

CHAPTER 4

PHOCENIC¹ ACID AND SOME PHOCENATES

SECTION 1

ISOVALERIC ACID

§1. COMPOSITION

260. The analysis of the dry lead salt of isovaleric acid gave the following data for isovaleric acid anhydride:

	BY WEIGHT	BY VOLUME ²
Oxygen.....	26.75	1.00
Carbon.....	65.00	3.17
Hydrogen.....	8.25	4.94

261. 100 parts of acid neutralize an amount of base that contains 8.65 parts of oxygen³. Accordingly, the ratio of the number of oxygen atoms in the neutral isovalerate to the oxygen in the base is near enough 3 : 1. Taking this into account and given that the acid consists of (by volume):

Oxygen.....	1.00
Carbon.....	3.34
Hydrogen.....	4.67

the composition of the acid anhydride is⁴:

	ATOMS	BY WEIGHT	
Oxygen.....	3	300.00 ⁵	26.030 ⁶
Carbon.....	10	765.30	66.390
Hydrogen.....	14	<u>87.36</u>	7.580
Total.....		<u>1152.66</u>	

262. When 0.500 g of free isovaleric acid having a density of 0.932 (g/mL) is mixed with 5 to 6 g of lead oxide at a temperature of 18°C, they react almost immediately under the evolution of heat. On heating, water evolves which tends to be alkaline rather than acid. The weight loss is 45 mg; accordingly the free acid consists of:

Composition
of the free acid

Isovaleric acid⁷.. 0.455 91 100
 Water..... 0.045 9 9.89, containing 8.792 oxygen

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

§ 2. PHYSICAL PROPERTIES

263. At ambient temperature, it is a liquid with a very low viscosity, like a volatile oil⁸. It does not solidify at 9°C below zero. It starts to boil at a temperature well in excess of 100°C⁹.

It can be distilled without decomposition.

264. At 28°C, its density is 0.932 (g/mL) since a flask that can contain 6.383 g water contains 5.948 g of isovaleric acid when full¹⁰.

265. It is colorless and it has a strong odor, which is reminiscent of both acetic acid and strong butter. However, once one has smelled it, it is impossible to confuse it with either of the latter.

266. Just like volatile oils, it will wet glass, paper and fabrics but it gives these materials a most disagreeable smell like that of slightly rancid dolphin oil.

267. It has a very sharp, acid taste¹¹ and an ethereal aftertaste like a russet apple. It leaves a white spot on the tongue where it has been applied. The taste is not at all reminiscent of cheese, unlike the flavor of butyric acid, which is distinctly cheesy.

The vapor of isovaleric acid has the sweet flavor of ethyl chloride.

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

Effect of water

268. It is not very soluble in water. You could say that 100 parts of water can dissolve 5.5 parts of acid at the most at a temperature of 30°C, since 5 g of water in which 250 mg of acid has been dissolved fail to dissolve an additional 30 mg acid.

* Assuming that the water that has been liberated has been formed from the hydrogen in the acid and the oxygen in the lead oxide, the acid radical that gets attached to the lead consists of:

	BY WEIGHT	BY VOLUME
Oxygen.....	32.670	1.00
Carbon.....	59.767	2.38
Hydrogen.....	<u>7.583</u>	3.72
Total	100.000	

269. The addition of phosphoric acid causes some of the isovaleric acid that has dissolved in water to separate out¹² in the form of oleaginous droplets.

270. It is miscible in all proportions with alcohol with a density of 0.794 (g/mL)¹³.

Effect of
alcohol

271. Concentrated sulfuric acid dissolves isovaleric acid at 15°C without changing it. On mixing, there is a rise in temperature. If water is added to the solution, part of the isovaleric acid separates but if the water is in excess, the acid dissolves again.

272. Nitric acid with a reading of 65° on a hydrometer has difficulty in dissolving it when cold and does not appear to change it.

273. If isovaleric acid is brought into contact with iron metal, there is no effervescence but the iron dissolves gradually, probably while absorbing oxygen from the atmosphere. The resulting solution is colored red. If not all the iron dissolved is in the form of iron peroxide¹⁴, adding water to the solution will cause a precipitate of this peroxide and of basic iron isovalerate¹⁵, whereas the ferrous isovalerate¹⁶ will remain in solution.

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

274. When isovaleric acid is heated in a retort that contains air, it will partially decompose. An aromatic substance results, the odor of which is similar to the aroma evolved when isovalerates are heated. This substance stays in solution in the part of the acid that did not react. This can be demonstrated by heating the product with lead oxide: the free acid reacts with this base and the aromatic compound and water are liberated.

