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IV. *On Malic Acid, and the Changes undergone by its Salts at High Temperatures.* By ROBERT HAGEN, *Ph. D.*

Read June 1, 1841.

AFTER the publication of Mr. Graham's observation, that phosphoric acid, in its different states, possesses the property of combining with one, with two, and with three atoms of base respectively, it was discovered by Liebig that the same law holds good in part with many organic acids; some of these acids requiring two, and some three atoms of base, to form neutral salts. The hydrates of each acid contain a corresponding number of atoms of basic water, which cannot be removed without the decomposition of the acids themselves. These chemists showed that, though a salt of any acid, with magnesia or with oxides isomorphous with it, possessed the power of combining with a potash salt of the same acid, and forming a double salt, such as the sulphate of magnesia and potash, that is not ground for doubling the atomic weight of the acid, or for viewing it as bibasic.

They proved at the same time that a monobasic acid is incapable of forming a double salt with two isomorphous bases. The proportion of base which unites with a polybasic acid is constant, generally either two or three atoms. In the memoir on organic acids by Liebig, here alluded to, he had made it not improbable that *malic acid* is bibasic. At his suggestion I have made several analyses of its various salts, which form the subject of this paper.

Malic acid was first discovered by Scheele in the juice of the apple; it was again discovered by Donovan in the juice of several plants, and described by him as a new acid. The identity of the acid of Donovan with malic acid was proved by Braconnot. This acid has been most fully described by Liebig. It has also been partially examined by Pelouze, Braconnot, and Richardson.

The malic acid used in the present investigations was prepared from the expressed juice of the berries of the *Sorbus occuparia*, or Service tree, in the following manner. The expressed juice was mixed in a copper pan with finely divided

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is therefore somewhat too high, and it contains more than one volume of oxygen; thus it is clear that the atomic weight of carbon, as calculated from this, is also too high. That, calculated from his specific gravity, at the pressure of one-third of an atmosphere, is 75·7. He has as yet, however, only made three weighings, which he considers as little more than introductory experiments of practice. I shall be present tomorrow at the fourth determination."

and levigated hydrate of lime, care being taken not to saturate the fluid completely, but to allow it to remain sensibly sour. Being placed on the fire, it was made to boil for some hours, during which time it gave off a peculiar pungent vapour, which strongly affects the eyes. By degrees neutral malate of lime precipitates, and may be removed with a ladle. By continued boiling, more of the salt is obtained. When no more falls, the vessel is removed from the fire, and allowed to cool, when a little more is precipitated. We must take care in the beginning not to saturate the expressed juice entirely with lime, or so much colouring matter falls with the malate of lime, as to render the acid impure. The neutral malate of lime thus obtained, is dissolved in dilute nitric acid (1 part acid to 10 of water), filtered and evaporated; upon cooling, acid malate of lime crystallizes out in perfectly colourless crystals. It must be well washed with cold water, again dissolved in boiling water, and precipitated by acetate of lead. The lead salt is decomposed by sulphuretted hydrogen, and the malic acid obtained pure by evaporation.

Malic acid forms with bases two neutral salts, one of which becomes anhydrous when dried at 100° C., while the other still retains water at that temperature. It possesses decided bibasic properties, and the hitherto received atomic weight is necessarily doubled.

The following salts have been examined :—

## MALATES OF LIME.

*a. Neutral anhydrous Malate of Lime.*

$$C_8 H_4 O_8 + 2\ Ca\ O,\ \text{or}\ M\ 2\ Ca\ O.$$

This salt is obtained by saturating a solution of malic acid with lime water. It is a crystalline powder, perfectly insoluble hot and cold water.

