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AERIAL ACID: a short history of artificial mineral waters

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Magical properties were long ago associated with natural waters and springs. Early physicians recognised that these natural waters contained a subtle spirit that imparted the waters with a refreshing taste that imparted a feeling of vitality. This spirit was assigned a variety of names including *Spiritus Silvestris, Gas Sylvestre, The Soul of the Waters* and an *Elastic Aethered Spirit*

Belief in the medicinal and healing properties of these waters spread and people went in search of cures. A demand was created for the waters to be available everywhere but transporting them was a problem, firstly they seemed to lose the lively taste, and secondly the ingredients appeared to leave the water in the form of a sediment. It was believed that the gas evolved by the waters was a powerful aid to its efficacy and searches were begun to identify this magical ingredient to enable the creation of artificial waters.

In the 1440s Michael Savanorola, an Italian physician, wrote a treatise on the hot baths of Italy. In 1560 Dr William Turner wrote an account of the waters at Bath, England. In 1572 Dr Jones, a physician from Derby, England, expanded the virtues of the waters at Buxton, and in 1602, Jacob Theodore mentioned a number of German mineral waters including the famous Seltzer Water.. None of these gentlemen made any attempt to analyse or comment on the contents of these waters.

The first mention of an ingredient is from Dr Thomas Guidott, a Somerset physician, who in 1676 wrote *A Discourse of Bathe and the Hot Waters there* in which he states "I am apt to believe that great part of the acidity is breathed off in evaporation".

In the 1660s the chemist Robert Boyle increased the knowledge of chemical analytical research. He discovered a number of indicators for acids including syrup of violets which turned red in acids. Mineral waters, it was found were acid but lost this property on standing as well as producing a precipitate which was not acid. In1685 Boyle published a book "*Short Memoirs for the Natural Experimental History of Mineral Waters*" in which he included 47 chapters each with one method of examination.

In 1726 Frederick Hoffman, "a most excellent and consumnate physician and curious chymist" wrote that mineral waters consisted of three parts:

1) a very subtile [sic] matter – in all probability an extremely moveable or subtile [sic] aether
2) of moisture or what for distinction's sake may be called elemental water.
3) Of a solid body, whether of an earth or saline nature.

He ascribed the most extravagant virtues to the first ingredient – "this noble, native spirit, it is, which by its penetrating nature and admirable faculty, renders itself perceptible to the smell and the sense; not only affording a grateful odour in its exhalation, but also filling the whole head therewith. This principle we take for their {mineral waters} most curious and effective part, or as it were the soul."

In the 1740s two men wrote notes on Pyrmont Water, found at Bad Pyrmont in Lower Saxony in Germany. F.G. P. Seif and a Dr George Turner described the "spirit" of Pyrmont water as an agent holding the ingredients of the water together because they precipitate on standing. Both recognised the similarity of the gas to the noxious exhalations of caves such as the Grotto del Cane, the gas issuing from mineral springs and the gas produced by fermenting liquors. Animals and man had been asphyxiated both in Italy and at Pyrmont.

The first complete analysis of a mineral water is attributed to a Dr Chrouet who, in 1713, analysed the waters at Spa in Belgium. He had a special pewter still to collect the vapour given off by the Spa water. He was convinced that the gas was air and not combustible spirits and that it was of such a nature that it was acidic and able to combine with potash. He called it **aerial acid**.

An English translation of his analysis of the water reads: *Thus a bottle of this water comes as a medicinal potion ready prepared from the bosom of the Earth, being composed of a great quantity of this **airy acid** lightly stuck to our salts, sulphurs, and to the matter of four grains of **Mars** divided into a million parts, of six grains of **double salt**, of seven and a half grains of **metallick sulphur,** and of a sample of a **sulphurous spirit**.*

Sometime before 1750 Monsieur G F Venel, a professor of chemistry in Montpelier, believed that the aerial acid was an extra part of the contained gas, as the amount of air in mineral water that had been standing, contained the same amount of air as ordinary solutions of chemicals. He found that by adding sulphuric acid until the deposits had been dissolved, in a closed vessel, the vitality of the water was restored. He later added an amount of sodium carbonate to water to just detect the taste then added a small quantity of hydrochloric acid – the result was a water with a taste that resembled that of Seltzer water.

