A Digest of Research on Succinic Acid, with special reference to its Metallic Salts.

by

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(Including an account of researches carried on at Edinburgh University and elsewhere by the author, in part independently, in part in conjunction with Dr. Hugh Marshall F.R.S.)

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The History and Preparation of Succinic Acid.

The first organic acid known to early chemists was acetic acid; they used it in the dilute form of crude vinegar. The litho-chemists obtained the concentrated acid by distilling verdigris. They used it orally medicinally. The glacial acid was obtained during the phlogiston period. Although the tartaric had been known from an early period, and the value of "tartar" and of "tartar emetic" was recognised by the litho-chemists, the acid itself was not isolated until Scheele prepared it in the 18th century. Thus succinic acid was the second organic acid known to the alchemists.

In his "De Nature Fossilium" (1550) Agricola states that the products of distilled amber include a saline substance. The litho-chemist Libavius refers to "flos succini, mistic siliciuis spirituosoque humidio abstractus floe elevatur." In describing the preparation of amber oil he mentions that crystals are deposited in the neck of the reagent. Croll, a follower of Paracelsus, was the first to recommend the medicinal use of "flos succini." Its application in medicine is of interest. At the time of Berzelius, ammonium succinate was part of a recognized preparation "liquor corona cerri succinatire." More recently it has been found that notwithstanding the very poisonous effect of malic acid and the oxalate, its homologue succino acid, and the succinates, are almost without effect on the system. They are no longer used in medicine.

The acid nature of succinic acid was first recognized by Henry 2 who remarks "J'ai reconnu que ce sel est acide, et semblerait a celui des plantes qu'on appelle essentiel." This resemblance to vegetable acids was disputed till Toll 3 showed the striking similarity. Stocker von Neumayr's investigation, "disparatia de Succino" established it as one of the proximate constituents of amber. Its name signifies this relationship.

\[ \text{L'acide succinique} = \text{L'acide de succin (amber)} \]

Bernsteinic= Amber acid.

It has since been obtained from many other natural sources, e.g.

- turpentine from various species of pine, linden, various kinds of poppy, hemp, grape, beet juice, and rhubarb, all yield small quantities.
- It also occurs in the system in very small quantities as a product of muscle decomposition.
- It is produced 1 by the action of nitric acid on many organic substances, including fats, fatty acids, from butyric acid upwards, and different waxes; 2 in the fermentation of sugar (alcoholic solution), of asparagus, of

2. Corso de Chemie 1649, p. 460.
calcium malate, or ammonium tartarate, and if usual. It can be prepared 1) by reducing
fumaric and malic acids with sodium amalgam, or malic and tartaric acids with
hydrobatic acid; 2) by heating its nitrate with alcoholic potash. To treat
it with dilute nitric acid, by a great many other synthetic methods, including
the electrolytic preparation of its ethyl ester from potassium ethyl malonate.

Succinic acid is obtained by the dry distillation of amber, other products being
amber oil in the distillate, and a resinous residue. The distillate contains the
acid partly as a mass of crystals, partly in solution. It is warmed, filtered, the filtrate
concentrated; yellow crystals of succinic acid separate. The colour is due to admixture
of oil, from which it is extremely difficult to purify the acid; the usual method
is to boil with nearly concentrated nitric acid.

The history of the purification of the acid may be briefly described. Berzelius mentions
the following methods: 1) Digestion with animal charcoal; hereafter, filtration and
concentration. Only a slight amount of impurity is removed. Fournaux's statement
that the nature of the acid is altered by this treatment is incorrect; 2) Sublimation
at as low a temperature as possible. Brilliant crystals result; 3) The impure acid
solution is saturated with potassium carbonate, boiled with powdered animal
charcoal and filtered; the filtrate is precipitated with lead acetate, and the lead
succinate washed, dried, and decomposed with the requisite quantity of sulphuric
acid. From the solution perfectly pure acid crystallises. (He especially recommends
this method). 4) "It has been proposed to boil with nitric acid, which destroys
the oil without affecting the acid," but, he objects, the products of decomposition
of the oil will affect the purity of the acid.

The third method was that commonly employed by early chemists. The
fourth method may be ascribed to Guyton de Morveau, who found that
nitric acid had no effect on succinic acid, and suggested this mode of
purification. In 1828 Lecait and Serbat 2 confirmed his statement; his
suggestion had not generally been adopted, they tested it, and found it
much preferable to the usual lead precipitation, being more rapid,
while the product is quite as pure. The comment of Berzelius in 1830 has
been given. D'Espagne & examined this question of purification at some
length, comparing the charcoal and nitric acid methods with that
of purifying the solution by a stream of gaseous chlorine. He decided
in favour of the nitric acid method, which appears to have come into

2. Journal de Pharmacie, 9, 89
The Constitution of Succinic Acid.

The first analysis was published by Berzelius (loc. cit.) in reality he analyzed the sublimed acid; that is to say, the anhydride. His figures compare well with those theoretically derived from the now accepted formula.

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calculated</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>48.48</td>
<td>47.985</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.96</td>
<td>4.030</td>
</tr>
<tr>
<td>Oxygen</td>
<td>47.56</td>
<td>47.985</td>
</tr>
</tbody>
</table>

This confusion of anhydride and acid, common to all the chemists of that period, hindered for a long time the recognition of the true character of succinic acid. Berzelius regarded the succinates as analogous with the formic; the acid was thus monobasic. L'Arcet in great part established the composition of the acid; his memoir was the first of any importance devoted to the subject. Liebig and Wöhler had previously analyzed the sublimed acid. They found it contained half an "atom" of water, which seemed indispensable to its existence. Summarizing L'Arcet's work from the light of present knowledge the following results become apparent:

Crystallized succinic acid of melting point (M.P.) 180°C, has the composition $C_4H_6O_4$; treated to about 140°C it loses half a molecule of water, subliming slowly to beautiful needles of composition $C_4H_6O_3$. This was probably the compound examined by Liebig and Wöhler. By repeated sublimation, or by heating the acid with phosphoric anhydride, pure succinic anhydride is often obtained; its composition is $C_4H_4O_3$. Both the latter compounds treated with water, give a solution from which the ordinary acid separates, while all the silver salts have the composition $H_2C_4H_4O_4$.

The existence of a dibasic acid of composition $C_4H_6O_7$ has not been confirmed and seems improbable. Possibly L'Arcet analyzed a mixture of acid and anhydride.

There are several reasons, however, in favor of this supposition. I have observed that at temperatures of about 140°C, succinic acid slowly sublimes, giving brilliant needles unlike the acid itself. L'Arcet finds the M.P. of the sublimed acid 160°C, its B.P. (boiling point) 242°C. (Succinic acid 181°C and 235°C). Ramsay and Young from an entirely different standpoint, endeavoring to account for the anomalous curve of dissociation of succinic acid, put forward as a mere conjecture the possibility of the existence of intermediate anhydride, as $C_4H_4O_4$.

$C_4H_4O_4$ This, of course, gives the formula $C_4H_6O_7$.

