CHAPTER 5

BUTYRIC ACID AND SOME BUTYRATES

SECTION 1

BUTYRIC ACID

§ 1. COMPOSITION

317. The analysis of butyric acid as present in dry lead butyrate, is as follows[1]:

	BY WEIGHT	BY VOLUME
Oxygen………………………..…	30.17	1.00
Carbon………………………...	62.82	2.72
Hydrogen…………………….	7.01	3.73

318. 100 parts of acid anhydride neutralize an amount of base that contains 10.3 parts of oxygen. Consequently, in the neutral butyrates, the ratio of the oxygen in the acid to the oxygen in the base equals approximately 3 : 1[2]. Thus assuming that the atomic ratio in butyric acid equals:

Oxygen………………………………………………..	1.00
Carbon……………………………………………...	2.67
Hydrogen…………………………………………..	3.67

its composition will be:

	ATOMS	IN WEIGHT	
Oxygen………………………..	3	300.00[3]	30.585
Carbon………………………..	8	612.24	62.417
Hydrogen……………………..	11[4]	68.64	6.998
Total………………………………		980.88	

Composition of the free acid

319. When an amount of 0.500 g free butyric acid having density of 0.9675 (g/mL) is mixed with 5 to 6 g of dry lead oxide at a temperature of 18°C, the two reagents react almost instantaneously under evolution of heat. On heating, water is evolved and this is alkaline rather than acid. The weight loss is 52 mg and the free acid therefore consists of:

Butyric acid anhydride..	0.448	100
Water……………………	0.052	11.6 containing 6.31[5] oxygen,

which is approximately one third of the oxygen in the acid anhydride*.

§ 2. PHYSICAL PROPERTIES

320. Butyric acid is liquid at ambient temperature, very fluid, similar to a volatile oil. It does not solidify at 9 degrees centigrade below zero[6]; it requires a temperature well above 100°C before starting to boil[7]; it can be distilled without decomposing.

321. At 10°C, its density is 0.9675 (g/mL).

322. It is colorless. Its odor is similar to that of acetic acid and rancid butter and therefore also of isovaleric acid. However, the odor is less pungent than that of the latter and once known, it is very easy to recognize. When placed on a glass plate, it evaporates completely. When put onto sized paper that does not immediately soak up water, it leaves an oily stain that smells like butter or according to some people, Gruyère cheese. The stain disappears as the acid evaporates.

323. Butyric acid has a very strong acid taste that is quite sharp and a sweetish aftertaste that is less pronounced than that of isovaleric acid vapor. Like the latter, it whitens those parts of the tongue that have come into contact with it.

§ 3. CHEMICAL PROPERTIES THAT ARE OBSERVED WITHOUT THE ACID BEING ALTERED

Effect of water

324. Water dissolves butyric acid in all proportions and what is remarkable is that a solution of 2 parts of acid in 1 part of water has a density of 1.00287 since a flask with a volume corresponding to 1.398 g water contained 1.402 g of this solution at 7°C.

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* Assuming that the water was formed by the hydrogen of the butyric acid and by the oxygen of the lead oxide, the acid moiety that is bound to the lead consists of:

	IN WEIGHT	IN VOLUME
Oxygen…………………………………..	36.700	1.00
Carbon…………………………………..	56.950	2.04
Hydrogen………………………………..	6.350	2.77

Effect of alcohol

325. Alcohol with a density of 0.794 (g/mL) dissolves the acid in all proportions: the solution has an ethereal flavor of a Cox's orange pippin apple[8] that becomes more and more pronounced with time[9].

Effect of sulfuric acid

326. Concentrated sulfuric acid dissolves butyric acid at 15°C without changing it; the temperature rises.

Effect of nitric acid

327. Nitric acid reading 35 degrees[10] on a hydrometer dissolves butyric acid at an ambient temperature, apparently without changing it. The solution evolves a light ethereal aroma.

Effect of iron

328. Butyric acid reacts with iron just like isovaleric acid except that the addition of water hardly causes a precipitate and that it seemed to me that this precipitate dissolved again in an excess of this liquid.

Effect of potassium

329. When potassium is floated on mercury under a bell jar containing butyric acid, it causes a lively effervescence because it decomposes the water of the hydrate.

