lead formate.

Since all the carbonates are decomposed by citric acid alone, we did not examine their behaviour with the nitro-citric and iodo-citric mixtures.

### *Behaviour of Sulphides, Arsenides, etc.*

Natural sulphides are very unequally decomposed by citric and other organic acids. Of the 35 species examined, five are attacked by citric acid alone in the cold, with liberation of sulphuretted hydrogen, and five are attacked on boiling the solution.

All the remainder are rapidly decomposed by heating with the nitro-citric mixture, except realgar, orpiment, cinnabar, molybdenite and proustite; of these the first three yield to the iodo-citric mixture, but molybdenite and proustite completely resist these reagents.

The decomposition of the natural sulphides by the nitro-citric mixture, affords a very interesting reaction; taking pyrites for example, the solution obtained contains ferric sulphate, and hydro-potassium citrate, while both nitric oxide and carbonic anhydride are abundantly evolved, consequently the reaction may possibly proceed as in the following equation:—

$$4\,FeS_2+26\,KNO_3+12\,H_3C_6H_5O_7=2\,Fe_2(SO_4)_3+2\,K_2SO_4+11\,K_2HC_6H_5O_7$$
$$+15\,H_2O+13\,N_2O_2+6\,CO_2$$

Oxalic acid mixed with potassium-nitrate acts similarly, and the reaction may be expressed thus:—

$$6\,FeS_2+32KNO_3+29\,H_2C_2O_4=3\,Fe_2(SO_4)_3+3\,K_2SO_4+26\,KHC_2O_4+$$
$$16\,H_2O+16\,N_2O_2+6\,CO_2$$

Certain sulphides treated with these reagents behave in such a way as to furnish additional means for their determination. Thus pyrrhotite and bornite are decomposed by citric acid alone, while their kindred compounds, pyrite and chalcopyrite (as well as chalcoite) are not attacked.

Since galenite is readily attacked and argentite is not, citric acid may be used to detect a mixture of the former with the latter. Pyrargyrite is decomposed by the nitro-citric mixture, while proustite wholly resists. When galentite is heated with the iodo-citric mixture, the mineral is completely decomposed,—sulphuretted hydrogen being evolved, and yellow lustrous flakes of plumbic iodide are formed; this characteristic precipitate also forms when bournonite is treated with the same reagents.

The most surprising result, however, is the decomposition of cinnabar by the iodo-citric mixture; this mineral is attacked even in the cold, and on heating the reaction proceeds with violence; on cooling the solution deposits scarlet crystals of mercuric iodide.

When cinnabar is heated with oxalic acid and potassium iodide, the action is even more energetic than with citric acid.

Sulphur is attacked by the nitro-citric mixture with difficulty, sulphuric acid being found in the solution.

The most easily decomposable sulphide seems to be alabandite, which is strongly attacked by citric acid alone in the cold. The reactions of the selenides, tellurides, arsenides, etc., are indicated with sufficient fulness in the table,

### *Behaviour of Oxides.*

This group includes such refractory minerals as corundum, rutile, cassiterite, quartz, and others, which naturally resist these methods of attack. A few oxides are more or less perfectly decomposed, as shown in the table; the decomposition of the manganese oxides is very complete, and is accompanied with oxidation of the organic acid used. The addition of sodium nitrate does not greatly increase the energy of the solvent, as respects oxides, except in the case of uraninite, which dissolves completely.

The iodo-citric mixture applied to oxides, affords no especially notable results.

### *Behaviour of Silicates.*

In its action on silicates, citric acid differs from hydrochloric more in power than in kind; those silicates which are decomposed by the mineral acid, with or without the formation of a jelly, are also attacked by the organic acid. Of the 76 species examined, 21 are decomposed in the cold, 14 on heating with citric acid, 12 are partially attacked by the iodo-citric mixture, and 29 resist these methods of attack; the names are given in the table. The most easily decomposed are the hydrous silicates of the Zeolite group.

Tartaric acid acts much like citric acid, as respects the silicates; but oxalic acid is less powerful. By treating silicates in platinum vessels with a strong hot solution of citric acid, to which ammonium fluoride is added, many of them dissolve very easily.

### *Behaviour of Sundry Minerals.*

Under this head are grouped 38 minerals, whose behaviour is as varied as their composition. They include fluorides, phosphates, sulphates, tungstates, columbates, etc., the reactions of which are shown in the table. We observe that all the phosphates are quite readily decomposed by citric acid alone; the fluorides are not attacked; of the tungstates wolframite is slightly attacked by citric acid, hübnerite yields to the nitro-citric mixture, and scheelite resists all the reagents. Gypsum seems to be somewhat more soluble in solution of citric acid than in water, but the sulphates of the other alkaline earths are insoluble. Wulfenite and crocoite are strongly attacked on boiling with citric acid. The native metals, silver, mercury, copper, arsenic, antimony, and bismuth, dissolve with more or less facility in the nitro-citric mixture; the energetic solvent-power of this reagent is further shown by the fact that it also dissolves lead and tin.