1. Annals de Chimie et de Physique, 1835, ii. 58, 282.
2. Philosophical Transactions, 1856, 177, 2, 103.
Doepping (loc.cit.) and Fehling, by their investigation on the succinate, contributed greatly to the elucidation of the constitution of the acid. This was especially so in the case of Fehling, who, by establishing the existence of acid salts, proved that the acid was polybasic except the alkali salt; thought the evidence for polybasicity inconclusive. Doepping, who could prepare no acid salts, thought the evidence for polybasicity inconclusive. Fehling argued the acid tribasic on four grounds: 1) The sulphur succinic acids 2) Succinate, 3) the basic lead salts, and 4) the composition of ethyl succinate. It is scarcely necessary to say that he had not grasped the nature of the sulphuric acid and succinic acid, while his work on the lead salts is very inconclusive; his analyses do not agree with his formulae—selected probably on the assumption of the tribasicity of the acid.

The constitution of the acid was determined by Maxwell Simpson ² who was the first to synthesise it. Starting with ethylene bromide, by treating with potassium cyanide in alcoholic solution, he obtained ethylene cyanide. This treated with alcoholic potash gave on crystallisation an acid possessing all the properties of, and having the same composition as, succinic acid. Simpson remarked that since ethylene bromide can be synthesised, the synthesis of the acid is complete.

Schmitt ³, in the same year, at the suggestion of Volle, reduced the male and tartaric acids to succinic acid by means of hydriodic acid. Other syntheses followed rapidly. Keule ⁴ established the composition of fumaric and maleic acids by reducing them to succinic acid with sodium amalgam, while Steine ⁵ obtained the acid from bromonic acid and reduced silver. Finally, Brown and Walker ⁶ synthesised it electrolytically from potassium ethyl malonate—a method slightly modified by Vanetti and Coppadoro ⁷ who used ethyl malonate as cathode solution and a 30% solution of potassium carbonate as anode solution.

Carpff discovered and investigated acetic, and malonic acids, and his work may be said to have established the position of succinic acid in the malic acid series, its composition by that time being recognised as

\[
\begin{array}{c}
\text{C}_2\text{H}_4\text{O}_4^- \\
\text{H}_2\text{C} = \text{O}^- \\
\text{C}_2\text{H}_4\text{O}_4^-
\end{array}
\]

The presence of the acid is usually recognised by the production of its barium salt in boiling solution (the chief method in use for its quantitative estimation) and by the red brown precipitate produced by ferric chloride. It most closely resembles benzoic acid in its reactions; hydrochloric acid does not, however, precipitate it from aqueous solution of its salt; moreover, it is insoluble in chloroform. These serve as distinctions

1. Annalen der Pharmacie 1846, 49, 154
3. Annalen der Chemie und Pharmacie 1860, 110, 166.
4. Annalen der Chemie und Pharmacie 1860, 110, 166.
5. Berichte 1873, 6, 314
7. Atti R. Acad. Lincei 1903, V, 12, 8, 299
8. Annalen der Chemie und Pharmacie 1860, 115, 103, 136, 172
9. Ib. 1864, 131, 348
The metallic succinates are treated below at some length. The other most important derivatives are briefly mentioned here.

Ethyl Succinate \((C_2H_5)C_4H_4O_2\) was first prepared by d'Arcet in 1835 (loc. cit.). He found that it had the composition \(C_8H_9O_2\), which either signified \(C_4H_4O_3 + C_2H_5 + H_2O\), or \(C_4H_4O_3 + C_2H_4O\).

His method of preparation was to distil a mixture of concentrated hydrochloric acid, succinic acid, and alcohol. Lebours' and Fehling (loc. cit.) improved the method. The latter obtained succinyl-succinic acid by the action of metallic potassium on the salt.

Ethyl Hydrogen Succinate \((C_2H_5)C_4H_3O_2\) was obtained by Kunito by heating succinic anhydride with alcohol. It gives several crystalline metallic salts, some of which have been of considerable service for synthetical purposes.

Fehling appears to be the first to prepare methyl succinate, \((CH_3)C_4H_3O_2\), the method used being similar to that for the ethyl salt. All these three compounds are ethereal oils at ordinary temperatures.

Phenyl Succinate \((C_6H_5)C_4H_4O_2\) can be obtained by warming phenol with succinyl chloride.

It is a crystalline solid, insoluble in water. Our knowledge of the compound is due to Weselkov and Bazinowski; the latter obtained it by heating phenol with a boiling solution of the acid.

Succinic Anhydride \(C_4H_4O_2\) was first prepared pure, as has been already mentioned, by d'Arcet. It can also be obtained by heating the acid with equimolecular proportions of phosphorus pentachloride, while Aldo and Manuelli state that acetic anhydride precipitates it from a solution of barium succinate. It crystallizes from alcoholic solution in long needles of mp. 118° C.

Gerhardt and Ghirard prepared succinyl chloride \(C_4H_5(C_2OCL_2)\) by heating the acid with twice its molecular proportion of phosphorus pentachloride. It has been shown that its composition is probably

\[
C_2H_4 - \text{C} = \text{O}
\]

\[
\text{C} = \text{O} - \text{C} = \text{O}
\]

Succinamide \(C_4H_6NH\) \(\text{CONH}_2\) was first prepared by Fehling from ammonia and ethyl succinate; it is insoluble, crystallising in needles.

Succinimide was obtained by d'Arcet by the action of dry ammonium gas on succinimide. Fehling called it "bisuccinimide." Laurant and Gerhardt 7 recognized its amide nature and gave it the present name. It crystallizes in transparent rhombic crystals, containing one molecule of crystallisation water; they slowly effloresce and lose their water completely below 100° C. The substance is soluble in water, to an acid solution, the amide hydrogen being replaced by metals. The silver salt has been studied by Laurant and Gerhardt 7, others by Bunse 8 and Menodochus 9.
Metallic Salts of Succinic Acid

Beauvau and Seriat were the first chemists to examine the metallic succinates in any detail. In the Journal de Pharmacie for 1823 (9, 92), in showing the difference between succinates and benzoates, he describes the appearance of the potassium, sodium, and ammonium, and barium salts. Anschütz in his "Kehrbuch" publishes a number of data observed by himself and others. These I have taken from the French edition of his work "Traité de Chimie". There is no reliance can be placed on his statements unless they are corroborated by later authors. In 1843, Bietting published a detailed examination of a number of salts; Fehling followed next year with a similar piece, largely corroboration, much of his work being finished prior to the publication of Bietting's. Brandt in 1858 published a crystallographical research, and included of the root measurement of the strontium, cobalt, and manganese salts; unfortunately, the composition was not given, so that we can only presume that he used the salts described by other investigators. More recently, succinates of some rare metals have been prepared, while much of the later work has been concerned with physical properties especially solubility.

I propose now to refer to the different salts under the usual metallic classification, referring to the above-mentioned chemists by name only, in other cases giving full references. As far as I am aware, the bibliography is complete. All the formulae given have been corrected in accordance with modern atomic weights and theory.

Succinates of Potassium.

1. Neutral potassium succinate. By neutralizing succinic acid with potash, Lecanu and Seriat obtained a very deliquescent salt; it only crystallized on evaporating the solution to syrupy consistence. Anschütz probably described this salt, relating that potassium succinate effloresces on heating, deliquesce in cold air. Bietting, from highly concentrated solution from a solution of acid saturated with the carbonate — obtained a salt separating in indistinct crystals. His analysis corresponded with the composition K₂Ca₄H₄O₈·2H₂O. The salt deliquesce in air, was soluble in spirits of wine (vinsgeist), insoluble in ether; some of the water was lost at 100°C.

