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# MINERAL AND AERATED WATERS

BY

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# MINERAL AND AERATED WATERS







TO  
WALTER WILLIAM FISHER,  
M.A. (OXON.), F.I.C.,  
ALDRICHIAN DEMONSTRATOR IN THE UNIVERSITY OF OXFORD.  
FROM  
HIS PUPIL.



## PREFACE

IN this book I have endeavoured to give an outline of the early methods of making artificial mineral waters, and to trace the gradual evolution of the primitive forms of apparatus first invented into the carbonating plant of the present day.

During the eighteenth century so much attention was given to the subject in the scientific journals of that time that it is possible to trace the beginnings of the mineral-water industry with much more detail than can be done in the case of many other industries.

Descriptions of aerating processes and diagrams of apparatus are to be found in many unexpected places, and I wish to acknowledge my indebtedness to Mr. William Kirkby's "Evolution of Artificial Mineral Waters" for several sources of information that would otherwise have escaped my notice.

My best thanks are also due to Mr. Kirkby for his permission to make use of the description and diagram of Withering's apparatus, and to Mr. A. Chaston Chapman, who has kindly supplied me with photographs of the wild yeasts illustrated in Chapter X.

I would also thank the different manufacturers of modern plant who have placed photographs and descriptions of their machines at my disposal and have given me every assistance in their power. Among them I may mention Messrs. W. J. Fraser & Co., of Dagenham, Messrs. Hall & Co., The Riley Manufacturing Company, Messrs. Wickham & Co., of Ware, and, in particular, Messrs. Hayward-Tyler & Co., who have been at great trouble to obtain for me descriptions and illustrations of the machines made by their firm in the early part of last century.

Messrs. Ingram and Royle have kindly allowed me to quote analyses from their compilation on natural mineral waters, and the Apollinaris Company have supplied me with information about their spring and with photographs of their works. To both these firms I tender my thanks for their assistance.

C. A. M.

WHITE COTTAGE,  
AMERSHAM COMMON,  
BUCKS.

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# MINERAL AND AERATED WATERS

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## CHAPTER I

### ORIGIN AND PROPERTIES OF NATURAL MINERAL WATERS— GASES IN NATURAL WATERS—HOLY WELLS—THE ZEM- ZEM WELL AT MECCA

IN its original signification the term “mineral waters” was restricted to those natural spring waters to which medicinal properties were attributed, either by reason of the salts that they contained in solution, or of the gases with which they were saturated.

These products thus formed a natural group in a series ranging from rain water at one end of the scale to sea water, brine springs, and petrifying wells at the other.

When freshly discharged from a cloud rain water is the purest form of natural water, but on its way through the atmosphere it becomes contaminated with various gases, and as soon as it reaches the soil begins to take up different salts, the nature and proportion of which will depend upon the kind of saline deposits with which it comes in contact. According to the amount of salts thus dissolved, natural waters are classified as soft or hard. In some waters, such as that of Loch Katrine, the water is very nearly as free from solid matter as rain water, and these leave only traces of organic matter on evaporation.

In others so large a proportion of salts may pass into solution that the product is a saturated saline solution. As an example of a natural water of this kind we have the water of the Dead Sea, which the writer has found to have a specific gravity of

1·2031 and to contain no less than 402 parts of solid matter per 1,000. Between extremes of this kind come river waters, ordinary well waters, and drinkable saline waters, which obviously differ more in the quantity than in the nature of their dissolved constituents.

**Alterations in Natural Waters.**—Another point in connection with natural waters is that, although in some cases their composition may remain fairly constant, as, for instance, soft lake waters, they may also show great variations from time to time, according to the nature of the season, and to alterations in the level of the pocket of water.

An interesting example of this alteration is afforded by the Government well in Trafalgar Square. In 1848 this water contained 99·15 parts per 100,000, whereas in 1900 an analysis by Mr. W. W. Fisher showed that it only contained 85·7 parts per 100,000. Between the years 1848 and 1857 the water lost 14 per cent. of its total saline constituents, but since the latter date has remained fairly constant. The loss consisted, in the main, of potassium carbonate.

In another case within the writer's experience the total solid matter in the water from a deep artesian well was 52 parts per 100,000 in 1895, while twelve years later the level of the water had sunk some 30 to 40 feet, and the water then contained only 43 parts of total solids per 100,000.

In moving waters alterations in the proportions of the various salts are often brought about by reactions that take place between the salts dissolved at one period and those with which the water subsequently comes into contact—with the result that some of the substances first dissolved are subsequently re-precipitated.

**Effect of Gases in Natural Waters.**—Another factor which affects the amount of saline matter in a water is the presence of carbon dioxide and other gases. For example, the carbonates of calcium and magnesium, which occur in many mineral waters and are the cause of the temporary hardness in drinking waters, are precipitated when the water is boiled

so as to expel the dissolved carbon dioxide which kept them in solution.

Many of the petrifying wells owe their power of incrustating objects with a deposit of calcium carbonate to this cause. The water is so saturated with the salt, which is solely kept in solution by the dissolved carbonic acid, that when a proportion of the gas escapes from the splashing water part of the carbonate is precipitated.

Another striking example of the part thus played by carbon dioxide in natural waters is afforded by the formation of stalactites in caverns. Each drop of water falling from the roof parts with a little of its dissolved carbon dioxide, and thus causes the deposition of some of the calcium carbonate with which it is also charged, until, finally, the succeeding drops traverse an envelope of the separated salt, and the stalactite gradually lengthens. At the point where the drop falls a stalagmite may be produced, and eventually may grow to a sufficient height to meet the descending stalactite and form a solid column.

To the same cause may sometimes be attributed the deposition of iron salts which takes place in certain chalybeate waters on standing. The iron carbonate in the water is kept in solution so long as the liquid remains saturated with carbon dioxide, but with the escape of the gas the iron salt is precipitated.

A good example of this is afforded by the chalybeate waters of Tunbridge Wells, which contain in solution about 0.025 part of iron per 1,000, corresponding to rather more than twice that quantity of iron carbonate, which is kept in solution by the free carbon dioxide. In one analysis the dissolved gas amounted to 69.35 c.c. per litre (or 19.19 cubic inches per gallon).

**Carbon Dioxide in Water.**—The degree of solubility of carbon dioxide in water under varying degrees of pressure and temperature is a factor of considerable importance in the manufacture of aerated beverages. This point is discussed in the section dealing with the production and properties of carbon dioxide.



In the case of natural mineral waters it is sufficient to state here that at the ordinary atmospheric pressure and normal temperature (60° F.), the gas is soluble in about an equal volume of water.

The proportion of carbon dioxide in natural mineral waters varies within wide limits. In some, the water is completely saturated with the gas as it leaves the spring, at a relatively low temperature, and on standing in the air it gradually attains the normal temperature, and bubbles of gas continually escape.

In others only traces of carbon dioxide are present in the dissolved gases.

**Hydrogen Sulphide.**—Another group of natural waters, which may be typified by the sulphur springs of Harrogate, contain large amounts of hydrogen sulphide. For example, from the water of the Old Sulphur Well, Muspratt separated 36·09 cubic inches of gases per gallon, consisting of 61·06 per cent. of carbon dioxide, 16·17 per cent. of methane, 8·08 per cent. of nitrogen, and 14·69 per cent. of hydrogen sulphide.

**Nitrogen and Inert Gases.**—In some mineral waters the gases in solution consist principally of nitrogen (including argon, neon, etc.). Thus in the case of the Buxton waters, Muspratt found 504 cubic inches of nitrogen and 3·5 cubic inches of carbon dioxide per litre. The therapeutic action of Buxton water has been attributed to this large amount of nitrogen, but is much more likely to be due to the presence of niton (radium emanation) (*see* Chapter IV.).

**Holy Wells.**—The medicinal properties of some of the more saline waters could hardly have escaped recognition at a very early period of man's history, and the good effects produced in some cases by a liberal use of certain springs frequently led to their acquiring a supernatural reputation and being regarded as the direct cause of many a miraculous cure.

For instance, long before the Reformation votive offerings were made to St. Anne at Buxton for the cures effected by the

use of the waters of her well, and the practice was finally forbidden by Henry VIII.

In many instances this holy reputation has been handed down to the present day ; in others all record of the well itself has disappeared, and only its name has survived. To this cause we can attribute the origin of the name " Holy Well," which is of such frequent occurrence in towns and villages all over Europe.

Some of the " holy " wells justify their medicinal fame by the fact that their waters contain Epsom salt, Glauber's salt, or sulphur compounds possessing a therapeutic action when applied externally.

In other cases the good effects claimed to have been brought about by the waters may have been mainly due to a simultaneous exercise of faith.

Take, for example, the water of St. Winifred's Well at Holywell in North Wales, which even yet retains some vestiges of its mediæval character of a health-giving spring, notwithstanding the fact that half a century ago it was shown that the salts it contained were remarkable neither in kind nor in quantity.

According to the analysis of J. Barrat,<sup>1</sup> it contained 30·4 grains per gallon of salts, consisting principally of calcium carbonate, calcium sulphate, and calcium chloride, with smaller quantities of magnesium carbonate, sodium chloride, and silica.

There remains, however, the possibility that this water may be strongly radio-active, and that it acquired its reputation from this cause and not from the nature of its saline constituents.

It is interesting to compare with this the composition of the water of the holy well, on the north shore of Morecambe Bay, which at one time was the property of the Priors of Cartmel.

It was highly esteemed as a cure for gout and diseases of the skin, and is mentioned in the pages of Camden as a medicinal spring.

The water, which issues from a fissure in a rock close to the

<sup>1</sup> *J. Chem. Soc.*, 1860, XII., p. 52.

sea, was examined by Mr. (now Sir Edward) Thorpe in 1868,<sup>1</sup> and was found to contain 7·19 parts per 1,000 of salts, consisting chiefly of sodium chloride and calcium sulphate, with smaller quantities of calcium carbonate, magnesium chloride and sodium sulphate, and minute quantities of barium, strontium and lithium salts (0·002 part), silica and iron carbonate (0·003 part).

**The Sacred Well of Mecca.**—Probably the most celebrated holy well in the world is the sacred well at Mecca, which tradition claims to be the actual well of Hagar.

To all Mohammedans, therefore, it is an object of especial veneration, though among Europeans it has the reputation of having been the means of distributing more than one outbreak of cholera.

Each pilgrim to Mecca is required to drink of this water and to bathe in it, and since the supply would be far too limited to meet the demand of the thousands of annual pilgrims, a conservative process has been evolved.

An Arab stands upon the parapet of the well and draws up the water in a bucket. A pilgrim then advances and receives the contents of the bucket on his head. He drinks what he can, and the remainder flows down over him, and falls back through a grating into the well, whence it is again drawn, to be poured over succeeding pilgrims.

When we reflect that this practice has been going on year after year with generations of pilgrims (70,000 to 80,000 a year), it is not surprising that the water of the Zem-Zem well shows extreme pollution, or that the well has been the medium for spreading infection far and wide.

The water is not only drunk in Mecca itself, but is exported to all parts of the world for the use of the faithful, and a great trade is done in the sale of the bottles to the pilgrims.

The curious tin bottle, shown in the accompanying photograph, is one of several brought back in 1853 by Sir Richard Burton from Mecca, and was given to the present writer by Lady Burton shortly before her death.

<sup>1</sup> *J. Chem. Soc.*, 1868, XXI., p. 19.



Readers of Burton's "Pilgrimage to Mecca" will remember how, disguising himself as a pilgrim dervish, he succeeded at the risk of his life in making his way to Mecca, and took part in all the ceremonies at the tomb of the prophet.

One of the objects of his pilgrimage was to see the Zem-Zem well and to obtain some of the water, and his account of the



FIG. 1.—Tin Bottle, containing Holy Water, brought from Mecca by Sir Richard Burton.

properties of the most renowned mineral water of the Old World is well worth quoting :—

“The produce of Zem-Zem is held in great esteem. It is used for drinking and religious ablution, but for no baser purpose, and the Meccans advise pilgrims always to break their fast with it. It is apt to cause boils, and I never saw a stranger

drink it without a wry face. Sale is decidedly correct in his assertion: the flavour is a salt-bitter, much resembling an infusion of a teaspoonful of Epsom salts in a large tumbler of tepid water. Moreover, it is exceedingly 'heavy' to the digestion. For this reason Turks and other strangers prefer rain water, collected in a cistern, and sold for five farthings a gugglet. It was a favourite amusement with me to watch them whilst they drank the holy water, and to taunt their scant and irreverent potations."

The analysis of the water made by the writer fully confirmed this description of its unpleasant character. It consisted, in the main, of a strong solution of magnesium sulphate and common salt, and showed an extreme degree of pollution, as is seen by a glance at the following figures:—<sup>1</sup>

Grains per gallon.				Grains per gallon.			
Aluminium	..	..	0·8	Potassium..	..	24·3	
Calcium	..	..	0·5	Ammonium	..	5·3	
Silica	..	..	3·0	Chlorine	..	69·3	
Magnesium	..	..	6·6	Sulphates	..	30·7	
Sodium..	..	..	38·3	Nitrates	..	19·9	

The proportion of salts left on evaporation was 219·5 grains per gallon. On bacteriological examination it was found to be sterile, but this was not surprising, considering that it had been sealed up for upwards of half a century in an air-tight vessel.

<sup>1</sup> *Proc. Chem. Soc.*, 1893, IX., p. 245.

## CHAPTER II

### SPAS AND THEIR SPRINGS

AN interesting book might be written upon the spas of Europe, their rapid rise into fame, their struggles for existence, and, in many cases, their final disappearance. In the eighteenth century the success or failure of a spa was frequently a matter of luck, and many a watering place has owed its fortune not so much to the nature of its springs as to its having attracted the notice of some celebrated person, who has believed himself better for taking the waters, and has proved an advertisement of the place to Society.

Thus Cheltenham first became really famous as a spa through being visited by George III. in 1788, and this visit started a period of prosperity for the town, which lasted until the fashion turned in the direction of the German spas, at the end of the war, in 1815.

A gradual decline in the popularity of the Cheltenham Spa then followed, and by the middle of the last century it had few visitors. Thus, according to Muspratt, writing in 1860, it "furnished a striking proof that the *furor* for saline and other springs is daily abating; thousands used to rush yearly to partake of its waters, whereas it is now almost entirely deserted." Since then Cheltenham has again revived as a watering place, and is now in a flourishing condition, although it is no longer the exclusive resort of Society that it once was.

Other spas have never revived after their first desertion. Epsom Spa, for example, which during the eighteenth century rivalled Bath and Tunbridge Wells in attracting London society, has sunk into an oblivion from which it will never arise. Of the vast crowds who yearly attend the races at Epsom it is safe to assert that not one in a hundred could say where the wells are situated. This partly came about from the nature

of the water itself, and the fact that the same results could be obtained by the use of Epsom salts at home.

Among other spas that once enjoyed some measure of popu-

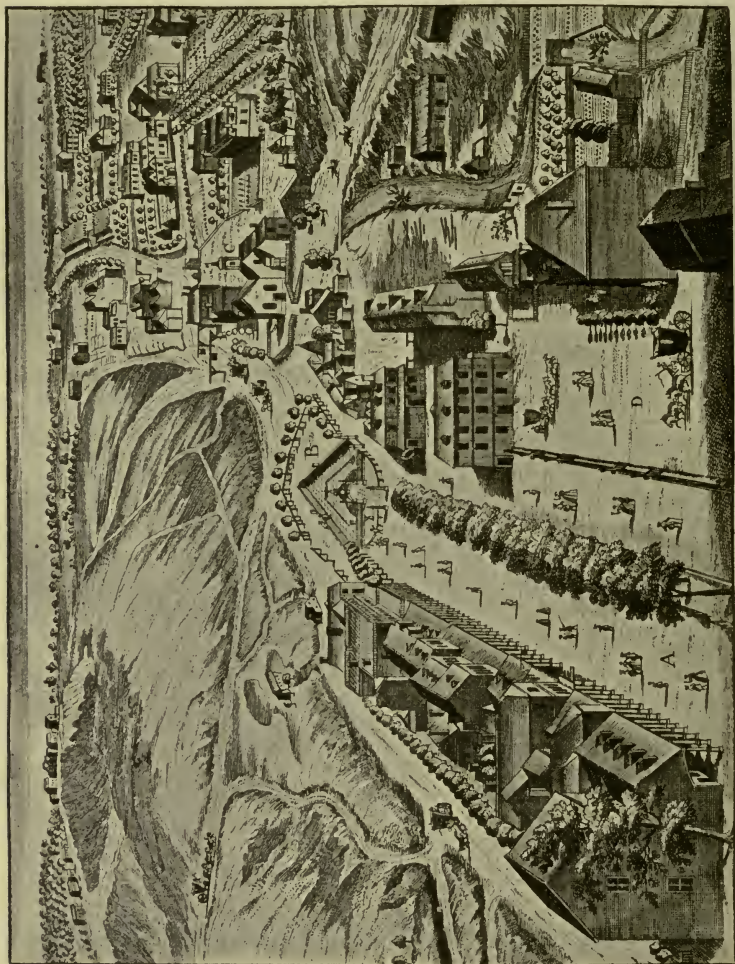


FIG. 2.—Plan of Tunbridge Wells in 1720.

A. The Public Walks. B. The Wells. C. The Chapel. D. The Market Place.

larity, and the memory of which is not always preserved even in local names, mention may be made of Islington, Dulwich, Streatham, and Hampstead.



The wells at Islington, the water of which was alkaline and non-effervescent, were still in use as late as the year 1860, and their name is recalled in the Sadlers Wells Theatre—now a music-hall.

The Streatham Spa has not even left so lasting a trace as this, although the present writer, a few years ago, was able to discover one of the springs, which then issued in a farmyard pool from which cattle were allowed to drink.

The Hampstead Spa, again, which was discovered in the early part of the seventeenth century, rapidly became famous, and was each year visited by crowds as great as those frequenting either Epsom or Tunbridge Wells. Its waters, which were chalybeate in character, are described by Elliott and other early writers upon the mineral waters of this country.

After a period of prosperity of more than half a century, Hampstead shared the fate of Epsom, and ceased to exist as a watering place, and finally the supplies of water to the wells themselves were affected by the excavations for the drainage system and the cuttings for the railways.

The shaded eighteenth-century raised pathway, still known as the " Pump Walk," is left as a reminder that there once was a spa at Hampstead.

During the early years of the Victorian period numerous books were published dealing in a more or less desultory fashion with the various springs of Germany, and some of these ran through many editions in this country. Their writers, who, by the way, frequently display an amusing animosity to one another, were medical men who established consulting practices in some of the German watering places that they recommended ; and their books proved good advertisements for the little towns—and for themselves.

The general effect, however, of this " booming " of the foreign watering places was that the well-known English spas were still further affected financially, while at the same time there was created a speculative movement for the establishment of new spas in various parts of England.

It was urged by the promoters of these schemes that since so much benefit was being derived from visits to the German

springs it ought to be possible to obtain the like benefits from similar springs at home. Hence, wherever a spring with any pretensions to being a mineral water was discovered it was exploited even when there was not the remotest chance of its proving a success. Companies were floated, each with an attractive prospectus, the money was subscribed and pump-rooms were put up in the approved style of a Grecian temple. The waters were there waiting to be "taken," but no one came to drink them, for in most instances these ill-fated spas, which were usually in out-of-the-way places, seldom survived their birth by more than a year or two, while some of them were still-born.

A striking monument of this folly may still be seen at Hockley, a small village in Essex. In the year 1842 a saline spring was found there, and its discovery was followed in the usual way by the building of a pump-room, with baths and a spa hotel. As was to be expected, the venture proved an absolute failure from the very first, and its abandoned Ionic pump-room still stands by the side of a country lane, while the "Spa Hotel" is now occupied by a coal dealer. The water itself appears to be quite unknown to any of the people in the village.

An amusing description of the struggle made by another of these mushroom spas to overcome the indifference of those whom it was so anxious to cure will be found in "The Chilterns and the Vale."<sup>1</sup> This spring was "discovered" at Dorton, a village at the foot of Brill Hill in Buckinghamshire, though, according to Lipscomb, the natives of the place had known of it long before, and had used its iron waters "in cutaneous diseases and for washing mangey dogs." A pump-room of the usual type was put up with its accompanying hotel, to which the attractive name of "Morris's Dorton Spa Rural Hotel" was given, and the advertisements described the place, which is about fifty miles from London, as "within a morning's drive of the metropolis."

But in spite of such specious advertising, and the giving of "*promenades musicales*" and fêtes, Dorton failed to capture

<sup>1</sup> "The Chilterns and the Vale," by G. Eland.

its share of the fashionable patients, who still preferred to go further afield to Bath and Tunbridge Wells.

In the absence of distinguished visitors the risk was too great for builders to put up houses, and this want of accommodation appears to have been another of the causes that accelerated the failure of the spa. After the year 1840 no further attempts seem to have been made to check the decline, and the pump-room was allowed to fall into ruins.

The well is still there, but only traces of the foundations of its ambitious pump-room can now be discovered.

**Classification of Spa Waters.**—Mineral springs are usually roughly classified into groups, in accordance with the chemical composition of the salts they contain or the physiological effects they produce. The varieties of waters typified by those of Bath and Buxton, which contain very little solid matter, were until recently often grouped together as “indifferent waters,” but the discovery of their radio-activity shows that this was a wrong description (*see* Chapter IV.).

For convenience of a general survey the principal waters may be considered under the heads of: I. *Alkaline Waters*; II. *Lithium Waters*; III. *Iron or Chalybeate Waters*; IV. *Aperient Waters*; V. *Sulphurous Waters*; VI. *Arsenical Waters*; and VII. *Barium Waters*.

Naturally, as in all classifications of natural objects, some of these groups overlap each other. Those waters that are more commonly used for drinking at table rather than medicinally are dealt with in the following Chapter.

### I. Alkaline Waters.

These waters are characterised by containing a considerable proportion of sodium carbonate, magnesium carbonate, or other alkaline salt as a main constituent, and are the most extensively used of all the mineral waters, especially in the treatment of digestive troubles and rheumatic complaints.

**AIX-LES-BAINS** (*Eaux des deux Reines*).—This is a slightly alkaline water, containing 1.99 grains of mineral solids per



pint, consisting almost entirely of calcium bicarbonate, with a very small quantity of magnesium bicarbonate and silica. The gases consist of carbon dioxide and oxygen.

AIX-LA-CHAPELLE (*Kaiserbrunnen*).—This water, which is also used as a digestive table water, contains 36 grains of total solids per pint, the chief constituent being sodium chloride (22·9 grains), sodium carbonate (5·8 grains), calcium carbonate (1·38 grains), sodium sulphate (2·48 grains), and potassium sulphate (1·34 grains), with smaller quantities of sodium sulphide, magnesium carbonate, silica and organic matter, and traces of many other salts.

BUXTON (*The Thermal Spring or St. Anne's Well*).—The waters of this spring have been used for centuries past for the treatment of gout, rheumatism, and similar troubles, but the undoubtedly good results that have been obtained are probably due, not to the alkaline salts, but to the radio-active properties of the water. According to an analysis quoted by Ingram and Royle the thermal water has the following composition :—Calcium bicarbonate, 1·762 ; magnesium bicarbonate, 0·752 ; sodium sulphate, 0·105 ; sodium chloride, 0·387 ; magnesium chloride, 0·118 ; silica, 0·118 ; carbon dioxide, 0·025 ; nitrogen, 0·025 grains ; and total solids, 3·416 grains per pint.

EMS.—The alkaline waters from the springs at Ems, in the valley of the Lahn, contain a large proportion of sodium bicarbonate, with a smaller amount of sodium chloride, calcium bicarbonate, and magnesium bicarbonate. According to an analysis of Fresenius, a sample of the Kesselbrunnen water contained 33·78 grains of total solids per pint, including 18·99 grains of sodium bicarbonate, 9·7 grains of sodium chloride, 2·27 grains of calcium bicarbonate, 1·79 grains of magnesium bicarbonate, 0·49 grain of potassium sulphate, together with traces of iron, phosphoric acid, and barium.

ÉVIAN.—The alkalinity of this water is mainly due to carbonates of calcium and magnesium, and is so small that the water is often used for drinking at table in France. An analysis of water from the Cachat Spring gave the following results :—Calcium carbonate, 1·72 ; magnesium carbonate, 0·71 ; sodium carbonate, 0·049 ; phosphates of iron and calcium, 0·007 ;



sodium sulphate, 0·069 ; potassium sulphate, 0·045 ; sodium chloride, 0·026 ; sodium nitrate, 0·025 ; and silica, 0·124 grains per pint, together with traces of lithium and iodine. Total solids, 2·78 grains.

KISSINGEN.—There are several saline springs at Kissingen, in Bavaria ; the best known of which is the “Rakoczy,” which was the name of its discoverer. Common salt is the main constituent in the waters, which contain much manganese chloride and calcium carbonate.

The following figures, quoted by Ingram and Royle, give the results of the analysis of three of the Kissingen springs :—

	Rakoczy Spring (by Liebig).	Pandur (1856).	Max Brunnen (1869).
	Grains.	Grains.	Grains.
Sodium chloride .. ..	50·943	48·306	20·267
Potassium chloride .. ..	2·510	2·112	3·290
Magnesium chloride .. ..	2·658	1·851	0·945
Lithium chloride .. ..	0·175	0·147	0·006
Manganese chloride .. ..	5·148	5·230	1·752
Calcium chloride .. ..	3·407	2·629	1·665
Magnesium bicarbonate .. ..	0·149	0·392	0·599
Calcium bicarbonate .. ..	9·283	8·879	4·945
Ferrous carbonate .. ..	0·276	0·242	0·021
Calcium phosphate .. ..	0·049	0·046	0·044
Silica .. ..	0·113	0·035	0·029
Sodium nitrate .. ..	0·814	0·031	0·676
Sodium bromide .. ..	0·073	0·062	—
Total solids, including other substances .. ..	74·867	79·96	34·24
Free carbon dioxide .. ..	11·42	13·17	11·0

VICHY.—The springs of Vichy, at the base of the Auvergne Mountains, are now under the control of the French Government, and the baths and bottling of the waters are supervised by State officials. Salts obtained by evaporation of the water are also sold for use in baths at home and are compressed into digestive lozenges.

The composition of the State springs as shown by the official analysis is as follows :—

—	Grande Grille.	Hôpital.	Celestins.
Sodium bicarbonate .. ..	2·442	2·515	2·552
Potassium bicarbonate .. ..	0·176	0·220	0·157
Magnesium bicarbonate .. ..	0·151	0·100	0·164
Strontium bicarbonate .. ..	0·001	0·002	0·002
Calcium bicarbonate .. ..	0·217	0·285	0·231
Iron bicarbonate .. ..	0·002	0·002	0·002
Sodium sulphate .. ..	0·146	0·145	0·145
Sodium phosphate .. ..	0·065	0·023	0·045
Sodium arsenate .. ..	0·001	0·001	0·001
Sodium chloride .. ..	0·267	0·259	0·267
Silica .. ..	0·035	0·025	0·030
Free carbon dioxide .. ..	0·454	0·533	0·525
Total grains per pint.. ..	<u>3·957</u>	<u>4·110</u>	<u>4·121</u>

WYCHIA WATER.—The water of the Wychia Spring at Droitwich differs from those given above, in that it is strongly saline (148 grains per pint), and contains relatively little carbonate, the principal salts being sodium chloride (87·0 grains) and sodium sulphate (58·3 grains). It is thus more akin to the aperient waters in Class III.

Among the numerous other waters which might also be mentioned here are St. Galmier, Perrier, Bath (Sulis), Malvern, and Taunus waters, which will be described under Table Mineral Waters.

## II. Lithium Waters.

Certain waters contain appreciable amounts of lithium salts, and have, therefore, been used in complaints for which lithium is prescribed. For example, the water of Bilin contains 0·062 grain of lithium carbonate per pint, while three of the Carlsbad springs contain from 0·106 to 0·12 grain. In some of the Royat waters the proportion of lithium is still greater, amounting to 0·306 grain of lithium chloride per pint.

Traces of lithium are present in the water of the Old Sulphur Well in Harrogate and in many other English mineral waters but not in sufficient quantity to have attracted special attention.

### III. Iron or Chalybeate Waters.

Many of the waters in this group are only distinguished from the alkaline and saline waters by the fact that they contain a notable proportion of iron, which is frequently kept in solution by the carbon dioxide.

Among the oldest and most celebrated iron waters are those of Tunbridge Wells (which are non-effervescent), Buxton, Pyrmont, and Spa. As a rule the proportion of iron in chalybeate waters ranges from 0.003 to 0.012 per cent.

**BUXTON CHALYBEATE WATER.**—This water, which is also bottled for table use, contains only 3.389 grains of mineral matter per pint, of which 0.42 grain is in the form of ferrous carbonate, 1.138 grains as calcium sulphate, and 0.612 grain as magnesium sulphate. It is commonly used as a tonic in anæmia.

**PYRMONT.**—The springs of Pyrmont in Waldeck are historically interesting from the fact that it was from experiments upon their water that the nature of the principal gas in mineral waters was discovered (*see* Chapter V.).

Pyrmont water was so much esteemed in the eighteenth century that it was bottled in large quantities and exported to Paris and London. Here, prior to the invention of soda water, it became a fashionable drink, and was extensively advertised by an agent who had his shop in Pall Mall.

The history of the spring and an account of experiments upon the nature of the water were published by Seip in 1712, who gives the curious plan (Fig. 3) of the place, and by his son in 1750. The water was also examined and described by many of the chemists of the latter part of that century.

The waters from the old Trinkbrunnen and the more recent Neu Brunnen are of very similar composition, both containing a little over 30 grains of mineral matter per pint, with from 0.6 to 0.7 grain of ferrous carbonate.