0·489 gramme of this salt gave 0·319 sulphate of lime, or 32·188 per cent. lime. This gives for the atomic weight of the salt the number 2212·40.

|  | Calculated. | Found. |
|---|---|---|
| 1 equivalent of Malic Acid 1461·39 | 67·24 | 67·81 |
| 2 equivalents of Lime . . . 712·04 | 32·76 | 32·18 |

*b. Neutral hydrated Malate of Lime.*

$$\overline{M}\ 2\ Ca\ O + 5\ aq.$$
$$\overline{M}\ 2\ Ca\ O + 4\ aq.\ (100°\ C.)$$
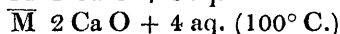
If acid malate of lime is saturated with potash, soda, or ammonia, and the solution evaporated at a gentle temperature, we obtain instead of a double salt, malate of lime with 5 equivalents of water, in hard shining crystals. When heated

to 100° C. this salt is converted into a porcellanous mass, and is found to have lost one atom of water.   At 150° C. it becomes quite anhydrous.   Of the salt in its first state of hydration, 0·422 gramme dried at the temperature of the atmosphere, gave 0·2655 sulphate of lime, or 26·113 per cent. lime, which makes the atomic weight of the salt 2725·0, and gives the following composition :—

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 eq. Malic Acid 1461·39 | | 53·44 | |
| 2 ... Lime . . . 712·04 | | 26·03 | 26·113 |
| 5 ... Water. . . 562·40 | | 20·53 | |
| 2735·83 | | 100·00 | |

Of the salt dried at 100° :—

(1). 0·6135 gramme gave 0·4045 sulphate of lime = 27·383 per cent. lime ; and consequently the atomic weight, 2600·0.

(2). 0·3660 gramme gave sulph. lime, 0·241, or 27·344 per cent. lime.

(3). 0·335 salt, gave 0·353 sulphate lime, and consequently the atomic weight, 2598·28.

These give—

|  |  | Calculated. | Found. | | |
|---|---|---|---|---|---|
|  |  |  | 1. | 2. | 3. |
| 1 Malic acid 1461·39 | 56·71 | | | | |
| 2 Lime . . . 712·04 | 27·14 | | 27·38 | 27·34 | 27·40 |
| 4 Water. . . 449·92 | 17·15 | | | | |
| 2623·35 | | | | | |

The previous analyses of the lime salt dried without heat, shows the necessity of doubling the atomic weight of the acid, as otherwise we should be obliged to give it the formula

$$C^4 H^2 O^4 Ca O + 2\tfrac{1}{2} \text{ aq.} ;$$
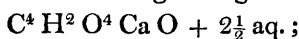
which is at variance with the atomic theory.

ACID MALATE OF LIME.   $\overline{M}$ Ca O H$^2$ O + 6 aq.

This salt is obtained when neutral malate of lime is dissolved in nitric acid.   It crystallizes in large transparent octahedrons.   Dried at 100° C. it loses water, and is converted into a viscid, stringy mass.

0·706 salt gave 0·2345 sulphate of lime, or 13·794 per cent. lime ; atomic weight, 2585·8.

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 atom Malic acid 1461·39 | | 56·10 | |
| 1 atom Lime . . . 356·02 | | 13·67 | 13·79 |
| 7 Water . . . . . 787·36 | | 30·23 | |
| 2604·77 | | | |

Richardson and Merydorf concluded the formula of this salt to be, $\overline{M}$ Ca O H$^2$ O + 8 aq.

## MALATES OF MAGNESIA.

*a. Neutral hydrated Malate of Magnesia.*

$\overline{M}$ 2 Mg O + 10 aq
$\overline{M}$ 2 Mg O + 2 aq (100° C.).
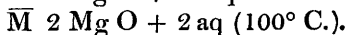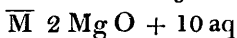
This salt is obtained by boiling magnesia in a solution of malic acid, and crystallizing. It loses 8 atoms of water by 100° C.

0·5505 salt gave 0·2708 sulphate of magnesia, equivalent to 16·713 per cent. of magnesia; and makes the atomic weight 3091·4.

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 eq. Malic acid | 1461·39 | 47·09 | |
| 2 ... Magnesia.. | 516·70 | 16·66 | 16·713 |
| 10 ... Water. . . | 1124·8 | 36·55 | |

3102·89

Of the salt dried at 100° C., 0·466 gave 0·109 sulphate of magnesia, equivalent to 23·390° per cent. magnesia.

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 at. Malic acid | 1461·39 | 66·34 | |
| 2 ... Magnesia . | 516·70 | 23·45 | 23·39 |
| 2 ... Water . . | 224·96 | 10·21 | |

2203·05

This salt was also analysed by Professor Liebig with the same result.