Fehling described a salt K₂Ca₄H₄O₈·½H₂O prepared in the same manner and crystallizing in rhombic tablets. This salt is stated to be unaffected by contact with air; a very slightly deliquescent salt crystallized from the mother liquor. On account of these differing observations, Fehling has, more recently, reinvestigated the matter. Using the same method, from a highly concentrated solution he obtained small deliquescent tablets; or standing over a disintegrator, these crystals separated. Their composition was K₂Ca₄H₄O₈·3H₂O, and they lost all their water below 100°C. Saller suggests that Fehling may have obtained the salt K₂Ca₄H₄O₈·½H₂O. My work on these compounds leads me to believe this extremely unlikely. Heischke, has published the crystallography of Saller's compound, which crystallizes in the rhombohedral system.

1. Annalen de Pharmacie 47, 253
2. 29, 157.
3. Bericht, 1883, 16, 3025
4. Zeitschrift fü Krystal 1883, 9, 525.
The action of normal potassium succinate solution in dissolving various metallic carbonates and hydrates will be dealt with under the heading of complex salts. Further particulars regarding potassium succinate will also be given in Part II.

2) Acid Succinate of Potassium \( \text{KHC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O} \) was prepared by dropping by saturating a solution of succinic acid with potassium carbonate and adding more acid. On evaporation, six-sided prisms are deposited, monoclinic, which effloresce slowly and are soluble in water and spirits of wine. All the water of crystallization is given up at 100\(^\circ\) C; the salt then remains unchanged by heat till above 200\(^\circ\) C when it melts.

3) Anhydrous Acid Succinate of Potassium \( \text{KHC}_4\text{H}_4\text{O}_6 \) was obtained by Flehling, using the same method, and just sufficient acid for half saturation. With more acid be obtained.

4) Potassium Supercrit Succinate \( \text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} \). According to this result, the salt when slowly deposed has \( \frac{1}{2} \) molecules water of crystallization. From hot solution it is anhydrous. Salzer (loc. cit.) examined these compounds from a solution which, he concluded, contained too much acid, the supercrit salt separated, anhydrous. In a second preparation be obtained dropings, hydrated salt. I shall show, in Part II, that all these salts exist, with the exception of \( \text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O} \), of which no trace has been obtained over a considerable range of temperature.

**Sodium Compounds**

1) Initial sodium succinate was probably prepared by leaching and sorbit from the acid and sodium bisuccinate. They state that it remains unchanged on standing in contact with air. In the same year H.T. Brooke published a series of crystallographical measurements of a "Sodium succinate" which crystallizes in doubly oblique prism.

2) Dropping, using the carbonate and acid, from slightly warm solution obtained the salt \( \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O} \) crystallizing in transparent rhombohedra, scarcely affected by air-contact. They are fairly soluble in water and spirits of wine, and lose all their crystallization water below 100\(^\circ\) C; Flehling confirmed these observations.

3) Three acid sodium succinates have been described. From half-saturated acid solution both dropping and Flehling obtained clear six-sided rhombic prisms of \( \text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O} \); the salt loses half a molecule of crystallization water on long exposure to air, the whole of the water below 100\(^\circ\) C, and is thereafter unchanged till above 200\(^\circ\) C. On one occasion only Flehling obtained indistinct crystals containing 2\(\text{H}_2\text{O} \), and unchanged by air-contact. On recrystallization the just salt separated; the preparation could not be repeated. Rammelsberg obtained the anhydrous salt from an acid solution; it crystallized monoclinic; the salt with 3\(\text{H}_2\text{O} \) then separated.

**Ammonium Succinate** \( (\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \): According to Sarret, it was unknown except in solution. Dropping obtained it by oversaturating a solution of acid with ammonia, and crystallizing in a beaker over lime. He gave it the composition stated. It crystallizes in transparent six-sided prisms, and gradually decomposes, giving off ammonia; it is easily soluble in water and spirits of wine. Flehling obtained the same salt, after saluting a solution, which had precipitated lead succinate, with ammonia — to obtain the basic lead salt.
Acid ammonium succinate was first obtained by Lemoine and Serboli, who got it in long, transparent crystals, slightly deliquescent, and readily soluble in water. They did not observe its acid character. Perséelius noted that the crystals obtained from neutral solution were acid. Dörrling obtained the compound in this way, and found that it had the composition \( \text{NH}_4 \cdot \text{C}_4 \text{H}_6 \text{O}_4 \). It crystallizes in six-sided monomineral prisms, unchanged by air contact, easily soluble in water and spirits of wine. It decomposes at 140°C. Broeker (loc. cit.) has described the crystallography of an ammonium succinate which was in all probability the acid salt.

Both Dörrling and Fehling were unsuccessful in attempts to obtain potassium-ammonium or sodium-ammonium succinate.

Lithium Succinate does not appear to have been isolated. Karrer (loc. cit.) has measured the refractivity of its solution, as well as that of the sodium salt.

The Rubidium and Cesium Succinates are being examined by Dr. Marshall.

Barium Succinate \( \text{Ba}_4 \text{C}_4 \text{H}_6 \text{O}_{12} \) is mentioned by Lemoine, and Serboli, and by Perséelius, who all note its slight solubility. Dörrling prepared the salt as a crystalloid powder from mixed barium chloride and sodium succinate solutions; and, isolated it. It is only slightly soluble in water, succinic acid solution, and potash, is insoluble in spirits of wine and ammonia, but dissolves easily in hot acetic acid, and dilute hydrochloric or nitric acids. Fehling confirmed these results.

Neither investigator could prepare an acid salt. Caruso \(^3\) has analyzed the salt, with the same result. Hauhofer \(^3\) gives a series of crystallographic measurements, the salt crystallizing in tetragonal tables.

Strontium Succinate \( \text{SrC}_4 \text{H}_6 \text{O}_{12} \) is mentioned by Perséelius as a "free soluble precipitate." Dörrling prepared it, using strontium chloride and sodium succinate solutions, and gives its analysis. It is probably the salt which Hauhofer examined crystallographically.

Calcium Succinate

Perséelius describes a salt crystallizing in needles, and unchanged by air contact.

Fehling describes a salt crystallizing in needles, and unchanged by air contact.

Both Dörrling and Fehling prepared the salt, and found that it had the composition \( \text{CaC}_4 \text{H}_6 \text{O}_{12} \cdot 3\text{H}_2\text{O} \). This was prepared from small crystals separated from the mixed calcium chloride and sodium succinate solutions; small crystals separated from the mixed calcium chloride and sodium succinate solutions; and not readily soluble in water or acetic acid.

They were readily soluble in succinic acid solution and dilute mineral acids. They were readily soluble in succinic acid solution and dilute mineral acids. They were readily soluble in succinic acid solution and dilute mineral acids.