Analyses by Wiggers of the chief constituents of these waters, expressed in grains per pint, were as follows :—



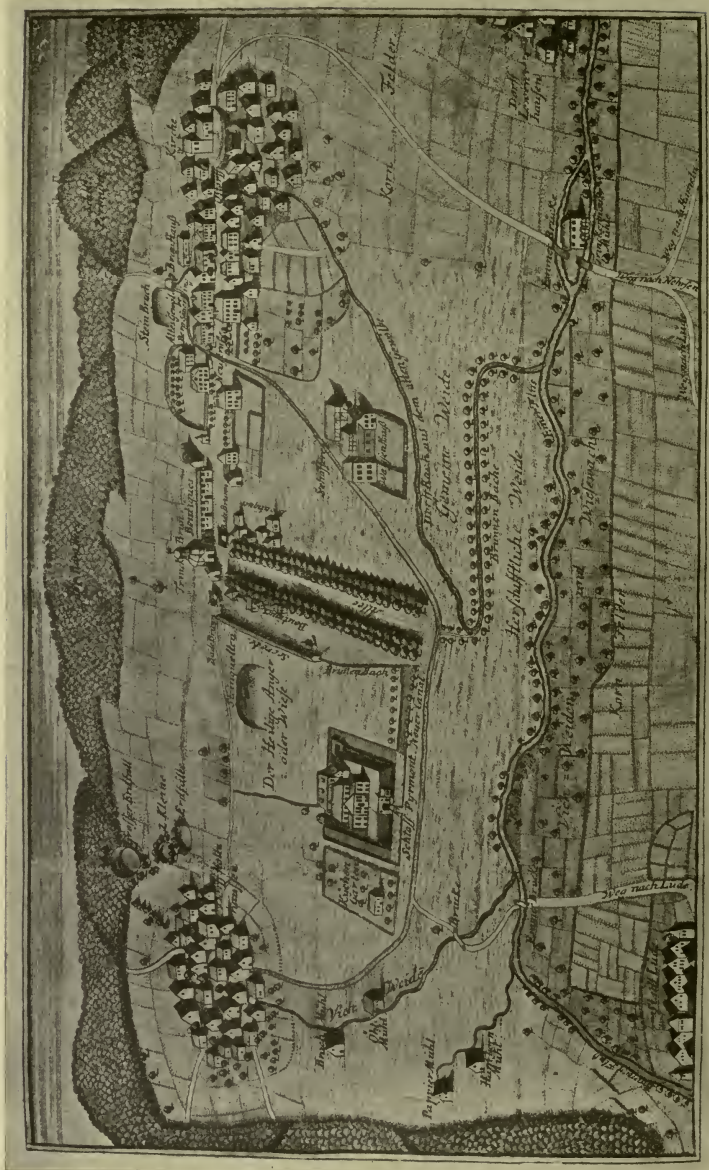


FIG. 3.—Plan of Pymont in 1712.

	Trinkbrunnen.	Neu Brunnen.
Ferrous bicarbonate .. ..	0·72	0·57
Calcium bicarbonate .. ..	13·10	15·47
Manganese bicarbonate.. ..	0·06	1·27
Magnesium bicarbonate.. ..	0·22	0·27
Calcium sulphate .. ..	11·32	0·59
Potassium sulphate .. ..	0·29	0·62
Sodium sulphate.. ..	—	2·77
Magnesium sulphate .. ..	4·86	3·69
Sodium chloride .. ..	0·64	11·13
Lithium chloride .. ..	0·03	0·02
Magnesium chloride .. ..	0·87	—
Silica .. ..	0·03	0·36
Total solids .. ..	32·16	36·93
Free carbon dioxide .. ..	19·26	17·08

SPA WATER.—Another water of historic interest, to which frequent reference is made in these pages, is that of Spa, or “Spaw” as it is termed by the early writers. In the later part of the eighteenth century this water shared, with the celebrated Pyrmont water, the place now occupied by soda water, and was imported into London in large quantities. With the development of the artificial mineral-water industry the sale of both these waters came to an end, and it is only recently that they have again been imported in bottles.

The Spa mineral water is obtained from four springs, which differ somewhat in composition ; that containing the largest proportion of iron is derived from the “Prince de Condé” Spring, which, according to a French analysis quoted by Ingram and Royle, has the following composition :—Total solids, 4·57 grains ; consisting of carbonates of sodium and potassium, 0·87 ; calcium carbonate, 0·96 ; magnesium carbonate, 0·87 ; sodium chloride, 0·22 ; sulphates of sodium and potassium, 0·17 ; iron oxide, 1·04 ; and silica, 0·44 grains per pint. Free carbon dioxide, 0·875 grains. The water of this spring and the other springs at Spa is cold, as it leaves the rock.

HOMBURG WATERS.—Among the best known of the Continental spas and most frequented by those in search of a “cure”

must be ranked the springs of Homburg. The predominating mineral constituents in the waters of the four springs are common salt, calcium and magnesium carbonates, magnesium chloride and iron carbonate.

The composition of the water from the Elisabethbrunnen was found by Liebig to be as follows :—Sodium chloride, 98.94 ; magnesium chloride, 9.74 ; ferrous carbonate, 0.57 ; calcium carbonate, 13.74 ; sodium sulphate, 0.47 ; magnesium carbonate, 2.51 ; and silica, 0.4 grains per pint. Total solids, 126.37 grains ; and free carbon dioxide, 26.85 grains per pint.

MARIENBAD.—The waters of the Marienbad springs contain about 100 grains per pint of mineral matter, about half of which is sodium sulphate. The other principal salts are bicarbonates of sodium, calcium, magnesium and iron, and sodium chloride. The amount of iron varies from about half to three-quarters of a grain per pint.

Other well-known waters containing iron include those of Fachingen, Schwalbach, Nauheim, and St. Moritz.

Iron mineral waters are frequently subdivided into “sulphated” or “aluminated” and carbonated. The former are often very strong and need dilution. Examples of such springs occur in Wales, Scotland, and the United States. The English chalybeate waters usually contain much less carbon dioxide than the Continental iron springs.

#### IV. Aperient Springs.

The waters classified under this heading contain a large proportion of magnesium sulphate or sodium sulphate, with smaller quantities of sodium chloride and other salts.

In the seventeenth century the waters of Epsom became celebrated all over Europe owing to their being strongly charged with magnesium sulphate (hence known as Epsom salts). The description of their discovery, as given by Nehemiah Grew in 1697,<sup>1</sup> merits quotation :—

“The mineral waters arising near Epsom in Surrey, the chief of all the bitter purging waters, were found out by a country-

<sup>1</sup> “A Treatise of the Nature and Use of Bitter Purging Salts Contained in Epsom and other such Waters.” Nehemiah Grew, M.D. London, 1697.



man in or about the year 1620. The country people first used them for external complaints. . . . Afterwards Lord North, having drank the Spaw waters in Germany, resolved to try the virtues of these Epsom waters (flattering himself, I suppose, that he had found chalybeate waters at his own door). A few years after the discovery was published others of the same sort grew into tolerable repute and use. The names of the principal are : Barnet, North Hall, Acton, Cobham, Dullidge, and Stretham."

Epsom soon attracted royalty. Charles II. often stayed there with his Court, and subsequently Queen Anne, before her accession, made it a favourite resort.

The fame of Epsom led to the discovery of similar springs abroad, and early in the eighteenth century Hoffmann published an account of the occurrence of the bitter Epsom salt in the waters of Seidlitz.

OLD SPRINGS.—The waters of Seidlitz and of Saidschutz are still bottled for exportation, whereas those of Epsom have long since ceased to be generally used.

The *Saidschutz Water*, which comes from a spring not far from Seidlitz, has a similar composition to the latter, containing about 178 grains per pint of mineral salts, of which 84 grains are magnesium sulphate and 47 grains sodium sulphate.

*Püllna Water* comes from a cold spring at Püllna, near Carlsbad, and was used by the villagers long before it was bottled for exportation. It contains about 310 grains of solid matter per pint, of which 155 grains are sodium sulphate and 116 grains magnesium sulphate.

*Friedrichshal.*—Originally this spring was used for the extraction of the salt it contained, and it was not until the middle of the last century that it began to be used medicinally. Since then the water has been bottled and exported in increasingly large quantities.

According to the analysis of the Municipal Chemists of Breslau, it contains 212·64 grains of salts, consisting of 54·39 grains of magnesium sulphate, 45·61 grains of sodium sulphate, 69·64 grains of sodium chloride, and 43·0 grains of magnesium chloride.

ENGLISH SPAS.—The chief English aperient waters, several of which are now bottled, are those of the Chadnor Well at Cheltenham, and Leamington.

*Cheltenham.*—The water of Chadnor Well, which is also described as the “magnesia sulphate saline,” contains 38 grains of mineral salts, including 14·7 grains of magnesium sulphate, 7·6 grains of sodium sulphate, and 3·0 grains of sodium chloride per pint.

*Leamington.*—In the Leamington spa water there are 155·3 grains of salts, consisting largely of sodium and magnesium chlorides and sulphates. The following analysis is quoted by Ingram and Royle:—Sodium, 52·53; magnesium, 3·31; calcium, 10·90; chlorine, 65·75; sulphuric acid, 22·81; iron oxide, 0·005, with traces of silica and carbonic acid.

MODERN SPRINGS.—Of the modern aperient springs, the water of which is bottled in enormous quantities and exported for sale all over Europe, the most widely known are “Aesculap,” “Apenta,” and “Hunyádi János.”

*Aesculap.*—This spring at Budapest was found in 1868 by a peasant, and was bought in 1881 by the present company. According to the analysis of Mohr, it has the following composition:—Sodium sulphate, 121·68; magnesium sulphate, 151·20; calcium sulphate, 18·19; sodium chloride, 25·42; sodium carbonate, 8·74; manganese carbonate, 0·375; and alumina, 0·303 grains per pint, with traces of potassium, ammonium sulphate, and silica. Total mineral matter, 326·216 grains per pint.

*Apenta Water.*—Another Hungarian spring, the waters of which are strongly saline, is described by the name of “Apenta.” Its chief saline constituents are magnesium sulphate and sodium sulphate in approximately equal quantities. An analysis of the water by Tichborne gave the following results:—Magnesium sulphate, 184·65; magnesium carbonate, 1·59; magnesium bromide, 0·1; sodium sulphate, 163·82; calcium sulphate, 23·09; potassium sulphate, 0·73; lithium sulphate, 0·66; sodium carbonate, 4·19; calcium carbonate, 1·03; ferrous carbonate, 0·67; alumina, 0·26; and silica, 0·28 grains. Total solids, 389·58 grains per pint.



*Hunyádi János.*—This aperient spring, which is also in Hungary, has been known for over half a century, and its waters are now bottled and exported to all parts of the world. According to Bunsen's analysis, it has the following composition:—Sodium sulphate, 197·32; magnesium sulphate, 195·56; potassium sulphate, 1·06; sodium bicarbonate, 5·91; strontium bicarbonate, 0·24; calcium bicarbonate, 6·99; sodium chloride, 14·92; ferrous bicarbonate, 0·005; and silica, 0·09 grains per pint. Total solids, 422·10 grains, and carbonic acid (free and as bicarbonate), 4·57 grains per pint.

### V. Sulphurous Waters.

Numerous springs owe their therapeutic effect to the presence of small quantities of sodium sulphide, sulphuretted hydrogen, and other sulphur compounds. The most celebrated of these are the springs of Aix-la-Chapelle, which have been used medicinally from the time of the Romans.

The Kaiserbrunnen water at Aix contains 31·5 grains of salts (mainly sodium chloride and sodium carbonate), with 0·073 grain of sodium sulphide per pint, while the gases in solution contain 0·31 per cent. of sulphuretted hydrogen.

Of the sulphur springs in this country, the Old Sulphur Well at Harrogate is the oldest. On standing this water becomes turbid from the separation of sulphur.

According to an analysis by Sir Edward Thorpe, it contained 1,047 grains of salts per gallon, largely in the form of chlorides and carbonates of sodium, calcium, and magnesium. The sulphur amounted to 6·53 grains per gallon, and the free hydrogen sulphide to 10·16 grains.

Other well-known sulphur springs are at Aix-les-Bains, Baréges, and Strathpeffer, the water of which contains 0·026 part of sodium sulphide per 1,000.

The sulphur springs of Aix-la-Chapelle, Aix-les-Bains, and Luchon, in the Pyrenees, are typical of hot sulphurous waters.

### VI. Arsenical Waters.

Owing to the fact that they contain medicinal doses of arsenic, the waters of certain special springs are frequently prescribed both for external and internal use.

The most celebrated of these springs are those of La Bourboule, in the South of France, which contain about 0·06 grain of arsenic per pint.

Other well-known arsenical springs are those of Levico, in South Tyrol, the Guber spring in Bosnia, and the springs of Royat and Roncegnon.

The following table gives the main constituents of some of these springs in grains per pint :—

—	Levico.	Guber.	La Bourboule.
Arsenious acid .. ..	0·0762	0·061	0·095
Sodium chloride .. ..	0·001	0·017	24·91
Ferrous sulphate .. ..	22·51	3·734	—
Ferric sulphate .. ..	11·42	—	—
Aluminium sulphate .. ..	5·56	2·27	—
Calcium sulphate .. ..	3·26	0·21	—
Calcium bicarbonate .. ..	—	—	1·67
Magnesium sulphate .. ..	3·36	0·22	0·28
Potassium sulphate .. ..	0·03	0·166	1·42
Sodium sulphate .. ..	0·27	0·037	1·83
Sodium bicarbonate .. ..	—	—	25·36
Silica .. ..	0·27	0·65	1·05
Free sulphuric acid .. ..	—	0·09	—
Zinc .. ..	—	0·08	—
Total solids .. ..	46·89	7·63	56·99

## VII. Barium Waters.

**BARIUM SALTS.**—In many natural spring waters relatively large quantities of barium are present in solution, and in some cases may account for the therapeutic action of the waters. Thus Muspratt, in 1867, discovered 0·05 part of barium as barium oxide in the water of the Old Sulphur Well at Harrogate, and it was still present in 1875, when Thorpe found 0·068 part per 1,000.

From 38·5 to 40·7 parts per 100,000 of barium chloride were found by White in deep-well water from Ilkeston, in Derbyshire. and 41·00 parts of barium chloride per 100,000 by Richards in the waters of Boston Spa.

Boston Spa was a popular inland watering place at the close of the eighteenth century, but it was gradually deserted as Harro-

gate became better known. At the time of the prosperity of the spa the water was drunk as a chalybeate water, although it only contains 1·5 parts per 100,000 of ferrous carbonate.

These mineral waters containing a high proportion of barium chloride have many points in common, their saline constituents including much calcium chloride and magnesium chloride, and a large percentage of sodium chloride (*e.g.*, 1,084 parts out of 1,271 parts per 100,000 in the Boston spa water).

*The Barium Spring of Llangammarch.*—About the year 1830 a remarkable spring was discovered by a peasant in the bed of the River Irvon, which was then almost dry. Examination of the nauseous water showed that it contained a large proportion of barium and calcium chlorides. After being used for many years by the natives for the treatment of chronic rheumatism, its fame gradually spread, and Llangammarch wells are now celebrated all over Europe. Soon after its discovery the well was protected by a wall from the river, but it was not until many years later, when the fame of the water had begun to attract visitors from outside, that a pump-room was built and the usual accompaniments of a spa were provided.

The water, which is largely prescribed for heart troubles and rheumatism, remains remarkably constant in composition, as is shown by the following analyses made by Dupré in 1883 and by the *Lancet* in 1896 :—

—	1883. Grains per gallon.	1896. No. 1. Grains per gallon.	1896. No. 2. Grains per gallon.
Sodium chloride .. ..	189·56	186·20	185·90
Calcium chloride .. ..	84·56	85·16	85·74
Magnesium chloride .. ..	24·31	20·10	20·31
Calcium carbonate .. ..	2·80	—	—
Silica and alumina .. ..	1·40	3·34	3·10
Bromine as bromide .. ..	trace	trace	trace
Lithium chloride .. ..	—	0·85	0·91
Ammonium chloride .. ..	—	0·26	0·26
Barium chloride .. ..	6·26	6·75	6·49
Total Solids .. ..	308·89	302·66	302·71

In connection with the presence of barium in natural waters it is interesting to note that under certain conditions both barium and sulphates may be simultaneously present. This is the case with the waters of Nérès-les-Bains, in the neighbourhood of which place several quarries of fluorides and one of the mineral barytes are being worked.

Experiments made by Carles<sup>1</sup> have shown the way in which this curious phenomenon may occur. If a mineral water contain sulphates and bicarbonates, and an excess of free carbon dioxide, it is capable of decomposing barium sulphate with the formation of a soluble barium bicarbonate, and it is probable that the lead which is also present in Nérès-les-Bains waters may owe its origin to an analogous cause.

<sup>1</sup> *Ann. Chim. Anal.*, 1902, VII, p. 9.



## CHAPTER III

### NATURAL MINERAL TABLE WATERS

It has long been a general custom in France and Germany to drink some of the less saline mineral waters at the table, either alone or mixed with wine, and in recent years the practice has gradually become fairly common in this country. It is only a certain kind of mineral water that is suitable for this purpose, since obviously the proportion of salts in solution must not amount to a medicinal dose. Hence, of the older spa waters, only those which, like the waters of Buxton, Bath and Malvern, are relatively poor in mineral constituents have been bottled for use in this way.

In the case of some of these waters, aeration with carbon dioxide under pressure is employed so as to render them more palatable and sparkling and to keep the salts in solution. This class of waters, therefore, forms a connecting-link between the strongly saline medicinal mineral waters and the purely artificial products of the manufacturer.

The natural mineral table waters are characterised by containing from about 4 grains to 22 grains of solid constituents per pint, usually consisting chiefly of carbonates of sodium, magnesium and calcium, sodium chloride, and sulphates of sodium and calcium.

The owners of most of the principal mineral springs of Europe and the United States now bottle their waters, and in many instances special carbonating plant has been erected so as to re-impregnate the water with its own gas.

It is, therefore, not possible to draw any sharp distinction between the old-fashioned spas where a "cure" is followed by drinking the waters and taking baths upon the spot, and the more modern mineral springs, which partake more of the nature of a factory than a spa.



Speaking generally, however, it may be said that as a rule the mineral waters that are used as table waters come from these natural mineral-water factories rather than from the spas in the old sense of the word.

The method of collecting and bottling these waters will be understood from the following details concerning the Apollinaris spring, for most of which the writer is indebted to the courtesy of the Apollinaris Company:—

*The Apollinaris Spring.*—The spring in the Valley of the Ahr, in Prussia, was discovered in the year 1852, and since the establishment of the company, twenty-one years later, has steadily risen in popularity. During the first year's work two million bottles of the water were exported, while last year the output had risen to thirty-seven millions.



FIG. 4.—General View of the Works at the Apollinaris Spring.

The water issues from the rock 50 feet below the surface, at a temperature of  $22^{\circ}$  C., and is highly charged with carbon dioxide.

The method of bottling employed is to collect in a funnel-shaped receptacle as much as possible of the gas emitted simultaneously with the water, and to conduct it into copper reservoirs. Thence it is drawn off, and is forced, under increased pressure, into bottles previously charged with the spring water. The process is thus analogous to that employed in the manufacture of soda water, the chief difference being that the

gas is derived from a natural source and has already been in association with the water itself.

We may assume that the water as contained within pockets in the rock is charged with the gas under a considerable pressure, and that most of this gas escapes upon exposure of the water to the ordinary atmospheric pressure.

The final product in the bottles thus consists of a slightly alkaline water re-charged under pressure with carbon dioxide derived from the same source, so that it shall contain, as far as possible, the same proportion of gas as is present in the water when it issues from the rock.

The composition of the mineral water corresponds with that of a solution containing the following proportions of salts :—

Analysis by Kyll (1907).	Parts per 1,000.
Sodium chloride .. .. .	0·438,
Sodium sulphate .. .. .	0·247,
Sodium bicarbonate ( $\text{NaHCO}_3$ ) .. .. .	2·015
Calcium bicarbonate .. .. .	0·400
Magnesium bicarbonate .. .. .	0·858
Iron bicarbonate [ $\text{Fe}(\text{HCO}_3)_2$ ] .. .. .	0·084.
Silicic acid (meta) ( $\text{H}_2\text{SiO}_3$ ) .. .. .	0·030.
	<hr/>
Free carbon dioxide .. .. .	3·996
(1,124 c.c. at 21·2° C. and 760 mm. barometer.)	2·042
	<hr/>
	6·038

During the bottling process part of the iron is precipitated, while, as stated above, carbon dioxide that has separated from the water is re-introduced under pressure.

The water of the Apollinaris spring is moderately radioactive, and according to Kyll's determinations shows about 3·78 Mache units per litre per hour.

*Gerolstein Water.*—A slightly alkaline table water is derived from a well sunk in the neighbourhood of the Casselburg Castle in the Eifel Mountains. According to analyses given by Ingram and Royle, this has the following composition in grains per pint :—

Sodium carbonate ..	..	..	..	7.18
Calcium carbonate..	..	..	..	5.00
Magnesium carbonate	..	..	..	3.99
Sodium chloride ..	..	..	..	2.19
Sodium sulphate ..	..	..	..	0.89
Silica.. ..	..	..	..	0.73



FIG. 5.—The Labelling Hall, Apollinaris Spring.

Together with minute quantities of lithium, iron, bromide and phosphate, and a trace of barium (0.00078 grain), the total solid matter is 20.03 grains, and the carbonic acid gas expressed as bicarbonates is equivalent to 7.28 grains per pint.

*Johannis Table Water.*—This is obtained from a spring which issues at a temperature of 50° F. from a rock near Aarthal, in Hesse-Nassau. Its chief constituents were found by Plaskuda to be as follows :—

Sodium bicarbonate	..	..	..	3·19
Potassium bicarbonate	..	..	..	0·11
Calcium bicarbonate	..	..	..	6·48
Magnesium bicarbonate	..	..	..	2·66
Sodium chloride	..	..	..	8·95
Sodium sulphate	..	..	..	0·26

Together with traces of manganese, iron, lithium and silica, the total solid constituents were 21·79 grains and the free carbon dioxide 21·33 grains per pint.

*Sulis Water.*—This is the name given to the natural mineral water of Bath after artificial saturation with carbon dioxide to keep the iron salts in solution. The following analyses, quoted by Ingram and Royle, show that, as regards its solid mineral constituents, the water as put up for table use is practically identical with that derived from the spring :—

					Natural Bath Water.	Aerated Sulis Water.
					Grains per pint.	Grains per pint.
Calcium bicarbonate	..	..			0·98	0·95
Calcium sulphate	..	..	..		11·76	11·88
Calcium nitrate	..	..	..		0·07	0·07
Magnesium bicarbonate	..	..	..		1·90	1·87
Magnesium chloride	..	..	..		1·90	1·87
Sodium chloride	..	..	..		1·89	1·92
Sodium sulphate	..	..	..		2·89	2·85
Potassium sulphate	..	..	..		0·83	0·86
Ammonium nitrate	..	..	..		0·13	0·11
Ferrous bicarbonate	..	..	..		0·15	0·14
Silica	..	..	..	..	0·33	0·32
Total solid constituents					21·00	21·02

*Tansan Table Water.*—This is an effervescent water derived from springs in volcanic rock near Kobé, in Japan. Its composition, as given by Ingram and Royle, is as follows :—Sodium chloride, 1·42 ; potassium chloride, 1·49 ; calcium sulphate,



0.09 ; calcium carbonate, 0.59 ; magnesium carbonate, 0.06 ; iron carbonate, 0.02 ; and silica, 0.28 grains. Total solid constituents, 3.95 grains per pint.

*Perrier Water.*—This table water, which is extensively used in France, is slightly alkaline and is naturally highly charged with carbon dioxide. According to an analysis made by Hake, it contains 3.36 grains of solids per pint, consisting of 2.37 grains of calcium carbonate, 0.38 grain of calcium sulphate, 0.22 grain of sodium chloride, and 0.21 grain of silica, with minute quantities of iron, magnesium, and nitrate.

*St. Galmier.*—Still more popular French mineral waters are those from the different springs of St. Galmier, which are now under the control of one company. The total sales of these waters are stated to exceed a hundred million litres per year.

The following analyses of the water from three of the St. Galmier wells are quoted by Ingram and Royle :—

	" Romaines " Spring.	" Badoit " Spring.	" Noel " Spring.
Sodium bicarbonate .. ..	5.91	4.90	2.62
Magnesium bicarbonate .. ..	7.18	{ 12.60 }	3.19
Calcium bicarbonate .. ..	10.08		5.86
Potassium bicarbonate .. ..	7.90	0.18	—
Sodium sulphate .. ..	0.13	{ 1.75 }	1.05
Calcium sulphate .. ..	0.30		0.62
Magnesium sulphate .. ..	0.15	—	—
Sodium chloride .. ..	0.74	—	0.58
Magnesium chloride .. ..	0.24	4.20	—
Calcium chloride .. ..	0.34	—	—
Aluminium silicate .. ..	—	1.17	—
Total solids .. ..	—	24.80	13.92
Free carbon dioxide ..	27.14	42.90	—

*Rosbach Water.*—This table water, which is obtained from a spring near Homburg, is alkaline and salt, and is naturally saturated with carbon dioxide. An analysis made by Sir Charles Cameron showed that the water contained 15.11



grains of mineral solids per pint, composed of 10·29 grains of sodium chloride ; 3·12 grains of calcium carbonate ; 1·63 grains of magnesium carbonate ; 0·07 grain of magnesium chloride, with traces of calcium sulphate, iron, silica, etc.

*Taunus Water*, which comes from a spring near Frankfort, is very popular in Germany as a table water. It contains a somewhat high proportion of mineral solids, mainly chlorides of sodium and potassium, and bicarbonate of calcium, and is saturated with carbon dioxide.

An analysis by Taylor gave the following results :—Total solids, 39·06 ; containing sodium chloride, 22·49 ; potassium chloride, 2·36 ; calcium bicarbonate, 11·99 ; magnesium bicarbonate, 1·54 ; sodium bicarbonate, 0·17 ; and calcium sulphate, 0·51 grains per pint ; together with traces of silica, aluminium, and calcium phosphate.

*Selters Water*.—The history of the Ober-Selters Spring, in Nassau, is curious. During the eighteenth century it was in great repute, and was the water of which the modern French water (*Eau de Seltz*) was originally an imitation. After the year 1794 its popularity had declined to such an extent that the spring was abandoned, and it was not until the year 1870 that the increasing demand for sparkling mineral waters caused the spring to be re-opened and works put up for bottling the water.

The water issues from the rock at a temperature of 53° F., and is so highly charged with carbon dioxide that it is bottled as it leaves the spring, any artificial process of carbonating being quite unnecessary.

According to Mohr's analysis, it has the following composition :—Total mineral matter, 32·54 grains ; consisting of potassium sulphate, 20·38 ; sodium bicarbonate, 7·31 ; calcium bicarbonate, 2·15 ; magnesium bicarbonate, 1·77 ; and silica, 0·46 grains per pint ; together with small quantities of iron, manganese, aluminium, arsenious acid, boric acid, phosphoric acid, and bromine. The gases consisted of 91·2 per cent. of carbon dioxide, 7·9 per cent. of nitrogen, and 0·9 per cent. of oxygen.

*Selters Water (Nieder)*, from a spring near the village of Nieder-

Selters, is also an alkaline table water containing about 39 grains of total solids per pint, consisting mainly of sodium chloride, 20·47; sodium bicarbonate, 10·84; calcium carbonate, 3·9; and manganese carbonate, 2·7 grains; with minute quantities of many other salts.

In addition to these typical table waters mention may also be made of Malvern table water, which contains 6·5 grains of mineral solids per pint (mainly carbonates of sodium, calcium and magnesium, sodium chloride, and a trace of sodium iodide); and of the Buxton water, which in addition to its medicinal uses is also bottled for table purposes.

## CHAPTER IV

### THERMAL SPRINGS AND RADIO-ACTIVITY—TEMPERATURES— HELIUM AND NITON IN MINERAL WATERS—MEASUREMENT OF RADIO-ACTIVITY—ARTIFICIAL RADIO-ACTIVE MINERAL WATERS

**Thermal Springs and Radio-activity.**—Although most of the mineral waters that issue from the earth at a high temperature have been mentioned under various other headings, they are so often grouped apart as “thermal waters” that they may be conveniently regarded as a separate class from this point of view. They are prescribed both for baths and for drinking, and, as is mentioned below, the results have been ascribed to a particular form of heat.

The following list shows the temperature of the water of some of the best-known thermal springs :—

		Deg. F.			Deg. F.
Buxton	..	80—82	Aix-la-Chapelle	..	113—140
Teplitz	..	101—120	Carlsbad	..	119—138
Bath	..	108—122	Bourbonne	..	114—149
Lucca	..	108—122	Caldas (Barcelona)	..	153—158

**Temperature of Mineral Springs.**—The high temperature of such springs as these has been made the subject of various ingenious speculations. In some cases volcanic action affords a probable explanation of the heat of the water, as, for example, the hot springs of the Auvergne district and the geysers of Iceland.

Gairdner, in his book upon natural mineral water,<sup>1</sup> gives a series of tables, in which it is shown that out of ninety-nine hot springs in Europe and America, no less than twenty-five issue from rocks of volcanic origin and thirty-five from rocks of primitive formation.

<sup>1</sup> Essay on Thermal and Mineral Springs, by Meredith Gairdner, M.D., 1832.

Granville was the first to put forward the theory that the heat in these thermal springs was of different origin to ordinary solar heat, and that the peculiar therapeutic effects of such waters must be attributed to the nature of their inherent heat.

“If you were to boil a Wildbad bath,” he remarks, “after a day’s exposure to the air, does anybody suppose that the effect would be the same on the human body as when the water employed is oozing from the rock? Most certainly not.”

The experiment, he points out, had already been tried on a large scale in the case of the hot springs of Carlsbad, Baden-Baden and Bath, and had utterly failed; and although at one time the waters from these springs had been bottled and sent all over the world, this was no longer attempted at the time when he was writing (1843).

To the impossibility of substituting artificial heat for what he termed *telluric* heat in hot spring waters, Granville also attributed the inferiority of Struve’s artificial Ems and Carlsbad waters, made in Brighton, as compared with the natural waters at the fountain-head.

On the other hand, Muspratt, writing in the year 1860, remarked:—“About forty years ago, when the fabrication of mineral and spa waters commenced, a very violent opposition arose with regard to them, especially from the members of the faculty. They were said to be devoid of all the good qualities of the natural ones—to be minus a certain *conditio sine quâ non* in the shape of a *spiritus rectus* or vital force, which imparted the medicinal properties. The Editor has lived to see such statements reversed. Chemistry, the great revealer of hidden treasures, has demonstrated to a certainty what the constituents of the natural waters are, and thus one is now enabled to produce artificial waters quite equal, if not superior, to the natural ones.”

As has happened in so many other cases, the negative “certainty” of one generation has been shaken by the discoveries of the next. In the light of the striking demonstration by Sir William Ramsay of the radio-activity of the waters of Bath, it seems probable that this mysterious “vital force” has been discovered.