Effect of lard

330. Butyric acid combines readily with molten lard. Once this has congealed, it is so similar to butter with respect to flavor and aroma that several people I asked to taste a sample did not notice the difference. However, what distinguishes this *artificial butter* from *ordinary butter* is that it loses all its acid by simple exposure to air. Fat that contains an excess of butyric acid has markedly sweet taste.

§ 4. CHEMICAL PROPERTIES THAT ARE OBSERVED WHEN THE ACID IS ALTERED

331. When butyric acid is distilled in contact with air, it behaves like isovaleric acid.

332. It burns in the same way as volatile oils.

333. When the solution of butyric acid in sulfuric acid is heated to 100°C, it discolors only slightly. At a more elevated temperature, it starts to boil and butyric acid evolves together with some sulfur dioxide. The liquid darkens much more slowly that the sulfuric acid solution of isovaleric acid (276) and much less carbon is formed.

§ 5. NOMENCLATURE

334. The specific name of this acid has been derived from *butyrum* meaning "butter".

§ 6. OCCURRENCE AND HISTORY

335. I reported the existence of butyric acid in soap made of butterfat and in buttermilk at the Academy on 19 September 1814; but it was not until 1818 that I managed to isolate caproic acid and capric acid. (See Book III, chapter 1).

SECTION 2

BUTYRATES

ARTICLE 1

BARIUM BUTYRATE

Preparation

336. Neutralization of baryta water with butyric acid and spontaneous evaporation of the resulting solution leads to the formation of flat prismatic crystals.

Composition

337. When 100 parts of butyrate that had previously been exposed to dry air were kept under a dry vacuum at a temperature of 20 to 25°C, the following losses were observed:

after 24 hours	1.50 parts
after 118	2.25

338. When the butyrate was exposed to a boiling bath of calcium chloride[11], there was no evolution of gas. When heated carefully in a crucible until it melted into a transparent glassy material, nothing was lost either. An amount of 400 mg of this butyrate gave 301 mg of barium sulfate, which corresponds to 197.5 mg of base; accordingly[12]:

Acid	0.2025[13]	50.625	100
Barium oxide.	0.1975	49.375	97.58 containing 10.197 oxygen

Appearance

339. It crystallizes in flat prisms with a width of 0.001 to 0.002 m[14] and a length of 0.032 m. The crystals are transparent and flexible, like several ammonia salts. They have a greasy sheen and keep their transparency when stored in a dry vacuum.

Odor and taste

340. Barium butyrate has a strong flavor of fresh butter. It has an alkaline, warm and barium-like flavor and a taste of butter.

341. At a temperature of 10°C, a saturated aqueous solution of barium butyrate consists of:

Water	100
Salt	36.07

342. A lump of barium butyrate thrown into water moves around rapidly just like a small piece of camphor. In the end, it dissolves.

343. An aqueous solution of this salt is slightly alkaline towards litmus paper. When carbon dioxide precipitates some barium carbonate, it liberates part of the butyric acid.

Effect of alcohol with a density of 0.792 (g/mL)

344. An amount of 10 g of dry barium butyrate was added to 70 g of alcohol[15] and kept at 5°C for three days.

345. When 10.025 g of the solution were evaporated, a residue of 25 mg was left.

346. An amount of 55 g of the alcoholic butyrate solution was subjected to distillation. The distillate had no effect on litmus. However, concentrating this distillate from barium hydroxide yielded 10 mg of dry butyrate. Consequently, the alcohol had separated some butyric acid from the barium butyrate[16].

347. The butyrate which did not dissolve in alcohol did dissolve in water, except for a trace of barium carbonate.

348. I kept a sample of solid barium butyrate for a period of nine years without observing anything that points to any significant change, except for the small amount of carbonate formed by the carbon dioxide in the air.

349. An aqueous solution of barium butyrate did not seem to change markedly, at least not during the period of time in which barium isovalerate decomposes.