Fehling found that this compound lost 24 molecules of water at 100°C, and 34 molecules of water at 140°C. From the warm mixed solutions he obtained a salt \( \text{CaC}_4 \text{H}_6 \text{O}_{12} \cdot 3\text{H}_2\text{O} \), which lost no water at 100°C. Milch \(^3\) has explained the break in the solubility curve of the salt (see below) by showing that when crystallized at 20-22°C it contained 3\text{H}_2\text{O}, while from solution at 80-85°C the compound contained only 1\text{H}_2\text{O}. These two salts changed into one another when shaken with water at 60-72°C respectively.

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1. J. prakt. Chem. 1835 (2) 31, 344.
2. Annalen der Chemie und Pharmacie 1867, 142, 144.
By adding succinic acid solution to finely powdered marble at a temperature of 50-600°C, Fehling obtained the normal salt, and at the same time an acid salt having the composition \( \text{Ca}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \cdot 2 \text{H}_{2} \text{O} \).

Neither Döpping nor Fehling succeeded in obtaining complex succinates from alkaline earths and alkaline metals.

**Glucinum or Beryllium Succinates.**

Berzelius notes the existence of a scarcely soluble "glucinum" salt. Our knowledge of the compound is due to Attems. By concentrating to syrupy consistency a solution of the oxide in succinic acid, he obtained small crystals of the salt together with \( \text{Ca}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \cdot 2 \text{H}_{2} \text{O} \); the crystallisation water is lost below 100°C. On adding ammonium succinate and glucinum sulphate solutions, a voluminous precipitate separates of composition \( \text{Ca}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \cdot \text{Cu} \left( \text{OH} \right)_{3} \cdot 2 \text{H}_{2} \text{O} \).

**Magnesium Salt.**

Berzelius knew of the existence of a magnesium succinate. Döpping and Fehling from the acid and magnesium carbonate obtained the salt \( \text{Mg}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \cdot 6 \text{H}_{2} \text{O} \) of crystals in prisms, uninfluenced by air or heat. It is readily soluble in water, insoluble in spirits of wine. Most of the water of crystallisation is lost at 100°C, the whole below 120°C. Fehling also describes the salt having 5½ and 6½ molecules of water. Jarugi and Checci appear to have obtained the least mentioned compound, \( \text{Mg}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \). If ammonia is added to a solution of the neutral salt a white precipitate of the basic compound \( \text{Mg}_{3} \text{H}_{2} \left( \text{C}_{4} \text{H}_{4} \text{O}_{4} \right)_{4} \) separates. (Döpping). The complex potassium-magnesium succinate is mentioned later.

**Zinc Succinate**, \( \text{ZnC}_{4} \text{H}_{4} \text{O}_{4} \), according to Berzelius is soluble, and crystallises in lamellae. Döpping prepared it as a sparingly soluble crystalline powder by treating freshly precipitated zinc carbonate with solution of succinic acid; its composition is that stated above. It is insoluble in spirits of wine, but readily soluble in acetic acid, dilute mineral acids, or alkalies. It is united till a temperature of above 200°C. Treatment with ammonia gives the salt \( \text{ZnC}_{4} \text{H}_{4} \text{O}_{4} \cdot \text{NH}_{3} \).

**Cadmium Succinate**, \( \text{CdC}_{4} \text{H}_{4} \text{O}_{4} \), has been examined by Schiff, who obtained it from the carbonate and acid; it deposits as a crystalline precipitate, insoluble in water and spirits of wine, scarcely soluble in succinic acid solution. He could not prepare an acid salt.

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The existence of mercury succinate is doubtful. Berzelius mentions both mercurious and mercuric salts as colourless and insoluble. Buehns and Geben had assumed that the white precipitate from admixture of mercurious nitrate and sodium succinate was the pure mercurious salt. Boepping showed it to be a mixture of basic nitrate and succinate. Both succinic acid and mercuric chloride solutions are unaffected by mixture; freshly precipitated hydroxide is partly changed into a white powder which may be a basic succinate. A highly concentrated mixture of sodium succinate and mercuric chloride deposits needles containing all four ions. Boepping suggests that a double salt is formed. A solution of mercuric oxide in acetic acid mixed with solution of succinic acid, gives a white precipitate containing no acetate.

Berzelius states that aluminium succinate is not easily soluble, and crystallises with excess of acid, while fluoruous succinate is produced by dissolving tin or the oxide in succinic acid. There is no other mention of these salts.

Lead Salts

According to Berzelius lead succinate is precipitated from solution as a white powder, anhydrous, soluble in excess of acid. Succinic acid solution gives no precipitate with the chloride or nitrate; lead acetate gives the salt in question. An insoluble basic salt — “subol” — is obtained by treating the neutral salt with ammonia, containing three times as much base for the acid present. This is completely confirmed by Boepping, the composition of the neutral salt being $\text{Pb}_2\text{C}_4\text{H}_6\text{O}_7$ of the basic salt $\text{Pb}_3\text{O}_2\cdot\text{C}_4\text{H}_6\text{O}_7$. Solutions of alkaline succinates mixed with lead salt solutions produce the neutral compound; it is scarcely soluble in water and acetic acid, easily in dilute nitric acid or potash. From solutions of acid succinates and lead acetate a basic salt precipitates of composition $\text{Pb}_2\text{O}$ ($\text{C}_4\text{H}_6\text{O}_7$). Feilng gets the precipitate containing one $\text{H}_2\text{O}$, and losing twice that quantity at 150°. He also describes precipitates of composition $\text{Pb}_3$ ($\text{C}_4\text{H}_6\text{O}_7$) and $\text{Pb}_2$ ($\text{C}_4\text{H}_6\text{O}_7$). His own analyses show close agreement with these formulas, which are based on the assumption, and intended to prove, that succinic acid is tribasic (compare p. 4). Carrio (loc. cit.) has confirmed the composition of the normal salt, F. Krug (reference unknown), that of the ammonium produced compound.

Berzelius says bismuth succinate is soluble in water and crystallises in lamellae; antimonial oxide is soluble in succinic acid, though the product has not been studied. Both Boepping and Feilng dispute the second statement.

Chromium Succinate? is unmentioned by Berzelius. Berlin, one of his students, (in a paper probably communicated to the Swedish Academy of Science, previously 1814) states that the chrome salt is produced when blue chrome chloride is added to sodium succinate. Feilng could obtain this neither with the blue, nor the green chloride. Boepping found that freshly precipitated chrome hydroxide dissolved very slightly in succinic acid, colouring the solution green, but forming no chemical compound. He could obtain no trace of Mores' salt, crystallising in violet octahedra. A solution of chrome oxide added to acetic acid gave forth succinic acid solution. On concentrating green coloured crystals of succinic acid were deposited.
E. A. Werner has remarked the comparative insolubility of chromic hydrosulphate in succinic acid, as compared with oxalic and malonic acids. By the interaction of finely powdered mixtures of potassium bichromate and succinic acid, heated to a considerable temperature, he obtained a chromium succinate of composition $\text{C}_8\text{H}_4\text{O}_8\cdot\text{Cr}_{3}\text{O}_8\cdot\text{H}_2\text{O}$. It has no properties of a chromorganic acid, is practically insoluble in water, and on ignition leaves a black modification of chromic oxide.