The simplest way to reproduce mineral waters was to evaporate the natural water then re-dissolve the residue in sufficient plain water. This method was successfully carried out by Nehemiah Grew on the waters at Epsom and he marketed the product as Epsom Salt. Similarly, Hoffman extracted the same salt from Seidlitz water. Chemists could increasingly determine the contents of mineral waters by chemical analysis, but the quest was to add the sparkling vitality of the water. Hoffman tried to produce the sparkle by adding alkali and acid, but shaking to dissolve the ingredients dissipated the gas.

As stated earlier, Dr Seif found that the vapours given off by the water at Pyrmont in Germany was similar to the noxious fumes at Grotto del Cane in Italy. It was Dr William Brownrigg who identified the vapour. Brownrigg was a physician in Whitehaven, in Cumbria, England. He investigated damps, that is, vapours in the coalmines. He concluded that it was these vapours that impregnated the underground water to impart the taste and effervescence and was the same vapour as found in Pyrmont and the Grotto del Carne. He also detected that the vapour was acid.

In 1752, Joseph Black, who would later become Chair of Chemistry at the University of Edinburgh, was researching the cause of causticity of lime and the effects of heat and acid on chalk. He found that both effects had the same result of driving off a gas which he named as **fixed air.**

Henry Cavendish, the English chemist and physicist, discovered that water could dissolve slightly more than its own volume of fixed air at room temperature and rather more at lower temperatures or under pressure, and that this combination could dissolve calcium carbonate while, at the same time, producing more fixed air.

In 1767, Joseph Priestley started experiments on fixed air which he could find in abundance as he worked very close to a brewery. He added very little knowledge to the subject but confirmed other people's experiments and declared fixed air to be a combination of oxygen and phlogiston (a hypothetical element that was said to be given off when a substance was burnt). The 'phlogiston' in the case of fixed air was, in fact, a black substance which Priestley was not prepared to identify as carbon – this task was completed by Lavoisier who proved that fixed air was a combination of 24% carbon and 76% oxygen. Lavoisier renamed fixed air as **Carbonic Acid.**

It is thought that the first person to aerate with carbon dioxide water was Brownrigg although he never published a paper. The gases from the local mine were passed to his laboratory by pipes and it may be inferred that aeration was effected by passing the gases directly into water. Venel had tried by adding hydrochloric acid and sodium carbonate but subsidiary products were left in the water.

Joseph Priestley first impregnated water by leaving it near the surface of beer in fermenting vats. In 1772 he used chalk and acid. At about the same time he heard of the work of Dr. Charles Irving, a naval surgeon and inventor from London, who produced distilled water from seawater. Priestley worked on a method of impregnating this water with carbonic acid gas and to use it for the prevention and cure of scurvy – an idea put forward by Dr David Macbride. Priestley produced an apparatus (see illustration) that was accepted by the admiralty and installed on two ships. He later produced a pamphlet which described his apparatus and how to use it.

"The bottle contains chalk just covered with water. Add sulphuric acid, press air out of bladder, cork bottle, allow a little time to expel air, then insert pipe. When half full of air, agitate. Allow to fill again and agitate. Cork and remove bottle."

The disadvantage was that although atmospheric air was removed, acid vapours were not.

Lavoisier took this a stage further by adding a funnel with a valve to control the amount of acid added. Purification was done by passing the gas through water to remove sulphuric acid and through a vessel containing lime and water to remove other impurities.

In 1775, Dr Nooth introduced what he called a Gazogene for making small quantities of aerated water. Gas was generated in the bottom chamber from chalk and sulphuric acid. It passes through a one-way valve to aerate water in the chamber above. Displaced water was returned via a bent tube into the aerated water.