275. Isovaleric acid ignites in the same way as volatile oils.

276. When the solution of isovaleric acid in sulfuric acid is heated to 100°C, it discolors only slightly. At a higher temperature, it starts to boil. Isovaleric acid is evolved together with some sulfur dioxide. The liquid darkens only slowly, which shows that sulfuric acid does not have such a strong effect on isovaleric acid as on many other organic substances. Finally, an ethereal smell develops and quite a copious carbon residue is formed.

277. An aqueous solution of isovaleric acid decomposes spontaneously when stored in a flask that is not completely filled; it develops a smell of leather that has been dressed with fish oil.

§ 5. PREPARATION

278. See Book III, Chapter 1.

§ 6. NOMENCLATURE

279. The word *Phocenic* has been derived from the *phocoena*, porpoise¹⁷.

§ 7. OCCURRENCE AND HISTORY

280. I discovered isovaleric acid in the oil of dolphins and porpoises in 1817. I described it in a presentation that I read at the Academy on 26 February 1818 under the name of *dolphinic acid*. At the end of the same year, I established its presence in the berries of *Viburnum opulus*¹⁸, where I was led to look for it because of the smell these berries release when they are squashed between the fingers. The berries of the tree cultivated in gardens contain less acid than the berries of the tree growing spontaneously in the woods. I seemed to observe that the isovaleric acid is only formed after the tree has reached full maturity.

The reason why I changed the name *dolphinic acid* to *phocenic acid* is that I have given the name *phocenin* to the substance in dolphin and porpoise oil that provided the first acid that I examined. If the vegetable alkali of the *delphinium* had not already been called *delphine*¹⁹, I would have preferred this name to *phocenin* because then the name of *dolphinic acid* could have been preserved.

SECTION 2

ISOVALERATES

ARTICLE 1

BARIUM ISOVALERATE

281. This salt is prepared by neutralizing baryta water with isovaleric acid and allowing the liquid to evaporate spontaneously.

Preparation

282. When 100 parts of transparent crystals of barium isovalerate were placed in a dry vacuum at 20 to 25°C, they became opaque and brittle. After a hundred and ten hours, 2.41 parts had evaporated.

283. An amount of 200 mg of barium isovalerate that had been dried under vacuum yielded 138 mg sulfate²⁰ that contained 90.57 mg of base. Therefore:

Acid anhydride.....	100 ²¹
Barium oxide.....	82.77 containing 8.649 oxygen

284. When humid barium isovalerate is heated in a calcium chloride solution, 1 part of acid evaporates together with some water. If the salt has been dried under vacuum beforehand, an aromatic smell develops that is not acid at all and that appears to be due to an alteration of the acid. If a weighed amount of 200 mg of isovalerate that has been heated dry in a bath of calcium chloride is placed on a sand bath that is so hot that the salt starts to decompose, no significant loss in weight will be observed. On the other hand, if the salt is heated gradually on a spirit lamp, it will be seen to melt partially and immediately discolor. In this state, it may only have lost 1 mg. Finally, if heating is continued, an aroma of basil²² develops without the aroma of isovaleric acid. A residue is obtained that yields 139 mg of barium sulfate corresponding to 91.74 mg of barium oxide. Thus the isovalerate consisted of:

Acid anhydride.....	100 ²³
Barium oxide.....	84.7, containing 8.89 oxygen

I think that the first result (283) is to be preferred.