In fact, Muspratt himself was not always so positive as in the passage quoted above, for in another place he speaks of "a certain mystery connected with the origin and mode of operation of some mineral waters," and continues:—"Many of these waters, and especially the thermal ones—Buxton *et cetera*—produce effects in general estimation far beyond what can be accounted for by their chemical composition and the power of their *known* ingredients, or by their temperature as shown by the thermometer in comparison with those of ordinary water baths."

The recent discovery that radio-active properties are associated with the gases argon, helium, and niton in mineral waters has opened up a fresh field of speculation as to the origin of the heat of hot springs. While in some cases volcanic action may still supply the explanation, in others the disintegration of radium is regarded as a more probable cause.

Thus, Dr. Julius Weszelsky has asserted that he has grounds for concluding that the celebrated hot springs of Ofen owe their temperature to the presence of huge deposits of radium below the town of Budapest. This assertion, however, stands in need of corroboration, although it is significant that the gases emitted by certain hot springs in different parts of the world contain appreciable quantities of helium and niton, the formation of which from radium involves the liberation of heat.

The property of radio-activity appears to be widely distributed in spring waters all over the world, and where its amount is considerable frequently occurs in association with uranium deposits in the vicinity of the well, as, for example, in the mining districts in Saxony. This is not an invariable rule, however, for strongly radio-active springs are known, in which the source of the radium cannot be so easily traced.

**Helium and Niton.**—The first discovery of helium in a mineral water was made in 1895 by Lord Rayleigh, a few years after the discovery of the element itself.

It was shown to be present in the gases escaping from the King's Well at Bath in the proportion of 1.2 parts per 1,000, but the significance of the fact was not made clear, until in



1903 there came the striking discovery by Sir William Ramsay and Mr. Soddy, that helium was a product of the disintegration of radium, and that its presence in the water was thus an indication of radio-activity.

The presence of radium itself was detected by the Hon. R. J. Strutt both in the waters of Bath and in the deposits from the hot springs, and this has been followed by the recent estimation by Ramsay of the amount of niton in different waters of Bath, and the natural gases given off by them.<sup>1</sup>

The gas from the King's Well was estimated to amount to 4,927 litres in twenty-four hours, and consisted of 360 parts of carbon dioxide and 9,640 parts of nitrogen, etc., per 10,000. There was no oxygen, hydrogen, or marsh gas.

The nitrogen contained 73·63 per cent. of argon, 23·34 per cent. of neon, and 2·97 per cent. of helium. The pump-room water contained in solution 18·5 parts of gas per 1,000, consisting of 6·9 parts of carbon dioxide and 11·6 parts of nitrogen, etc.

The inert gases argon, neon, and helium have also been found in numerous other spring waters in England and on the Continent, and they appear always to occur in association with niton (radium emanation).

Thus in the case of three of the well-known thermal springs at Wiesbaden, the gases contained in the waters were found by Henrich<sup>2</sup> to have the following percentage composition :—

	Kochbrunnen.	Adlerquelle.	Schutzenhofquelle.
Carbon dioxide (absorbed by KOH) .. .. .	84·8	77·6	32·4
Oxygen .. .. .	0·2	1·2	0·2
Nitrogen .. .. .	12·7	18·4	62·05
Methane .. .. .	0·6	0·8	0·45
Argon, neon, helium, etc., and radium emanation .. .. .	1·7	2·0	4·9
	100·0	100·0	100·0
Temperature of the Spring ..	68·7° C.	64·6° C.	49·2° C.

<sup>1</sup> *Chem. News*, 1912, CV., p. 134.

<sup>2</sup> *Ber. d. d. Chem. Ges.*, 1908, XLI., p. 4,196.

The composition of the gases varied in an irregular fashion at different seasons of the year.

It is probable that the gases have their origin in rocks in the neighbourhood of the springs, judging by the fact that fragments of the rocks, when heated, emitted oxygen, nitrogen, helium, and argon. The oxygen would be absorbed by the ferrous carbonate in the water.

Some of the French mineral springs give off natural gases particularly rich in helium. For example, the following results have recently been obtained by Moureu and Lepape <sup>1</sup> in the examination of certain well-known waters :—

Spring.	Per cent. of Helium in Natural Gas.	Yield in litres per annum.	
		Natural Gas.	Helium.
Sautenay (Côte d'Or)— Source Lithium .. ..	10·16	51,000	5,182
„ Carnot .. ..	9·97	173,000	17,845
„ Fontaine-Salée .. ..	8·40	—	—
Maizières (Côte d'Or)— Source Romaine .. ..	5·92	18,250	1,080
Grisy (Saône-et-Loire)— Source d' Ys. .. ..	2·18	—	—
Bourbon-Lancy— Source du Lymbe .. ..	1·84	545,500	10,074
Néris (Allier)— Source César .. ..	0·97	3,504,000	33,990
La Bourboule (Puy-de-Dôme)— Source Choussy .. ..	0·1	30,484,800	3,048

Assuming the helium to have been originally derived from the disintegration of radio-active substances, these French chemists consider that it probably consists of dissolved helium

<sup>1</sup> *Comptes Rendus*, 1912, CLV., p. 197.

taken up by the water at some former period from surrounding minerals, since the quantities are too large to be attributed to recent nascent helium emitted immediately after its production.

It is pointed out as a curious fact that these and similar springs, rich in helium, are approximately upon a line drawn through the towns of Vesoul, Dijon, and Moulins.

**Measurement of Radio-activity in Mineral Waters.**—The general methods of measuring the radio-activity of radium and other radio-active bodies are based upon two principles—viz., (1) the measurement of the  $\gamma$ -rays emitted by a given weight of the substance, by means of a sensitive electro-scope; (2) the measurement of the emanation emitted within a given time from a definite weight of the substance.

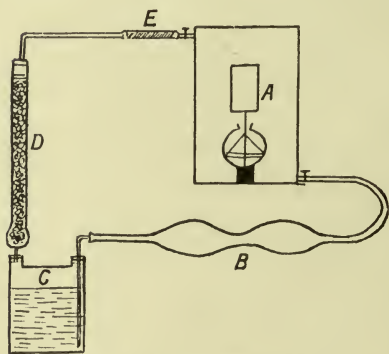


FIG. 6.—Henrich's Apparatus for measuring Radio-activity.

In applying these methods to the valuation of the radio-activity of natural mineral waters, the amount of emanation contained in a litre of the water is first determined. It is then distributed throughout a definite volume of air, which may be made to circulate through the liquid until fully charged with emanation, after which the effect of this air upon a sensitive electro-scope is ascertained, and the fall in

potential during sixty minutes is measured and calculated into the corresponding electrostatic units. This value multiplied by the factor 1,000 gives what are termed the "Mache units."

A form of special apparatus devised by Henrich<sup>1</sup> for this purpose is shown in the accompanying diagram, where A represents an Elster-Geitel electro-scope; B, a pressure bulb; C, a Woulff's bottle, holding about 1.5 litres; D, a calcium chloride tube to dry the air; and E, a tube filled with fine wire.

A blank test is first made with distilled water to ascertain the

<sup>1</sup> *Zeit. angew. Chem.*, 1910, XXIII., p. 340.

degree of leakage of air from the apparatus, and this is followed by an experiment upon the mineral water itself. The "induced activity" is found by a third measurement, in which the influence of the air of the room upon the electroscope is ascertained.

For details as to the calculations the reader may be referred to the original paper.

In most cases the radio-activity of natural waters is not very high. According to the measurements recently made by Landin,<sup>1</sup> the most radio-active water known is that yielded by an old Roman well in the Island of Ischia, which shows an activity of 30,800 units.

The values obtained with the waters from other mineral springs were as follows :—

				Units.
Joachimsthal Spring	..	..	..	14,000
Grabenbäcker Spring	..	..	..	12,000—14,000
Büttel Spring, Baden	..	..	..	9,000—10,000
Porla Spring, Sweden	..	..	..	800
Hög Spring, Sweden	..	..	..	500—600

The objection to this method of measuring radio-activity in mineral waters is that it is based upon an arbitrary standard, and demands the use of a particular apparatus and mode of working.

By Sir William Ramsay's method the actual amounts of radium and its emanation (niton) are estimated, the niton being calculated into the corresponding quantity of its parent radium which would have produced it.

In the disintegration of radium one atom of helium is thrown off in the form of  $\alpha$ -rays, and a gaseous residue, originally termed "radium emanation," but now recognised as a distinct element, *niton*, is left. In this change, two other kinds of rays, known respectively as  $\beta$ - and  $\gamma$ -rays, are emitted. Unlike the  $\alpha$ -rays (or helium), these rays possess great penetrative properties, and are capable of traversing layers of metal of considerable thickness. The  $\gamma$ -rays, in particular, will readily pass through a thick screen of lead, and advantage is taken of this property in separating them from the other rays.

<sup>1</sup> *Chem. Zeit.*, 1910, XXXIV. (Rep.), p. 102.



It is to the emission of these  $\beta$ - and  $\gamma$ -rays that the therapeutic action of radium and of niton is to be attributed.

Niton itself also undergoes disintegration in the course of a few days, with the successive formation of a series of products termed radium A, B, C, D, E, F, and G, the last of which is regarded as being probably identical with lead.

This method of expressing the radio-activity of waters and natural gas in terms of the amount of radium equivalent to the quantity of niton found is best made clear by quoting Sir William Ramsay's words <sup>1</sup> :—" Suppose 1 gramme of radium to be dissolved in water, say as chloride or bromide. It is continually giving off niton ; but at the same time, the niton is as continuously disappearing, owing to the formation of radium A, B, C, and D. There will arrive a time when the production of niton from the radium will have ceased to increase, because as it is produced it decays, and the rate of production is then equal to the rate of decay. The amount of niton will therefore increase up to a certain point ; that point is when 6.6 of a cubic millimetre of niton has been produced. The weight of 1 cubic millimetre of niton is almost exactly  $\frac{1}{100}$ th of a milligramme ; hence 0.6 cubic millimetre weighs  $\frac{6}{1000}$ ths of a milligramme. This is the weight of the niton, which is in equilibrium with 1 gramme of metallic radium."

Estimated by this method, the following results were obtained in the examination of the waters of Bath :—

— — — — —				Milligrammes per million litres.
Radium in the water of the King's Well	..	..		0.1387
Niton (radium emanation) in King's Well	..	..		1.73 <sup>2</sup>
Niton       "       "       Cross Bath	..	..		1.19 <sup>2</sup>
Niton       "       "       Hetling Bath	..	..		1.70 <sup>2</sup>
Niton       "       in gas from King's Well	..	..		33.65 <sup>2</sup>

The Buxton water is also radio-active, as is shown by the recent determinations of Makower,<sup>3</sup> who found niton in the pro-

<sup>1</sup> *Chem. News*, 1912, CV., p. 135.

<sup>2</sup> These figures are the weights of radium capable of forming the amounts of niton found.

<sup>3</sup> *Chem. News*, 1912, CV., p. 135.



portion of 0.83 milligramme per million litres in water from the Hospital Natural Baths and the Crescent Pump-room, Buxton, while the water from the "Gentlemen's Natural Baths" yielded 1.1 milligramme.

The gas emitted naturally by the Buxton Springs contained from 7.7 to 8.5 milligrammes of niton per million litres. All these figures represent the quantities of radium capable of forming the volume of niton found (Cf. p. 37).

**Artificial Radio-active Mineral Waters.**—It is possible to obtain mineral waters of any desired degree of radio-activity by immersing therein an insoluble compound of radium, until the water is sufficiently charged.

According to Landin,<sup>1</sup> a suitable radio-active strength for mineral waters for drinking purposes is 10,000 units, and for baths 200,000 units. The radio-activity of these prepared waters is estimated by the method outlined on a preceding page (p. 40).

Quite recently bottles of special construction, containing artificial radio-active mineral waters, have been put upon the market in Sweden.

It has frequently been asserted that artificial mineral waters prepared from mixtures of salts strictly corresponding to the analysis of natural spring waters do not produce the same medicinal effects as the natural products. In the light of recent investigation it seems probable that the more pronounced therapeutic action of the latter may be due partially, at all events, to their containing radio-active bodies. For further particulars of the methods of preparing these artificially radio-active products see p. 83.

<sup>1</sup> *Chem. Zeit.*, 1910, XXXIV. (Rep.), p. 102.

## CHAPTER V

### CARBON DIOXIDE—ITS PREPARATION, PROPERTIES, AND USES IN THE MINERAL WATER FACTORY

**Nature of Carbon Dioxide.**—A supply of pure carbon dioxide under pressure is one of the main essentials of the mineral water industry, and the artificial preparation of the gas, which until a relatively recent date was almost entirely restricted to soda-water manufacturers, is now being carried out on a large scale to an increasing extent—in some cases as a means of utilising the by-products of other industries.

Carbon dioxide, or, as it is more popularly termed, carbonic acid, is a compound of one atom of carbon with two atoms of oxygen.

Historically it is of interest as being the first gas to be recognised as distinct from ordinary air. To the elder van Helmont is due the credit of the discovery of the preparation of the gas from burning wood and from mineral carbonates treated with acid, while its property of combining with caustic (or fixed) alkalies, which was discovered by Black, suggested the name of “fixed air,” by which, for many years, it was known.

It was also termed “mephitic air,” when its identity with the poisonous exhalation in caverns became known and its property of extinguishing both life and flame was recognised.

For a long period it was considered to be an individual substance, and it was not until 1781 that its real nature as a compound of carbon and oxygen was proved by Lavoisier.

**Occurrence.**—Carbon dioxide in the free state occurs in the atmosphere to the extent of about 4 parts in 10,000, and is emitted abundantly from volcanic fissures all over the world. It is also present in solution in natural water, and in some mineral waters, such as those of Selters, Vichy, and the

Apollinaris Spring, is present under pressure, so that the water effervesces when the pressure is released by the escape of the water from the rock. A description of the character and methods of bottling these naturally super-carbonated mineral waters will be found on a subsequent page.

In the case of other springs the gas pours forth in a copious torrent from the water, as, for example, at Franzensbrunn, near Eger, in Polterbrunnen.

The most celebrated instance of the exhalation of carbon dioxide through fissures in the rock in volcanic areas is in the Grotto del Cane, at Naples, where a constant layer of the gas is present to the depth of 2 or 3 feet.

Another famous spot where carbon dioxide collects in this way is the "Valley of Death," in Java. This is a deep valley that was once the crater of an active volcano. Here the gas is poured forth from time to time from fissures in the ground, and at such periods it means death for any animal that is tempted to enter the valley.

In its combined state as carbonate, carbon dioxide forms one of the principal constituents of the structural materials of the globe. The volcanic rocks are continually absorbing the gas from the air and forming soluble carbonates, which are dissolved by rivers and pass into the sea, where they are taken up by animal and vegetable organisms, and again deposited in the form of precipitated carbonates of calcium and magnesium.

Some conception of the vast extent of the deposits of limestone and the like thus produced may be formed from the calculation of Högbom, that these rocks upon the surface of the earth contain over 25,000 times the quantity of carbon dioxide found in the air.

Another means by which the gas is removed from the atmosphere is by the action of plants, which breathe in carbon dioxide and decompose it through the agency of sunlight, retaining the carbon and giving off the oxygen.

**Properties.**—At the ordinary temperature and pressure, carbon dioxide is a colourless gas with a sourish taste and odour. Its weight, as compared with an equal volume of

hydrogen, is about 22, and as it is thus heavier than air it may be collected by pouring it downwards into a jar, from which it will at once displace the air.

**Solubility of Carbon Dioxide.**—It is soluble in about its own volume of water at a temperature of 15·5° C. (60° F.), the solubility decreasing rapidly with the rise in temperature.

Its “absorption coefficient,” or, in other words, that volume of the gas (reduced to standard temperature (0° C.) and pressure (760 mm.)) which is absorbed by 1 c.c. of a liquid at standard pressure at a given temperature, is shown in the following table, which gives the corresponding values for carbon dioxide, oxygen, and nitrogen at various temperatures :—

ABSORPTION COEFFICIENTS.

—	0° C.	10° C.	20° C.	30° C.	50° C.
	C.c.	C.c.	C.c.	C.c.	C.c.
Carbon dioxide ..	1·7134	1·194	0·878	0·665	0·436
Oxygen .. ..	0·0489	0·0297	0·031	0·026	—
Nitrogen .. ..	0·0239	0·0196	0·0164	0·0138	0·0106

The solubility is now more commonly expressed in terms of Ostwald’s “coefficient of solubility,” which represents that volume of a gas which is dissolved by one volume of the liquid at a definite temperature.

At zero the two modes of expressing the solubility will give the same result, while for other temperatures the relationship between the “coefficient of solubility,”  $x$ , and the “absorption coefficient,”  $y$ , may be calculated by means of the formula  $\frac{x}{y} = \frac{(273 + t)}{273}$ , where  $t$  represents the temperature of the liquid in degrees Centigrade.

Under pressures below about four atmospheres, the law of Henry holds good for the solubility of carbon dioxide in water—i.e., the amount of the gas absorbed by water at a definite temperature varies in proportion to the pressure of the gas. At higher pressures, however, the solubility of carbon dioxide in water is lower than that required by the law.



Thus, for example, Wroblewski found that water at  $12.5^{\circ}\text{C}$ . dissolved the following proportions of carbon dioxide under increasing pressures :—

Pressure in Atmospheres ..	1.	5.	10.	20.	30.
Solubility .. .. .	1.086	5.15	9.65	17.11	23.25

The practical bearing of these factors, of pressure and temperature upon the solubility of carbon dioxide, will be seen later in considering the question of the pressures for bottling aerated liquids.

**Carbon Dioxide from Carbonates.**—Until within the last few years, the carbon dioxide used in mineral water factories was almost invariably obtained by the interaction of an acid and a carbonate.

In America, coarse white marble dust was the favourite raw material, while in England the preference was given to whiting or sodium bicarbonate, the latter of which yields a very pure carbon dioxide, and has the advantage of leaving a soluble carbonate in the generator.

The objection to the use of marble is that it frequently contains iron and bituminous impurities, which in the decomposition with the acid yield hydrogen and volatile vapours of unpleasant odour. This is more liable to occur with black than with white marble.

Another and less pure form of calcium carbonate sometimes used as the raw material for the gas is whiting (purified chalk). It requires to be mixed with a larger proportion of water than does marble, and thus entails the use of larger apparatus. The evolution of the gas is more violent, and the gas itself is liable to contain more impurities.

Both marble and whiting have the drawback of leaving in the generator an insoluble mass of gypsum, of which it is not always an easy matter to dispose.

Other carbonates which were used in certain places, and are probably still employed where they can be obtained plentifully in a relatively pure condition, are magnesite, a carbonate of magnesium (containing 52 per cent. of carbon dioxide) and purified limestone.

Sodium bicarbonate (containing 52.4 per cent. of combined carbon dioxide) is extensively used in this country, but in America is regarded as too expensive except for the highest grade of mineral waters.

The acids used for the decomposition of the selected carbonate are sulphuric acid, sold under the name of *oil of vitriol*, and hydrochloric acid, sold as *muratic acid*.

Both acids, if not carefully purified, are liable to contain traces of volatile bodies that will impart an unpleasant flavour to the gas, and this is particularly the case with hydrochloric acid. The impurities in the latter acid are much more difficult to remove from the gas by washing, and for this reason sulphuric acid has always been preferred.

Whatever the acid used, an addition of water is made to the carbonate in the generator before the sulphuric or hydrochloric acid is introduced, and the proportion is so calculated as to leave a small excess of alkali in the residue.

**Carbon Dioxide from Coke.**—Several processes have been devised for preparing carbon dioxide from coke or charcoal, which when burned yield gases containing about one-fifth of their volume of carbon dioxide.

Most of these are based upon the well-known property of solutions of potassium carbonate to combine with more carbon dioxide and form potassium bicarbonate, which readily parts with the gas again on heating.

In Stead's patent process the furnace gases produced in the combustion are cleansed, cooled, and made to circulate through a solution of potassium carbonate. This absorbs the gas with the formation of potassium bicarbonate, and on now boiling the liquid the carbon dioxide is expelled again, leaving a solution of the original carbonate ready for a further absorption.

The processes of "bicarbonating" and "decarbonating" are carried out in a cycle in different parts of the apparatus.

The furnace gases are first forced under pressure through the "bicarbonators," and leave behind practically the whole of their carbon dioxide, while the other gases and steam escape from a suitable outlet.

The bicarbonated lye is then boiled by means of steam-heat or otherwise, and the carbon dioxide expelled in the process is conducted through a cooling apparatus into a gas-holder, whence it can be drawn off for direct use in aeration or for compression into liquid carbon dioxide.

The two operations involved are thus independent, and are controlled by valves which are worked by means of a hand wheel.

The quality of the gas leaves nothing to be desired, and in the writer's experience is superior to that produced from whiting, and fully equal to that obtained from bicarbonate.

The apparatus is made in various sizes, intended to produce from 1 cwt. to 5 tons of carbon dioxide per day, and is claimed to effect a net saving of £5 to £8 per ton of gas over that produced in the old way from acid and whiting.

A further advantage of the process is that it obviates the necessity of pumping the alkaline lye from one vessel into another.

In Candia and Merlini's French patent (No. 387,874 of 1908), the furnace gases are washed with water, then cleaned in scrubbers containing coke and chalk, where they encounter a current of cold water. They are next cooled and passed through a vessel containing a sodium hydroxide or potassium carbonate solution. In the first case solid sodium bicarbonate is formed, and the absorbed carbon dioxide may be expelled by calcining the salt, while in the second case the solution of potassium bicarbonate is transferred to another vessel, and heated to expel the absorbed carbon dioxide.

**Liquid Carbon Dioxide.**—The gas was first obtained in a liquid form by Faraday, who used for the purpose a strong glass tube, about 8 inches in length and  $\frac{1}{4}$  inch in diameter, which was bent at an obtuse angle a short distance from one end. This was fused, and dilute sulphuric acid was introduced by means of a long funnel, in such a way as not to come in contact with other parts of the tube, after which fragments of ammonium carbonate were placed in the longer limb, and that too was hermetically sealed. When the tube was turned

so that the acid ran down on to the salt, carbon dioxide was produced, and being confined within the closed tube became liquefied by its own pressure and formed a colourless liquid at the other end.

**Properties of Liquid Carbon Dioxide.**—In its liquid form carbon dioxide is a transparent, very mobile fluid, which boils at  $79^{\circ}$  C. Its vapour pressure at  $0^{\circ}$  C. is equivalent to 35 atmospheres, increasing to 58 atmospheres at  $20^{\circ}$  C., and falling to 14 atmospheres at  $14^{\circ}$  C. It dissolves readily in alcohol and ether, but does not mix with water.

When liquid carbon dioxide is allowed to escape through a small aperture into a canvas bag, part of the fluid becomes solidified through loss of heat absorbed in the spontaneous evaporation of the remainder.



FIG. 7.—Faraday's Tube for Liquefying Carbon Dioxide.

The solid product is a snow-white deposit with a specific gravity of 1.5, and under the ordinary atmospheric pressure vapourises without having previously melted.

When mixed with ether or alcohol, solid carbon dioxide is used as the starting-point for obtaining the low temperatures required for the liquefaction of other gases that do not so readily assume the fluid condition. By means of this mixture an initial temperature of about  $80^{\circ}$  C. is produced. Solid carbon dioxide is now obtainable as a commercial article at a moderate price.

Liquid carbon dioxide is now largely employed in the mineral water industry, in which to a great extent it has displaced the production of the gas from carbonates and mineral acid.



The gas is obtained, either from the combustion of coke or from the gaseous products of fermentation, by means of processes described in outline below, and is forced by pressure pumps into steel tubes, which have been tested to withstand pressures far in excess of that exerted by the liquefied carbon dioxide.

The risk of explosion is still further reduced by leaving a small amount of gas in the cylinder, and elaborate tables have been drawn up, showing the amount of liquid which may safely be put into the tube.<sup>1</sup> The effect of leaving 1 per cent. of air in a cylinder is to increase the pressure inside by about 4 per cent.

The general adoption of gas purchased in tubes, in place of preparing it from acid and whiting, has been the chief development in the manufacture of mineral waters during the last ten years.

This substitution has many advantages to recommend it, both from the points of view of convenience and of economy. Thus it has eliminated the use of sulphuric acid from the factory, the handling of which was always attended with some degree of danger, and owing to the greater simplicity of working with the tubes, has reduced the labour bill to a considerable extent.

It has also effected a great saving in the cost of materials. Thus, if we take the cost of a ton of carbon dioxide produced from acid and whiting at about £13 10s. 0d., and that of the gas as purchased ready-made in tubes at about £12 per ton, there will be a saving of £1 10s. 0d. in this direction alone.

In addition to this there is the further advantage of obtaining a purer gas, for the oil of vitriol used in the generator frequently contained arsenic, and there was some risk of this impurity being introduced into the mineral waters.

In the earlier types of apparatus for preparing liquid carbon dioxide upon a large scale, the gas was generated by the action of an acid upon a carbonate in a *generator*, whence it was forced over by the pressure of the gas into the *receiver*.

<sup>1</sup> Stewart: *Trans. Amer. Soc. Mech. Engineers*, 1909, XXX., p. 1,111.

The first successful apparatus appears to have been that of Thilorier, which is represented in diagrammatic form in Fig. 8.

This consisted of a cylindrical leaden chamber, A, enclosed in copper, and strengthened with rings of wrought iron, and of a second chamber, B, of similar construction.

The generator, A, which was about 2 feet long by about 4 inches internal diameter, was charged with  $6\frac{1}{4}$  lbs. of tepid water,  $2\frac{3}{4}$  lbs. of powdered sodium bicarbonate, and 1.47 lbs. of strong commercial sulphuric acid, these proportions being chosen so as to leave an excess of alkali salt. It was then turned several times upon its axis, *pp*, after which it was

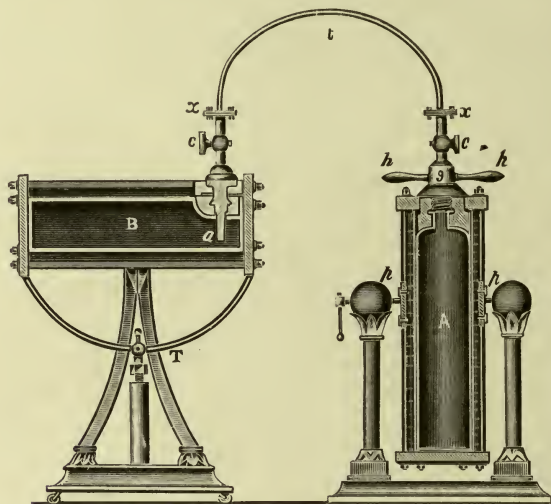


FIG. 8.—Thilorier's Apparatus for Liquefying Carbon Dioxide.

allowed to stand vertically, with its screw-plug, *s*, closed. The liquefied carbon dioxide rose to the surface, and when the generator was connected with the receiver by means of the copper tube, *x*, *t*, *x*, and the valves were opened, the liquid was forced over into the other vessel, which was meanwhile chilled in ice water. By opening the stopcock, *c*, in the receiver, the liquid could escape through the tube, *a*, a portion of it being immediately solidified.

**Natural Gas Sources.**—In Germany liquid carbon dioxide is prepared from the natural gas as it issues from fissures in the earth. This gas is first purified by washing and treatment with suitable solutions to remove other gases, and is then dried, and liquefied in cylinders by means of powerful pumps.

**Marble.**—Another source whence a pure liquefied gas is obtained upon an industrial scale is broken marble, which, when strongly heated in a kiln of special construction, is decomposed, with the liberation of carbon dioxide. The gas is conducted through cooling apparatus, and condensed to the liquid form, while the residue of lime left in the kiln is used for mortar in building.

Carbon dioxide derived from white marble by this process is particularly pure, for the small quantities of impurities which it may contain are not removed by the kilning, as they may be when the marble is decomposed with a mineral acid.

**Carbon Dioxide from Breweries.**—The vicinity of a large brewery first suggested to Priestley in 1772 the possibility of utilising the carbon dioxide liberated in the process of fermentation.

In a postscript to his pamphlet<sup>1</sup> he writes :—" In large vessels containing liquors in a state of fermentation, as at a public brewery or distillery, fixed air may be found in great plenty ready made ; and if water be poured from one vessel into another held as near as possible to the surface of the fermenting liquor (by means of long handles) for about four or five minutes, it will acquire the acidulous taste of Pyrmont water."

Cylinders of liquid carbon dioxide obtained, in the first instance, from the brewers' fermenting tuns, have now been for some years upon the market, and are sold to the mineral water manufacturers to be used as the source of gas for the aeration of their products.

The mode of collecting it is shown in Fig. 9, which represents

<sup>1</sup> Priestley: *Directions for Impregnating Water with Fixed Air*, London, 1772, p. 21.

a vertical section of a modern brewery. The fermenting tuns upon the first floor are closed in at the top, and the carbon

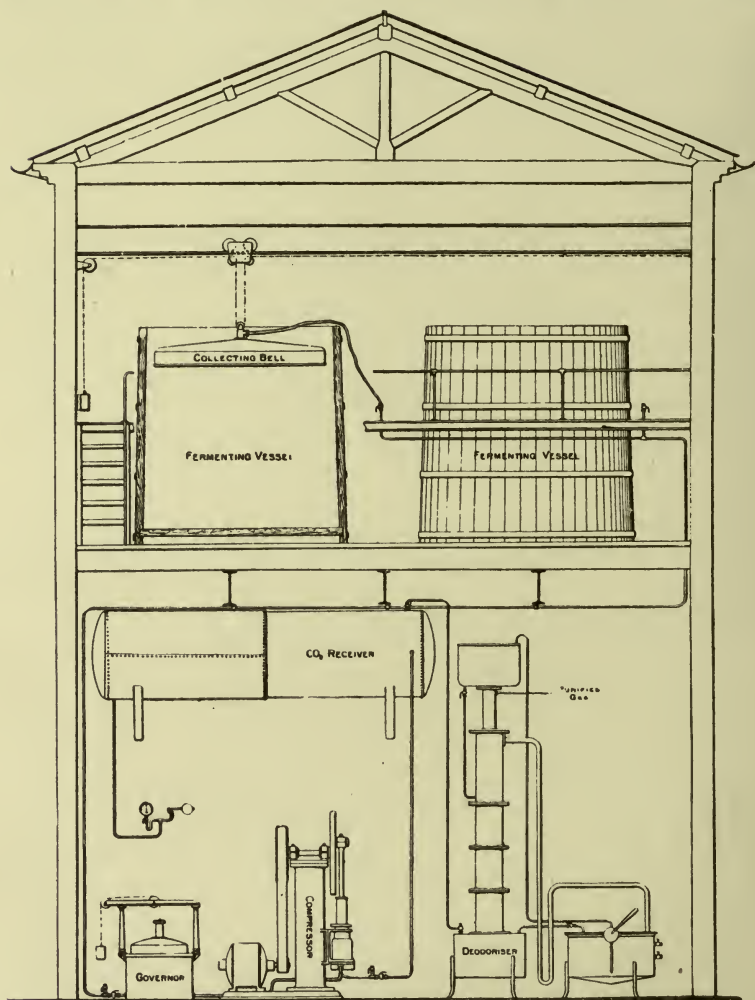


FIG. 9.—Fraser's Apparatus for Collecting, Compressing, and Deodorising Carbonic Acid Gas from Brewers' Fermenting Vessels.

dioxide is drawn off from above the yeast and passes through a main, which conducts it to the purifying and liquefying plant upon the ground floor.