*b. Neutral anhydrous Malate of Magnesia.* $\overline{M}$ 2 Mg O.

This salt is obtained by precipitating a saturated solution of the former salt (*a.*) with alcohol, and drying at 100° C.

0·344 salt gave 0·0935 magnesia, equivalent to 26·945 per cent.; atomic weight, 1906·88.

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 atom Malic acid | 1461·39 | 73·83 | |
| 2 atoms Magnesia | 516·70 | 26·12 | 26·94 |

1978·09

ACID MALATE OF MAGNESIA. $\overline{M}$ Mg O H$^2$ O + 3 aq
$\overline{M}$ Mg O H$^2$ O + aq (100°).

Obtained by dividing and saturating one half of the malic acid with carbonate of magnesia, and evaporating to crystal-

lization.   It loses 2 atoms of water by 100° C.; at a higher temperature it melts.

1·1755 salt gave 0·1405 magnesia, equivalent to 11·952 per cent.; and for the atomic weight, 2161·5.
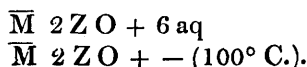
|  | | | Calculated. | Found. |
|---|---|---|---|---|
| 1 atom Malic acid | 1461·39 | | 67·35 | |
| 1 ... Magnesia | 258·35 | | 11·91 | 11·952 |
| 4 atoms Water ... | 449·91 | | 20·74 | |

<div align="center">2169·66</div>

Of the salt dried at 100° C., 0·698 gave 0·0795 magnesia, or 13·294 per cent.; atomic weight, 1943·0.

|  | | | Calculated. | Found. |
|---|---|---|---|---|
| 1 eq. Malic acid | 1461·39 | | 75·147 | |
| 1 ... Magnesia | 258·35 | | 13·285 | 13·294 |
| 2 ... Water . . | 224·96 | | 11·568 | |

<div align="center">1944·70</div>

### MALATES OF ZINC.

*a. Neutral Salt.*

$$\overline{\text{M}} \ 2\,\text{Z}\,\text{O} + 6\,\text{aq}$$
$$\overline{\text{M}} \ 2\,\text{Z}\,\text{O} + - (100° \text{ C.}).$$

Is prepared by digesting carbonate of zinc with malic acid, at a temperature not above 30° C.   Dried at 100° C. it becomes anhydrous.

Of this salt, 0·4570 gave 0·2935 sulphate of zinc, or 32·179 oxide of zinc, making the atomic weight 3127·8; the calculated one being 3142·77.

0·695 of the salt dried at 100° C. gave 0·566 sulphate of zinc, or 40·302 oxide of zinc; making the atomic weight 2463·6; the calculated is 2467·6.

### ACID MALATE OF ZINC.   $\overline{\text{M}}. \ \text{Z}\,\text{O}\,\text{H}\,\text{O} + 2\,\text{aq}.$
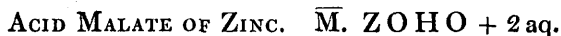
Prepared by adding excess of malic acid to the neutral salt.

0·190 of this salt gave 0·082 sulphate of zinc, or 21·343 per cent. of oxide of zinc; the atomic weight deduced from which is 2351·7.   The composition of the salt is therefore -

|  | | | Calculated. | Found. |
|---|---|---|---|---|
| 1 eq. Malic acid . . | 1461·4 | | 63·480 | |
| 1 ... Oxide of zinc | 503·2 | | 21·861 | 21·343 |
| 3 ... Water . . . . | 337·4 | | 14·659 | |

<div align="center">2302·0</div>

Braconnot analysed this salt with the same results.

## BASIC MALATE OF ZINC.

If malic acid is long boiled with excess of carbonate of zinc, there falls down a sandy powder; of this salt dried at 100°,

(1.) 0·3935 gave 0·178, or 44·66 per cent. of oxide of zinc; atomic weight, 2253·3.

(2.) 0·255 gave 0·224 sulphate of zinc, or 44·015 per cent. of oxide of zinc; atomic weight, 2286·8.

(1.) 0·474, burnt with oxide of copper, gave 0·1075 water, and 0·329 carbonic acid.