Distillation of barium butyrate

350. An amount of 0.3 g of butyrate was distilled in a small glass tube that had previously been filled with mercury and that was connected to a graduated glass jar also filled with this metal. The salt melted, gases evolved and a white vapor that condensed as a yellow liquid developed. The distillation was started with a spirit lamp and completed using charcoal; the tube was heated to a cherry red. It was only at this last stage of the process that the residue started to turn noticeably black because a little carbon was liberated. In this respect barium butyrate differs from the isovalerate of the same base, which turned black immediately on heating.

A. Residue

This was a mixture of barium carbonate and carbon. It was only present in a very small amount since it weighed 1 mg.

B. Liquid

It was orangey yellow and very fluid. It had a very strong odor like that of aromatic plants of the basil[17] family, but several people thought they recognized the aroma of absinth or quinces. It did not turn dry litmus paper red. I have the impression that potassium caused hydrogen to evolve slowly but in very small amounts. The volume of this liquid was more or less the same as that of the liquid produced from barium isovalerate.

C. Gaseous product

It consisted of 14.3 mL of ethylene and 0.5 mL of carbon dioxide

ARTICLE 2

STRONTIUM BUTYRATE

Preparation

351. It is the same as for barium butyrate.

Composition

352. An amount of 0.1 g of dry strontium butyrate was heated in a platinum crucible: it scorched and melted almost simultaneously. The residue yielded 72 mg strontium sulfate, which corresponds to 40.58 mg of strontium oxide.

Acid anhydride…	59.42[18]	100
Strontium oxide..	40.58	68.3, containing 10.55 oxygen

Odor

353. Its odor is similar to that of barium butyrate.

Appearance

354. It crystallizes in long flat prisms, similar to those of barium butyrate.

Effect of water

355. At 4°C, a saturated solution of this salt consists of:

Water……………………….…………………	100
Salt………………………………………………..	33.34

ARTICLE 3

CALCIUM BUTYRATE

Preparation

356. It is the same as for barium butyrate.

Composition

357. When 100 mg of dry calcium butyrate were placed in a platinum crucible, they melted and gave off an aroma of essential oil of basil. They left an amount of base that corresponds to 65 mg calcium sulfate; thus:

Butyric acid anhydride..	73.005[19]	100
Calcium oxide………..	26.995	36.97 containing 10.39 oxygen

Odor

358. Its odor is similar to that of barium butyrate.

Appearance

359. It crystallizes in needles or very thin prisms that are perfectly transparent.

Effect of water

360. At 15°C, a saturated solution of this salt consists of:

Water	100
Salt	17.58

This solution crystallizes so profusely when heated that it sets as a mass. The crystals redissolved completely when the material was cooled again to a temperature of 15°C. To observe these phenomena properly, the solution must be introduced into a narrow glass tube that is then sealed with a burner. By first heating the bottom part of the tube with the flame of a match and then the upper part, the crystals can be seen to form from the bottom upwards; this crystallization cannot be attributed to the evaporation of the liquid. After the crystals have been formed, the tube can be inverted without any liquid falling out. Finally, the crystals dissolve again when the tube is immersed in cold water.

361. When 2 parts of calcium butyrate and 3 parts of barium butyrate are dissolved in water, they yield octahedral crystals of the two butyrates when the water is allowed to evaporate spontaneously.

ARTICLE 4

POTASSIUM BUTYRATE

Preparation

362. It is prepared by neutralizing a solution of potassium carbonate or bicarbonate with butyric acid dissolved in water.

Composition

363. When 0.100 g are decomposed by hydrochloric acid, they yield 60 mg of potassium chloride[20] which corresponds to 37.96 mg of potassium oxide: thus:

Butyric acid anhydride.	62.04[21]	100
Potassium oxide	37.96	61.2, containing 10.37 oxygen

Odor and taste

364. It has the aroma of butyrates, a sweetish taste and the flavor of fresh butter.

Appearance

365. It will only crystallize in the shape of rather indistinct cauliflowers and only at a temperature of 25 to 30°C.

366. It is very deliquescent. At 15°C, 100 parts of water dissolved 125 parts of potassium butyrate and the solution was not saturated.

Effect of potassium butyrate on butyric acid

367. When 500 parts of potassium butyrate (which contain 307 parts of acid[22]) are dissolved in 400 parts of water and 115 parts of free butyric acid (which contain 102 parts of the acid anhydride) are added, a solution is obtained that has no effect on dry litmus paper at ambient temperature, despite the fact that it contains more than enough acid to neutralize the base[23].