In this case the carbon dioxide is utilised in a refrigerating machine, which keeps the storage cellars at a constant low temperature.

If the carbon dioxide is only to be used for this purpose and for carbonating the beer in the brewery itself, no special purification

is necessary, since the other volatile products of fermentation will already be present in the beer. In such cases, too, it is not necessary to liquefy the gas, but it is sufficient to store it in suitable receivers at a pressure of about 200 lbs. to the square inch.

If, however, the gas is to be sold for aerating mineral waters it must be washed, purified, and condensed to a liquid in strong steel cylinders. Sufficient attention is not always paid to this question of purification before liquefying the gas, and it is within the present writer's experience that some of the carbon dioxide thus derived from breweries will impart a slight but distinct and unpleasant odour and flavour to the mineral water.

Passing the gas through a solution of potassium perman-

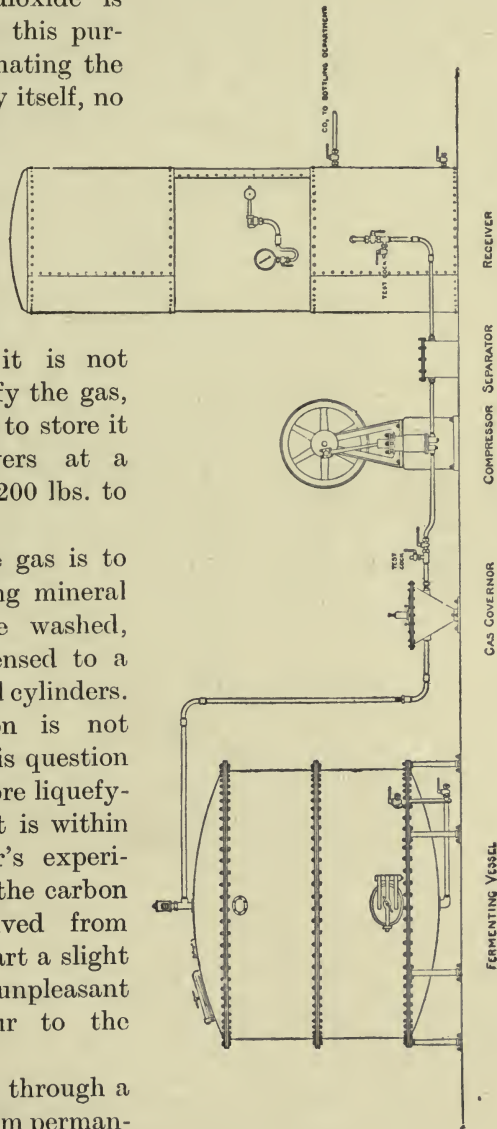


Fig. 10.—Fraser's Apparatus for Collecting Carbon Dioxide from a Closed Fermenting Vessel.

ganate on its way to the bottling machine will eliminate more or less completely the volatile substances.

A type of apparatus, made by Messrs. Fraser & Co., suitable for the collection, purification, and bottling of the gas derived from fermenting liquors in a closed vessel of enamelled steel is shown in Fig. 10. The gas governor is designed to prevent air being drawn over into the compressor.

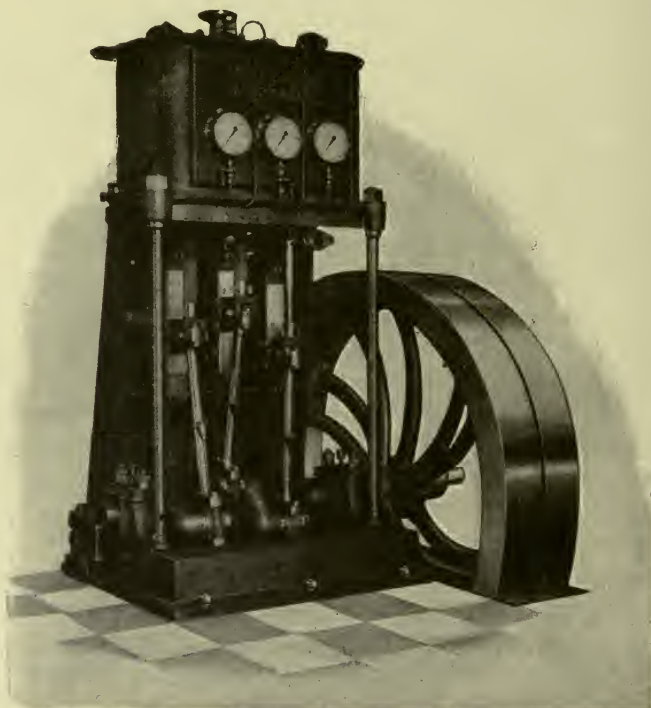


FIG. 11.—Hall's Plant for Collecting Carbon Dioxide from Fermentations.  
The Three-Stage Compressor.

The external appearance of other machinery used for this purpose is shown in Figs. 11 and 12, which represent the collecting apparatus of Messrs. Hall & Co.

Fig. 11 represents the three-stage compressing pump, which is driven by a belt passing over the large wheel, and connected with a steam engine or electric motor.

The gas entering this pump is forced through a connecting pipe (not shown) into the cylinders of the condenser (Fig. 12).

**Carbon Dioxide Refrigerating Machinery.**—The use of liquid carbon dioxide for refrigerating purposes is being increasingly extended in mineral water factories where a supply of cold water from an artesian well is not obtainable.

In order to obtain proper saturation of the liquids with the gas in the bottling process it is essential that the temperature should not be too high, the reason for which will be seen by a reference to the table on p. 46, which shows the solubility of carbon dioxide at various temperatures.

Sufficient cooling of ginger beer is also essential to the production of a good-keeping product, in order to lessen the time of cooling, and reduce the risk of infection with foreign micro-organisms prior to the introduction of the chosen yeast.

This is especially necessary in hot climates, where the water available for cooling purposes may often be as high as 90° F., so that without the use of a suitable refrigerating machine it would be only by good luck that a well-aerated mineral water or stable ginger beer could be manufactured.

Carbon dioxide refrigerating machinery is rapidly displacing

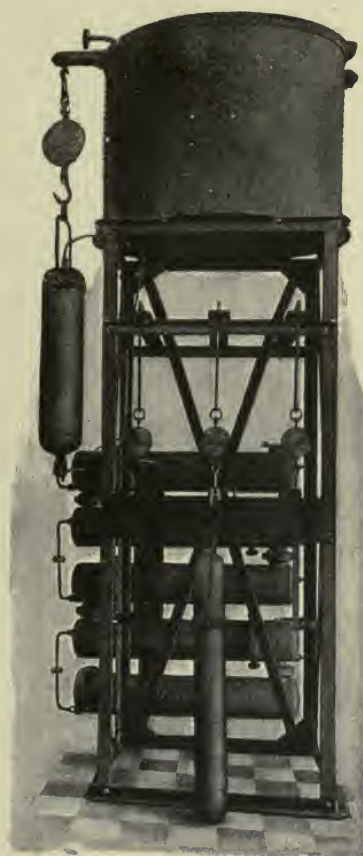


FIG. 12.--The Condenser Purifier and Bottling Machine.

the more costly ammonia and sulphur dioxide plants, over which it has also many advantages in addition to economy in working.

Thus the gas may be blown off through the safety-valve without risk of injury to persons in the room, which is not the case with ammonia; and, unlike the latter, it does not attack copper or its alloys.

There is also the great advantage that, being the gas subsequently used in carbonating mineral waters, it cannot, when

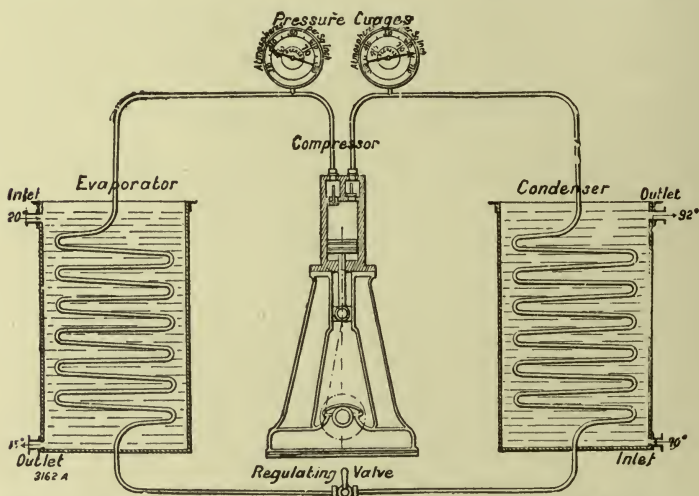


FIG. 13.—Diagrammatic Section of Hall's Refrigerating Machine.

pure, impart any flavour to liquids with which it comes into contact.

Assuming the price of the carbon dioxide to be about  $1\frac{1}{2}d.$  per lb., the price of the material required for working a carbon dioxide plant would only be about one-twentieth of that needed for an ammonia plant.

The principles upon which the refrigerating plant of Messrs. J. & E. Hall (the originators of the system in this country) depend may be gathered from the diagrammatic section of one of their machines shown in Fig. 13.

It consists of four main parts—viz., (1) *The Compressor*, in which the gas drawn from the evaporator is subjected to



sufficient pressure to liquefy it ; (2) *The Condenser*, composed of coils of pipes in which the gas is cooled by means of water, and thus becomes liquefied ; (3) *The Evaporator*, in the coils of which the liquid carbon dioxide evaporates, and in so doing abstracts heat from the surrounding liquid ; and (4) *The Regulating Valve*, by means of which the degree of compression

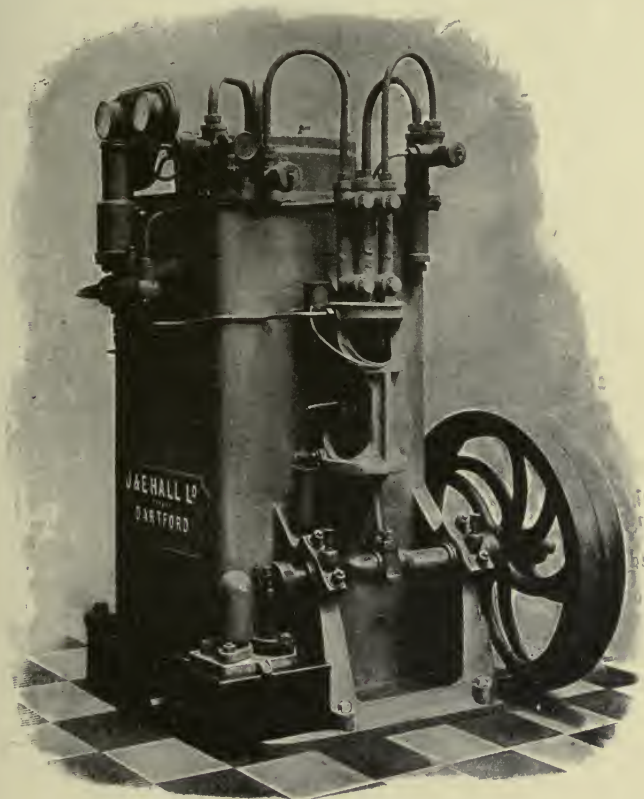


FIG. 14.—Hall's Vertical Combined Land Type CO<sub>2</sub> Refrigerating Machine and evaporation is controlled in accordance with the readings of the two pressure gauges.

The external appearance of one of these machines is shown in Fig. 14, while its internal construction may be seen from the vertical section shown in Fig. 15.

These machines are made of iron, steel, bronze or copper, according to the purpose for which they are required, and are tested to a pressure three times as great as that to which they will be exposed under working conditions (often about 950 lbs. per square inch).

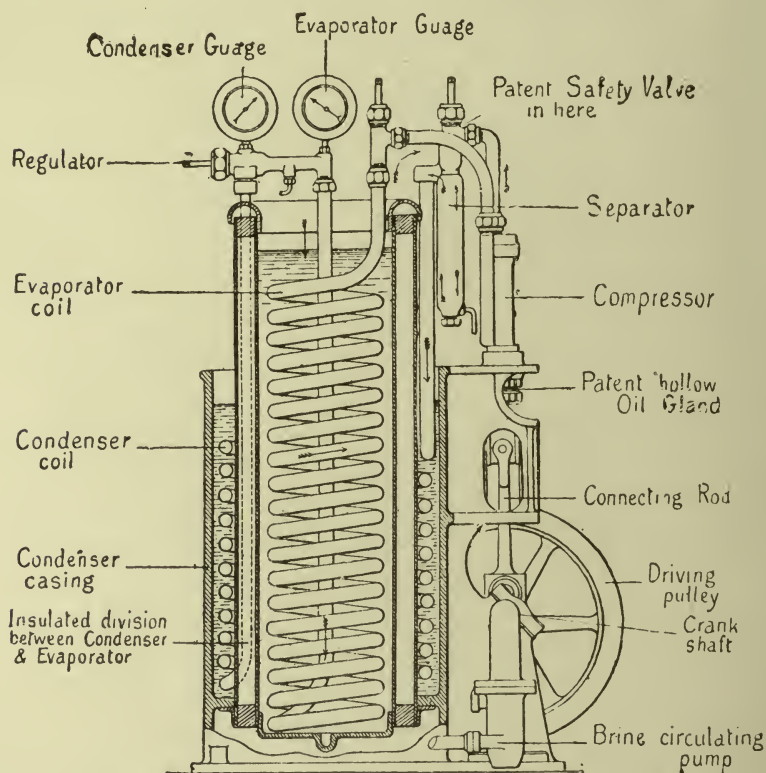


FIG. 15.—Diagram illustrating construction of Hall's Land Type Machine.

In another modification of the apparatus, the coils of the condenser, which are constructed of wrought-iron pipes, are arranged so that water trickles over them, instead of being immersed in a tank of water. The machines are also adapted for cooling the air of a room, but except in tropical climates, this is hardly necessary in mineral water factories, though there would be some advantage in doing this in the brewing of ginger beer, so as to obviate the risk of infection of the yeast.

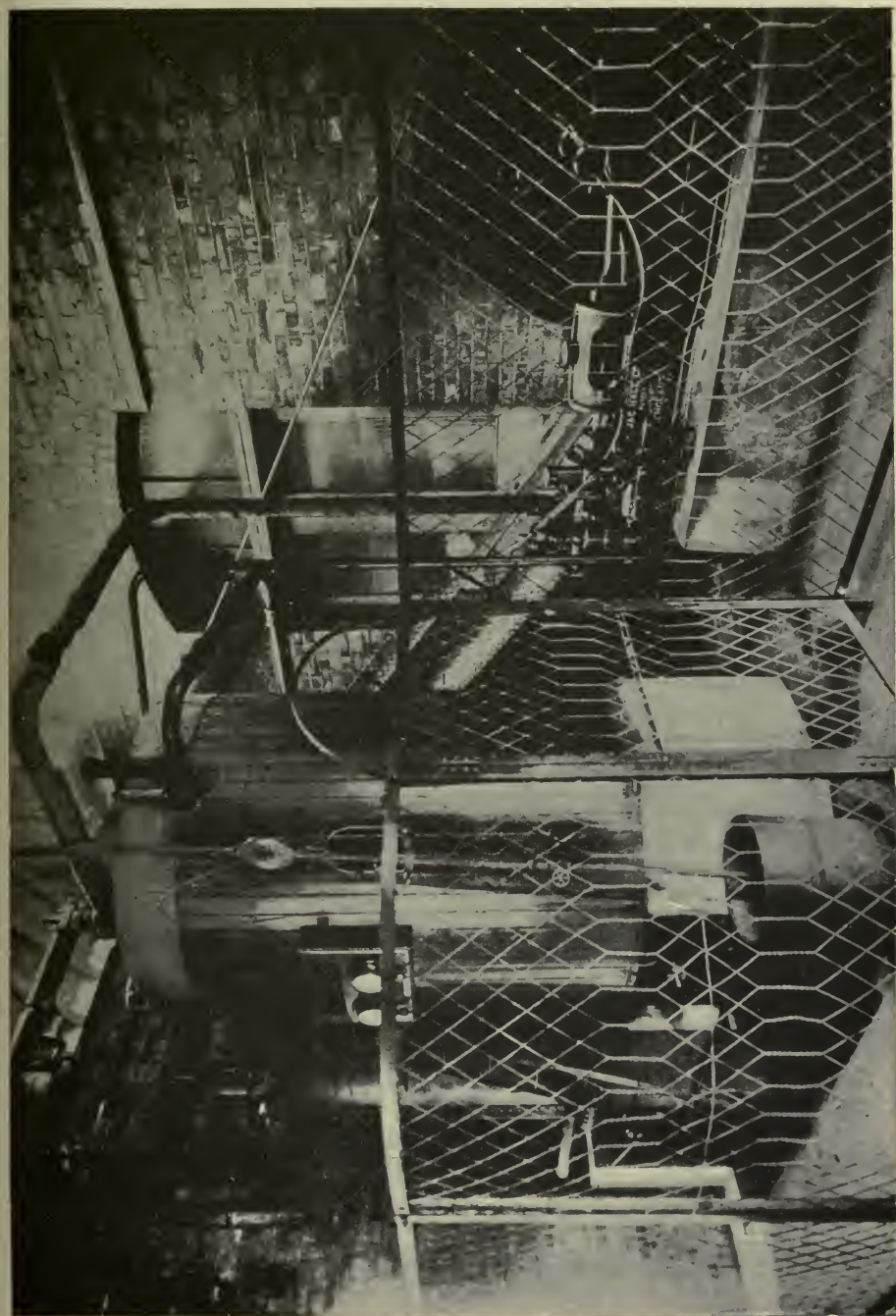


FIG. 16.—Hall's Refrigerating Machine installed in Mineral Water Factory.



Where it is desired to cool a room in this way the air may be made to pass across a system of chilled brine pipes, or the chilled brine may be made to circulate through pipes arranged round the chamber, special precautions being taken to prevent heat entering the room by way of the walls.

A refrigerating machine installed in a large mineral water factory is shown in the accompanying figure (Fig. 16).

**Pressure Gauges.**—The pressure at which the carbon dioxide is forced into the saturating vessel, and consequently the pressure it will exert within the bottle, is indicated upon a gauge.

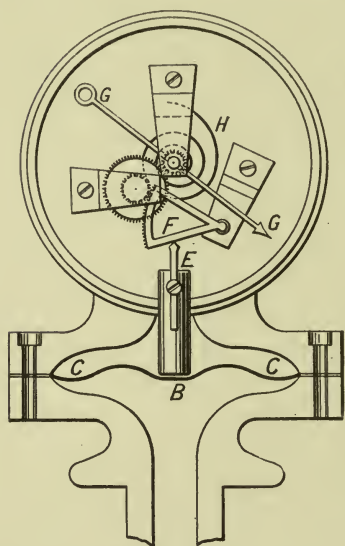


FIG. 17.—Diagram illustrating the construction of a Pressure Gauge.

This contains a spring, which, when acted upon by the gas, sets in motion a lever which controls an indicator upon the face of the dial.

Thus in a common type of pressure gauge, the carbon dioxide enters the space, B, which has a closely fitting spring cover, C. The pressure the gas exerts upon this spring lifts the steel rod, E, and this in turn raises the triangle, F. The indented edge of this fits into a cog-wheel, which moves a second wheel connected with the indicator, GG, while a spiral spring, H, prevents a too-rapid motion of the indicator (Fig. 17).

The values recorded upon the dial vary in different countries. In England and the United States the ordinary atmospheric pressure (14·7 lbs. to the square inch) is represented by zero, while the higher readings are given in lbs. to the square inch. In Germany zero also represents the normal pressure, but the pressures in excess thereof are represented as so many atmospheres, and are not expressed in lbs. or their metric



equivalent; while in France the figure 1 represents the normal pressure, and the figures 2 and so on the *super* pressures.

Thus, for example, a pressure of three atmospheres would be represented by the figure 2 on the German scale, 3 on the French scale, and by 29 lbs. on the British and American scales.

## CHAPTER VI

### ARTIFICIAL MINERAL WATERS

THE miraculous cures which were directly attributed to the waters of some of the mediæval springs could not fail to give birth to the speculations of the natural philosopher as to their cause.

In the doctrines of alchemy, which gradually developed into the science of chemistry, water was termed the *phlegm*, and was a passive principle like *earth*. There were also three active principles—viz., (1) the *Spirit* (or mercury), a subtile, piercing light substance “causing all Bodies to grow in more or less time, according as it abounds in them more or less”; (2) the *Oil*, “a subtile unctuous substance that rises after the Spirit, and causes the Diversity of Colours and Smells”; and (3) *Salt*, “which remains disguised in the Earth after the other principles are extracted. It preserves bodies from Corruption and causes the Diversity of Tastes, according as it is diversely mixed.” Salts again were further divided into three different groups, known as *Fixt*, *Volatile* and *Essential*.

It is not surprising that the sparkling character of many natural spring waters, due to the escape of dissolved carbon dioxide, should have lent support to the commonly accepted belief that there was present in such mineral waters some volatile vital essence, or *Spiritus sylvestris*, to which they owed their beneficial effects. This idea received confirmation from what were believed to be the facts that the waters of certain wells did not produce the same results when bottled and sent away as when they were used upon the spot, the cause of this being due, so it was alleged, to the loss of some of this volatile first principle, the “Soul of the Waters.”

“This noble Spirit it is,” wrote Hoffmann in 1731,<sup>1</sup> “which by its penetrating Nature and admirable Faculty renders itself

<sup>1</sup> “Experiments on Mineral Waters,” English trans., 1731.

perceptible to the Smell and Sense, not only affording a grateful Odour by its Exhalation, but also filling the whole Head therewith."

Further, he remarks that this principle is the "most curious and effectual part" of mineral waters, and concludes that "the delicate Nature of this Spirit is the true and principle Cause of the great Difficulty, even by the utmost Address of Art, of preparing Waters that shall perfectly resemble and have the noble Virtues of the natural hot or cold medicinal Springs."

Early in the seventeenth century Van Helmont (1577—1644) discovered carbon dioxide, and showed that it was distinct from ordinary air, for prior to his discovery, all known gases had been regarded as merely so many different varieties of air.

He invented the name "gas," and described his newly-found substance as the *gas sylvestre*, probably from the fact that he first prepared it by burning wood. The later name of "fixed air" was given to carbon dioxide in 1757 by Black, from the fact that it was absorbed by caustic alkalies.

This *gas sylvestre* gradually came to be regarded as the chief active first principle or spirit in all mineral waters.

In 1712 J. Seip published an account of the water of the Pyrmont Spring,<sup>1</sup> and his investigations were continued by his son, F. G. P. Seip, who, in 1750, described the results of his observations on the "Spirit" and salt of these mineral waters,<sup>2</sup> in which he quotes from an English work by Dr. Turner upon the same subject.

In Seip's opinion this spirit of the waters was identical, or had much in common with the gas that was emitted from fissures in the floors of caves, such as the Grotto del Cane, and with the gas that was set free in the process of fermentation.

He considered this "genuine mineral spirit" to be a volatile vitriolic acid.

In the year 1741 William Brownrigg read a paper before the Royal Society on "The Use of a Knowledge of Mineral Exhalations when Applied to Discovering the Principle and Properties of Mineral Waters."

<sup>1</sup> "Beschreibung der Pyrmontischen Gesund Bruñen," 1712.

<sup>2</sup> "Beschreibung der Pyrmontischen Mineral Wasser und Stahlbrunnen," 1750.

In this paper, which was not published until 1765, he gave reasons for his conclusion that the "subtile and fugitive principle, the spirit of mineral fountains," was closely related to the choke damp found in coal mines and in various other parts of the earth.

He also described experiments which indicated that the class of waters known as *acidulæ* were really impregnated "with a mephitic exhalation resembling the choak damp," as was also made manifest by the effects produced upon ducks swimming upon the surface of certain springs, such as those of Pymont.

And with regard to the therapeutic action of these waters, he remarked that "the elastic spirit of the *acidulæ* seems to have a great share in the admirable effects which those waters exert upon the body."

His later paper was published in the Transactions of the Royal Society,<sup>1</sup> under the title of "An Experimental Enquiry into the Mineral Elastic Spirit or Air contained in Spa Water as well as into the Mephitic Qualities of this Spirit," and his former communication was given as an appendix.

Here he elaborated his experiments and the deductions drawn from them, and still laid stress upon the point that this mephitic air entered into the composition of all sharp and pungent waters like those of Pymont and Spa, and that it was the volatile spirit upon which their prime virtues depended.

In the interval between the two papers of Brownrigg, Dr. Springfield wrote, in the year 1748, a treatise in Latin on the waters of Spa ("Iter Medicum ad Aquas Spadanas"), in which he expressed the opinion that ordinary air was the cause of the clear solution of the contents of "subtile mineral waters." And this view was supported by Venel in his memoir upon Seltzer water (1755), in which he gave reasons for his belief that the "mineral spirit" was air itself.

He also attempted to prepare Seltzer water artificially, by adding sodium carbonate and hydrochloric acid to ordinary water, so that the gas produced saturated the liquid.

Although Venel was mistaken as to the nature of the "air" that he produced, his method of impregnation marks a great

<sup>1</sup> *Phil. Trans.*, 1765, LV., p. 218.



advance in the direction of the successful imitation of naturally carbonated mineral waters, since the proportions of acid and sodium carbonate were chosen so as to yield approximately the right amount of sodium chloride in the finished water.

Both Springfield and Venel were evidently unacquainted with the results of the experiments of Brownrigg and others upon the nature of the "air" in this type of mineral waters, and their conclusions were once more shown to be erroneous by Bergmann and subsequently by Priestley.

Bergmann (1735—1784), who was Professor of Chemistry at Upsala, in Sweden, proved that the principle of the "fluid called fixed air" was common to the Seltzer, Spa, and Pyrmont waters, and he appears to have been the first to attempt an artificial imitation of these waters, so as to include both the volatile "fixed air" and the dissolved saline constituents (see p. 74).

He also showed that solutions of carbon dioxide had an acid reaction, and for this reason described the gas as the "aërial acid," which could be expelled with effervescence from substances with which it was united, by means of a stronger acid.

The essays of Macbride,<sup>1</sup> which were published in 1767, contained many ingenious speculations upon the physiological properties of fixed air. From the facts that more of that gas was liberated in the putrefaction of vegetable than of animal matter, and that the use of vegetable food was admitted to be a remedy against sea-scurvy and other "putrid diseases," he drew the inference that these good effects of a vegetable diet were due to the greater proportion of fixed air set free in the decomposition of the food by the digestive organs.

This gas, he argued, would then be absorbed into the system, and would tend to check any putrefactive changes that had set in. Thus on p. 87 he remarks:—"Seeing then that *dead bodies* become putrid from the *loss* of their *fixed air*, may not the immediate cause of putrefaction in *living* bodies be the detachment of too large a proportion of their *fixed air*?"

<sup>1</sup> "Experimental Essays on Medical and Philosophical Subjects," by D. Macbride, M.D., London. 1767. Second edition.

And so by replacing this loss the course of the disease would be arrested.

To give practical effect to his theory he suggested the employment of a mixture of fresh lime-juice with a carbonate as a remedy against sea-scurvy and yellow fever, his prescription being "to give the patients repeated doses of alkaline salts in fresh lime-juice and the like, and let it always be swallowed during the effervescence."

Priestley adopted the view of the carbon dioxide being the principal medicinal constituent of naturally carbonated waters, and in his pamphlet on "Directions for Impregnating Water with Fixed Air in order to Communicate to it the peculiar Spirit and Virtues of Pyrmont Water," he remarks:—"If any person chuse to make this medicated water more closely resemble genuine Pyrmont water, Sir John Pringle informs me that from 8 to 10 drops of *Tinctura Martis cum Spiritu Salis* must be mixed with every pint of it. It is agreed, however, on all hands that the peculiar virtues of Pyrmont water or any other mineral water which has the same brisk or acidulous taste depend not upon its being a chalybeate, but upon the fixed air which it contains."

And later, he emphasises the point that ordinary water saturated with carbon dioxide will be of most service in "diseases of a putrid nature, of which kind is sea-scurvy." "It can hardly be doubted," he continues, "that this water must have all the medicinal virtues of Pyrmont water and some other medicinal waters similar to it, whatever they be; especially if a few iron filings be put into it to render it chalybeate like genuine Pyrmont water."

Priestley's belief in the efficacy of carbon dioxide as a therapeutic agent was based upon the then widely accepted view that carbon dioxide, or fixed air, acted as an antiseptic agent when introduced in a free state into the circulatory system—the theory that had been put forward so plausibly by Macbride (see p. 67).

His pamphlet was published in 1772, and was dedicated to the Earl of Sandwich, First Lord Commissioner of the Admiralty, in recognition of the favourable manner in which

the inventor's proposal for improving water at sea had been received.

An illustration of the apparatus, which may be regarded as one of the earliest predecessors of the carbonating machines of to-day, is given on a subsequent page.

**Sulphurous Waters.**—With the general advance in knowledge of the carbonated waters the sulphur-bearing springs, of which Aix-la-Chapelle was then the most celebrated, were also made the subject of investigation.

The existence of sulphur in such waters was the subject of much controversy, and its presence was denied by various chemists, including Hoffmann and Lister, who asserted that the unpleasant odour was due, not to sulphur, but to the effects of stagnation.

In 1759, however, Dr. John Rutty read a paper before the Royal Society upon "Thoughts on the Different Impregnations of Mineral Waters,"<sup>1</sup> in which he described a series of systematic tests applied to various so-called hepatic waters, and showed that the reactions were caused by sulphur, and were not merely the accompaniments of a stagnant water.