(2.) 0·5510 gave water 0·1335, and 0·3835 carbonic acid. This salt is therefore composed of

|  | Calculated. | | Found. | |
|---|---|---|---|---|
| 12 at. Carbon . . . | 917·22 | 20·19 | 19·191 | 19·24 |
| 9 ... Hydrogen. . | 112·32 | 2·47 | 2·52 | 2·69 |
| 15 ... Oxygen . . . | 1500·00 | 33·03 | 33·62 | 34·04 |
| 4 ... Oxide of zinc | 2012·9 | 44·31 | 44·66 | 44·015 |

$$4542·44$$

Heated to 100° C. it lost 4 atoms of water; and 0·420 gave 0·411 sulphate of zinc, or 49·082 per cent. oxide of zinc; atomic weight, 2052·3. 0·4225 gave 0·0715 water, and 0·334 carbonic acid, which gives the formula $C^{12} H^5 O^{11} + 4 Z O$. This salt, however, is then essentially altered, part of its malic acid being converted into fumaric acid, as will be shown in the sequel.

ACID MALATE OF COPPER. $\overline{M}$ Cu O H$^2$ O + 2 aq
$\overline{M}$ Cu O H$^2$ O (100° C.).
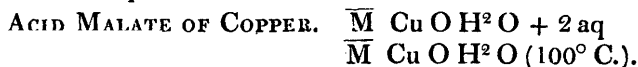
Prepared by dissolving hydrated oxide of copper in malic acid, and evaporating at a temperature of 30° to 40° C., as a small blue crystalline body. 0·690 of this salt gave 0·149 oxide, or 21·521 per cent. of oxide of copper; atomic weight, 2302·17. The composition calculated from this, is as follows:—

|  |  | Calculated. | Found. |
|---|---|---|---|
| 1 atom Malic acid . . . . | 1461·39 | 63·69 | |
| 1 ... Oxide of copper | 495·70 | 21·60 | 21·821 |
| 3 atoms Water . . . . . | 337·44 | 14·71 | |

$$2294·53$$

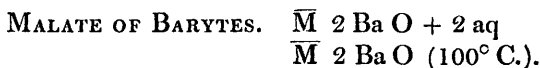Dried at 100° it loses 2 atoms of water, and its atomic weight becomes 2069·57.

## MALATE OF SILVER. M 2 Ag O.

0·2877 salt gave 0·1777 silver, or 66·339 per cent. of oxide of silver. Hence

|                           |          | Calculated. | Found. |
|---------------------------|----------|-------------|--------|
| 1 eq. Malic acid. . .     | 1461·39  | 33·48       | 33·66  |
| 2 ...  Oxide of silver    | 2903·21  | 66·52       | 66·33  |

$$4361·60$$

MALATE OF BARYTES.    $\overline{M}$ 2 Ba O + 2 aq

$\overline{M}$ 2 Ba O (100° C.).

A solution of malic acid is saturated with barytes water, and evaporated at a very moderate temperature. The salt found crystallizes. At 30° C. it loses one atom of water; at 100° C. it becomes quite anhydrous.

Of the salt, 0·5575, dried at the ordinary temperature, gave 0·452 sulphate of baryta, or 53·207 per cent. of barytes; which makes the atomic weight 3956·8, the calculated one being 3600·10. The salt dried by 30° C. gave 54·426 per cent. barytes. That dried at 100° C. is composed of 1 atom of malic acid and 2 atoms of barytes.

MALATE OF STRONTIAN.    $\overline{M}$ 2 St O + 3 aq

$\overline{M}$ 2 St O + 2 aq (100° C.).
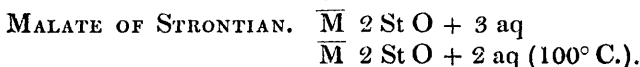
### FUMARATE OF OXIDE OF ÆTHYL.

This æther is formed whenever malic acid is brought into contact with muriatic æther. Malic acid also, when long mixed with absolute alcohol, or with strong fuming hydrochloric acid, is converted into fumaric acid.