368. If the litmus paper is then held close to the fire, the part impregnated with the butyrate becomes perfectly blue. If water is then added to the same part, it turns red. Heating the paper to evaporate the water makes the color revert to blue and wetting it again causes it to become red once more. These changes can be repeated quite a number of times but there comes a moment where they can no longer be reproduced because all the excess acid has been volatilized.

369. The liquid I mentioned does not dissolve calcined potassium carbonate at ambient temperature but on heating, it dissolves it with effervescence[24]. When water is added, the liquid acquires the property of turning litmus paper red and of dissolving potassium carbonate with effervescence.

370. The experiments that I have just reported demonstrate that:

1. The affinity of the red dye of the litmus in the paper for the alkali which colors it blue is stronger than the affinity for alkali of the butyric acid which is present in excess in the concentrated solution of potassium butyrate;
2. The addition of water to this solution causes the affinity of the butyric acid to predominate over that of the litmus dye;
3. After the water that had been added has been removed by gentle evaporation, the butyric acid which was combined with the alkali of the litmus is liberated because the coloring constituent recombines with that base[25].

ARTICLE 5

SODIUM BUTYRATE

Preparation

371. It is prepared in the same way as the previous compound.

Composition

372, An amount of 100 mg of sodium butyrate that had been dried until it lost no more weight, using a heat source that was insufficiently strong to decompose it, yielded 540[26] mg sodium chloride, which corresponds to 28.78[27] mg of sodium oxide; hence:

Acid anhydride...	71.22[28]	100
Sodium oxide.....	28.78	40, containing 10.23 of oxygen

Properties

373. They are similar to those of potassium butyrate but the salt is less deliquescent.

ARTICLE 6

LEAD BUTYRATE

374. When a solution of lead butyrate containing an excess of acid is allowed to evaporate, a fusible residue results in the form of a neutral butyrate.

375. When the solution of neutral butyrate is evaporated in a dry vacuum, it crystallizes in fine, silky needles. When 200 mg of these needles were decomposed, they yielded 121 mg of lead oxide; thus:

Acid anhydride.	39.5	100
Lead oxide.......	60.5[29]	153.16, containing 10.95 oxygen

375 *bis* When the neutral lead butyrate is distilled in a tube that has been filled with mercury, it yields some water, a very small amount of odorous oil in comparison with the amount of oil obtained from barium butyrate, some carbon dioxide and ethylene. The ratio of the volume of the first of these gases to that of the second is 9 : 1. The distillation residue is a mixture of lead oxide and lead.

ARTICLE 7

BASIC LEAD BUTYRATE

376. I have already described (319) what happens when an excess of butyric acid is brought into contact with lead oxide. If cold water is then mixed with the reaction product, a solution results that on evaporation in a dry vacuum leaves a butyrate that contains three times as much lead as the neutral butyrate[30]; 500 mg of this butyrate decomposed with nitric acid gave 405 mg of lead oxide.

Acid anhydride	95	19	100
Lead oxide...	405	81	426.3, containing 30.57 oxygen

377. Basic lead butyrate does not melt when heated over a flame. It has little odor; it did not seem to me to be very soluble in water. The solution rapidly absorbs carbon dioxide from the air.

378. It is remarkable that butyric acid and isovaleric acid have in common with acetic acid that their basic lead salts contain three times as much base as their neutral salts[31].

ARTICLE 8

COPPER BUTYRATE

Composition

379. When 100 parts of crystallized copper butyrate* are exposed to a dry vacuum for one month, hardly 1 part is lost. The salt keeps it shape and its color and only its transparency is changed.