He summarised his conclusions in the following words:—"Thus it appears that sulphur is not confined to the hot baths of Aix-la-Chapelle and a few more abroad, but is found also in the cold waters of both England and Ireland."

Priestley, at the end of his pamphlet on the impregnation of water with fixed air, also described the manner in which his apparatus might be used in the preparation of mineral waters impregnated with sulphur compounds. Instead of limestone, chalk or marble, he charged the small receptacle with *liver of sulphur*, which he then decomposed in the same way with dilute sulphuric acid.

"The *hepatic* air will arise," he observes, "the water will be impregnated, will smell strongly sulphurous, and will resemble the celebrated waters of Aix-la-Chapelle, etc."

**Salts in Mineral Waters.**—But as it was not only in the direction of the search for the "soul" of mineral waters,

<sup>1</sup> *Phil. Trans.*, 1759, LI., p. 275.



which culminated in artificial carbonation of the water, that frequent attempts had been made to imitate natural mineral waters.

The concentration of sea water by evaporation to obtain the dissolved salts in a crystalline form obviously suggested a similar process for the separation of the second active principle, the *salt*, from mineral waters.

In the year 1697 a "Treatise of the Nature of the Waters of Epsom" was published by Dr. Nehemiah Grew, in which the properties of the water are described and directions are given for preparing the active salt (magnesium sulphate) by evaporation of the water and crystallisation of the salt.

In the patent granted to him in the following year (Eng. Pat. No. 354 of 1698) his process is described as "The Way of Making the Salt of the Purgeing Waters perfectly Fine and in Large Quantities very Cheape, so as to be commonly Prescribed and Taken as a Generall Medicine."

Analogous processes were introduced about the same time abroad, for we find in Lemery's "Course of Chymistry"<sup>1</sup> that "Many acid bituminous Salts which are drawn by the Evaporation of certain Mineral Waters, such as those of Balerac in Languedoc, and Digne in Provence, do perform the same Effects [as sea salt] when they are mixed with *Oil of Tartar*."

Lemery also describes a method of preparing a medicinal salt *Sal Polychrestum* (πολυχρης "good for many uses"), which was an impure potassium sulphate, obtained by heating nitre and sulphur in a crucible.

He recognised that this was not the same substance as the salt made and sold under that name by Seignette of Rochelle. "Monsieur Seignette, an Apothecary of Rochelle," he remarks, "hath put in Use a certain *Sal Polychrestum*; the composition is known to none but himself, who having given it a Reputation in the Chiefest Towns of France hath left some Quantity of it with me to distribute and make Use of here in Paris."

This salt, which is still known as *Rochelle* or *Seignette salt*, was the double tartrate of potassium and sodium.

Yet another passage from Lemery deserves quotation as

<sup>1</sup> Translated from the French. Fourth English edition, 1720, p. 254.



foreshadowing the preparation of artificial medicinal mineral waters.; "One may make an Aperitive Mineral Water," he writes, "by dissolving eight or nine grains of *Gilla Vitrioli* [zinc sulphate] in two pints of Common Water."

Early in the eighteenth century it was discovered by F. Hoffmann<sup>1</sup> that the purgative character of the water of the springs at Sedlitz, in Bohemia, was due to the presence of Epsom salt (magnesium sulphate) in considerably greater proportion than even in the water of Epsom itself. He showed that the salt might be obtained in a solid form by evaporating and crystallising the residue as in the case of Epsom water, and to his discoveries the town of Sedlitz (or Seidlitz) owed its fame.

The crystals of magnesium sulphate prepared from the water were put upon the English market early in the nineteenth century under the name of *Seidlitz salts*.

Hoffmann also published a treatise upon mineral waters in general, in which, as has already been mentioned, he found the three main constituents:—A volatile principle; a solid salt or earthy substance; and "moisture" or "elementary water."

This book was translated into French, and an English edition was published in the year 1731.

The methods of analysis then used in the examination of mineral waters were mainly due to the earlier investigations of Boyle and of Du Clos.

In the year 1663 Robert Boyle made use of several substances to precipitate various ingredients in water, and showed that syrup of violets was reddened by acids, that water tinged with logwood became yellow with acids, and so on. Then, in 1684, he published a treatise in which he described several reagents for examining mineral waters.<sup>2</sup>

Thus he employed an infusion of galls, oak leaves or myrobalaus for the detection of iron in water, and showed how sulphurous waters might be recognised by the changes of colour given by them with solutions of various metals. He also described tests for detecting the presence of arsenic in

<sup>1</sup> "Bericht von der Wurekung des Brunnens zu Sedlitz," 1725. .

<sup>2</sup> "Short Memoirs for the Natural Experimental History of Mineral Waters." London, 1684.

water, and dealt in some detail with the salts contained in English mineral waters.

In estimating the residue left on evaporation of waters—the *caput mortuum* as he termed it, Boyle used a rough balance with which to weigh the residual salts, and gave the comparative results obtained with different mineral waters such as those of “Dulledge,” Acton, Epsom, and Islington (“From the Musick House”).

In discussing the question of ferruginous waters, he observed that “most of them, even such as will bear removing, have something of Freshness and Quickness at the Spring head, perhaps from some *Spirituos* and Fugitive Exhalations that there arise with them, but presently vanish, that they have not anywhere else.”

“And if it be with some such *Spirituos* and Volatile Exhalations that a Mineral Water as that of Tunbridge or of Islington is impregnated, ’tis not hard to conceive that they may easily lose their chief Vertue, by the avolation of most or many of their fugitive Parts, upon their being removed to a distance from the Spring head.”

At the beginning of the eighteenth century other substances were employed in testing mineral waters. Thus Du Clos, who began a systematic examination of all the mineral waters of France, which he continued for many years, made use of many other reagents, including juice of iris flowers, martial vitriol (iron sulphate), and turnesole (turmeric).

Hoffmann was the first to detect sodium carbonate (which he termed “nitre”) in several mineral springs, while Allen, in 1711,<sup>1</sup> discovered a salt containing vitriolic acid and lime” (calcium sulphate), which he termed *selenite*, in certain of these waters.

In the year 1755 Dr. Peter Shaw published his “Chymical Lectures,” in which there is a section dealing with “The More Commodious Method of Examining Mineral Waters.” He describes the behaviour of Pyrmont water towards several reagents, and classifies mineral waters in general into three classes—chalybeate, purgative, and alterative.

<sup>1</sup> “Natural History of Mineral Waters of Great Britain,” 1711.

He then proceeds to show how "the mineral waters are imitable by Art," and gives the following prescription for the artificial preparation of Pymont water :—

"We took a quart of the lightest and purest Water we could procure, and added to it about thirty drops of a strong Solution of Iron, made with Spirit of Salt, a dram or more of *Oleum Tartari per deliquum*, and twenty, thirty, or forty drops of Spirit of Vitriol, but so as that the Alkali of the Oil of Tartar might prevail. We now shook all briskly together and poured out into a glass for tasting; upon which it was found very remarkably to resemble Pymont Water."

From his analyses, Shaw concluded that the ingredients of Pymont water were "a subtile aqueous fluid, a volatile iron, and a predominating alkali, all joined into one brisk, pungent, spirituous water."

Referring to the imitation of mineral waters in general, Shaw remarks that the imitation of the common purgative mineral waters, such as those of Epsom, is "facile," but that the imitation of the "alterative waters such as those of Bath, Buckston, and Holt has hitherto scarce been attempted, nor can be rationally for want of their respective just analyses, upon which such imitations should always be founded."

The exact nature of the substances that Peter Shaw dissolved in water, in his attempts to imitate Pymont water, is not quite clear, but apparently there was iron sulphate, hydrochloric acid, and a solution of potassium carbonate, obtained by igniting cream of tartar, and extracting the mass with water. Carbon dioxide would be liberated by the interaction of the carbonate and mineral acid and would impregnate the liquid.

The importance attached to the presence of "fixed air" in a mineral water caused less attention to be paid to the saline constituents, and as has already been mentioned (p. 68), ordinary carbonated water came to be regarded as possessing all the medicinal virtues of the effervescing mineral waters.

Bergman, however, clearly recognised that to imitate a natural mineral water it was not sufficient merely to saturate ordinary water with carbon dioxide, but that the different character of these waters was due to their containing different

salts in different proportions. "Hence," he remarks,<sup>1</sup> "water by bare impregnation with fixed air cannot be called either Seltzer, Spa or Pyrmont, nor can he be said to understand the artificial preparation of these waters who merely knows the method of saturating water with fixed air."

Bergman's account of how he came to prepare artificial medicinal waters in Sweden is sufficiently interesting to deserve quotation :—

"In the year 1770," he writes, "being attacked by a severe colic, I was obliged to take above eighty bottles of foreign medicated waters. By these the symptoms were somewhat mitigated; in the meantime I examined the nature and principles of these waters with the greatest attention, as I most earnestly desired to imitate them; for besides their extreme dearness in this country at the beginning of the spring, when not only diseases, the foundations of which have been laid in winter, but my complaints are also particularly troublesome, these waters cannot be had fresh and good at any price. I soon reaped the wished-for fruit of my labours, for the year following I substituted the artificial to the natural waters, and not only used them myself but gave them to many of my friends with like success."

And in another passage Bergman remarks :—"In the year 1771, at Upsal, several persons made use of waters artificially prepared, which exactly resembled the natural waters of Seltzer, Spa and Pyrmont, not only as to the volatile part, but as to the entire contents; and the use of these waters afterwards obtained through most of the provinces of Sweden."

The apparatus used by Bergman in impregnating these waters with carbon dioxide is described elsewhere (see p. 85).

About the year 1768 Thomas Bewley had introduced a form of soda water, obtained by mixing an acid and a carbonate. This he described by the singularly ill-sounding name of "mephitic julep," the term "mephitic" being that which he had previously given to carbon dioxide.

<sup>1</sup> "Essays of Torbern Bergman," translated by E. Cullen, M.D. London, 1788, p. 107.



This preparation was in great demand as a remedy for various diseases, and according to Henry, writing in 1781, "the materia medica perhaps does not afford a more efficacious or more grateful medicine in putrid fevers, scurvy, dysentery, bilious vomitings, hectic, etc."

Henry in his pamphlet already quoted gives the following directions for the preparation both of artificial mineral waters and of Mr. Bewley's mephitic julep by means of his impregnating apparatus (see p. 92):—

#### PROCESS FOR MAKING ARTIFICIAL PYRMONT WATER.

To every gallon of spring water add one scruple of magnesia, 30 grains of Epsom salt, 10 grains of common salt, and a few pieces of iron wire or 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.

#### THE PROCESS TO MAKE ARTIFICIAL SELTZER WATER.

Add one scruple of magnesia alba, six scruples of fossil alkali,<sup>1</sup> and four scruples of common salt to each gallon of water, and saturate the water, as above, with fixed air.

#### TO PREPARE MR. BEWLEY'S JULEP.

Dissolve three drams of fossil alkali in each quart of water, and throw in streams of fixed air, till the alkaline taste be destroyed. This Julep should not be prepared in too large quantities; and should be kept in bottles very closely corked and sealed. From four ounces of it may be taken at a time, drinking a draught of lemonade, or water acidulated with vinegar, by which means the fixed air will be extricated in the stomach.

In the year 1798 Cavallo published his "Essays on Factitious Airs,"<sup>2</sup> in which he gives the following directions for the preparation of "acidulous soda water":—

One ounce of soda is dissolved in four or five pints of rain or of boiled soft water, and the solution is then impregnated as much as possible with carbonic acid gas.

Incidentally he remarks, that although only a moderate, though efficacious, quantity of gas can be introduced by the use of Nooth's glass apparatus, the soda water then "prepared

<sup>1</sup> An old term for soda.

<sup>2</sup> "An Essay on the Medicinal Properties of Factitious Airs," by T. Cavallo, F.R.S. London, 1798.

and sold in London by a Mr. Schweppe contains an incomparably larger proportion of carbonic acid gas, and accordingly is much more efficacious." As to the method by which this is done, however, Cavallo admits his ignorance.

This passage is of historical interest, since it shows that "soda water" was made in England before the end of the eighteenth century, and prior to the establishment of Paul's factory.

The manufacture of artificial mineral waters upon a large scale may be said to have begun in Geneva about 1789, when Nicholas Paul became associated with Gosse, an apothecary of that town, and started a factory where all kinds of natural medicinal waters were imitated.

After a branch establishment had been set up in Paris, a report was issued in 1799 to the National Institute of France upon the nature and preparation of the mineral waters manufactured by this firm, and subsequently, when, in 1802, a business, had also been opened in London, a translation of this report was issued as an advertisement.<sup>1</sup>

From this circular we learn that the following varieties of waters were prepared:—(1) Strong Seltzer water; (2) mild Seltzer water; (3) strong Spa water; (4) weak Spa water; gaseous alkaline water (commonly called *mephitic*); (6) Seidlitz water; (7) oxygenated water; (8) hydrocarbonated water; and (9) sulphurated or hepatic water.

The method of carbonating some of the waters is described on p. 102.

It was claimed, further, that numerous combinations of these waters could be prepared, which "might be more effectual in particular cases than those Nature affords."

So successful was the venture at Geneva that ten years later no less than 40,000 bottles of artificial Seltzer water were annually sold, and while scarcely any mineral waters were imported into Geneva, from 40,000 to 50,000 bottles were exported every year.

<sup>1</sup> A Report made to the National Institute of France in December, 1799, by Citizens Portal, Pelletal, Fourcroy, Chaptal and Vauquelin, respecting the Artificial Mineral Waters prepared at Paris by Nicholas Paul and Co. London, 1802.

These figures were supplied by Paul himself, in a paper read before the National Institute of France in the year 1799.

An appendix to Paul's circular of 1802 contains a communication by Dr. W. Saunders to the *Medical and Physical Journal* of that year, which is noteworthy for the following passage :—“The gaseous alkaline water commonly called *soda water* has long been used in this country to a considerable extent.”

This shows that the name “soda water,” was in general use in this country long before the beginning of the last century.

It was not long before there were many other factories preparing imitation mineral waters (as distinct from ordinary carbonated water), although during the first ten years of the last century they had to contend with violent opposition on the part of medical men.

Thus, again, to quote the words of Muspratt, though in another connection :—“They [artificial mineral waters] were said to be devoid of all the good qualities of the natural mineral and spa waters—to be minus a certain *conditio sine quâ non* in the shape of a *spiritus rectus*, or vital force, which imparted the medicinal qualities.”

This prejudice against artificial mineral waters gradually died away, because—to use Muspratt's grandiloquent words—“Chemistry, the great revealer of hidden treasures, has demonstrated to a certainty what the constituents of the natural waters are ; and thus one is now enabled to produce artificial waters quite equal, if not superior, to the natural ones.

“The rapid increase and spread of the manufacture of artificial waters is the best proof that physicians find the medical and therapeutic effects of them are *identical* with those of the natural ones, whilst their *identity* in a physical and chemical point of view can hardly be questioned.”

It may be remarked that the “proof” given in this passage is not convincing, nor is it in accord with other observations made by the same writer (*see* p. 37).

Similar attempts were made about the same time in France, Germany, and Sweden to substitute artificial preparations for the natural waters. Thus imitation Carlsbad and Friedrich-

shalle waters were manufactured on a large scale, the ingredients of which were based upon an analysis by Liebig, and met with a ready sale.

**Struve's Artificial Mineral Waters.**—The rise of Struve's establishments for the preparation of artificial mineral waters forms an interesting chapter in the history of the industry.

Struve, who was a doctor in Dresden, underwent a course of "taking the waters" at Marienbad, and received such unexpected benefit from them that he began to study the chemical and medicinal properties of all the leading German mineral waters, and to attempt to imitate them exactly.

He made minute analyses of the waters of the different springs, and by the year 1820 had prepared artificial waters, which he gave to his friends. Then, owing to an increasing demand in many directions for his imitation waters, he opened a public pump-room in 1821 in Dresden for their manufacture and sale, and this was followed in the two next years by similar establishments in Leipzig and Berlin.

In the year 1825 a pump-room was started at Brighton, and other branches were opened in the following years at various places in Russia and in other towns in Germany, until, finally, there were fourteen thriving establishments in all.

From a contemporary account<sup>1</sup> we learn that hundreds of invalids came to these pump-rooms in preference to the natural springs, and that medical men in Germany recommended them as being quite equal to the natural waters.

In a pamphlet published in 1823<sup>2</sup>, Struve mentioned that upwards of 4,000 patients had already used his artificial waters made by means of apparatus which he had invented. "Mineral waters thus prepared," he remarks, "are found to contain all the properties and qualities, in the most minute degree, of their corresponding natural mineral springs, as well in effect produced on the human body in its most refined distinctions,

<sup>1</sup> "Observations on the Artificial Mineral Waters of Dr. Struve," by W. King, M.D. Brighton, 1826.

<sup>2</sup> "Remarks on an Institution for the Preparation and Use of Artificial Mineral Waters in Great Britain," by F. A. Struve, M.D. London, 1823.



as in their chemical analysis, taste, intensity of union, and manner of their decomposition when exposed to air."

In these respects Struve claimed that his products differed materially from the artificial mineral waters previously manufactured, which were very different from the natural waters they professed to imitate. Attempts had only been made to introduce the chief saline ingredients, whereas the action of natural mineral waters was the result of the combined action of all the elements present. None of them were without their influence.



FIG. 18.—The "German Spa" at Brighton.

The prospectus issued by Struve in 1826, concerning his "German Spa in Brighton for the Preparation of Factitious Mineral Waters," contains many further curious details. It describes the classes of hot and cold waters to be obtained at the pump-rooms, and gives a table of Struve's analyses of the principal natural mineral waters, together with rules as to diet while taking the artificial preparations.

The charge for "taking the waters," hot and cold, at the Brighton Spa was £1 1s. 0d. per week, and the cold waters, including imitations of those of Spa, Pyrmont, Eger, Marienbad, Seidschutz, Püllna, Seltzer and Geilna, could be obtained in

quart bottles at Brighton or from London agents at the price of £1 4s. per dozen.

The prospectus also stated that Faraday had examined the artificial Carlsbad water, and allowed a reference to be made to him as to its chemical correctness.

Although the venture at Brighton met with a large measure of commercial success, over three hundred thousand pint bottles of the different artificial mineral waters being sent out every year from the "Spa" to all parts of the kingdom, these products were nevertheless made the subject of much adverse criticism.



FIG. 19.—Preparation of Artificial Mineral Waters at Struve's Establishment in Dresden, 1853.

For example, Granville, writing in 1843<sup>1</sup> of the so-called Ems and Carlsbad waters prepared at Brighton by Struve's process, described them as merely watery solutions of the same chemical ingredients contained in the natural springs, charged with *artificial* heat, and therefore incapable of producing the effects of the genuine waters when taken at the springs.

Granville attributed the different results produced by the natural and artificial waters to the temperature of the former as being due to a peculiar form of heat, which he described

<sup>1</sup> "The Spas of Germany Revisited," by A. B. Granville, M.D., F.R.S. London, 1843.

as "telluric," and when that heat was dissipated it was impossible to supply its place by artificial means (see p. 36).

Struve died in 1840, but his "spas" were then firmly established, and thirteen years later an account of their progress and of the method of preparation of the artificial waters in the parent establishment in Dresden was published.<sup>1</sup>

Freshly distilled water formed the basis, and the carbon dioxide was made from crushed marble or magnesite (magnesium carbonate) and sulphuric acid in the leaden cylinder, shown on the right of the illustration. The gas passed through the series of washing bottles into the gasometer, whence it was drawn off by means of a pump, and forced under pressure into tin cylinders (on the left). These had previously been charged with the distilled water, and had received the requisite proportions of the different salts in the form of solutions, each of these being introduced in the proper order.

The carbonated water was then bottled under pressure (say about four atmospheres) in strong glass bottles.

The process was thus very similar to that used with the early German apparatus described on p. 106, with the exception that patent machinery (p. 107) was employed.

Fashion alters, however, even in medicine, and according to Hirsch and Siedler<sup>2</sup> the manufacture of artificial mineral waters in Germany has now developed in another direction.

During the first years after their introduction, the aim of their producers was to make exact imitations of natural waters, every ingredient being slavishly added without any attempt at criticism.

But since many natural waters contain substances which modify the chief medicinal action of these waters, or which, like calcium sulphate and carbonate, are even injurious to digestion, it is now regarded as more rational to use the artificial waters as the media for special drugs.

Substances are therefore introduced into them which do not occur in natural mineral waters, or are only present in a

<sup>1</sup> "Die Struve'schen Mineral Wasser Anstalten." Leipzig, 1853.

<sup>2</sup> "Die Fabrikation Künstlichen Mineralwasser," by B. Hirsch and P. Siedler Brunswick, 1897.



small proportion, and the predominant medicinal qualities of a given natural water are thus accentuated.

In these writers' opinion the manufacturer who advertises that any artificial mineral waters may be regarded as the complete equivalent of a "cure" at the springs themselves makes an unjustifiable claim and injures his reputation, since the use of either natural or artificial mineral waters at home cannot take the place of treatment with the natural waters upon the spot.

In this country, too, the demand for the artificial mineral waters made in exact imitation of the natural products gradually waned, their place being taken by soda, potash, and lithia waters, the first two of which became recognised as official drugs in the London Pharmacopœia of 1836, and the third in the British Pharmacopœia of 1867.

Another factor that led to the decline in the manufacture was the introduction and increasing use of natural spring waters, carbonated under pressure so that they would keep well (see p. 28).

Occasionally artificial preparations may still be made to meet a special order, but with the exception of Seltzer water, which now seldom corresponds in composition with the natural *Selterswasser*, the manufacture of imitation mineral spring waters in this country is but rarely attempted.

The formulæ for such imitations, however, still continue to be published in handbooks, especially those of American origin. Thus to quote from one of these:—"All that is required is that this compound be properly carbonated with pure gas, and suffering humanity have no occasion to visit the 'springs' for the benefits derived from the use of any particular natural mineral waters, . . . but the preparation of the artificial waters must be left in the hands of responsible, practical manufacturers of carbonic acid gas waters, not such as follow old 'formulas' or 'theories' copied from cook books and family recipes of their grandfathers, and make a stuff which, instead of the mild, soft, and pungent taste of the genuine, produced by effectual carbonation, tastes just like any other salt water."



**Artificial Radio-active Mineral Waters.**—The discovery of the radio-activity of many natural spring waters (see p. 37), and the growing belief that the therapeutic action of the so-called “indifferent” waters of Bath and elsewhere is to be attributed to this property, has led to the manufacture of waters rendered radio-active (or of increased radio-activity) by artificial means.

For this purpose a minute quantity of a salt of radium, such as the sulphate, is dissolved in a definite quantity of either a water already radio-active, such as that of Kreuznach, or in ordinary water (see also p. 43).

In the case of naturally radio-active mineral waters the property of radio-activity rapidly disappears after the water has been drawn from the spring, and it remains to be seen to what extent a water rendered radio-active by artificial means is as effective physiologically as the natural water, and for how long a period it retains its properties.

The methods of estimating the radio-activity of waters, whether natural or artificial, are described elsewhere (p. 40).

## CHAPTER VII

### EARLY FORMS OF CARBONATING APPARATUS

THE notion of artificially impregnating water with carbon dioxide dates back to the latter half of the eighteenth century, and was evidently suggested by the discovery that the effervescence of the waters of Spa and Pyrmont was due to their being saturated with "fixed air" (see p. 65).

In the year 1767 Cavendish described an experiment which showed how much of the gas a given volume of water could be made to absorb, but did not turn his results to any practical purpose.

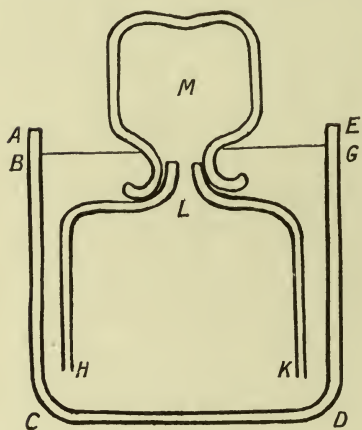


FIG. 20.—Cavendish's Apparatus for Estimating Carbon Dioxide in Water.

The apparatus used by Cavendish in estimating the amount of carbon dioxide in Rathbone Place water was of the simplest description, as is seen in Fig. 20, reproduced from the rough sketch in his original paper.<sup>1</sup>

A tin vessel, HKL, was inverted in another vessel of the water, ACDE, and a bottle, M, also filled with the water, was placed over the neck of the inner vessel. On heating the outer vessel, the dissolved gases were collected in the bottle, M, and the amount of carbon dioxide was estimated by absorption with a solution of caustic alkali.

The notion of impregnating water with carbon dioxide may be traced in the writings of several chemists at about that

<sup>1</sup> "Experiments on Rathbone Place Water," by the Hon. H. Cavendish. *Phil. Trans. Roy. Soc.*, 1767, LVII., p. 92.

time ; but there is some doubt as to whom should be given credit for its practical utilisation.

On the whole, it appears probable that the process was independently devised by Bergman and by Priestley, and that the former was a little ahead of the English chemist.

Bergman has related in his " Physical and Chemical Essays " (see p. 74) the circumstances that induced him in the year 1770 to attempt to imitate naturally effervescent waters,

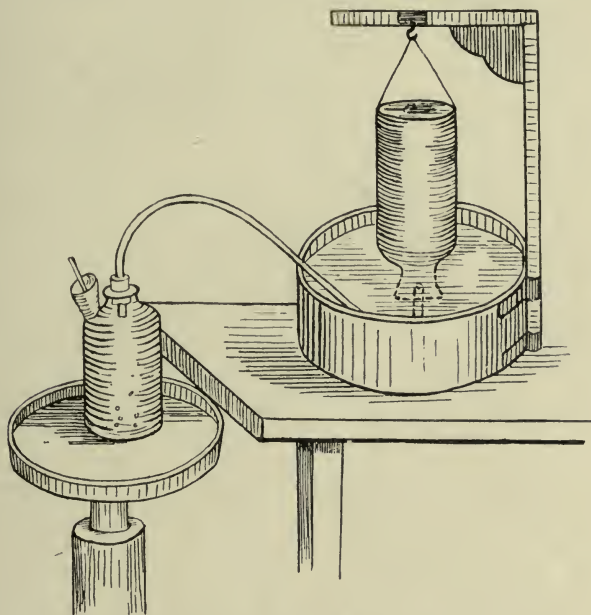


FIG. 21.—Bergman's Impregnating Apparatus, 1770.

and in another place<sup>1</sup> he describes and gives the annexed illustration (Fig. 21) of the apparatus he used for the impregnation. It consisted of a bottle, A, which was half filled with water and coarse lumps of chalk, and into which sulphuric acid was allowed to drop through the funnel, O, the tube of which was loosely closed by a glass rod, in the manner suggested by Lavoisier.

The gas was conducted through the tube into the inverted bottle, which was partially filled with water and suspended in

<sup>1</sup> *Loc. cit.*, p. 265.

the basin of water. Round the tube, passing up into its neck, was tied a wet bladder to confine the "aerial acid," and the escape of the gas was regulated by having a small pinhole in the bladder.

Bergman also describes an apparatus for impregnating water with the fixed air derived from a fermenting liquid, but mentions that it is inconvenient owing to its requiring a very large vessel to contain the fermenting gas.

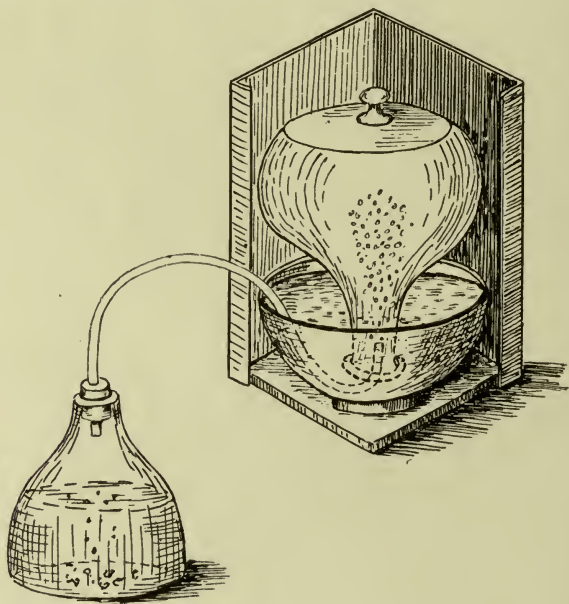


FIG. 22.—Priestley's Original Apparatus, 1772.

In the year 1772 Priestley published his pamphlet (see p. 68), and in the following year Bergman became acquainted with Priestley's method, and from that time onwards used it in place of his own.

In Priestley's first apparatus the method of collecting the carbon dioxide was the same as that used by Bergman, the gas being led from the bottle in which it had been generated from marble and sulphuric acid into a flask containing water, and inverted in a basin of water. The pipe between the flasks



was made of leather, the end being kept open by pieces of quill (Fig. 22).

Subsequently, Priestley improved his apparatus by placing between the "effervescing vessel" and the collecting flask a bladder, which would serve as a primitive form of gasometer, and by the compression of which the gas would be driven forward with some degree of force into the water to be impregnated.

The mode of working this apparatus will be understood without further description from the accompanying figure (Fig. 23), taken from Priestley's pamphlet (p. 68).

A passage in another paper by Priestley<sup>1</sup> is of interest in this connection, since it foreshadows the invention of the process of carbonating liquids under high pressure on a large scale with the aid of a force-pump:—"I do not doubt," he remarks, "but that by the help of a condensing engine, water might be much more highly impregnated with the virtues of the Pyrmont Spring,

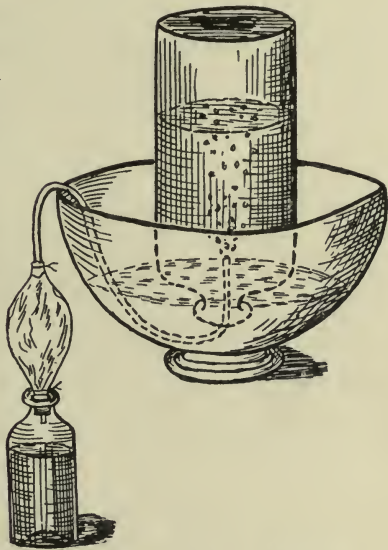


FIG. 23.—Priestley's Modified Apparatus, 1772.

and it would not be difficult to contrive a method of doing it."