I have observed that the succinic acid deposited from solution containing chromic hydrosulphate has its crystal habit considerably altered, becoming markedly tabular. I cannot doubt that complex chromium succinate was present in solution. If a solution containing potassium bichromate and twice its molecular proportion of succinic acid and a reducing agent is added, e.g. sulphurous acid, hydrogen, or better, hydrogen peroxide, a deep ruby colour is at once produced, containing no trace of bichromate orange. On evaporation, however, bichromate and succinic acid, and sometimes chromic hydrosulphate, are obtained; all my attempts to isolate a red compound have failed.

I describe the results of a further series of experiments in Part II.

Berselius mentions too molybdenum salts, or rather, precipitates. The observations lack confirmation.

Uranium salts of composition $(\text{UO}_4)^{2-}\cdot\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, $K(\text{UO}_4)^{2-}\cdot\text{C}_4\text{H}_4\text{O}_4\cdot\frac{1}{2}\text{H}_2\text{O}$, and $\text{Na}(\text{UO}_4)^{2-}\cdot\text{C}_4\text{H}_4\text{O}_4\cdot\frac{3}{2}\text{H}_2\text{O}$, have been described. Seekamp observes that uranium succinate is deposited as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium 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powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutions of acid, and uranium succinate, as a green powder from 5% solutio

Manganese Succinate, according to Berselius, crystallizes in regular, almost colourless crystals, insoluble in alcohol, soluble in the parts of water at 13°C. Debney prepared it from the carbonate and hot acid solution; the flesh-coloured crystals have the composition $\text{MnC}_6\text{H}_4\text{O}_4\cdot4\text{H}_2\text{O}$. The crystallization water is given up below 100°C. Händel has examined the crystallography of this salt.

Succinate of Iron

Berselius mentions a ferric succinate. The same chemist states that the ferric salt is a red-insoluble powder, and is therefore used to separate iron and manganese. Ferric chloride and sodium succinate give a very voluminous red-brown precipitate, easily soluble in hot acetic and dilute mineral acids. Bridal at 200°C has the composition $\text{Fe}_2\text{O}_3\cdot\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$ (Deion). The usually ascribed formula, $\text{Fe}_2\text{O}_3\cdot\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, is that

obtained after drying the precipitate at 100° C.

Doeppping mentions a salt of composition Fe₂9, O₁₂, C₆H₁₂O₁₆; he obtained it by adding excess of ammonia to the red precipitate; it consisted, probably, of ferrous hydroxide mixed with a very small quantity of undecomposed succinate. He himself states that Wiesels "acid feric succinate" is only the acid colored by ferrous succinate. Fehling states that the composition of the red precipitate does not remain constant.

Cobalt succinate is dismissed by Berzelius with the customary note, "not soluble." Handel has described its crystallography. Although several investigators have worked with it, no one has yet published an analysis of it.

Among my experiments with acid potassium succinate solution, I tried sodium hydroxide, hot solution dissolved it in quantity, turning a deep blue color—red when cold. On cooling a red salt was always deposited, of composition Co₂C₄H₆O₇, 4H₂O. By a somewhat similar method Reynolds obtained potassium cobalt succinate.

Nickel succinate Ni₂C₄H₆O₇, 4H₂O, crystallizes in small green transparent crystals, "not soluble." (Berzelius). Doeppping obtained it from freshly precipitated nickel hydroxide and hot acid solution, decomposed and analyzed it. It is soluble in water, acetic acid, and ammonia.

Copper succinate crystallizes in pale green crystals. Digestion with copper oxide gives an insoluble basic green salt (Berzelius). Doeppping prepared the salt from copper carbonate and the acid; its composition is Cu₂C₄H₆O₇. It is slightly soluble in water and in succinic acid solutions, easily in acetic acid. Barrio (loc. cit.) confirmed the analysis. Schjibf⁵ has described the compounds Cu₂C₄H₆O₇, 2NH₃, blue, and 4NH₃, violet, obtained by dissolving copper succinate in ammonia.

Silver succinate Ag₂C₂H₆O₆ was first analyzed by d'Arcet, who obtained it by mixing neutral silver nitrate and ammonium succinate solutions. Berzelius merely notes its existence. Doeppping and Fehling both confirm d'Arcet's statement.

Salts of the Rare Metals

Yttrium succinate crystallizes in cubes from a mixture of yttrium and succinate solution. (Berzelius) Clevé and Hoeglund⁶ gave the formula Y₂(C₂H₆O₇)₂. It is obtained in little colourless needles from mixed solutions of the nitrate and ammonium succinate.

Lanthanum succinate La₂(\(\text{C}_7\text{H}_4\text{O}_4\))₅\(\text{H}_2\text{O}\) is described by Cleve. 2. Czudnowicz had assigned \(\text{H}_2\text{O}\). Meyer examined it microscopically. He found it isomorphous with the cerium salt, and concluded that microscopic methods could not be used for its detection.

Thorium succinate is a white flocculent precipitate obtained either from mixed neutral solutions of sulphate and sodium succinate or from hydroxide and acid. Succinic acid gives no precipitate with titanium salts. Lutecium succinate is insoluble. (Berschlie)

Cerium succinate is "pre soluble" (Berschlie). Czudnowicz prepared the salt \(2\text{Ce} \cdot \text{C}_7\text{H}_4\text{O}_4 \cdot 3\text{H}_2\text{O}\) by mixing cerium sulphate and ammonium succinate solution. (Compare Meyer, above)

Vanadium succinate has only been obtained as a white powder mixed with succinic acid (Berschlie).

Samarium succinate has the composition \(5\text{Sm}_2(\text{C}_7\text{H}_4\text{O}_4)_3 \cdot 5\text{H}_2\text{O}\). It loses \(2\text{H}_2\text{O}\) at 100°C. It is obtained as a voluminous crystalline precipitate on warming mixed solutions of the acetate and acid. Meyer examined it microscopically along with the neodymium and praseodymium salts.


erbium succinate \(\text{Er}_2(\text{C}_7\text{H}_4\text{O}_4)_5\) is prepared from the acetate and ammonium succinate. Alcohol added precipitates microscopic needles of the salt.

**Complex Succinates**

Reynolds is responsible for most of the work on these salts. His procedure was to dissolve the carbonate or hydroxide in, or add some other salt of the metal to, a fairly concentrated solution of neutral potassium succinate. In this way he prepared the following salts:

- \(\text{K}_2\text{Cu} \cdot (\text{C}_7\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}\)
- \(\text{K}_2\text{Co} \cdot (\text{C}_7\text{H}_4\text{O}_4)_2\)
- \(\text{K}_2\text{Mn} \cdot (\text{C}_7\text{H}_4\text{O}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}\)
- \(\text{K}_2\text{Fe} \cdot (\text{C}_7\text{H}_4\text{O}_4)_3 \cdot 2\text{H}_2\text{O}\)
- \(\text{K}_2\text{Ca} \cdot (\text{C}_7\text{H}_4\text{O}_4)_3 \cdot 2\text{H}_2\text{O}\)
- \(\text{K}_2\text{Mg} \cdot (\text{C}_7\text{H}_4\text{O}_4)_3 \cdot 5\text{H}_2\text{O}\)

The magnesium salt had previously been described by Bopping.