In 1781, Thomas Henry, an apothecary from Manchester produced an apparatus that could produce10 to 12 gallons of aerated water in one operation. Here the generator containing chalk and acid is on the right side. Two bladders are fitted, one to conserve gas, the other to take the displaced water. With his apparatus he prepared Pyrmont water, Seltzer water and something called Mr Bewley's mephitic julep.

His formula for Pyrmont Water was:

"To every gallon of spring water add one scruple of magnesia alba (magnesium carbonate), 30 grains of Epsom Salts (Magnesium Sulphate), 10 grains of common salt, and a few pieces of iron wire or iron filings. The operation is then to proceed as in the process for impregnating water with fixed air; and the water, if intended for keeping, must be put into bottles, closely corked and sealed."

Seltzer water contained magnesium carbonate, sodium carbonate and salt. And Mr Bewley's julep contained sodium carbonate and the instruction was to take 4 fluid ounces with a draught of lemonade or vinegar water by which means the gas could be released in the stomach. This was probably the first "Soda Water". The first mention of Soda Water was by Tiberius Cavallo, a member of the Royal Society, in about 1798, when he stated "the soda water which is now prepared and sold in London by a Mr Schweppe, contains an incomparably greater proportion of carbonic acid gas".

One refinement of Henry's apparatus was performed by the famous inventor James Watt. It was hydraulic bellows or gasometer to receive and store gas produced.

The 1790s saw a sharp increase in the manufacture of artificial waters, pumps were introduced and glass bottles replaced earthenware bottles. Bottles were filled using pressure and agitation. Specialised bottles were invented such as that by Hiram Codd that had a marble built into the bottle. The bottle would be filled and the pressure would hold the marble in the neck. A wooden apparatus would release the marble foe emptying the contents.

Continuous machines were produced to be used in pharmacies to make their own brands of mineral water. Here is one such apparatus as recommended in the Pharmaceutical Journal of 1849/50. (See illustration)

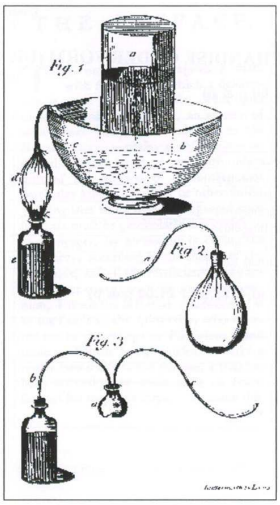
It was also recommended that the man carrying out the task of bottling should wear a thick woollen sweater as the bottle might shatter when being filled.

Other machines were developed for the over-the-counter sales of carbonated drinks

For production at home of small quantities of aerated water the gazogene was further developed by various manufacturers using mainly tartaric acid and sodium bicarbonate to produce the carbon dioxide. These were eventually replaced by the soda syphon with its charged mini-cylinders of carbon dioxide.

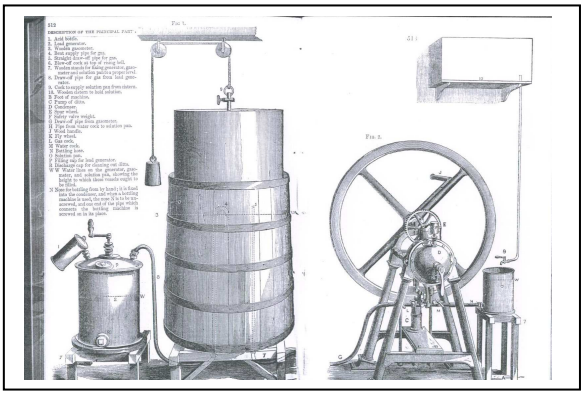
I cannot finish without mentioning a famous pharmacist who was arguably the worlds greatest beneficiary from the discovery of aerial acid, John S Pemberton, the inventor of Coca-Cola.

Main reference: William Kirkby; The Evolution of Artificial Mineral Waters; Jewesbury & Brown, Manchester, 1902.



Priestley's Apparatus

Nooth's Gazogene



Soda Water Apparatus
Pharmaceutical Journal 1849/50.9.512