The method of regulating the supply of the acid to the chalk, described on p. 85, appears to have been adopted by Bergman from a device of Lavoisier,<sup>2</sup> who suggested the two forms of apparatus shown in Fig. 24.

In the first of these a glass rod was ground with emery powder until it fitted closely into the neck of the funnel. The acid could then be made to enter the flask as slowly as desired by gently raising the glass rod.

<sup>1</sup> *Phil. Trans. Roy. Soc.*, 1772, LXII., p. 155.

<sup>2</sup> Lavoisier: "Traité Elementaire de Chimie," Paris, 1789.

In the other apparatus a long bent tube ending in a capillary opening at D, and having a funnel at the other end, was fitted into the cork of the flask. Any acid poured into the funnel would pass the bend and fall slowly into the bottle, and so long as there was a constant supply of the liquid its introduction into the flask would proceed regularly.

In these two devices we have the beginnings of the automatic feeding arrangements, controlled by valves, which have been fitted to the acid tanks in various forms of mineral water plant, with the object of regulating the supply of acid to the generator (see p. 132).

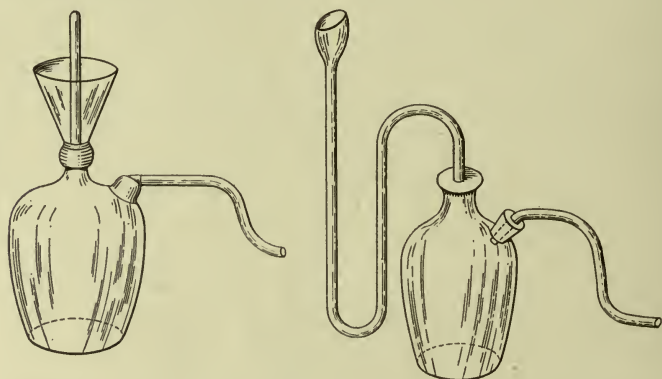


FIG. 24.—Lavoisier's Devices for Regulating an Acid Supply.

**Nooth's Apparatus.**—Priestley's apparatus had the drawback of requiring some degree of skill to handle, so that it was not altogether suitable for general use by the public. Being constructed in separate parts, it was not readily portable, and leakage of the gas was liable to occur at the points of connection.

It was thus a great advance on anything previously devised, when Nooth designed his compact apparatus for impregnating water and other fluids with fixed air.

In the paper that he read before the Royal Society<sup>1</sup> he gave full credit to Priestley for his suggestion of the idea, but claimed that he had obviated the drawbacks in his predecessor's apparatus.

<sup>1</sup> *Trans. Roy. Soc.*, 1775, LXV., p. 59.

A glance at the illustration (Fig. 25) of this apparatus shows that it may be regarded as the prototype, both of the modern *gasogenes* and of the well-known Kipp's gas apparatus used in every chemical laboratory to-day.

It consists of three glass vessels, the fittings of which were ground so as to form perfectly air-tight joints. The chalk and acid were placed in the lower vessel, *c*, while the middle chamber, *b*, was open, both above and below, and was charged with water. In the neck, *h*, of this vessel was fitted a glass valve, made from two pieces of tube, with a movable plano-convex lens between them (see Fig. 26).

This valve opened upwards and allowed the gas to pass, while water was prevented from returning by the action of the lens, and also on account of the glass tube having only a capillary bore.

The uppermost vessel, *a*, received the water forced upwards by the pressure of the gas, and the air was expelled from the apparatus through the opening, *k*, at the top, which could be closed by the stopper, *f*.

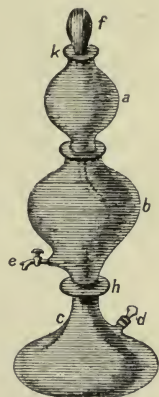


FIG. 25.—Nooth's Apparatus, 1775.

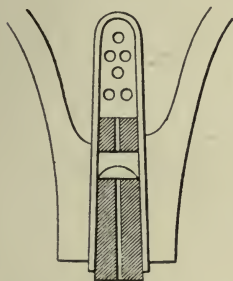


FIG. 26.—Valve in Nooth's Apparatus.

In order to accelerate the impregnation of the liquid in the middle chamber, the two top vessels were disconnected from the bottom one and shaken.

Nooth stated that by means of this apparatus he had been able to imitate very perfectly the common mineral waters.

He claimed that there was no risk of any explosion in using his apparatus; but, as a matter of fact, the defective working of the valve sometimes caused the lowest

vessel to burst.

The reason for this was that the gas was not forced through the capillary tube until considerable pressure had been produced in the generator, and occasionally

the glass was not strong enough to withstand this pressure.

**Modifications of Nooth's Apparatus.**—Hence, Skrimshire, writing in 1804 on the use of Nooth's apparatus, remarks<sup>1</sup>:—"When the mixture of the acid and chalk is carelessly made there is so much gas suddenly evolved as frequently to burst the vessel and inconvenience the operator."

Several modifications of Nooth's apparatus were proposed, and improved vessels were devised by Parker and others, and were sent all over the world.

In the year 1777 J. Magellan published a pamphlet in the form of a letter to Priestley, in which he gives a description of "a glass apparatus for making Mineral Waters like those of Pyrmont, Spa, Seltzer, etc., in a few minutes and with a very little Expence."

Essentially, this apparatus consisted of two separate Nooth's vessels, each containing the two upper bulbs. When the water in the first of these was saturated with the gas, the upper portions were removed and placed in a stand, while their place was taken by the similar bulbs from the other vessel. The complete absorption of the gas by the water in the first bulbs was then effected by shaking them in their stand.

In Withering's<sup>2</sup> apparatus, which was brought out as an improvement upon that of Priestley, the use of bladders was still further extended. The gas was generated from acid and chalk in the conical vessel, A, which was closed by a cork with three openings for tubes. To one of these was tied a bladder by the pressure of which the gas could be driven forward through the central tube into the saturating vessel, B, while the third tube was intended for the introduction of fresh acid.

By closing the lower tap above the saturating vessel the

<sup>1</sup> "Series of Chymical Essays," p. 131, by F. Skrimshire, M.D. London, 1804.

<sup>2</sup> There is no mention of this apparatus in the "Miscellaneous Tracts of the late William Withering, M.D., F.R.S.," 1822; and the present writer wishes to acknowledge his indebtedness to Mr. W. Kirby's "Evolution of Artificial Mineral Waters" for the details upon which this description and diagram have been based.



two bladders, C, C, were filled with the gas, after which this tap was opened and the water impregnated with the gas. The upper tap was then closed, and the vessel, A, detached from the generator, B, as shown in Fig. 27. The saturation of the liquid with the gas was now completed by shaking the vessel, the process being assisted by the pressure of the carbon dioxide in the two bladders, C, C. The tap at the bottom of this bottle was intended for drawing off the carbonated water.

The use of a barrel in place of small glass vessels to contain the water to be impregnated with the gas must have suggested itself both to Bergman and to Priestley, but the first forms of apparatus for making larger quantities of carbonated water actually described were those devised by Duchanoy in 1780 in France, and by Henry in 1781 in this country.

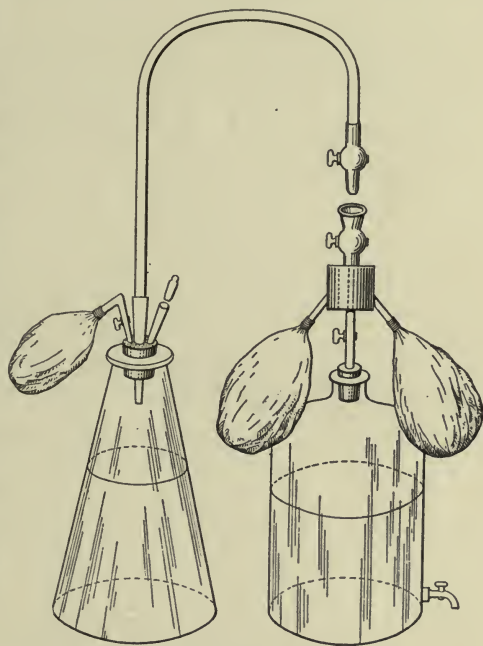


FIG. 27.—Withering's Apparatus.

### Duchanoy's Apparatus.

In Duchanoy's apparatus, a description of which is given in his book<sup>1</sup> on the imitation of mineral waters, the gas was generated from chalk and acid and conducted through a glass tube into a barrel of water, as shown in the illustration (Fig. 28).

Duchanoy also quotes, in the inventor's words, a description of the agitator invented a few years previously by the Duc

<sup>1</sup> "Essais sur l'Art d'Imiter les Eaux Minérales." M. Duchanoy, Paris, 1780.

de Chaulnes, the object of which was to accelerate the impregnation of the water by the gas.

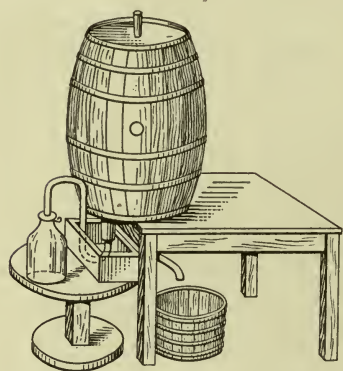


FIG. 28.—Duchanoy's Carbonating Apparatus, 1780.

This agitator consisted of a spindle, which passed through an opening in the barrel, and was capable of being moved up and down. Near the end, at intervals of an inch or two, were fixed four small cross pieces about six inches long so as to form radial arms, and these were connected together by a number of pliable twigs arranged at different angles. A handle could be attached to the top of the spindle outside the barrel, and by giving this a few turns, three or four gallons of liquid could be saturated with carbon dioxide in the course of a few minutes.

**Henry's Apparatus.**—Henry's aerating apparatus was primarily intended for medicinal purposes, so as to obtain larger quantities of the new remedy against scurvy.

As Nooth's vessel was only sufficient for family use, and "would be too small for the sickly crew of a large ship," Henry substituted a small barrel, holding from 10 to 12 gallons, for the glass vessel containing the water (Fig. 29).

The water or other liquid to be carbonated was placed in this barrel, while the gas was generated in the small glass vessel, which, as in the case of Priestley's apparatus,

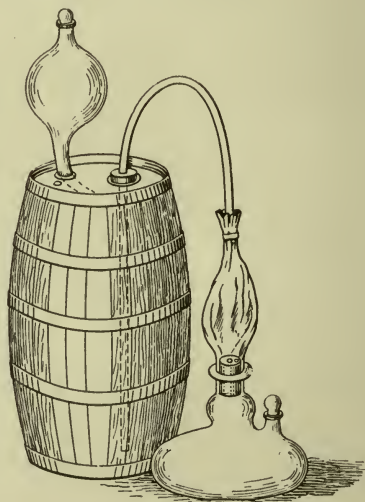


Fig. 29.—Henry's Aerating Apparatus, 1781.

was provided with a bladder to retain particles of acid and to drive the gas forward into the water.

The original air was expelled from the cask through a small vent in the top, and this also served to reduce the pressure when necessary. Some of the water was at first driven upwards into the glass funnel, the stopper of which was then replaced, and in proportion as the water in the cask absorbed the gas, this water in the funnel was drawn downwards again.

Henry published a pamphlet giving directions for the use of this apparatus in preparing various mineral waters, and aerating beer or cider.<sup>1</sup>

His directions for the preparation of artificial mineral waters by means of this apparatus are given elsewhere (p. 75).

The agitator of the Duc de Chaulnes, described by Duchanoy, was subsequently also added to this apparatus, and a valve was placed between the bladder and the generating vessel, with the object of preventing any of the gas being driven backward instead of forward.

**Haygarth's Impregnating Machine.**—At about the same time that Henry had devised his apparatus an ingenious impregnating machine had been constructed by Haygarth, who was also a medical man, and he gave the idea and plans of his apparatus to Henry to publish.

In the year 1781 the latter read a paper before the Literary and Philosophical Society of Manchester on the "Preservation of Sea Water from Putrefaction," and to this he added as an appendix "An Account of a Newly-invented Machine for Impregnating Water or other Fluids with Fixed Air," which had been communicated to him by Dr. Haygarth.

It was not until four years later that a description, illustrated by plates, of this machine was published in the first volume of the "Memoirs of the Society."<sup>2</sup>

<sup>1</sup> "An Account of a Method of Preserving Water at Sea, to which is added a Mode of Impregnating Water in large Quantities with Fixed Air. For the Use of the Sick on Board of Ships and in Hospitals," by Thomas Henry, F.R.S., Warrington, 1781.

<sup>2</sup> "Memoirs of the Lit. and Phil. Soc., Manchester," 1785, I., p. 51.

As will be seen from the accompanying figure (Fig. 30), Haygarth's machine consisted of two communicating chambers and an "effervescing vessel" or generator, in which the carbon dioxide was prepared from chalk and oil of vitriol, and a pair of bellows fixed above the cylinders.

The gas on leaving the generator, E, entered the "air

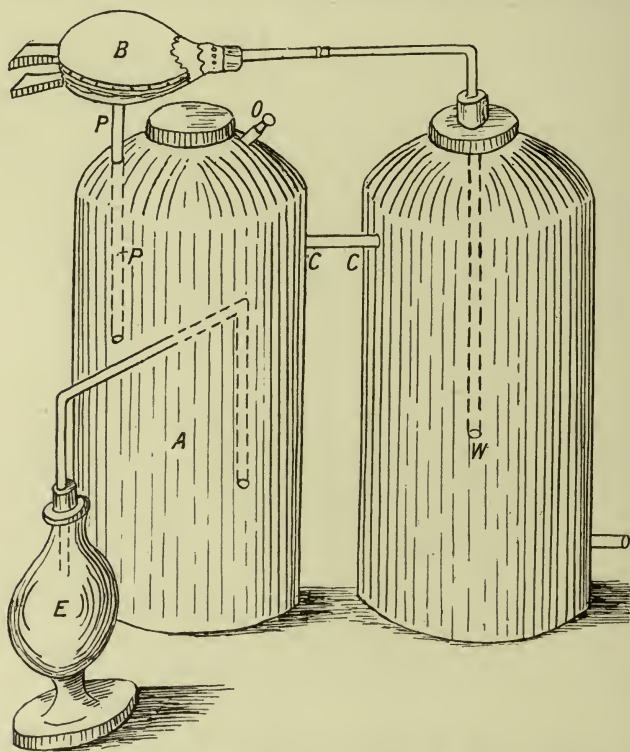


FIG. 30.—Haygarth's Impregnating Machine, 1781.

vessel," A, the original air being expelled through the opening, O. It was then drawn up into the air valve of the bellows, B, through the pipe, PP, and thus forced forward into the "water vessel," W, which had previously been charged to about half its capacity with water or other liquid to be impregnated.

The gas not absorbed by the water returned to the "air vessel" through the pipes, c, c, above the level of the liquid, and was thus brought into the circulation again, this process being



continued until the saturation under the low pressure obtainable was complete.

As it was found in practice that the working of the bellows was very difficult, a bladder filled with carbon dioxide was tied over the opening, O, in the air vessel, after all air had been expelled from the apparatus, and with this addition the gas could readily be driven forward.

The impregnated water was drawn off into bottles through the tube at the bottom of the "water vessel," this opening being kept corked and wired until the end of the impregnation.

The principle of Haygarth's machine was adopted in practice as a manufacturing process, and as late as the year 1825 "carbonated water and other liquors such as spirituous,

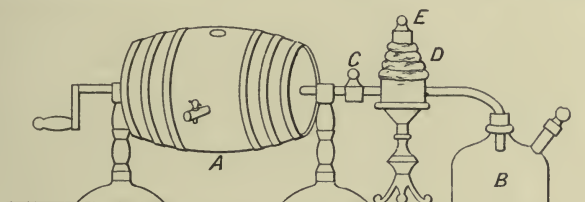


FIG. 31.—Carbonating plant used in London in 1825.

saccharine and aromatic" were thus impregnated by the gas. According to Mackenzie,<sup>1</sup> who gives the accompanying diagram of the machine used for the impregnation "in a large way," these liquors were saturated with the gas under considerable pressure, which was reduced in part when they were bottled.

This machine consisted of an air-tight barrel, which could be made to rotate by turning the handle. The gas was generated from chalk and dilute sulphuric acid in the bottle, B, and entered into the bellows, D, which were varnished to make them air-tight. As soon as the bellows had been distended to their full extent, the cock, C, was opened, and a weight, E, was placed upon the top of the bellows, with the result that the gas was driven forward under a certain degree of pressure into the barrel (Fig. 31).

<sup>1</sup> "One thousand Processes in Manufacture," by C. Mackenzie, Operative Chemist. London, 1825.

This had meanwhile been filled to about half its capacity with distilled or spring water, and, after expulsion of the air by the carbon dioxide, the bung was replaced and fixed down by means of a jointed hoop.

The barrel was provided with a perforated false bottom, and the impregnation of the water was accelerated by quickly turning the handle backwards and forwards a few times, and finally stone bottles were rapidly filled from the tap with the "carbonated water," and their corks bound down with copper wire.

As thus prepared the carbonated water is stated to have kept well for many months. It could be obtained as a drink at "various establishments in London."

**Hydraulic Bellows.**—The next advance in the development of carbonating machinery was the substitution of "hydraulic bellows" for the primitive air bellows of the first machines.

The origin of the gasometer of the aerating plant of to-day has been attributed, though incorrectly, to an invention of James Watt, who devised "hydraulic bellows" for the collection of the various "airs," then being advocated as a remedy for most diseases.

Writing from Heathfield to his friend, Dr. Thomas Beddoes of Bristol, in June, 1794, Watt observes :—

Having never made the art of medicine my particular study, I should not have troubled you with my crude ideas on the use of pneumatic medicines, if your approbation of what I mentioned to you, joined to my earnest desire to aid your endeavours with the hope that possibly some idea might be started, which may save other parents from the sorrow that has unfortunately fallen to my lot,<sup>1</sup> had not urged me to step over the bounds of my profession.

It appears to me that if it be allowed that poisons can be carried into the system of the lungs, remedies may also be thrown in by the same channel.

As fixed air is a saturated solution of charcoal in oxygene air, is it not probable that the lungs can decompose it? We should therefore only look to its effects as an antiseptic.

The species [of fixed air] I would recommend is that from fermentation, and the means keeping a vessel of fermenting wort close to the patient, which will in general be grateful to him.

<sup>1</sup> His daughter had recently died of consumption.

A month later Watt writes to Beddoes that he is forwarding drawings of his apparatus for "producing and receiving the various airs which may be supposed to be useful in medicine."

These letters and drawings, together with numerous accounts of cures effected by means of "airs," are published in a pamphlet, of which the first (or medicinal) part was written by Beddoes and the second (or mechanical) part by Watt.<sup>1</sup>

That part of the apparatus intended for the collection of fixed air and other gases was termed the *Hydraulic Bellows*, and is shown in the accompanying figure (Fig. 32).

It consisted of an outer vessel, H, and an inner movable vessel, J, which was suspended by a cord passing over two pulleys, and bearing a counter weight, L.

The outer vessel was made double to obviate the use of much water, and a space of about 2 inches was left for the inner vessel, J, to move up and down, while a channel in the rim, W, prevented the water from overflowing.

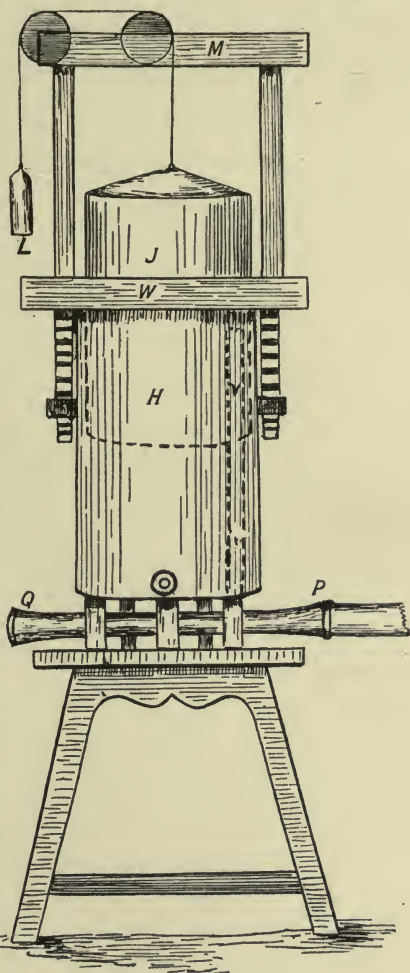


FIG. 32.—Watt's Hydraulic Bellows.

<sup>1</sup> "Considerations on the Medicinal Use of Factitious Air and on the Production of Factitious Air." Part I., by Thomas Beddoes, M.D. Part II., by James Watt. London, 1795.

The "air," which in the case of carbon dioxide was obtained by igniting chalk, entered the bellows through the pipe, P, and passed upwards through the vertical pipe, V, causing the inner vessel, J, to rise until it was stopped by the cross-piece at the top.

When it was required to fill a gas bag or gas holder the gas was forced out through the discharge pipe, Q, by lifting the weight, L, and allowing the inner vessel to descend by its own weight.

The apparatus was made of japanned tin-plate or iron, and in two sizes, the larger (12 inches in diameter) holding about a cubic foot of air, and the smaller ( $8\frac{1}{2}$  inches in diameter) holding about a third of the quantity.

In order to wash gases when prepared with acids they were made to pass through a vessel of water on their way to the hydraulic bellows, the contents of this being meanwhile stirred by means of an inverted T-shaped agitator, which was turned by a small winch at the end of its stem.

**Lavoisier's Gasometer.**—There can be no question, however, that the credit of the invention of the gasometer itself, if not its application to the manufacture of mineral waters, belongs to Lavoisier, who published the account of his invention five years before Watt invented the *hydraulic bellows*.<sup>1</sup>

Lavoisier's apparatus (*see* Fig. 33) was, as its name denotes, primarily intended for the measurement of gases, but had the further object of enabling a continual and uniform supply of the gas to be directed wherever required.

The bell of the gasometer was made of hammered copper, 18 inches in diameter and 20 inches in depth, and it had an external ridge with compartments in which leaden weights were placed when pressure to expel the gas was needed.

This bell was inverted in a vessel of water, and was attached at the top to one end of a curved beam, having at each end a

<sup>1</sup> "Traité Elementaire de Chimie," by A. Lavoisier, Paris, 1789, Vol. II., p. 346 :—"Je donne le nom de Gazomètre à un instrument dont j'ai en la première idée, et que j'avois fait exécuter dans la vue de former un soufflet que pût fournir continuellement et uniformément un courant de gaz oxygène pour d'expérience de fusion."



segment of a circle of iron. The beam rested upon large movable brass wheels, the axes of which ran on rock crystal to reduce the friction.

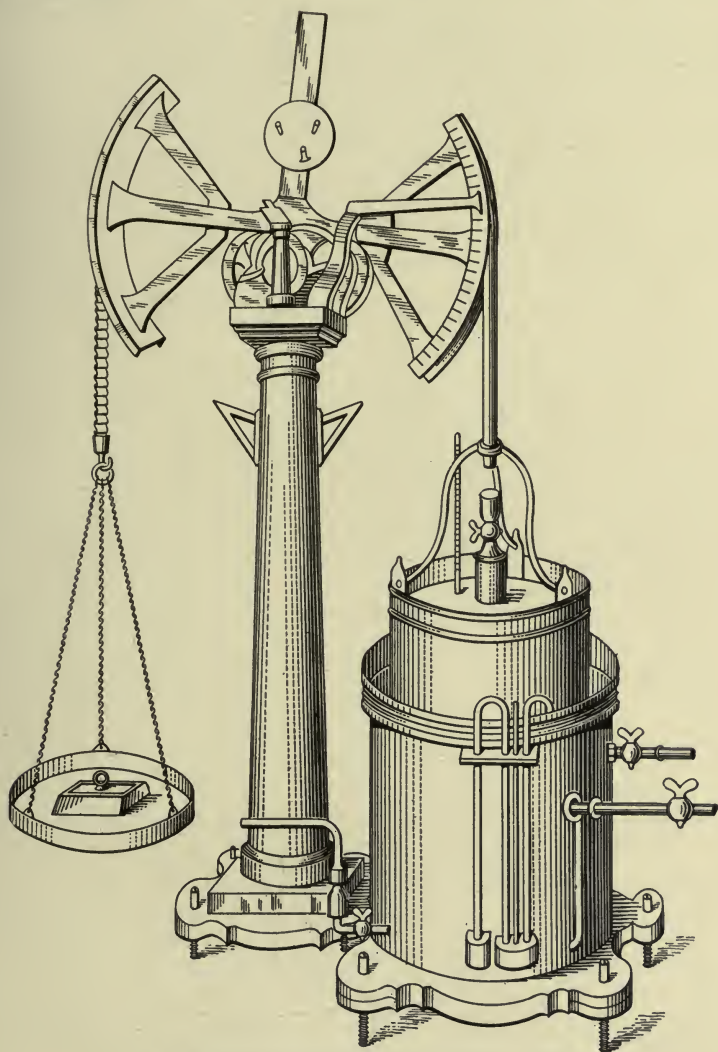


FIG. 33.—Lavoisier's Gasometer. 1789.

The other end of the beam carried a pan, in which weights could be placed when the pressure within the bell was to be

reduced and the bell was to be raised. This was equivalent to the counter weight of Watt's hydraulic bellows. By reducing the weight in the pan, the bell would sink and expel the gas, and, as was mentioned above, the pressure could be still further increased by putting weights upon the bell.

A thermometer passed through an opening in the top of the bell, and the volume of the gas could be measured upon a scale by means of an indicator at the top.

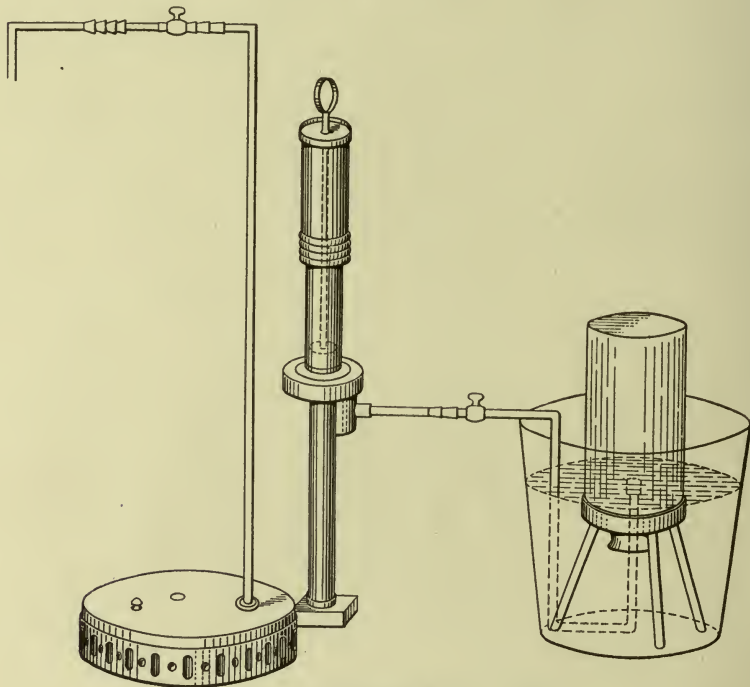


FIG. 34.—Lavoisier's Pump. 1774.

It was not long before Watt's hydraulic bellows, which soon became known as "gasometers" (after Lavoisier's invention), became generally adopted as an essential part of most mineral water carbonating machines, although, as was mentioned above (p. 95), the old air-bellows type of apparatus still continued to be used in the smaller factories.

Another improvement added to in the early manufacturing plants was a washing bottle between the generator and the

carbonating vessel, its object being to remove traces of sulphuric acid and other impurities from the gas before it came in contact with the liquid that was to be impregnated. The adoption of this device is usually attributed to the French chemist, Macquer.

**Early Pumps.**—The use of a force-pump for impregnating water with fixed air under pressure had been suggested by Priestley (see p. 87), and a type of pump suitable for the purpose had been devised and described by Lavoisier shortly afterwards.<sup>1</sup>

The application of such a pump (Fig. 34) to the plant for making aerated water was rendered more practicable when a gasometer was also employed, although in France it was extensively used on a limited scale with small apparatus by the pharma-

cists, in whose hands the manufacture of aerated mineral waters remained as a monopoly.

Bouillon-Lagrange, writing in 1811 on the subject,<sup>2</sup> gives a description of Planche's compressor (Fig. 35), by means of which a liquid could be charged in the course of a few hours with four to five times its volume of carbon dioxide.

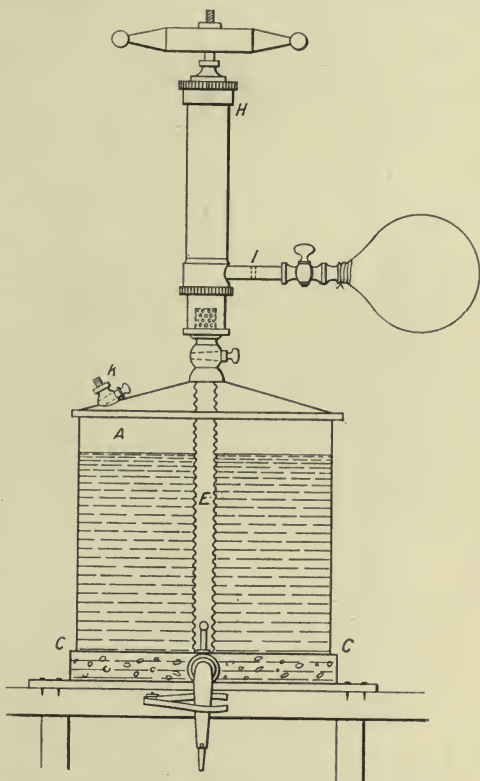


FIG. 35.—Planche's Compressor. 1811.

<sup>1</sup> "Opuscules Physiques et Chymiques," Paris, 1794.

<sup>2</sup> "Essai sur les Eaux Naturelles et Artificielles," Paris, 1811.

The vessel, A, was filled with water, and about an eighth of the quantity then run out, and the space filled with carbon dioxide from the bladder or flask affixed to the side tube of the pump. At the bottom of A, which was made of polished copper tinned inside, was a perforated false bottom, with a central opening for the pipe, E, the object of the perforations being to assist in the distribution of the gas. After being

impregnated with the gas under pressure, the liquid could be drawn off through the tap at the base.

Planche, who was a pharmacist in Paris, also devised an apparatus for the preparation of small quantities of *Eau de Seltz*, in which the gas was forced into the liquid by its own pressure, and the process of impregnation was accelerated by a wooden agitator of the type of that of the Duc de Chaulnes (*see* Fig. 36).