- Form and cohesion 285. Barium isovalerate comes in large transparent colorless crystals with a greasy sheen. I have had polyhedra that were as thick as a thumb and appeared to be octahedral. The crystals shatter easily when crushed.
- Odor and flavor 286. The salt has no smell when kept in a small sealed²⁴ bottle. But if the salt is wet and if the atmosphere in the bottle contains carbon dioxide, the latter displaces some of the acid, which then makes the atmosphere aromatic. The isovalerate odor also becomes apparent when the salt is rubbed between the fingers or when filter paper or fabric is impregnated with a solution of barium isovalerate²⁵.
287. It is crunchy when chewed. It has a warm, pungent, alkaline and sweetish flavor and then the taste of isovaleric acid.
- Effect on litmus 288. Barium isovalerate is slightly alkaline towards red litmus paper.
- Effect of water 289. An amount of 10 g of barium isovalerate in the form of large crystals were dissolved in 20 g of water at 15°C. If a thin layer of the solution is carefully concentrated on a sand bath and the dish is placed on a heating element under a bell jar in which the temperature is such that the liquid, which would be viscous at 15°C, is sufficiently fluid to allow the particles to crystallize into polyhedra²⁶ as the water evaporates.
290. At 20°C, 1 part of water can dissolve 1 part of barium isovalerate.
291. In air, barium isovalerate is not noticeably deliquescent.
292. When a dilute solution of barium isovalerate is exposed to air, it decomposes spontaneously. A deposit of barium carbonate²⁷ and flakes is formed and the solution smells like Roquefort cheese.
- Distillation of barium isovalerate without contact with air 293. When 0.3 g of isovalerate is distilled in a tube filled with mercury, it melts and turns black. The following products are obtained:
- A. *A residue* of barium carbonate and carbon; in one of my experiments, it weighed 4 mg;
- B. An orangey yellow *liquid* that is very fluid and smells strongly. It is not acid and does not dissolve in aqueous potassium hydroxide, at least not immediately;
- C. *A gaseous product* consisting of 1 mL of carbon dioxide and 27.5 mL of ethylene.

ARTICLE 2

STRONTIUM ISOVALERATE

294. Strontium isovalerate is prepared by neutralizing an aqueous solution of strontium hydroxide with isovaleric acid.

Preparation

295. If this solution is evaporated in an atmosphere that is kept dry by quicklime, efflorescent, elongated prismatic crystals result.

296. If the solution is evaporated while exposed to the air, the surface of the resulting residue looks as if it had been varnished.

297. 100 parts of isovalerate obtained by evaporation of a solution while open to the ambient air lose 8.46 parts of water²⁸ when exposed to a dry vacuum.

Composition

298. When 100 mg of this isovalerate is heated in a platinum crucible, it melts almost at the same time as it begins to show signs of decomposition. An aromatic scent of herbs develops. Finally, a residue results that corresponds to 63 mg of strontium sulfate²⁹.

Acid anhydride ³⁰ ..	63.46	100
Strontium oxide...	36.54	57.58 containing 8.89 oxygen

299. It smells like isovaleric acid and its taste is similar to that of barium isovalerate.

Properties

300. It is highly soluble in water. If the water in this solution is completely evaporated and the residue is ground to a fine powder when removed from the fire, this powder will be seen to move and agglomerate into small grains.

ARTICLE 3

CALCIUM ISOVALERATE

301. It is prepared by neutralizing an aqueous solution of isovaleric acid with calcium carbonate³¹ and heating slightly. When the solution is evaporated in air that has been dried by quicklime, prismatic crystals are obtained.

Preparation

302. When the solution is evaporated in the ambient air, it crystallizes into a mass of long white needles that have the sheen of satin spar³².

Composition 303. 100 parts of calcium isovalerate obtained from a solution that was evaporated in the open air lost 13.96 parts in a dry vacuum but some acid was also volatilized with the water.

304. An amount of 100 mg of dry isovalerate yields an amount of base that corresponds to 59³³ mg of calcium sulfate. Thus:

Acid anhydride..	75.515	100
Lime.....	24.485	32.42 containing 9.129 oxygen ³⁴

Properties 305. Its properties are similar to those of the previous salt. It is soluble in water.

ARTICLE 4

POTASSIUM ISOVALERATE

Preparation 306. It is prepared by mixing an excess of isovaleric acid with a solution of potassium carbonate or bicarbonate. By evaporation, the excess of acid separates off and if the solution is too dilute, a significant amount of acid contributes to the neutralization of the alkali being released.

307. When 200 mg of potassium isovalerate^{*} is decomposed by hydrochloric acid, this yields 111 mg of potassium chloride³⁵ which corresponds to 69.586 mg of potassium oxide; thus:

Acid anhydride..	130.414	65.202	100
Potassium oxide.	69.586	34.798	53.37 containing 9.046 oxygen

308. Calculating the composition of potassium isovalerate in the same way as for barium isovalerate gives:

Acid.....	65.53	100
Potassium oxide.....	34.47	52.6

Properties 309. It has a sharp, slightly alkaline taste with a sweetish aftertaste of isovaleric acid. It reestablishes the blue color of reddened litmus paper. It is one of the most deliquescent salts I have come across: when a sample of 0.25 g was exposed to an atmosphere that was saturated with water at 20°C, the sample was completely liquefied three hours later:

	GRAMS
After 3 hours, the amount absorbed was.....	0.09
24.....	0.30
48.....	0.43

^{*} It was obtained by evaporation and then dissolved again in absolute alcohol. In this way the salt was separated from the potassium carbonate.