380. On decomposition by nitric acid, 100 mg of butyrate which had been exposed to a dry vacuum yielded 30 mg of brown copper oxide. This means that the salt contains water of crystallization since in view of the composition of barium butyrate, 100 parts of butyric acid anhydride should correspond to 53.04 oxide[32] instead of the 42.85 as found. If we calculate the composition of the copper butyrate that I analyzed, it must contain:

Water……………………	13.21, containing 11.74 oxygen
Acid anhydride………..	56.79
Copper oxide……………	30.00, containing 6.05 oxygen

Appearance

381. Haüy has described the morphology of copper butyrate crystals as follows:

"The most intricate morphology of these crystals is that of an eight-faceted prism with oblique facets on both ends bordering three additional facets, each of which replaces one of the edges situated on the circumference of these oblique facets. Figure 5[33] represents the upper half of one of those crystals. The letters *c, d, f* and *g* indicate the four prism facets that face towards the front; *a* is the oblique facet, *b* is one of the additional facets that face to the front and *h* and *n* the two others facing backwards. The facets *d* and *g* appear to be perpendicular to each other."

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* I have to mention that the crystallized copper butyrate that I describe here was prepared eight years ago, at a time when I did not yet have a fully reliable method of obtaining butyric acid in a high degree of purity. Therefore I do not assert that these crystals should be regarded as equally pure as the other butyrates dealt with in this section.

382. When an aqueous solution of copper butyrate is kept at 100°C, it becomes cloudy and deposits a blue material that changes to brown copper oxide and is completely soluble in acetic acid. On distillation of the butyrate solution after removal of the deposit, butyric acid is collected in the recipient. If the distillation residue is evaporated repeatedly, eventually all the acid is distilled and all the base is precipitated. This result is all the more remarkable since the copper butyrate crystals themselves can be exposed to 100°C for several hours without showing the slightest change.

ARTICLE 9

ZINC BUTYRATE

383. After dilution with water, butyric acid dissolves basic zinc carbonate[34] at ambient temperature, with effervescence. The solution colors litmus paper red, even after is has been in contact for a month with an excess of carbonate[35].

384. When the solution is filtered and the filtrate is evaporated to dryness in a dry vacuum, it yields shiny, lamellar crystals that smell and taste like butyrates.

385. When 100 mg of these crystals that had been exposed to a dry vacuum for a month were decomposed by nitric acid and calcination, they yielded 35 mg of oxide; therefore the zinc butyrate consists of:

Acid anhydride…	65[36]	100
Oxide……….	35	53.84, containing 10.69 oxygen[37]

386. The solution of zinc butyrate becomes cloudy before it boils. As it is concentrated, butyric acid is volatilized and a white deposit is formed which is either a basic butyrate or an oxide. Eventually, a residue results that melts at a low heat but is apparently also mixed with a material that does not melt, either a basic butyrate[38] or pure zinc oxide. If water is added to the residue and it is heated gently, more butyric acid evolves and finally, an infusible residue is obtained that retains the less butyric acid, the more often it has been treated with water and heat. In one of my experiments, the residue consisted of:

Acid………………………………………..	100
Oxide………………………………………	1525

ARTICLE 10

AMMONIUM BUTYRATE

387. Butyric acid reacts with ammonia gas in the same manner as isovaleric acid does. Crystals are formed that are then reduced to a thick, transparent and colorless liquid. Accordingly, there is probably a solid butyrate and a liquid butyrate.

388. I have observed that in the end, the liquid butyrate solidifies in the form of needles when left in an atmosphere containing ammonia.

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[1] Lead butyrate is $Pb(CH_3CH_2CH_2COO)_2$. Removing PbO leaves the butyric acid anhydride $(C_3H_7CO)_2O$ or $C_8H_{14}O_3$. Accordingly the oxygen/carbon-ratio of 2.72 is quite close to the expected value of 8 : 3 = 2.67 but the value for the oxygen/hydrogen-ratio of 3.73 is quite a bit lower than the expected value of 14 : 3 = 4.67.

[2] Yes indeed: 3 oxygen atoms in the 'butyric acid anhydride' or 'dry acid', and 1 in the lead oxide. See also endnote 4 on page 86 of the preceding chapter

[3] This is in accordance with the atomic weights according to Berzelius, who set oxygen at 100.00.

[4] As pointed out in endnote 2, this should really be 14. Similarly, the footnote of subsection (319) mentions 2.77 for hydrogen instead of 3.5 in what we would now call the butyrate anion $CH_3(CH_2)_2COO^-$ or $C_4H_7O_2$. The value for carbon at 2.04 on the other hand is correct within the margins of experimental error.