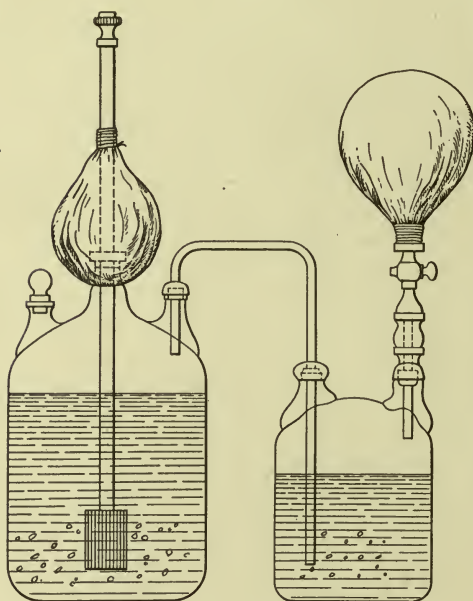


FIG. 36.—Planche's Apparatus with Wooden Agitator.

gas was prevented by enclosing the neck of the vessel through which it passed within a bladder.

From the veiled description given in 1799<sup>1</sup> by the French Committee that reported upon the artificial mineral water establishments of Nicholas Paul in Geneva and Paris (*see* p. 76), it would seem that Paul's carbonating plant probably included a gasometer and a force pump. "The gases," it is stated,

<sup>1</sup> "Rapport sur les Eaux Mineral Artificielles du Cit. Paul, etc., par le Cit. Fourcroy." *Annales de Chimie*, An. VIII., XXXIII., p. 125.



“are conveyed through purifiers into strong closed casks, where they meet with filtered water, and are dissolved by joint assistance of agitation and pressure. The gas, whether produced by heat or effervescence, is drawn out by the same pump and conveyed into the same casks.

“The saline and other fixed matters are put, in due quantities well mixed and powdered, into each bottle before it is filled with gaseous water drawn immediately from the cask.

“The hissing noise and bursting of the bottles occasionally at the moment they are corked convinces the spectator that the water is supersaturated with gas.”

The gas was prepared either from chalk and sulphuric acid, or by decomposing chalk alone by heat.

Exact details of the machinery employed are not given, for “the Inventor reserves to himself the complete knowledge of the apparatus used to compress the gas.”

By way of criticism the Committee remarks that the machinery did not compress into the water as much as six times the volume of carbonic acid gas, and that the impregnated waters suffered constant and successive losses of gas during the corking, storing, and uncorking of the bottles.

In the preface to his pamphlet, Paul observes that for many years previously he had used glass bottles instead of those of earthenware, which he had found too porous.

**The Geneva Process.**—This method of carbonating by compression of the gas with the aid of a force pump into water contained in a cask became known as the “Geneva process,” from the fact of its having been first introduced on a manufacturing scale by Paul in Geneva, about the year 1790.

The same firm started a branch business in London in 1802, and other mineral water factories using the same type of machinery were established about the same time, both in England and various European countries.

Shortly before the establishment of Paul’s factory in London, the manufacture of aerated mineral waters was started by A. R. Thwaites & Co. in Dublin and in the year 1799 that firm was selling “soda water of single and double strength.”

Their method of manufacture was kept strictly secret, but the machinery was probably very similar to that employed by Paul.

In a pamphlet published in 1869 by J. Briggs, manager to Messrs. Hayward-Tyler & Co., it is stated that the first machine used in the Dublin factory was made of wood, while strong glass bottles were used for generating the gas. Subsequently cisterns excavated from large blocks of granite took the place of the wooden aerating vessel.

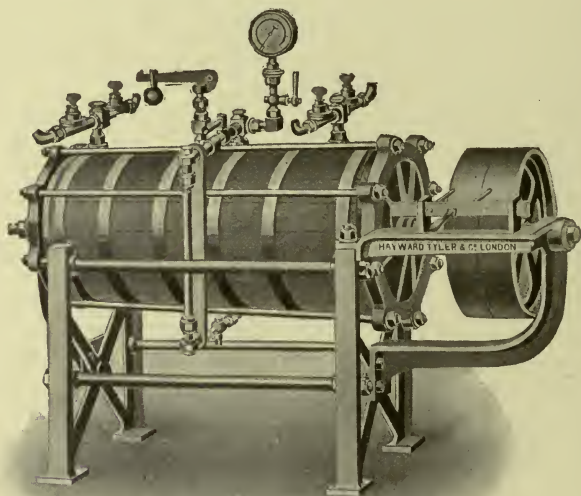


FIG. 37.—Old English Wooden Carbonating Cylinder.

Early in the last century William Russell began to manufacture machinery for the preparation of soda water, and after his death, in 1835, the business was acquired by the present firm of Hayward-Tyler & Co., who may thus claim to be the earliest makers of mineral water plant in this country.

The machinery first made by them was constructed on the "Geneva system," and was worked upon the principle already described, of saturating a given quantity of liquid with gas by means of a force pump.

The illustration (Fig. 37) represents the carbonating cylinder

of the old type of English machines as made by Hayward-Tyler & Co. in 1835. It was constructed of oak  $2\frac{1}{2}$  to 3 inches thick, strongly bound with iron hoops, and having ends of plate-iron secured with bolts and nuts. It contained a horizontal shaft supported in the iron end, and carrying stirring blades which were made to revolve by a band passing over the end wheel. This was connected with a steam engine, or in other cases was worked by hand. The pressure of the gas within the cylinder was recorded on the pressure gauge, while a safety-valve was provided at the top. Air was first pumped out, so as to create a partial vacuum, and on opening the cock in the pipe connected with the supply tank, the solution containing the weighed quantity of soda rushed in. The gas was then forced in by the pump, the contents stirred with the agitator, and the "batch" drawn off into bottles.

The generator for the production of the carbon dioxide, the gasometer, and the force pump are not shown in the illustration.

According to J. Briggs, whose pamphlet has already been quoted, the output of soda water from one of these early machines with a single bottler was from 60 to 80 dozen bottles per day, though the quantity could be increased by having two bottlers to a machine.

In the modern types of machines plant worked by a single pump will yield from 300 to 700 dozen bottles per day, according to the degree of power applied.

The pressure within the cylinder of the early machines could be kept fairly constant by pumping in more gas during the process of bottling, but the objection to this course was the accumulation of a large amount of gas which would be left after all the liquid had been withdrawn.

Before the cylinder could be re-charged this gas had to be expelled, and was either allowed to escape into the air or was returned to the gas-holder. The former course involved waste, while in the latter the gas usually became mixed with more or less air.

To prevent this loss some manufacturers pumped air into the cylinder during the bottling, but soda water bottled under those conditions was pretty sure to contain air as well as carbon



dioxide, and the contents of the bottle would then rush violently from the bottle when opened, and would become flat almost immediately on standing.

The principle involved in this early apparatus is found in

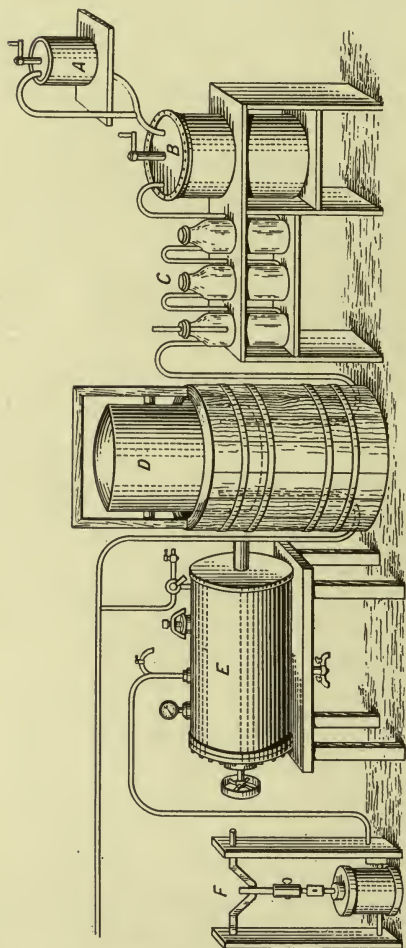


FIG. 38.—Old German Carbonating Plant.

plant still used to a small extent in mineral water factories at the present day, especially where a small quantity of a liquid such as cider is to be carbonated.

The arrangement of plant including these machines will be seen by reference to the accompanying figure (Fig. 38), which represents a German carbonating apparatus of the early part of last century.

The small vessel, A, at the top was charged with sulphuric acid, the flow of which into the generator, B, below was regulated by the handle.

Lumps of chalk and some water were placed in the generator, which was provided with an agitator, worked by the handle outside, for mixing the contents.

The carbon dioxide passed through washing bottles, C, to remove particles of acid mechanically carried over with the gas, and then into the gasometer, D, whence it was drawn by means of the pump, F, and forced under pressure into the closed carbonating cylinder, E.



The pipe at the top of this apparatus must have turned downwards and have formed a connection with the bottom of the pump on the left side.

The impregnation of the liquid in the cylinder by the gas was accelerated by the movement of agitating blades fixed to a horizontal shaft, which was made to revolve by applying power to the wheel outside at the end of the cylinder.

The gas pumps of these earlier machines were open at the top, and had pistons packed with leather. The gas was drawn into the barrel by an up stroke of the piston, and forced out by a down stroke, just as in the case of an ordinary water pump.

Hence leakages of gas were very liable to occur when the leather of the piston became at all worn, and apart from the wastage involved, it then became difficult to obtain the necessary pressure within the cylinder.

#### Struve's Apparatus.—

A modification of this type of apparatus was patented in 1823

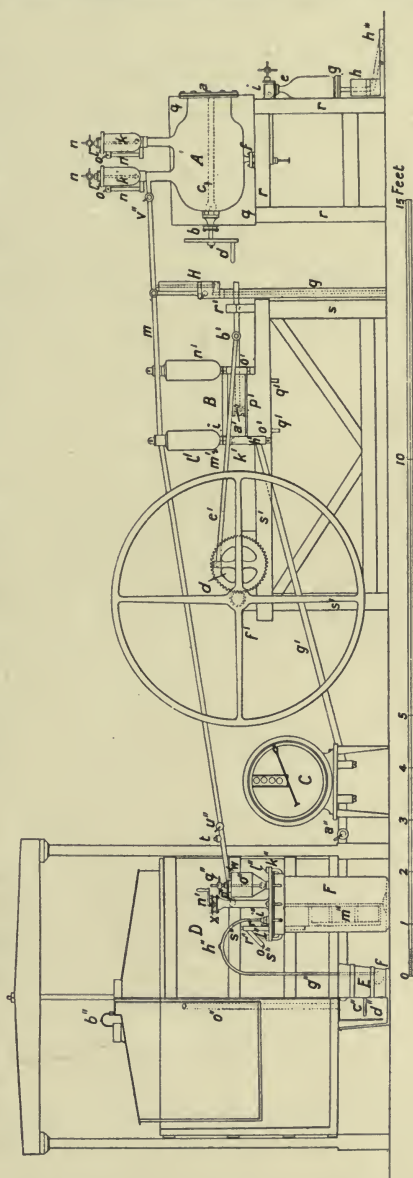


FIG. 39.—Struve's Carbonating Plant, 1823.

by Swaine acting on behalf of Struve (English Patent, 4,851 of 1823). This is of interest both from the ingenious way in which its various parts are combined, and from the fact that it was the apparatus used by Struve in manufacturing his artificial mineral waters at his "spas" in Brighton, Germany, and Russia.

The pump and "preparing vessel," A, are shown in the accompanying diagram (Fig. 39). The pump, B, which was capable of acting both as a suction and compressing pump, drew the carbon dioxide from a gas-holder, D, through a measuring meter, C, delivering into the pipe, *g'*, and forced it under pressure into the preparing vessel through the pipe, *m*. The piston of the pump, *b'*, was connected with the wheel, *d'*, which was put in motion by the large fly-wheel that was worked either by hand, or, at a later period, by steam power. The barrel of the pump was enclosed in a cylinder of water, *p'*, so that any escape of gas could be readily detected, while a chamber, *l'*, was provided for condensing any vapour from the pump, and a chamber, *n'*, containing distilled water for moistening and cooling the leather packings of the piston.

Above the preparing vessel were two receivers K, *k*, made of tin or other metal, which were intended to hold the concentrated solutions of salts to be introduced in regulated quantities into the vessel of water beneath, the supply being regulated by means of the stop cocks, *o*, *o*.

The preparing vessel, A, was surrounded by a cistern of water, *q*, *q*, for cooling purposes, and was provided with a manual agitator *a*, *b*, *c*, to accelerate the impregnation of the liquid by the gas.

When the required degree of pressure was indicated upon the pressure gauge, H, the aerated liquid was drawn off through the tap, *f*, at the bottom of the vessel and entered the bottle, which had previously been brought into position by pressing the treadle, *h*, and so raising the platform, *g*. As soon as the pressure within the bottle was equal to that in the vessel, A, a small air-vent, *i*, in the side of the cock, *e*, was opened. This let a small quantity of air escape, and allowed the filling of the bottle to be completed, immediately after

which the cork was introduced, and secured by a wire or a string.

The other parts of the apparatus, not shown in the diagram, included an ordinary carbon dioxide generator, purifying vessels containing a solution of a barium salt to absorb any particles of sulphuric acid carried forward with the gas, and a gas-holder or gasometer of the usual type.

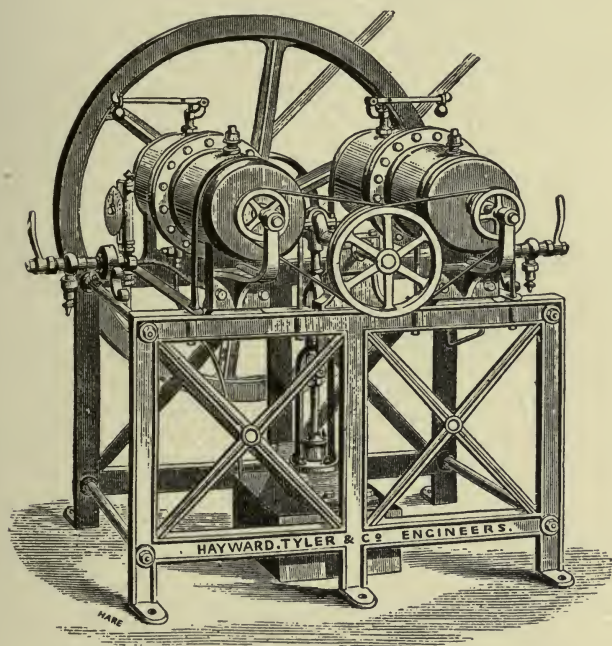


FIG. 40.—Double Cylinder Carbonating Machine.

An illustration, in which this plant is shown in working order in Struve's main establishment in Dresden in 1853, is given on p. 80.

Apart from the gradual diminution of pressure during bottling, the drawback of all forms of apparatus working upon the "Geneva system" is that the process of bottling must be interrupted in order to re-charge the cylinder with a fresh quantity of liquid.

Various attempts were made to remedy this defect. Thus,

in 1821, an apparatus was devised by Laville-Delaplagne, in which the carbon dioxide was stored in two gas-holders, communicating with a double pump, while the liquid to be aerated was placed in two wooden barrels containing agitators. The gas could be pumped into either of these at will, so that while one was being drawn from for bottling, the other was being aerated.

An early machine on this principle, made by Hayward-Tyler & Co., is shown in Fig. 40. The cylinders here were put side by side, with the pump below working between them, while the agitators were set in motion by cords from a wheel in common.

**Saturation by Chemical Pressure.**—In 1824 Cameron constructed an apparatus in which the saturation of the liquid was effected by the pressure of the gas itself upon a larger scale. In other words, it was a reversion to eighteenth century apparatus.

The generator was made of iron lined with steel, and contained an agitator also covered with lead for stirring the chalk and sulphuric acid. The gas was conducted into a lead-lined iron vessel with very thick walls in which it was washed, and thence passed into the saturator, which was of ovoid form, and was provided with a vertical agitator with three superposed blades. This vessel was made of copper or iron, tinned inside, and the pressure was indicated upon a mercury manometer.

An apparatus upon the same principle was brought out in France in 1830 by Barruel, with the difference that his saturator was in the form of a cylinder, which could be rotated upon an axis.

The difficulty of controlling the pressure of the gas evolved from the generator rendered both of these apparatus, in which the gasometer was omitted, dangerous to use.

**Bakewell's Apparatus.**—In the year 1832 F. C. Bakewell took out a patent (English Patent, No. 6,238) for a carbonating machine, which is interesting from its ingenious construction and from being one of the earliest attempts in this country



to bring the carbonating cylinder and the generator together in one compact piece of apparatus.

As will be seen from the diagram in Fig. 41, which represents a side section of this machine, Bakewell's invention consisted essentially of a strong cylindrical vessel of iron, divided into two compartments by a partition about two-thirds of the height from the bottom. The lower chamber was intended to serve as the generator, and was preferably lined with lead or earthenware to protect it from the action of the acid, while the upper chamber served as the carbonating vessel. The whole cylinder was supported by pinions resting upon standards at the side, so that it could be turned or made to vibrate at will.

In making soda water the machine was turned so that the opening, *b*, was uppermost. Chalk and water were introduced through the opening, *c*, which was then screwed down, after which the acid was poured through a funnel placed in *b*, in the acid chamber, *n*, whence it could only reach the chalk through the opening, *p*.

The cap having been screwed down on to the opening, *b*, the machine was turned to a vertical position, and the water to be carbonated was poured into the upper compartment through the opening, *a*, upon which a cap was also screwed.

Upon now causing the cylinder to vibrate upon its pinions, a little of the acid passed through the opening, *p*, and acted upon the chalk. The gas evolved could only escape through the opening, *f*, and passing through the tube, *g*, and thence into the tube, *i*, where it was washed, escaped through the perforations, *m*, at the end of the tube, *l*, into the water to be impregnated.

The stirring of the chalk during the gradual introduction of the acid was effected by means of a pendulum agitator, *v*,

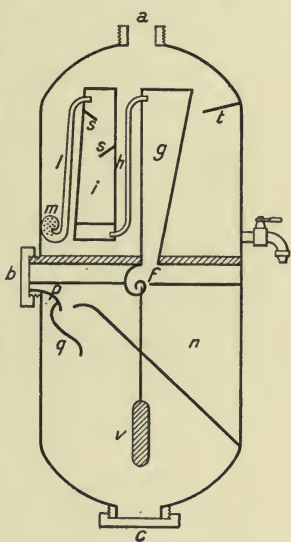


FIG. 41.—Bakewell's Apparatus. 1832.

which was suspended at two points from the top of the lower compartment, and was made to vibrate when the machine was rocked on the pinions, which are not shown in the diagram. Shelves or baffles, *s*, *s* and *t*, were provided to bring the gas into contact with the water and promote the washing and subsequent impregnation, while the carbonated liquid was drawn off through the tap at the side.

The size of the cylinder described in the patent was 18 inches in height and about 8 inches in diameter, while the internal washing tube, *i*, was about 2 inches in diameter at its widest end.

It will be noticed that no safety-valve or other means of guarding against excessive pressure from a sudden evolution of gas was provided, and the risk of explosion with this machine must have been very considerable.

**Savaresse's Apparatus.**—In 1837 Savaresse devised an improvement upon the apparatus of Barruel, in which he regulated the production of gas in such a way that the quantity to be evolved was determined beforehand, and so fixed that its force should not be greater than the strength of the walls of the apparatus. In this way he claimed that all risk of explosion was prevented.

The carbon dioxide was generated in the usual leaden vessel, provided with an agitator, from dilute sulphuric acid and chalk, the latter being introduced in paper cartridges as required.

The gas produced was made to pass through two purifying vessels, the second of which was provided with a manometer to indicate the pressure, and then into an oscillating cylinder, the axis of which was made hollow to receive the conducting pipe.

Here the water or other liquid was rapidly impregnated, and was thence drawn off into bottles by means of a special bottling machine (*see p. 149*).

Subsequently, in 1838, Savaresse improved upon this machine by using two cylinders, one of which was charged with the gas, while the other was being drawn off into bottles, and he thus made the process more continuous.

This latter apparatus was also patented in this country by an agent, Miles Berry (English Patent, No. 7,899 of 1838), and its construction was illustrated by the accompanying diagram (Fig. 42).

Here *b* represents the generator, a hollow globular vessel, to the upper part of which was secured a conical tube, *c*, of copper lined with tin.

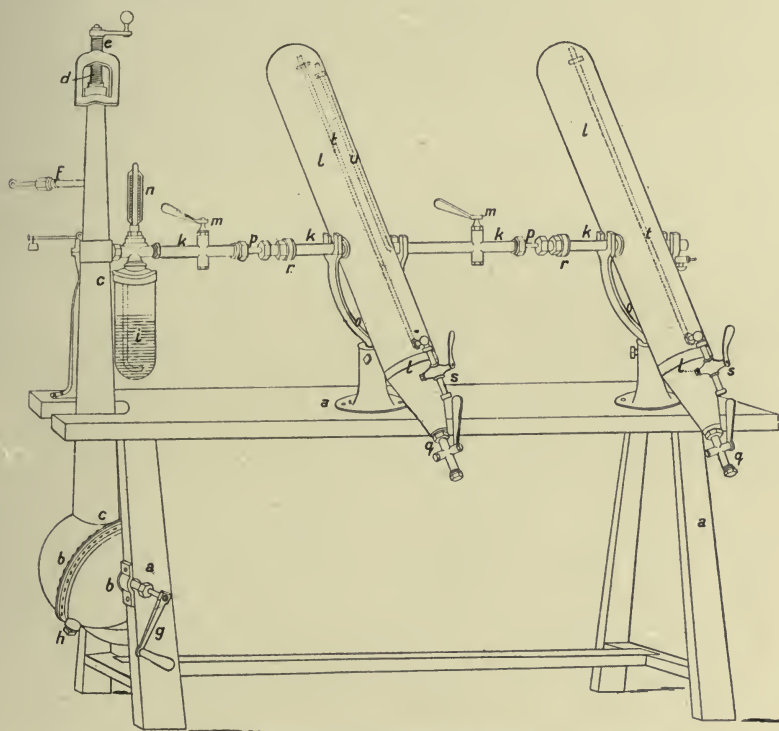


FIG. 42.—Savaresse's Carbonating Machine. 1838.

The cartridges containing the charges of calcium carbonate were introduced into the top of this tube, and could be admitted one by one, as required, into the generator by withdrawing the sliding shutter, *f*. The top of the tube, *c*, was closed by a plug with a leather collar, which was screwed down by turning the handle, *e*.

The gas was washed by bubbling through water contained in

the vessel, *i*, from the upper part of which it passed into the two oscillating cylinders, *l, l*, which had previously been charged with the liquid to be impregnated.

The bottling machine and the method of filling syphons by its means are described elsewhere (p. 149, 167).

**Ozouf's Apparatus.**—A few years later an intermittent apparatus of the same type as those of Savaresse was devised by Ozouf in France. It consisted of a spherical saturator made of copper lined with lead, and was provided with an internal agitator, a manometer, and a safety-valve. This vessel was charged with the water or mineral salt solution, and was connected with the gas generator, which was in the form of a copper cylinder lined with lead. Within the cylinder were contained the vessel for the sulphuric acid and a washing chamber, and the whole apparatus was mounted on a compact stand.

The objections to the use of this machine were that the gas received insufficient washing, and conveyed impurities to the water in the sphere, and that, as in other plant constructed on the same principle, the risk of explosion from a too sudden evolution of gas had not been altogether eliminated.

Mention may also be made here of a machine devised in 1861 by François, since it combined many of the features of the machines of Savaresse and Ozouf. It had a vertical washing chamber inside the generating cylinder, and all its separate parts were mounted so as to form a single apparatus that occupied a small space and was easily worked. It did not, however, completely overcome the drawbacks of the machines that it succeeded.

**The Mondollot System**—The various attempts made in France to simplify the machinery by omission of the gasometer without incurring risk of explosion culminated in Mondollot's system of carbonating.

In its main essentials this system differs only from the ordinary continuous process of carbonating in its mode of generating the gas. The supply of acid to the generator is



dependent upon the amount of gas drawn off by the pump, so that acid is only introduced when required for the decomposition of more chalk or sodium carbonate. To prevent still further the risk of explosion a safety water-valve, in the form of a U-tube, is affixed to the top of the generator, so that any excess of pressure within the apparatus is at once indicated by the water being expelled from this tube and leaving a clear passage for the gas.

The gas withdrawn by the pump from the cylinder passes through a small washing vessel containing water, and is forced, together with the water to be carbonated, into a spherical condenser, where the impregnation is promoted by the action of an agitator.

When the gas is thus withdrawn from the cylinder through the pipe, B (Fig. 43), at each stroke of the pump, the dilute sulphuric acid in the outer chamber of the generator passes through the holes, *a*, and rising into the tube, *t*, and traversing the perforations comes into contact with the chalk or

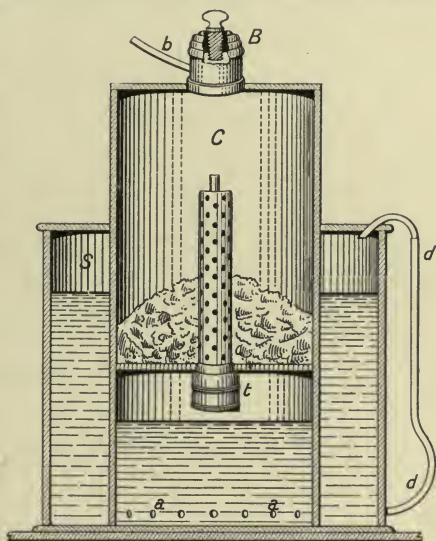


FIG. 43.—Section of a Mondollot Apparatus.

sodium carbonate in the inner chamber. Carbon dioxide is immediately produced, and thereby a backward pressure is created, which drives the acid down again through the tube, *t*, and the evolution of gas stops, until, upon the next stroke of the pump, the back pressure is again removed and the acid once more comes into contact with the carbonate. This process will continue, with alternate evolution and stoppage of the gas, until the whole of the materials are spent.

After impregnation of the liquid in the saturating condenser, bottling is done by any kind of bottling machine.

This French system presents many points of analogy with the more recent Riley system described on p. 139 ; but in the case of the latter not only is the gasometer omitted, but the saturation is also effected without the use of any agitator.

**Other Intermittent Apparatus.**—The loss of gas after bottling with intermittent machines was met to some extent by the invention of apparatus having two stationary cylinders, each provided with an agitator.

Machines of this type were made by Vernaut and by Berjot, and were intended more especially for the manufacture of mineral waters by pharmaceutical chemists.

The cylinders communicated, so that when one had been drawn down, leaving only an atmosphere of gas, it could be connected with the other cylinder, and sufficient water drawn from the latter to absorb this residual gas, and equalise the pressure within the two cylinders. The cock of the communicating pipe was then closed, and the saturation of the water completed with gas direct from the generator. By this means the loss of gas was reduced to about half the quantity of that inevitable when only one cylinder was used.

In neither of these double-cylinder machines, however, was the drawback of irregularity of pressure inherent in this type of machine overcome. Thus bottling would begin at a pressure of about eight atmospheres, and would steadily fall until, finally, when the cylinder was nearly empty, the pressure would have been reduced to about five or six atmospheres.

**The Continuous Process.**—In the invention of William Hamilton, which was secured by two patents (English Patents, No. 3,232 of 1809, and 3,819 of 1814), we have the beginning of the continuous process of aeration—a process that has now been almost universally adopted.

Hamilton's apparatus, according to the description given in his later patent, was based on the principle of forcing a measured quantity of the liquid and of the gas simultaneously into a small condenser, whence after impregnation had taken place under regulated pressure, the aerated product was drawn

off and bottled. The supply of both liquid and gas could be maintained without interruption, and the process was thus

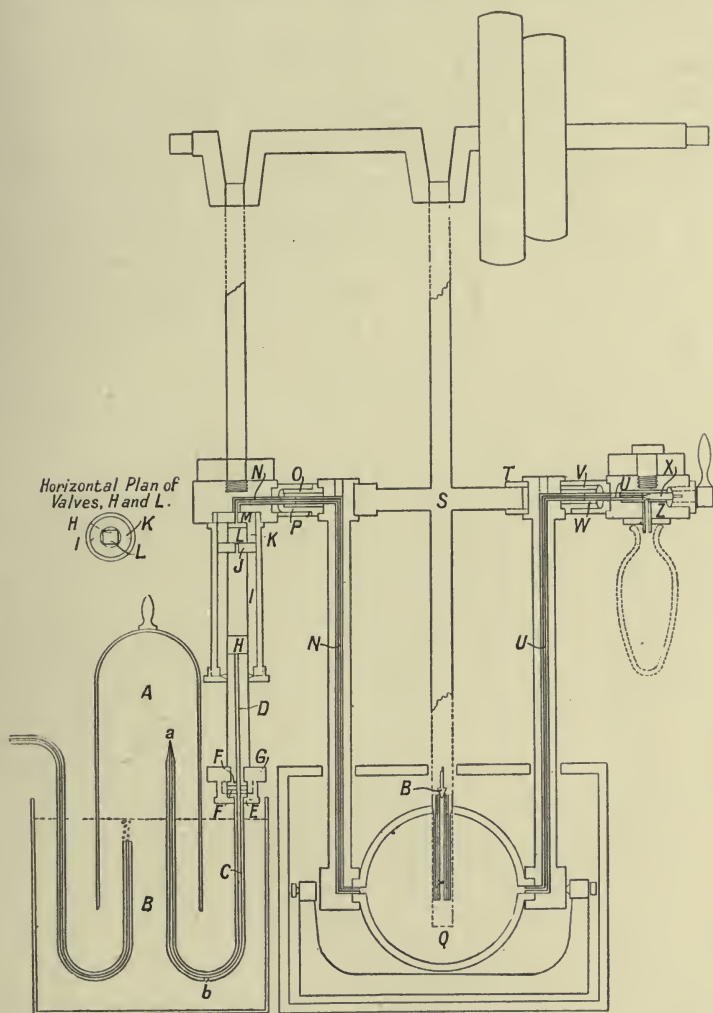


FIG. 44.—Hamilton's Continuous Process Machine. 1814.

both more rapid and less wasteful than in the case of the old cylinder machines.

The construction of the machine is shown in the accom-

panying diagram (Fig. 41), which Hamilton annexed to his patent specification.