310. Potassium isovalerate is very soluble in alcohol since at 20°C, 100 parts of alcohol with a density of 0.792 (g/mL) dissolved 25.8 parts of isovalerate; the solution was not saturated.

ARTICLE 5

SODIUM ISOVALERATE

311. It is obtained by neutralizing an aqueous sodium carbonate solution with an excess of isovaleric acid. It is then evaporated to dryness. When the residue is dissolved in water, it does not spontaneously crystallize unless the air is very dry since sodium isovalerate is very deliquescent. A solution that had been concentrated to a syrup had not formed any crystals after having been exposed for eight days to an atmosphere where the temperature was 20 to 26 degrees centigrade. When the temperature was raised to 32°C, the isovalerate formed crystals shaped like cauliflowers; after twelve hours, these crystals had liquefied by absorbing water from the atmosphere.

Preparation
and properties

ARTICLE 6

LEAD ISOVALERATE

312. When isovaleric acid is poured over lead oxide mixed with some water, it dissolves this very well. If the solution is allowed to evaporate on a sand bath while an excess of isovaleric acid is maintained, the resulting meltable residue is a neutral isovalerate. On decomposition by nitric acid, 650 mg of this salt yielded 358 mg³⁶ of lead oxide:

Isovaleric acid anhydride.	292	100	
Lead oxide.....	358	122.6,	containing 8.76 oxygen

313. I obtained this salt in the form of beautiful, transparent, ductile flakes by evaporating a solution of lead isovalerate in a dry vacuum. An amount of 200 mg yielded 111 mg of lead oxide.

Acid anhydride..	89	44.5	100
Lead oxide.....	111	55.5	124.7, containing 8.94 oxygen

ARTICLE 7

BASIC LEAD ISOVALERATE

314. We have seen above that isovaleric acid tends to lose its hydration water³⁷ when reacting with lead oxide on heating. If lead oxide was in

excess and cold water is mixed into the material after the reaction, a solution results that on evaporation to dryness crystallizes as small, brilliant needles that are arranged in half-spheres. These crystals consist of basic lead isovalerate in which the amount of base is three times that in the neutral salt since decomposing 0.500 g of this salt with nitric acid yielded 0.390 g of lead oxide; thus:

Acid.....	110	100 ³⁸
Lead oxide.....	390	354.5 containing 25.34 of oxygen

315. The salt has a faint smell of isovaleric acid and is not very soluble in water; it attracts carbon dioxide from the air. It does not melt.

ARTICLE 8

AMMONIUM ISOVALERATE

316. When a small vial containing isovaleric acid is placed in a bell jar containing dry ammonia, crystals are formed without giving off a white cloud, which shows that the vapor pressure of the acid at ambient temperature is quite low. The absorption continues slowly and the crystals change into a thick liquid that is totally colorless and perfectly transparent. Afterwards, there are likely to be two ammonium isovalerates, one solid and the other liquid.

¹ The term "phocenic acid" was coined by the author from the Greek word φωκη that led to the genus *phocaena*, porpoises, which some authors confuse with turtles. Nowadays, this branched acid is called 'isovaleric acid' (3-methyl butanoic acid, $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$, MW = 102) and this is the name that will be used in this chapter and thereafter; salts will be referred to as 'isovalerates'.

² In the lead salt $\text{Pb}(\text{C}_5\text{H}_9\text{O}_2)_2$, one of the oxygen atoms is reckoned to belong to the lead so the anhydride has the formula $\text{C}_{10}\text{H}_{18}\text{O}_3$. That means that the hydrogen content has been underestimated.

³ This value is reasonably accurate because it needs two molecules of isovaleric acid to combine with one oxygen atom in the base.

⁴ When discussing the composition of stearic acid in Chapter 1 of this Book (sub-sections 28-30), the author also started by reporting his analytical data. Then he reported how much water was released when the free acid reacted with lead oxide and this allowed him to arrive at a correction factor for the oxygen to be used when calculating the molecular composition of the anhydride. Since the number of atoms must be integers - after all, the Greek word ἀτομος means indivisible - the smallest possible integer is chosen for oxygen and then the values for carbon and hydrogen are arrived at by multiplication and rounding off to the nearest integer.

This has also been done for isovaleric acid. The analytical data are reported in sub-section (260). The first column where oxygen is quoted as 26.75 gives these analytical data as weight percentages. In the second column, these percentages are converted

to atomic ratios, whereby the oxygen is put at 1.00 and the relative atomic weights of 12.244 and 0.9984 are used for carbon and hydrogen respectively (see endnote 19 on page 12).