I have previously mentioned the strong probability that complex chromium succinates exist in solution (p. 11)

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2. Zeits. anorg. Chem. 1902, 93, 51 and 1113.
5. Cleve and Nørgaard, I:/ 1872, 18, 296.
Physical Properties of Succinic Acid and its Salts.

Solubilities of the acid, and various salts, have been determined by a number of investigators, with regard to the acid, considerable discrepancy of statement existed until Bougon published his results. Most of the classic "Lehrbucher" say that one part of succinic acid is soluble in five parts of water. Bougon thinks this is due to the incorrect figures published by Beccari and Serboli. He quotes a number of varying figures from Lavoisier, Klaproth, Berzelius, and Weideweber. His own method is not conducive to accurate results. He warms his solution to just above the temperature of measurement, and allows it to cool while agitating with excess of acid.

Ganio (loc. cit. 1867) had given previously some figures for 15°, 17°, and 19° C. Mieszyński, by a slightly improved method, but not working at constant temperatures, has published figures which are probably nearer to the correct values than Bougon's. As will be mentioned in Part II, in my research with Dr. Marshall, I have determined the solubility at 0°, 20°, 25°, and 40° C, working at constant temperature. A comparison of the figures at these temperatures may be interesting. The figures express parts by weight in 100 parts of water.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Ganio</th>
<th>Bourgon</th>
<th>Mieszyński</th>
<th>Cameron</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>2.88</td>
<td>2.804</td>
<td>2.768</td>
<td></td>
</tr>
<tr>
<td>14.5°</td>
<td></td>
<td>5.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15° (3.52)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17°</td>
<td>5.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18°</td>
<td>6.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>6.893</td>
<td>6.836</td>
<td>8.577</td>
<td></td>
</tr>
<tr>
<td>25°</td>
<td></td>
<td>8.414</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°</td>
<td></td>
<td></td>
<td>16.214</td>
<td>14.861</td>
</tr>
<tr>
<td>40°</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.5°</td>
<td></td>
<td></td>
<td>15.37</td>
<td></td>
</tr>
</tbody>
</table>

The solubility of calcium succinate has been investigated by Mieszyński and — at 15° and 20° C only — by Tarugi and Checchi, who attribute to it two molecules of water if crystallisation. Its solubility increases till above 50° C, when it gradually decreases. Milofko has shown (see p. 5) that this is due to the change in hydration. Cantoni and Broccoli have determined the solubility by a more accurate method. All these figures give figures for the barium salt also. Tarugi and Checchi have studied the magnesium salt, cantoni and Broccoli the lead, and copper succinate.

The solubility curves are shown on the diagram facing this page. All the results are expressed in parts by weight per 100 parts of water.

Very little work has been done on the solubilities in other solvents. The following results by Bourgin and Roux may be compared (Temperature 15° C):

5. Ib. 29, 843.
100 parts of pure Ether, 90% alcohol, 96% Alcohol, Abs. Alcohol, Methyl Alcohol, Acetic
Bouorou
Rau
1.129
1.193
11.904
11.984
6.98
9.96
15.73
8.57
parts succinic acid

Figures for the acid and neutral potassium salt in absolute alcohol are given in part II.

There is some difference of opinion regarding the Melting Point of Succinic Acid. The early investigators state that it melts at 180-181°C. Davidoff 1 using a thermometer standardised according to Ramsay and Young's method 2 obtained the figure 185. Ramsay and Young 3 give the figure 181. My own determination is 187°, my thermometer, however, was not standardised. Melting points of some of the salts are given in Part II.

Dye 4 gives some value for the sublimation temperature of the acid at reduced pressures, showing that at very low pressures it is possible to vaporise it below its melting point, while Ramsay and Young give considerable data on the same subject.

Bancroft 5 and Stade 6 have studied the equilibrium of anhydride and acid, and anhydride acid and water.

The following densities have been determined.

Crystallised succinic acid 1.552, Boden 7
1.572, Tanatar and Sehlebrieff 8
Sublimed ...
1.532, Boden 7
1.529, Boden 7
Succinic sodium
3.518, Husemann 7
3.800
Lead ...

As these were determined previously to the publication of Retger's method in 1890, their accuracy is questionable. That for succinic acid I have found incorrect (see part II).

Thermal data are given by Thomasen 9, Hess 10, Stohmann 11, and Thome. 12, Massol 13, and Stohmann and Husemann. 14

Electrical data are given by Ostwald 16, Walden 7, Loomis 18, Bie 19, and Towe 20.

End of Part I.

3. Phil. Trans. 1886, 177, 103.
5. T. Physical Chem. 1896, 3, 72.
Part II

I was led to the study of succinate by an accidental discovery made in the summer of 1902; I was then a student in the Chemical Laboratory of Edinburgh University. Having to prepare potassium chromate, I was directed to examine the literature of the subject. E. L. Wrenn has remarked that analogous organic salts should be capable of preparation. I tried to prepare the complex succinate. From mixed solutions of succinic acid and potassium bichromate, these compounds crystallized unchanged, the bichromate having no action on homologues of oxalic acid notwithstanding its violent action with that acid itself. I next tried to dissolve freshly precipitated chromic hydroxide in a hot acid potassium succinate solution. Precipitated from chrome alum solution by sodium hydroxide the solution hydroxide is little soluble; precipitated by ammonia it dissolves to a much greater extent. I obtained a dark green solution, which, concentrated to almost syrupy consistency, deposited dark green crystals. D. Marshall was the first to observe that these contained scarcely a trace of plane faces, being in fact double cones crystallizing in the monoclinic system, with the y-axis passing through the apices.

I was unable to continue the investigation for some time. The results of my earlier work were published as a preliminary note in 1905. My later work, carried out for the most part in collaboration with Dr. Marshall, is at present ready for publication, and will appear shortly. Our present knowledge of these curved crystals may be shortly summarised.

The original crystals were potassium supersuccinate containing a small quantity of chromic salt. Two analysed crystals from different preparations gave respectively 0.688% and 0.548% Cr. (The complex potassium chromic succinate of the usual type would have the composition \(K_3Cr\left(C_4H_6O_7\right)_2\cdot3H_2O\), containing 9.14% chromium.)

Much better crystals are obtained by adding acid solution of ferric chloride to acid potassium succinate solution until it is on the point of depositing ferric succinate. From such solutions which have been allowed to stand a considerable time I have obtained almost perfect birefringent crystals of a dark brown colour. A single crystal analysed by colorimetric methods gave 0.61% Fe. A quantity of lighter coloured crystals analysed in the same way gave 0.44% Fe. They were only drawn; the acidity determined by titration with barium solution was respectively 1.031% H_2 and 1.133% H_2O. The supersuccinate salt \(K_3Cr\left(C_4H_6O_7\right)_2\) contains 1.095% H_2O.

The pure sulphuric salt crystals in monoclinic prisms, showing a marked cleavage. The curved crystal show the same symmetry and cleavage, but the prism faces have vanished; the pyramidal faces appear to be infinitely thinned. The amount of iron or chromium in the solution and taken up by the crystals has a marked effect on the crystals. Light coloured crystals always show some plane faces.