This combination, or fumaric æther, is heavier than water, and has a grateful odour, like that of fruit. It is slightly soluble in water, and is therefore better separated from muriatic æther, when mixed with the latter by distillation, than by means of water. By potash, fumaric æther is converted into alcohol and the fumarate of potash. Kept long in contact with ammonia, it is converted into fumaramide. Purified by being distilled over chloride of calcium, 0·3315 æther gave 0·208 water, and 0·669 carbonic acid. Hence

|                          |         | Calculated. | Found.  |
|--------------------------|---------|-------------|---------|
| 8 atoms Carbon . .       | 611·48  | 56·29       | 55·803  |
| 6  ...  Hydrogen         | 74·87   | 6·89        | 6·97    |
| 4  ...  Oxygen . .       | 400·00  | 36·82       | 37·22   |

$$1086·35$$

### FUMARAMIDE.    $C^4 H O^2, N H^2$.
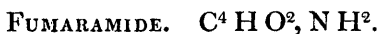
This amide is obtained when fumaric æther is left a long time in contact with an excess of caustic ammonia. Its formation is quite analogous to that of oxamide and the other com-

pounds of amide. In cold water and absolute alcohol it is quite insoluble. It is soluble in boiling water, and again precipitates as the water cools. Left long in contact with water, it is completely converted into fumarate of ammonia. Ammonia is disengaged by the fixed alkalies, and a fumarate formed. By distillation it is decomposed into ammonia; a white body, probably maleinic acid, and a residue of charcoal are left.

0·426 of fumaramide gave 0·1335 water, and 0·2780 carbonic acid. By a qualitative determination of the nitrogen, the latter was found to be to the carbonic acid in volume as 1 to 4.

| | |
|---|---|
| Carbon . . . . | 42·37 |
| Hydrogen . . . | 5·33 |
| Nitrogen . . . | 24·53 |
| Oxygen . . . . | 27·77 |
| | 100·00 |

This gives—

| | | | | Calculated. |
|---|---|---|---|---|
| 4 atoms | Carbon . . . . | 305·74 | | 42·46 |
| 3 ... | Hydrogen . . . | 37·44 | | 5·19 |
| 1 ... | Nitrogen . . . | 177·04 | | 24·59 |
| 2 ... | Oxygen . . . . | 200·00 | | 27·76 |
| | | 720·22 | | 100·00 |

### MALATES AT HIGH TEMPERATURES.

If malates of the earths or alkalies are kept for some time at a temperature varying from 250° to 300° C., they are changed into fumarates, water being the only other product. The changes produced are best observed in the following manner. The fumarate produced is dissolved in as small a quantity of boiling water as possible, and a small excess of nitric acid is added to it. The fumaric acid crystallizes from the solution in its peculiar form, possessing all the properties ascribed to it by Pelouze. I have prepared its silver salt to identify it with certainty. 0·2726 acid gave 0·0885 water, and 0·4115 carbonic acid. This gives the following formula for its composition :—

| | | | Calculated. | Found. |
|---|---|---|---|---|
| 4 atoms | Carbon. . . | 305·74 | 41·84 | 41·73 |
| 2 ... | Hydrogen | 24·95 | 3·41 | 3·60 |
| 4 ... | Oxygen . . | 400·00 | 54·75 | 54·683 |
| | | 730·69 | | |

0·3735 of the silver salt gave 0·3205 chloride of silver, or

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69·422 oxide of silver; and 0·4270 gave 0·029 water, and
0·224 carbonic acid.

|  |  | Calculated. | Found. |
|---|---|---|---|
| 4 atoms Carbon . . . . | 305·74 | 14·77 | 14·50 |
| 1 atom Hydrogen . . . | 12·48 | 0·60 | 0·75 |
| 3 atoms Oxygen . . . . | 300·00 | 14·49 | 15·31 |
| 1 atom Oxide of silver | 1451·6 | 70·14 | 69·42 |

2069·82

This remarkable change of malic acid salts into those of
famaric acid, appears to me to bear a strong analogy to the
formation of the pyro- and metaphosphates, but this is as yet
not sufficiently proved by experiment.    1 have kept a satu-
rated solution of fumaric acid at a boiling temperature for
several days without the slightest change in it.    And I have
also kept a like solution, in a tube hermetically sealed, for a
considerable time at a temperature of $250°$, under a pressure
therefore of nearly 15 atmospheres, without its being altered
in any of its properties.    Hence fumaric acid does not appear
to be reconvertible into malic acid.