Then, in sub-section (261), the ratio of the oxygen content of the bound acid and that of the base is established as near enough 3 : 1 and the carbon and hydrogen contents are slightly adjusted so that when multiplied by 3, they lead to integers. So the carbon value is raised from 3.17 to 3.34 and the hydrogen value is decreased from 4.94 to 4.67. Finally, the composition is calculated on the basis of this molecular formula, again using the relative atomic masses mentioned in endnote 19 on page 12. So the oxygen content equals: $3 \times 16.00 : (3 \times 16.00 + 10 \times 12.24 + 14 \times 0.9984) \times 100 = 26.028$ as weight %.

The same method of treating the analytical data was also used for palmitic acid in Chapter 2, sub-sections (133-135), and oleic acid, sub-sections (185-187) and will be used in subsequent chapters dealing with other fatty acids.

⁵ These are the Berzelius figures where oxygen is set at 100.

⁶ The figures in this column were derived from the previous column by dividing by the total.

⁷ This refers to the anhydride that has a relative molecular mass of $2 \times 102 - 18 = 186$. Accordingly, the amount of water corresponding to 0.455 parts of anhydride equals: $0.455 \times 18 : 186 = 0.044$ parts which is close enough to the 0.045 parts listed in the table.

⁸ This could perhaps be a volatile hydrocarbon.

⁹ The atmospheric boiling point of isovaleric acid is 176.5°C.

¹⁰ The author has not taken into account that at 28°C, water has a density of 0.99523 kg/L. If he had done, he would have arrived at a density of 0.927 kg/L. The current literature value is 0.934 (g/mL) at 20°C.

¹¹ This is just one of the many examples where unknown products are tasted as part of their characterization. So when 2,4,6-trinitrophenol was tasted and found to be extremely bitter it was given the name of picric acid. Modern safety regulations would prevent such naming procedure.

¹² The isovaleric acid in solution will be partially dissociated. By adding phosphoric acid, the degree of dissociation will be reduced and this increases the concentration of the non-dissociated acid. Before acidification, the solution was saturated with respect to the non-dissociated acid so that on acidification, it became supersaturated and some acid separated out.

¹³ This is about as absolute as you can get since the 17th edition of the *List of Tables* that the Dutch Chemical Society published in 1952 gives a density of 0.794 (g/mL) for 100% alcohol at 15°C and adding water only raises the density.

¹⁴ 'Iron peroxide' is an old name for ferric oxide (Fe₂O₃); it is orange-red.

¹⁵ The "sous-phocénate de peroxide de fer" is presumably a basic ferric isovalerate which could be FeO{(CH₃)₂CHCH₂COO} or FeOH{(CH₃)₂CHCH₂COO}₂ or a mixture of both.

¹⁶ Ferrous isovalerate could well be Fe{(CH₃)₂CHCH₂COO}₂.

¹⁷ In Dutch, porpoises are called “bruinvissen”, which means ‘brown fish’; porpoises are not fish but mammals like dolphins and whales.

¹⁸ According to Google, the *Viburnum opulus* (Caprifoliaceae) could be the common snowball plant but then it is reported to be sterile and would not produce any berries. Accordingly, the ‘Guelder rose’ or the ‘European cranberry bush’ are more likely sources of isovaleric acid.

¹⁹ This remark is typical for the French language because a dolphinarium (with an ‘o’) in English is a ‘delphinarium (with an ‘e’) in French. So in French the mammal and the flower have the same vowel, which could be confusing.

²⁰ With the following atomic and molecular relative masses: Ba = 137; BaSO₄ = 233; barium isovalerate = 339, the figures work out quite well: $(0.200 : 339) \times 233 = 0.1375$ for the sulfate and $(0.1375 : 233) \times (137 + 16) = 0.897$ for the oxide.

²¹ These data allow the relative molecular mass of the anhydride to be calculated as: $100 \times (137 + 16) : 82.77 = 185$, which is very close to the value of $2 \times 102 - 18 = 186$ as calculated on the basis of the molecular formula and loss of water.

²² ‘Huile de labiées’ generates only two hits in Google, one of which is sub-section (284) in the book being translated. Widening the search by looking for ‘huile’ AND “labiées” reveals that the botanical family of the *Lamiaceae* is in French also called ‘Labiées’. Accordingly, the oil could well be a basil oil (Basilic exotique) used in aromatherapy.