The hydrated acid salt is similarly affected. Fully effloresced curved crystals have been examined; they contained 0.33 %. Fe. On one occasion a solution depositing the curved crystals was seeded with small rose prisms of the hydrated salt. The prism faces alone grew, the ends becoming curved. In time the out-growing curved ends would have caused the disappearance of the prism faces. The crystals were only slightly coloured and analysis gave 0.05 % Fe.

I have obtained curved crystals from such solutions when cobaltic, copper, or aluminium salts were added; with cobaltic salts, well marked double cones of both acid salts were obtained, coloured a dark olive.

In one experiment, with an almost neutral solution and ferrie chloride, completely pointed pyramids were obtained, which effloresced in air, though analysis gave the composition \( \text{K}_2 \text{Cu}_4 \text{H}_4 \text{O}_6 \cdot 3\text{H}_2 \text{O} \).

Whatever metallic salt or other "impurity" was added to these solutions, the habit of the crystals was always changed, though only in the case mentioned did curved crystals result. Some idea of the state of the added metal in these crystals can be obtained from the observation that their solution does not colour with ammonium thiocyanate (in the case of ferrie salts) until hydrochloric acid is added; the iron complex present is therefore stable and less ionised (into \( \text{Fe}^{3+} \) ions) than ferrie thiocyanate—which is almost colourless. This leads some support to belief in a complex cyanate, though all my endeavours to isolate such have failed (compare page 11).

Having ascertained most of these facts, D. Marshall and I were confronted with several difficulties. Though our solutions were always made up in theoretically exact proportion for acid potassium succinate, the supersaturated salt usually deposited, the acid salt depositing later. We found by experiment that a theoretical supersaturated salt solution deposited the free acid, while a solution neutral to litmus deposited the acid salt. Again the existing literature on the subject was by no means conclusive (compare pages 5, 7). Bopp and Fehling's work showed no agreement, Salzer had solved the deciding riddle of the question of the neutral salt, without finding the cause of the different statements concerning the acid salts. We decided to study the complete system of potassium succinates and their acid, selecting the method of solubilities for that purpose.
Since we found that a solution of the superacid salt deposits succinic acid, if the acid salt, the superacid, it is scarcely correct to speak of the "solubility" of such compounds. We were in reality measuring the ratio of potassium and hydrogen solid containing in solution in equilibrium with varying proportions of the acid and its salt, at a constant temperature.

The following method was finally decided on:
A mixture of the solid salts was introduced into a small glass specimen tube; insufficient water was added for complete solution. The tube was closed by a well fitting rubber stopper and rotated for two hours or longer in a thermostat accurate to 0.1°C. It was found that constant results were obtained after from one to two hours. The cork was then removed, i.e., of solution filtered out through filter-paper, and transferred to a weighed wide-mouthed glass dish having an accurately ground lid. The whole was weighed, and heated in a water oven till the weight became constant. The dried salt was dissolved in water and titrated with baryta of known strength, phenolphthalein being the indicator employed. From the titer found the amount of succinic acid was calculated; this subtracted from that of the dried salt gave the weight of potassium succinate. We thus considered that the solution contained so much acid, and so much normal salt, expressing the result in molecules per 100 molecules water. The greatest number of measurements were made at 20° and 25°C; sufficient were obtained at 0° and 40°C to show the nature of the curve at three temperatures. For the determinations at 0°C a vertical stage was caused to revolve in a large tube of stout glass containing the solution and solid in small quantity; the tube was embedded in a mixture of finely powdered ice and water, the whole being surrounded by non-conducting material.

The breaks in the curves obtained determined the double points of the system; in some cases they were determined by one experiment only, making certain that considerable excess of each of two salts remained in contact with determined solution. Theoretical considerations occasionally gave these points. Thus a solution of pure acid salt in contact with solid contained more than the theoretical percentage.

1. The operation was tedious, often involving heating for 25-30 hours before constancy of weight resulted. If a higher temperature was employed, an appreciable quantity of succinic acid volatilized; the alternative method of first neutralizing with baryta and then evaporating the neutral solution allowed more rapid heating, but gave great errors in the potassium determination, when only small amounts of potassium were present. Experiments made under the usual working conditions with pure dry salts gave the following results:

<table>
<thead>
<tr>
<th>In 33 hours pure dry succinic acid lost</th>
<th>0.47%</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.738%</td>
</tr>
<tr>
<td>30</td>
<td>0.473%</td>
</tr>
</tbody>
</table>
Diagram showing the equilibrium of solutions and solutes for the potassium selenocyanate and their acid products.
of potassium; therefore the superacid salt had been deposited; consequently the results indicated the double point K\(\text{H}_2\text{C}_4\text{H}_4\text{O}_4\) \(\cdot\) KH\(\text{C}_4\text{H}_4\text{O}_4\) \(\cdot\) 2H\(\text{O}\), that is to say, the point at which these salts would be deposited together from solution. These results may be quoted as showing the accuracy of the method; one was obtained from an acidified neutralised neutralised solution, and confirms the theory just stated. At 25° the following figures were obtained.

<table>
<thead>
<tr>
<th>Molecules of $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ per 100 of water</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$</td>
<td>3.392</td>
<td>3.350</td>
<td>3.353</td>
<td>3.318</td>
</tr>
<tr>
<td>$\text{K}_2\text{C}_4\text{H}_4\text{O}_4$</td>
<td>3.486</td>
<td>3.481</td>
<td>3.444</td>
<td>3.523</td>
</tr>
</tbody>
</table>

At the same temperature the following results were obtained for potassium succinate.

<table>
<thead>
<tr>
<th>Molecules per 100 of water</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$</td>
<td>12.997</td>
<td>12.936</td>
<td>12.866</td>
</tr>
</tbody>
</table>

The figures need not be quoted in extenso. The resulting curves are given in the diagram facing this page.

Transition point temperature for the hydrate and anhydrous salts were obtained by the dilatometric method. The acid salt shows a well marked change in volume at 23.5° in presence of $\text{K}_2\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, at 14° in presence of $\text{K}_2\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, 3H\(\text{O}\). The change in composition $\text{K}_2\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, 4H\(\text{O}\) \(\rightarrow\) $\text{K}_2\text{C}_4\text{H}_4\text{O}_4\cdot\text{H}_2\text{O}$, 3H\(\text{O}\)$, 3H\(\text{O}\). Slight temperature points were also obtained at 3° and 5° respectively, showing possibly the existence of a salt with 3 or more molecules of crystal water. The triple points corresponding to these results were determined either by extrapolation, or for the point at 14° by actual experiment. No other transition points were obtained from the series of curves shown. These quite check the anomalous results which I previously described and easily understood. Between the limits of 0° and 80°C a theoretical solution will deposit its salt in the case of the pure acid and the normal succinate only. At 40° a solution of acid salt will deposit its anhydrous; it seems probable that at a much higher temperature the same result will be obtained with the superacid salt. The results will be further discussed in connection with the nature of the superacid salt (see page 22).

The physical constants, and some further results have been determined. These will now be given, preceded with an account of the best method of preparation of the different salts.

1. The agreement of these results shows that Salze's statement that the neutral salt does not give up all its crystallisation water till 130° is incorrect. If sufficient time is allowed all the water is lost at 100°.