[5] This is a printing error. It should read 10.31.

[6] Pure butyric acid melts at – 5.3°C.

[7] The atmospheric boiling point of butyric acid is 164°C.

[8] In H. Kolbe, *Ausfürliches Lehr- und Handbuch der Organischen Chemie,* 2nd edition by E. von Meyer, Friedrich Vieweg und Sohn, Braunschweig, 1880, a book the editor inherited from his father, the aroma of ethyl butyrate is described as similar to that of pineapple.

[9] The ethyl ester of butyric acid is formed gradually and consequently, its flavor also develops gradually.

[10] There appear to be several different hydrometers and they probably all have their own scale. However, if 35° were to mean a density of 1.35, the acid strength would be some 55 % by weight.

[11] This cannot be pure calcium chloride since that boils >1 600°C. It is probably a saturated aqueous solution which, according to a footnote on page 307 of the *Journal de Pharmacie et des Sciences Accessoires,* Volume 2, 1816, boils at 154°C. The annotator would therefore not be surprised if the use of a boiling, saturated solution of calcium chloride enabled heating to a set temperature, just as boiling water provides a temperature of 100°C.

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[12] This table is straightforward. The first column with numbers represents the experimental observations whereby the acid number is obtained by deducting 0.1975 g from the 0.400 g starting material. In the next column, these figures are normalized to percentages by multiplying with 250, and in the last column, the acid is set at 100 and the oxide is calculated in proportion. Given the currently accepted atomic weight of barium of 137.3 and of barium oxide of 153.3, the oxygen content equals 16 x 97.58 : 153.3 = 10.1845. This value differs slightly from the value of 10.197 given in the table because the author uses a slightly different value for the atomic weight.

[13] This value permits the relative molecular mass of butyric acid anhydride to be calculated as (0.2025 : 0.1975) x (137.3 + 16) = 157.5. This value is very close to the theoretical value of 2 x 88 – 18 = 158.

[14] The author is a strict adherent to the metric system. Nowadays, we would express this length as from 1 to 2 mm.

[15] The density of the alcohol is mentioned in the side note of this sub-section; it corresponds to absolute alcohol.

[16] Barium butyrate is a salt of a strong base and a weak acid. When it is dissolved in alcohol, the acid will only be partially ionized so when the solution is then heated, some of the non-ionized acid will also distill off and the condensate will be an alcoholic solution of butyric acid which, given the low polarity of alcohol in comparison with water, will be dissociated even less in alcohol than in water. Accordingly, the alcoholic solution does not turn litmus red.

[17] See endnote 21 in the previous chapter on page 88.

[18] Just as in the case of the barium butyrate (endnote 13 above), the value for strontium butyrate also allows the relative molecular mass of the butyric acid anhydride to be calculated: (59.42 : 40.58) x (87.6 + 16) = 152.

[19] Similarly, (73.005 : 26.995) x (40 + 16) = 151.

[20] When determining the barium content of a salt, use can be made of the insolubility of barium sulfate in water; its precipitate can therefore be isolated by filtration, dried and weighed. Since potassium salts are soluble in water, another method must be used to isolate its salt: an excess of a volatile acid such as hydrochloric acid. With the relative molecular masses of (2 x 39.1 + 16) = 94.2 for potassium oxide and of 39.1 + 35.5 = 74.6 for potassium chloride, 60 mg of chloride contains 60 :74.5 x (94.2 : 2) = 37.93 mg of potassium oxide equivalent.

A third method employs nitric acid. It can be used for metals yielding a stable oxide since on heating, nitrates decompose and form oxides.

[21] This leads to relative molecular mass of the anhydride of: (62.04 : 37.96) x 94.2 = 154.

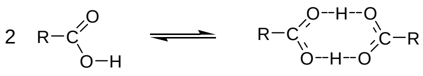
[22] Again, this is the acid anhydride.

[23] Although quite a number of observations had been reported, for example that salts of weak acids and strong bases have a soapy taste, the theoretical background was still lacking since the concept of ionisation had not yet been firmly established.

[24] It is not immediately clear what happens during this calcination. Perhaps the salt melts and has a much smaller surface after solidification than the original powder. This would explain the observations.