²³ Accordingly, 200 mg of barium isovalerate contained 91.74 mg of barium oxide and $200 - 91.74 = 108.26$ mg of isovaleric acid anhydride. 100 mg of this anhydride thus contained $91.74 : 1.0826 = 84.74$ mg of barium oxide.

²⁴ This will probably have been a stoppered bottle since the neck of the bottle and the stopper could be ground into a matching pair.

²⁵ Presumably, the carbon dioxide in the surrounding air then plays a similar role as it did in the aforementioned bottle.

²⁶ The author is clearly aware that growing large crystals requires small temperature gradients and thus time. If this was a novel finding, the author was not aware of its novelty.

²⁷ In the French text, this is called ‘sous-carbonate de baryte’. Reading what has been written about this compound at around the time the author used it and in some later works, it looks as if the compound may well have been just barium carbonate (BaCO₃) and not a kind of basic carbonate (BaOBaCO₃) or bicarbonate {Ba(HCO₃)₂}. The fact that Ostwald (*Grundlinien de Anorganischen Chemie*, 1912) only mentions barium carbonate supports this interpretation.

²⁸ This corresponds to 3 molecules of water per 2 molecules of strontium isovalerate.

²⁹ When using the current relative molecular masses: strontium isovalerate = 289; SrSO₄ = 183; SrO = 103, 100 parts of isovalerate yield: $100 \times 183 : 289 = 63.32$ parts of SrSO₄ which correspond to: $63.32 \times 103 : 183 = 35.64$ parts of strontium oxide. These are then normalized to 100 parts of acid according to: $100 \times 35.64 : 64.36 = 55.38$ which contain: $55.38 \times 16 : 103 = 8.60$ parts of oxygen.

³⁰ Working backwards, the relative molecular mass of the isovaleric acid anhydride can be calculated as: $100 \times 103 : 57.58 = 179$, which is a bit lower than the actual value (186) and lower than the value calculated from the barium isovalerate data (185).

³¹ Again the text mentions 'sous-carbonate' but according to M.J.B.P. Orfila, *Éléments de Chimie Médicale*, Vol. I, page 235, Crochard, Paris, 1817, this compound shows all the properties of calcium carbonate.

³² Satin spar is a fibrous variety of gypsum.

³³ When 100 parts of isovalerate yield 59 part of calcium sulfate (M.W. 136.8; see also next endnote), the relative molecular mass of the calcium isovalerate can be calculated to equal: $(100 : 59) \times 136.8 = 231.9$. Subtracting the relative molecular mass of calcium oxide (56.8) leaves $231.9 - 56.8 = 175.1$ for the isovaleric acid anhydride. So 100 parts of the calcium isovalerate consist of $(175.1 : 231.9) \times 100 = 75.49$ parts of anhydride and $(56.8 : 231.9) \times 100 = 24.49$ parts of calcium oxide as more or less reported.

³⁴ If 32.42 parts of calcium oxide contain 9.129 parts of oxygen and the relative atomic mass of oxygen equals 16.00, the relative molecular mass of calcium oxide equals: $32.42 \times 16.00 : 9.129 = 56.82$. Accordingly the relative atomic mass of calcium equals: $56.82 - 16.00 = 40.82$, which is only slightly higher than the value of 40.08 used nowadays.

³⁵ Using a relative molecular mass for potassium isovalerate of 140 and for KCl of 74.5, 200 mg of the isovalerate corresponds to $200 \times 74.5 : 140 = 106$ of potassium chloride, which is near enough to the 110 mentioned in the text. The difference is so small that it does not demonstrate the presence of residual potassium carbonate in the sample.

³⁶ When using the following relative masses: Pb, 207; lead isovalerate, 409; PbO, 223; 650 mg lead isovalerate will yield $650 \times 223 : 409 = 354$ mg of lead oxide.

³⁷ Free acids were still considered to be a combination of the actual acid and the water of hydration. However, the author gradually moved towards the notion that the hydrogen of the acid might react with the oxygen in the metal oxide and accordingly, he devotes some footnotes to this revolutionary notion.

³⁸ The relative molecular mass of the isovalerate anion equals 101. Accordingly, the molar equivalent of the lead oxide equals: $(354.5 \times 1.01) : 223 = 1.60$ whereas in the neutral salt, 2 isovaleric anions combine with a single lead cation. The molecular formula of the basic lead isovalerate could therefore be: $(\text{PbO})_2\text{Pb}(\text{isovalerate})_2$.