2. I have compared results with those previously published on page 111.
Preparation of the Potassium Succinate

Neutral potassium succinate \(K_2C_4H_6O_4 \cdot 3H_2O\). Fine potassium carbonate is added to boiling succinic acid till the solution is alkaline; acid is added till pink phenolphthalein is just turned colourless. (Prepared in any other way the dried salt contains carbonate, which materially reduces its solubility.) The solution was concentrated and allowed to stand in a desiccator of over sulphuric acid.

Anhydrous acid potassium succinate \(KH_3(C_4H_6O_4)\) may be obtained from alcohol-water solution caused to evaporate in a desiccator over pure alcohol. As the proportion of alcohol in the solution increases, well marked crystals are deposited. Nearly neutral solutions also deposit this salt at ordinary temperatures.

Hydrated acid potassium succinate \(KHC_4H_6O_4 \cdot 2H_2O\) is deposited from acid solution somewhat more than half neutralised with potassium carbonate, and allowed to cool slowly.

Superacid potassium succinate \(KH_3(C_4H_6O_4)\) is deposited from acid solution which has been one-third neutralised with potassium carbonate.

Succinic Acid, used in determining the physical constants given below, was obtained by recrystallising Merck's purest acid. This itself was used for the determination of the solubilities.

**Densities**

Rietz's method was used, k bromoform and turpentine, and benzene and acetylene tetrobromide being the liquids employed. (Compare page 15.)

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>Mean</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic Acid</td>
<td>1.561</td>
<td>1.563</td>
<td></td>
<td>1.562</td>
<td>14.4°C</td>
</tr>
<tr>
<td>(KH_3(C_4H_6O_4))</td>
<td>1.558</td>
<td>1.559</td>
<td>1.559</td>
<td>1.559</td>
<td>14.0°C</td>
</tr>
<tr>
<td>(KHC_4H_6O_4)</td>
<td>1.766</td>
<td>1.768</td>
<td>1.768</td>
<td>1.767</td>
<td>18.5°C</td>
</tr>
<tr>
<td>(KHC_4H_6O_4 \cdot 2H_2O)</td>
<td>1.619</td>
<td>1.613</td>
<td>(1.616)</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>(K_2C_4H_6O_4 \cdot 3H_2O)</td>
<td>1.564</td>
<td></td>
<td>(1.564)</td>
<td>17.5°C</td>
<td></td>
</tr>
</tbody>
</table>

**Melting Points**

Succinic Acid 181°, Superacid salt 182°, Anhydrous acid salt 240-245°C.

**Crystallography.**

The three acid salts have been examined by Dr. Marshall. They all crystalline monoclinic. The three compounds \(K_2C_4H_6O_4 \cdot 3H_2O\), \(KH_3(C_4H_6O_4)\), \(KHC_4H_6O_4\), show no relationship which would lead one to suppose that the second one is a molecular mixture of the other two.
Solubility in Alcohol.

All early observations on this subject are valueless, spirits of wine having been used, and often diluted spirit of wine.

We obtained the following qualitative results. Potassium succinate is practically insoluble, the acid salt is very slightly soluble, the superacid salt is decomposed into succinic acid and acid salt. Bischoff has noticed that the quadravalent is similarly acted on. To see whether it was in this phase was completely absent in alcoholic solution, a series of solubility determinations were made at 25°. The enormous decrease in solubility found, brought about by the smallest quantity of acid succinate in solution, and the very slight solubility of the succinate led to the following modification of method.

An accurately stopped bottle contained the solution and solid during rotation. Six or seven grams were precipitated out, weighed, transferred to a platinum crucible, taken to dryness in a water-bath, ignited, and weighed as K₂C₂O₄; at the same time two or three grams were precipitated out, weighed and titrated for the amount of free acid. The figure for the normal salt, compared with that obtained by evaporation to dryness and weighing as K₂C₂O₄, shows that the method is moderately accurate.

\[ \begin{align*}
0.0107 \\
0.0090
\end{align*} \]

The results are shown in the diagram. They prove the complete absence of a phase corresponding to the superacid salt. Therefore it will be observed that the K₂C₂O₄ values have had to be multiplied by 62.5, in order to show the curve at all. A curve of solubility of acid at different temperatures is also given. All the results are in molecules free 100 molecule solvent.

Nature of the Super-Acid Salt Ion.

In textbooks the graphic formula of potassium quadravalent is assumed to be of the nature

\[
\begin{array}{c}
\text{K-O-} \\
\text{C-O-N}
\end{array}
\]

Such a substance would be a succinate and would not give a succinate ion in solution; it might easily decompose to a mixture of succinate ions. As far as we know, no reasons have hitherto been put forward for the assumption. The only other possible hypothesis is that the crystalline solid is a molecular mixture of the acid and acid salt, and that solution immediately resolves the mixture into its constituents. If this were true the density of the...
Superacid salt should be a rough mean of the densities of the other two compounds. The results actually found are:

<table>
<thead>
<tr>
<th></th>
<th>Succinic Acid</th>
<th>Superacid salt</th>
<th>Acid salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.562</td>
<td>1.559</td>
<td>1.767</td>
</tr>
</tbody>
</table>

Again both quaternary and quin succinate are decomposed by absolute alcohol. In the case of the succinate the acid is very soluble, the acid salt slightly soluble. The superacid salt cannot be said in this case to behave like a mixture of its constituents. It has a distinct melting point, showing that there is no transition till that temperature is reached.

Reference to the diagram of solubilities will show the very marked increase in the solubility of succinic acid caused by addition, and that at temperatures above 20° the increase is strictly proportional to the amount of salt added. We could understand this on the assumption that a double ion \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \) is produced, which is much more soluble than the ion \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4^+ \) into which we know the acid salt dissociates.

The existence of complex salts of the type \( \text{K}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \) and the suggestion that intermediate anhydride-acids exist (see page 3) support the existence of double derivatives of \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \) or \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \text{O}^- \). We regard it as extremely probable that the salt \( \text{K}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \) is a derivative of \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \) and not of \( \text{H}_2 \text{C}_4 \text{H}_4 \text{O}_4 \text{H}^+ \text{O}^- \). In this case the very clumsy nomenclature employed hitherto, and such a term as potassium bissuccinate employed (the term "bi" for acid salts has now been no longer used in fine chemistry). We are proceeding to add further physical work on the succinate, malonate, and oxalate, in an attempt to solve this question.

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**Conclusion**

In this essay I have attempted to give complete information concerning the metallic salts of succinic acid. It is evident that much of the work published in the first half of last century is not exact; its truth is very doubtful. It has, however, not been disproved to the present time, and is the basis of the information given in the dictionaries. Although such researches are not of first importance, still it is desirable that much of the work be repeated, so that it is less to correct errors in work commonly accepted as correct than to publish fresh work liable to the same errors. Such work therefore is well suited to students just commencing research work.

The elucidation of the problem "how" plane crystals become curved by admixture with a small quantity of foreign substance may prove very difficult. It seems, however, very important, leading possibly to some idea of the internal structure of crystals. Any attempt, such as that of Barlow and Pope (J. Chem. Soc. Nov. 1906), to theoretically explain this structure will pass a very severe test if it includes the possibility of formation of such curved crystals.