### *Summary of Results.*

The accompanying table, to which we have frequently referred, summarises the results obtained by the application of these reagents to two hundred minerals. From this it appears that citric acid has a power of decomposing minerals little short of that possessed by hydrochloric acid, and this difference in degree evidently gives the organic acid an advantage over the mineral acid in the determination of species. Many of the reactions are characteristic, yet we do not regard the table as a scheme for determining minerals.

That this table is entirely free from errors we dare not claim; without a fuller investigation than time allowed, it is, in certain cases, difficult to ascertain whether a mineral is merely attacked (one or more constituents being partially removed by the solvent), or whether it is truly *decomposed.*

### *Application to Field Work.*

The advantages of these methods in the examination of minerals and rocks *in the field* are evident. Many geologists and mineralogists add to their outfit for blowpipe work, a glass bottle of hydrocloric acid, carried in a protecting wooden case, for the purpose of testing carbonates; but notwithstanding great care, the fragile glass often gives rise to unhappy accidents. To avoid such inconveniences, we propose to substitute for the liquid acid, the solid citric acid, which can be readily carried in a strong pasteboard box, and dissolved in water obtained in the field, when required for use. The facility with which potassium nitrate (or nitrite) is decomposed by citric acid, makes it possible to carry nitric acid also practically in a solid form; and the addition of solid potassium-iodide to this list of *dry reagents* for *wet analysis*, greatly increases the means of studying the chemical characters of minerals in the field.

Hydro-potassium sulphate,—furnishing sulphuric acid in a solid form—has already been proposed by E. Jannettaz (*Compte Rendu,* 1874).

The writer has tested in the field the methods above described, applying them to the more common minerals with success. For the purpose of working with solutions, a nest of test tubes (12 c.m. long) in a cylindrical pasteboard case is found convenient; the innermost test tube may be used to hold pulverized citric acid. In the absence of test tubes, the writer finds the hollow palm of his hand a convenient and portable apparatus for testing carbonates by their effervescence.

## *Application to Geological Phenomena.*

The disintegration and erosion as well as the consolidation of rocks has been attributed in part to the chemical action of various solvents, among which carbonated waters play an important rôle; if, however, we are permitted to reason by analogy, it appears probable that many changes, imperfectly understood by geologists, may be explained by referring them to the action of the organic acids of the soil. If citric, tartaric, and oxalic acids are able to decompose minerals, rapidly and completely in the hands of the chemist, may not humic, geic, crenic, apocrenic, and other acids of humus, in the lapse of long periods of time, accomplish much in the disintegration of rock-material on the surface of the earth?

The very existence in the soil of compounds of ulmic (?), humic, crenic, and apocrenic acids, with ammonia, soda, potassa, lime, magnesia, alumina, iron, and manganese, is *proof* that these organic acids exert considerable influence. This is also shown by the existence of minerals, of which organic acids form component parts;—such as whewellite, thierschite, succinite, mellite, pigotite, etc.; as well as the occurrence of limonites, containing 12·5 to 15· per cent of humic acid (Sterry Hunt, Geol. Canada, 1863, 510); and of acid hydrocarbons, containing the ill-defined bodies, geoceric, georetinic, and butyro-limnodic acids.

Paul Thénard has remarked the extraordinary power of azo-humic acid to dissolve silica (*Compte Rendu* LXX, 1412,); Bischof, Mülder, Herrmann, Detmer, Senft, and many others, have recorded observations on the geological action of the acids of humus; these notices are widely scattered throughout Journal literature; and, since we began these researches in the laboratory, our friend Alexis A. Julien, of Columbia College School of Mines, New York, has collated all papers bearing on this subject, and has recently published a review of them, together with the results of original study, under the title "Geological Action of the Humus Acids." This will be found in the Proceedings of the *Am. Assoc. Adv. Science*, vol. 28, 1879 (80).

## TABLE SHOWING THE BEHAVIOUR OF CERTAIN MINERALS WITH CITRIC ACID ALONE, AND WITH REAGENTS.

### I.

DECOMPOSED (IN FINE POWDER) BY A SATURATED SOLUTION OF CITRIC ACID.