[25] Because the author does not yet think in terms of pH but in terms of competing affinities of the base and the acid for the litmus dye, he has to assume a change of affinity when water is added. A solution of a salt of a strong base (such as potassium hydroxide) and a weak acid (butyric acid) and some additional weak acid is a buffer solution. Buffer solutions have the property that on addition of an acid or base, their change in pH is less than the pH change of pure water, so how can the author's observations be explained?

Perhaps the dimerization equilibrium of carboxylic acids can help to explain:



In a concentrated buffer solution, the acid will be more strongly dimerized than in a dilute solution, so diluting this particular buffer solution with water will liberate monomeric acid which will take part in the dissociation/ionization equilibrium and cause the pH to drop. This drop appears to be just enough to induce a colour change in the litmus indicator.

[26] This is a typesetting error. It should be 0.054 g or 54 mg. Using this value to calculate the oxide content gives: (54 : (23 + 35.5) x 0.5 x (2 x 23 + 16) = 28.6

[27] The $0^{g}02878$ in the original is also a typing error. It should be $0^{g}2878$ or 28.78 mg.

[28] So the relative molecular mass of the anhydride equals: (71.22 : 28.78) x 62 = 153.

[29] This value is on the high side; the theoretical value for the lead oxide content of $Pb(C_4H_7O_2)_2$ is 58.53%. Accordingly, the relative molecular mass of the anhydride that can be calculated from these data: (39.5 : 60.5) x (207.2 + 16) = 146 is quite a bit lower than the theoretical value of 158.

[30] A compound with three times the amount of lead could be $(PbO)_2Pb(C_4H_7O_2)_2$ and 500 mg of this compound does indeed yield 405 mg of lead oxide:

{500 : (2x(207+16) + 207 + 2x(4x12 + 7 + 2x16)} x 3x(207+16) = 404.5

[31] As mentioned in end note 37 on page 89, the basic lead isovalerate could well be $(PbO)_2$Pb(isovalerate)$_2$. It has three lead atoms per two isovalerate moieties. The neutral salt, Pb(isovalerate)$_2$ has only one lead atom per two isovalerate moieties so there is indeed a threefold difference in lead content.

[32] Since 100 parts of copper butyrate yield 30 parts copper oxide, they should contain 100 - 30 = 70 parts of butyric acid anhydride. Then 100 parts of the anhydride would correspond to (30 : 70) x 100 = 42.86 parts of oxide. However, when using the relative molecular mass calculated for the anhydride of 157.5 in endnote 13, the amount of copper oxide should be (100 : 157.5) x (63.5 + 16) = 50.48. The amount found is less and this means that the crystals contain something else besides just copper butyrate. The amount of butyric acid anhydride that corresponds to the 30 parts of copper oxide equals: (30 : 79.5) x 157.5 = 59.4. This value should be compared with the 56.79 that the author calculated and included in the table listing the composition of the crystals.

[33] This figure is on page 343.

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[34] According to Ch. Gerhardt and Gustave Chancel in *Précis d'Analyse Chimique Qualitative,* 1855, the 'sous-carbonate de zinc' is formed by the addition of potassium or sodium carbonate to an unspecified zinc compound and according to Ostwald, *Grundlinien der Anorganischen Chemie,* 3rd edition 1912, aqueous solutions of zinc salts yield basic zinc carbonates on the addition of alkali carbonates; hence the translation 'basic carbonates'.

[35] When butyric acid reacts with the insoluble basic zinc carbonate, some CO_2 is evolved and the zinc goes into solution. The resulting solution will contain non-dissociated butyric acid since this is a weak acid, butyrate anions, hydroxyl anions and hydrogen cations whereas the zinc will probably be present as the $Zn(OH)^+$ cation. Apparently, the equilibria involved have such constants that the hydrogen cation concentration exceeds the hydroxyl concentration, so that the solution turns litmus red.

[36] Accordingly, the relative molecular mass of butyric acid anhydride can be calculated as: (65 : 35) x (65.4 +16) = 151.

[37] The amount of 10.69 oxygen allows the relative atomic mass of zinc to be calculated as 64.6; the modern value is 65.4.

[38] This basic zinc butyrate can be regarded as an impure zinc oxide.