1. IN THE COLD.

| A.<br>*Without evolution of Gas.* | B.<br>*With liberation of $CO^2$.* | C.<br>*With liberation of $H_2S$.* | D.<br>*With separation of $SiO_2$.* |
|---|---|---|---|
| Clausthalite | Calcite ! | Stibnite | Wollastonite |
| Leucopyrite | Dolomite* | Galenite | Rhodonite ! |
| Atacamite | Gurhofite ! | Alabandite ! | Chrysolite |
| Brucite | Ankerite* | Sphalerite | Willemite ! ‡ |
| Gummite | Rhodochrosite* | Pyrrhotite | Nephelite |
| Pyromorphite* | Smithsonite * |  | Lapis lazuli |
| Mimetite | Aragonite ! |  | Chondrodite |
| Triphylite | Witherite ! |  | Pectolite !‡ |
| Triplite | Strontianite ! |  | Laumontite !‡ |
| Vivianite ! | Barytocalcite ! |  | Chrysocolla ! |
| Libethenite ! | Cerussite ! |  | Calamine !‡ |
| Olivenite ! | Malachite ! |  | Apophyllite |
| Pseudomalachite | Azurite* |  | Thomsonite ! |
| Wavellite |  |  | Natrolite !‡ |
| Pharmacosiderite ! |  |  | Mesolite ! |
| Torbernite |  |  | Analcite |
| Autunite |  |  | Chabazite |
| Ulexite ! |  |  | Herschelite ‡ |
| Cryptomorphite ! |  |  | Stilbite |
| Anglesite |  |  | Deweylite |
| Brochantite ! |  |  | Prochlorite |

2. ON BOILING.

| E.<br>*Without evolution of Gas.* | F.<br>*With liberation of $CO^2$.* | G.<br>*With liberation of $H_2S$.* | H.<br>*With separation of $SiO^2$.* |
|---|---|---|---|
| Cuprite ! | Hausmannite † | Bornite | Tephroite ‡ |
| Zincite | Pyrolusite !† | Jamesonite* | Ilvaite |
| Malaconite | Manganite† | Bournonite* | Phlogopite* |
| Goethite* | Psilomelane !† | Boulangerite | Datolite !† |
| Limonite* | Wad !† | Kermesite | Prehnite* |
| Allanite (?) | Magnesite ! |  | Heulandite |
| Apatite* | Siderite ! |  | Serpentine |
| Wolframite* |  |  | Chrysotile |
| Wulfenite |  |  | Retinalite |
| Crocoite |  |  | Bastite |
| Gypsum* |  |  | Genthite |
|  |  |  | Gieseckite* |
|  |  |  | Jeffersite |
|  |  |  | Masonite* |
| *and those in A.* | *and those in B.* | *and those in C.* | *and those in D.* |

## II.

DISSOLVED BY BOILING WITH CITRIC ACID WITH THE ADDITION OF:—

| I. *Sodium nitrate.* | | K. *Potassium iodide.* | |
|---|---|---|---|
| Silver | Cobaltite ! | Realgar* | Pyrope |
| Mercury | Ullmannite ! | Orpiment* | Colophonite |
| Copper | Marcasite ! | Cinnabar ! | Epidote |
| Arsenic | Arsenopyrite ! | Hematite* | |
| Antimony | Nagyagite | Menaccanite* | |
| Bismuth | Covellite ! | Washingtonite* | *and most of those in A, B, C, D, E, F, G, H, and I.* |
| Sulphur * | Berthierite ! | Magnetite* | |
| Bismuthinite | Pyrargyrite | Franklinite | |
| Domeykite ! | Tetrahedrite ! | Braunite | |
| Argentite | Tennantite ! | Enstatite | |
| Hessite | Stephanite | Paulite | |
| Chalcocite ! | Polybasite ! | Augite | |
| Tiemannite ! | Enargite ! | Spodumene* | |
| Millerite ! | Uraninite ! | Hornblende* | |
| Niccolite ! | Hübnerite | Actinolite* | |
| Pyrite ! | | Pargasite* | |
| Chalcopyrite ! | | Olivine | |
| Linnæite | *and those in C. and G.* | Almandite | |
| Smaltite ! | | | |

## III.

L. MINERALS NOT DECOMPOSED BY THE ABOVE REAGENTS.

| | | | |
|---|---|---|---|
| Graphite | Hyalite | Wernerite | Titanite |
| Molybdenite | Diopside | Leucite | Staurolite |
| Proustite | Petalite | Anorthite | Bowenite |
| Fluorite | Asbestus | Labradorite | Talc |
| Cryolite | Beryl | Oligoclase | Kaolin |
| Corundum | Zircon | Albite | Ripidolite |
| Spinel | Vesuvianite | Orthoclase | Columbite |
| Chromite | Zoisite | Tourmaline | Samarskite |
| Chrysoberyl | Iolite | Andalusite | Scheelite |
| Cassiterite | Biotite | Fibrolite | Barite |
| Rutile | Muscovite | Kyanite | Celestite |
| Quartz | Lepidolite | Topaz | Anhydrite |

Completely decomposed or dissolved. * Feebly attacked. † The $CO_2$ evolved is derived from the Citric Acid. ‡ Gelatinizes.

N.B.—The gases evolved are to be examined with acetate of lead test paper, the solutions with appropriate reagents.