The carbon dioxide was contained in a gas-holder, A, and the solution to be aerated was introduced into the tank, B. By the action of the piston of the pump, D, which received its motion from the crank above, gas was drawn into the tube, C, through its capillary opening, *a*, and soda solution into the same tube through the opening, *b*. After passing the valve, H, the mixture of gas and liquid was driven forward by the pump into the cylinder, Q, which was made of glass, and was provided with a safety-valve, R, which could be regulated so as to allow excess of either liquid or gas to escape. This condenser received an oscillating movement, communicated to it from the crank above through the distending cross-piece, S, the object of which was to accelerate the incorporation of the carbon dioxide with the liquid.

After being saturated with the gas under the desired pressure in the condenser, the liquid was drawn off through the tube, U, into the bottles, which were applied below the valve, X, controlled by the handle at the side.

It will be observed that the soda-water bottle shown at Z in the diagram is of the well-known conical shape. This form of bottle was invented by Hamilton, who thus describes it in his specification :—" I generally use a glass or earthen bottle or jar of a long oval form, for several reasons—viz., not having a square bottom to stand upon, it can only be on its side, of course ; no leakage of air can take place, the liquid matter being always in contact with the stopper. It is much stronger than a bottle or jar of equal weight made in the usual form."

Another distinctive feature about Hamilton's machine was that the pump had a solid piston, which worked beneath the pump through leather packing.

In the old type of machine the piston of the pump was of leather, fitting tightly into the barrel, and, as is mentioned elsewhere, leakage of gas readily occurred, notwithstanding constant cooling of the pump to prevent heating through condensation of the gas.

Hamilton sold all the rights secured by his two patents for



the sum of £600; but his machine did not long retain its position, for by the year 1820 it had been displaced by Bramah's continuous machine, which adopted its principle, but improved in many directions upon its mechanism.

**Bramah's Continuous Machine.**—In Bramah's machine, too, the water and the gas were pumped together into an oval condenser capable of resisting the pressure, and after mechanical agitation to complete the absorption of the gas, the aerated liquid was discharged through a tap provided with a nipple for bottling.

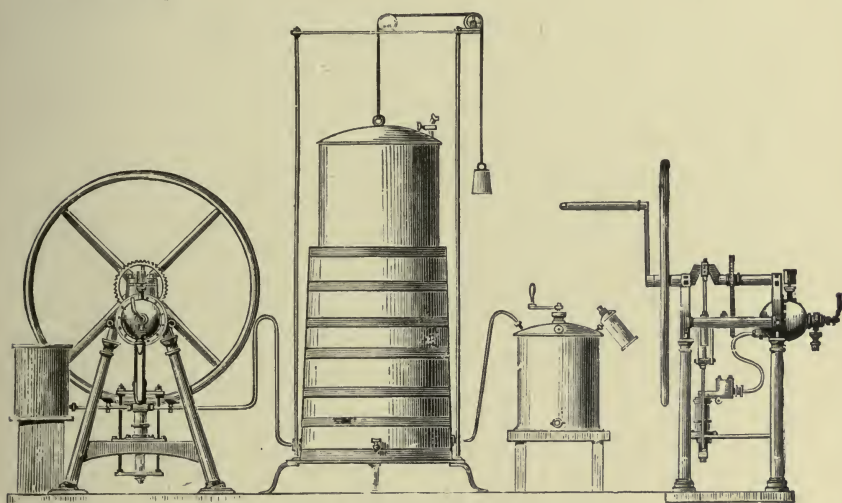


FIG. 45.—Bramah's Original Machine.

The arrangement of the different parts of Bramah's first machine is shown in Fig. 45, which is reproduced from an original drawing by John Briggs.

The essential novelty in the apparatus was the pump and condenser, which are shown in full view on the left, and in side view on the right of the diagram.

The carbon dioxide was drawn from the gasometer through a pipe to the right of the condenser, while, simultaneously and by the same stroke of the pump, liquid was drawn from the solution tank on the other side of the condenser.

As in the case of Hamilton's machine, Bramah's pump had a solid piston surrounded by a flexible collar, which became tighter with the increase of pressure. Unlike the pumps in the older machines, the pump of Bramah's machine had its piston working upwards, so that the water and gas were drawn in by the down stroke, and driven forward by the up stroke.

The advantage of this arrangement was that the gas preceded the water in the pump, and that the water, being at the bottom, formed a seal that effectually prevented the loss of any gas if the piston were defective. The necessity of cooling the pump was also obviated, and the valves could readily be removed for cleaning. According to Briggs attempts were made by various manufacturers to adapt their old pumps to the new type of machinery, but the results were invariably unsatisfactory when they were used for gas and liquid at the same time.

This was obviously due to the fact that the water, being heavier than the gas, was expelled first by the down stroke of the piston, while the gas, being left without any water-seal as in Bramah's pump, was liable to escape when there was the slightest defect in the packing. In fact, pumps thus adapted were in constant need of repair, and, to quote Briggs, "a machine of this kind was about the worst that could be made."

Bramah added the manufacture of soda water machines to his other industries, and after Bramah's death in 1815, his pupil, William Russell (who was the founder of the firm of Hayward-Tyler & Co.), also began to make machines upon the same pattern.

One of the earliest machines made by the firm is represented in the accompanying figure (Fig. 46). This was capable of producing from 120 to 130 dozens of bottles of soda water per day by hand power, or about 300 dozens when steam was used.

As will be seen by reference to the preceding diagram (p. 119), its construction was essentially the same as that of Bramah's original machine, the difference being that it was larger and more strongly made.

Of the letters indicating the different parts of the apparatus,

A denotes the gas generator, with its acid bottle, B ; C, the gasometer ; D, the condenser ; G, the pump ; M, the solution tank ; E, the bottling cock ; and F, the wheel for driving the agitator within the condenser and for working the pump.

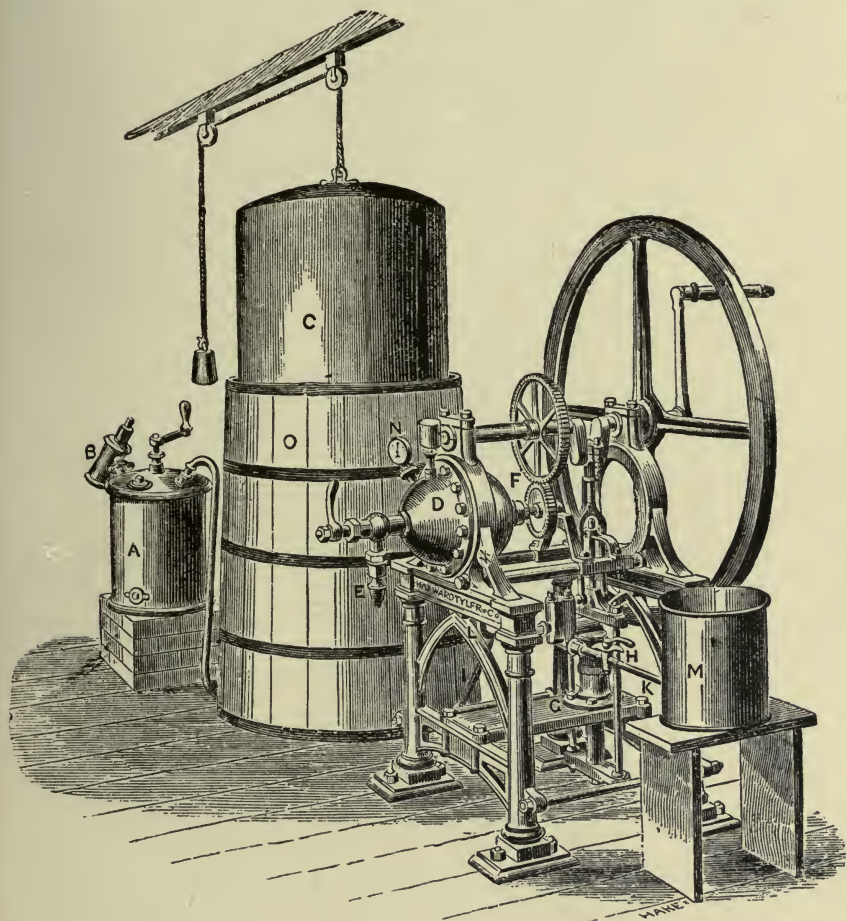


FIG. 46.—Hayward-Tyler's Earliest Continuous Machine.

In all essential details, Bramah's original machine is that which, in one or other of its modifications, is still used in mineral water factories all over the world.

A beam action machine upon Bramah's principle was



patented by Hayward-Tyler in 1840 (English Patent, No. 8421), the novelty of which was that the pump was worked by the oscillation of the beam, an arrangement that allowed two handles to be fixed to the crank shaft, so that, where only hand power was available, the machine could be worked by two men, one at each end of the shaft.

The arrangement of this machine, without the connected generator and gasometer, may be seen in the accompanying illustration (Fig. 47).

A machine upon the same principle with double pumps and double condensers was also made.

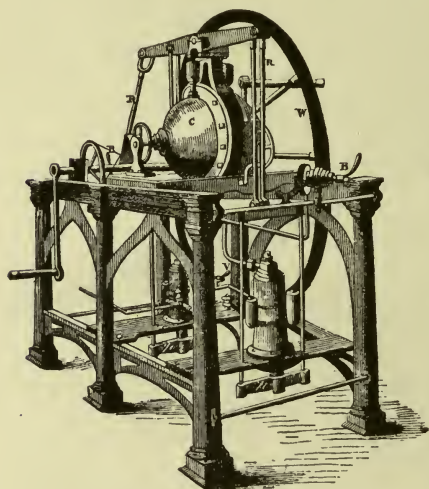


FIG. 47.—Hayward-Tyler's Beam Action Machine.

### Early French Machinery.

—Until the year 1840 the French mineral water industry was restricted by law to the pharmacists, who jealously protected themselves against any encroachment upon their rights. Mineral waters were looked upon as pharmaceutical preparations, and ordinary soda water was sold at the prohibitive price of a franc to a franc and a-half a bottle.

The outbreak of cholera in Paris in 1832 created a greater popular demand for aerated waters (*Eau de Seltz*), the carbonic acid in which was regarded as a remedy and preventative against the disease. But the price still remained very high, until in the year 1840 Fèvre put upon the market separate packets of tartaric acid and sodium bicarbonate, which were brought together in a gasogene. The ready sale with which these powders met at 5 centimes per packet caused the Parisian pharmacists to contest their legality, since, as they alleged, their sale was an infringement of the legal monopoly to dispense



medicinal preparations. Judgment was given against the pharmacists in 1845, and this eventually had the result of destroying the monopoly of the druggists in ordinary aerated waters ; for Fèvre's packets were now sold everywhere, and the

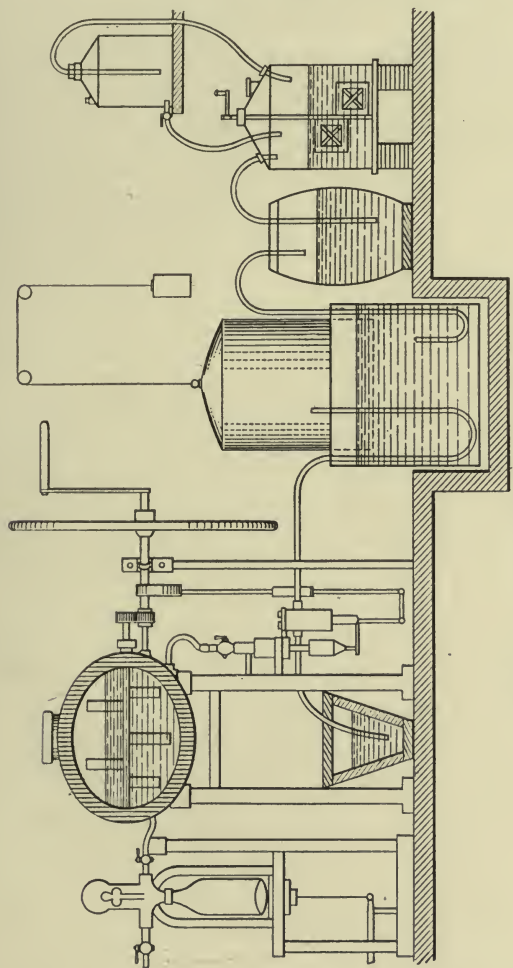


FIG. 48.—Early French Continuous Plant.

manufacture of soda water could no longer be kept within its former narrow and profitable limits.

Yet the fact that for over fifty years the mineral water industry had been artificially restricted had had its effect upon

the type of machinery used in France. The general trend was to produce apparatus that would yield only a limited amount of aerated waters, such as, for example, the machines of Planché, described on a previous page (p. 101). And when larger plant became necessary, the aim of the inventors was to produce a machine that should take up very little room and be easily handled by a single individual.

This probably accounts for the great attention given in France to intermittent apparatus without a pump or gasometer, many of which machines were designed by pharmacists.

When the industry became "free" the necessity for a more rapid process of manufacture soon made itself felt, and modifications of Hamilton's and Bramah's continuous machines came into general use.

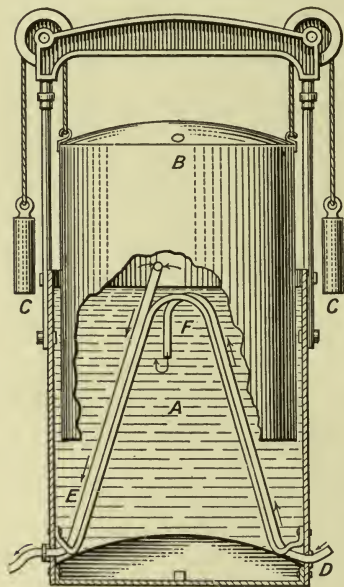


FIG. 49.—Early French Gasometer.

As will be seen from the accompanying diagram (Fig. 48), in which one of the early French machines is shown, the arrangement of the plant was similar to that of the English machines.

The gas was generated in the vessel on the right, which was provided with a vertical agitator, and was fed by an acid bottle above; thence it passed through a barrel of water, where it was washed, and into the gasometer. The pump, which was constructed on Bramah's principle, drew the gas from the gasometer on one side and from a solution tank on the other, and pumped them simultaneously into the saturator above, where the mixture was mechanically agitated, and finally was drawn off into the bottling machine on the extreme left.

The construction of the gasometer used in French machines

is seen in Fig. 49, which represents one of those made fifty years ago by Hermann-Lachapelle.

The difference between German and French and English gasometers was that in the first the gas was conveyed above the water in the surrounding tank, while in the two latter it was made to bubble through the water, and thus received an additional washing.

**The American Intermittent System.**—The principle of carbonating by impregnating the liquid directly in a cylinder without the intervention of any gasometer, which was tried in so many of the early French machines, has been adopted extensively in the United States largely on account of the great demand for portable “soda fountains.”

Although during the last quarter of a century modifications of the continuous system have gradually come into general use, the older method is still widely employed, the chief modification having been the substitution of gas tubes for the generators.

One of the earlier forms of apparatus is shown in Fig. 50, which represents a sectional view of Matthews' vertical generator connected with a portable fountain.

In this machine the marble or other carbonate is made to fall through the dilute acid, thus obviating the necessity for constant agitation, and preventing too violent evolution of gas.

The required proportion of acid and water is first poured into the lower chamber V, through the opening, A, which is then screwed down. The weighed quantity of crushed marble is then introduced through the larger opening, B, where it rests upon the wings, P, of the agitator, E, which has previously been turned so as to close the openings in the diaphragm. The generator is now charged and ready for connecting with the portable fountain, L. On slowly turning the handle, E, a little of the marble dust falls through the diaphragm into the acid in the lower chamber, the process being continued until the desired pressure is shown on the indicator, after which the handle is placed so as to close the diaphragm openings.



The gas produced is passed through purifiers, X, Y, containing water and chips of marble, and enters the fountain by the pipe, T, at the top. This fountain is mounted on a frame,

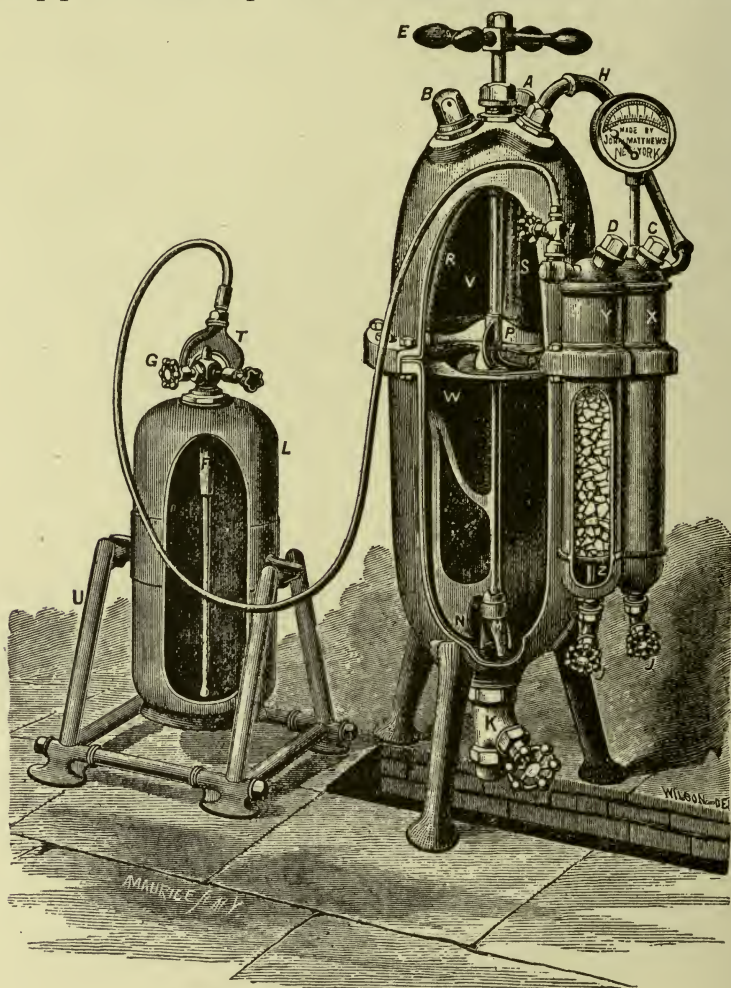


FIG. 50.—Matthews' Vertical Generator.

so that it can be rocked to promote the saturation of the liquid by the gas.

The portable "fountain," or "cylinder" as it is more commonly termed in this country, is then detached from the



generator, and is ready for delivery to the customer, who usually places it beneath the counter in connection with a draught column (*see* p. 171).

The method of charging these portable cylinders by means of liquid carbon dioxide is very simple, the gas being made to pass slowly through a pressure gauge into a fountain. It is safer to have an automatic pressure governor, which as soon as the desired pressure is reached automatically cuts off the supply of gas.

The cylinder may also be charged by means of any large soda water machine.

## CHAPTER VIII

THE MACHINERY OF TO-DAY: THE PUMP—GENERATORS—GAS  
TUBES—SODA WATER MACHINES—COMBINED COOLING,  
ETC.—CONDENSERS—SODA-WATER BOTTLING MACHINERY.  
ARRANGEMENT OF A SODA WATER FACTORY

**Carbonating Machinery of To-day.**—In modern mineral water factories the carbonating machinery chiefly employed is still based upon the principle of the continuous process invented by Hamilton and perfected by Bramah, the improvements that have been made of recent years having been mainly in the directions of simplifying the working of the machines and increasing their speed, and in the processes and machinery for bottling.

The older cylinder or intermittent process (*see* p. 103) still survives, however, as an auxiliary method in many factories, and is useful in cases where a relatively small amount of liquid, such as lithia water, for which the demand is restricted, has to be carbonated.

In some factories, indeed, the oldest part of this machine, the wooden cylinder described on p. 104, may even now be found, the idea being that a liquid carbonated within a wooden vessel is less liable to become contaminated with metallic impurities than when the saturation is effected in cylinders of metal.

Since, however, the interior of all soda water machinery is now usually lined with pure tin, the risk of contamination from this source is infinitesimal; while, on the other hand, the chance of bacterial infection of the soda water is greatly increased when vessels of wood are used in the manufacturing processes.

This so-called intermittent process of aeration is more commonly used for carbonating light beers or cider than for mineral waters. It still has the drawbacks, mentioned on a

previous page, of the pressure diminishing during bottling, and of the loss of gas in the cylinder when the pressure is kept up by pumping in the course of the bottling process.

The cylinders are generally made of copper either washed with tin inside, or, preferably, lined with block tin. As was



FIG. 51.—Twin Carbonating Cylinders.

discovered long ago, the intermittent character of the process is largely modified by the use of twin cylinders, one of which is being charged while the other is being drawn down. The loss of gas is in this way restricted to that remaining in the final cylinder at the close of the operation.

A pair of these twin cylinders, made by Messrs. Wickham & Co., of Ware, is shown in Fig. 51. Each of the cylinders has a capacity of over 40 gallons, and is capable of carbonating 36 gallons at a charge. The liquid within the cylinders is agitated by the action of fans, which are made to revolve by turning the handles, while in the larger sizes with cylinders taking charges of 108 gallons, the agitators are worked by power.

When intended for carbonating soda water the cylinders are more strongly made and tested against higher pressures than those used in breweries.

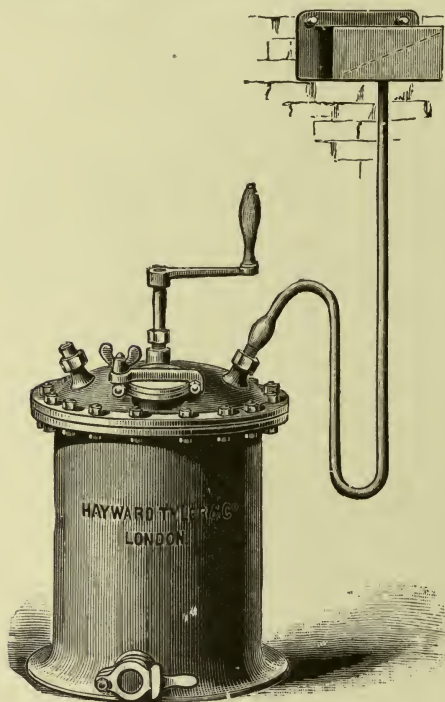


FIG. 52.—Upright Generator.

**The Generator.**—Although in a large number of mineral water factories the generator has been superseded by tubes of liquid carbon dioxide, which is made on the spot or is bought in cylinders, there are yet many places where these courses are not practicable, and some

form of generator must be used for the production of the gas.

Various forms of these generators are employed, ranging in capacity from about 3 to over 150 gallons.

One of the smaller sizes, made by Messrs. Hayward-Tyler & Co., is shown in Fig. 52, which represents an upright generator holding 14 gallons. This is made of thick lead, and has a central vertical agitator for mixing the whitening and water, while the acid is introduced through the inverted syphon-feeding device (*see* p. 88) from the acid box above, which is



also made of lead. At the bottom of the generator an opening, which is controlled by a valve of special construction, is provided for the removal of the calcium sulphate formed in the reaction.

**Horizontal Generators.**—The horizontal form of generator, an example of which is given in the accompanying figure (Fig. 53), presents several advantages over the vertical form. Thus the whiting is more readily distributed and prevented from caking

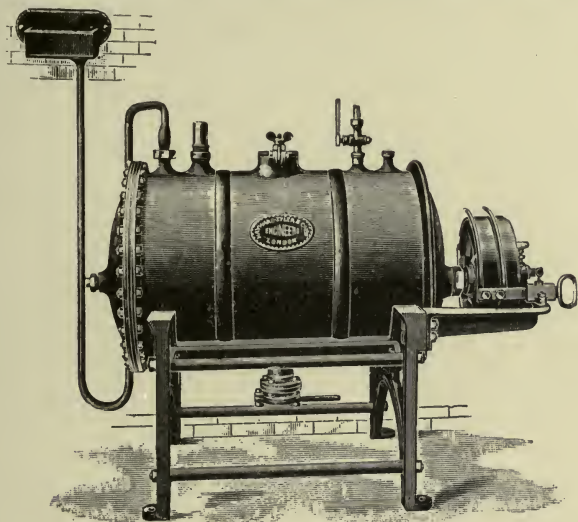


FIG. 53.—Horizontal Generator.

at the bottom, while the agitator, being also in the horizontal position, is better adapted for the application of steam power. If intended to be used with sodium bicarbonate instead of whiting, this generator is made of a specially strong metal.

Any risk of explosion through the sudden evolution of too much gas is prevented by the use of the siphon tube for the introduction of the acid, any excessive pressure having the effect of driving the acid back into the acid box.

The gas leaving the generator bubbles through the water in the lower part of the gasometer into the bell, and is thence drawn off by the soda water pump.

An automatic arrangement for regulating the supply of acid to the generator (and consequent development of more gas) is shown in Fig. 54.

The outlet in the acid cistern at the top is closed by a valve, which is controlled by a lever connected with the bell of the gasometer.

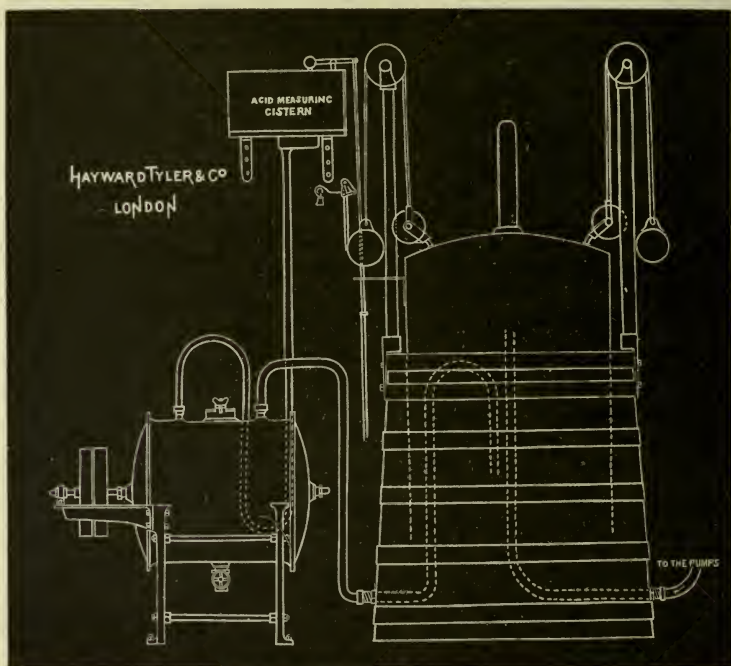


FIG. 54.—Automatic Device for Regulating the Supply of Acid.

When the gas is drawn off by the soda water pump the bell sinks in the gasometer and the valve is opened, admitting more acid to the generator. The gas produced raises the gasometer bell again, and at the same time simultaneously closes the valve in the acid box and shuts off the supply of acid. The supply of gas is thus made entirely dependent upon the amount drawn off by the pump, and renders the process an intermittent one.

**The Riley "Safety" Generator.**—The generators made by the

Riley Manufacturing Company, are of cast iron lined with sheet lead, and are provided with agitators working upon a vertical shaft, and put in motion by power applied to the wheel at the top.

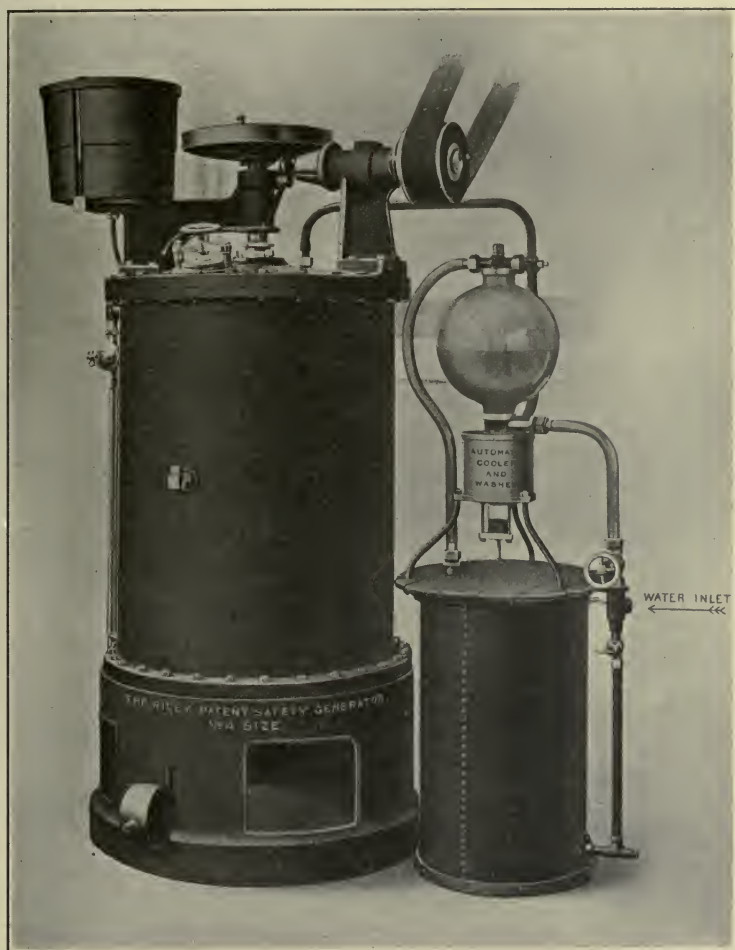


FIG. 55.—The Riley "Safety" Generator.

A specially constructed automatic cooler and washer is placed between the generator and soda water pump to wash and cool

the gas, as shown in Fig. 55, and there is a device by means of which, when a charge is finished, a plunger that is drawn up by the action of the pump automatically closes the pipe leading to the pump. In this way any injury to the lead lining of the generator through suction is obviated.

A charge of sodium bicarbonate or whiting and water is introduced into the generator, and the requisite quantity of sulphuric acid is placed in the acid box at the top. As soon as the pressure within the generator attains about 3 lbs. the supply of acid is automatically cut off, while an additional safeguard against accident is furnished by an outlet valve at the bottom. This is kept tightly closed by a lever, upon which is a weight sufficiently heavy to withstand even an abnormal pressure within the generator. Should, however, the pressure attain 25 lbs. the resistance of the weight is overcome, the valve is opened, and the gas escapes while the other contents of the generator flow out on to the ground. This would only happen when the agitator had been stopped while the supply of acid was still being admitted.

A generator of the size illustrated is 7 feet in height and 3 feet 3 inches in diameter at the base. It is constructed to receive a charge of 224 lbs. of sodium bicarbonate and 130 lbs. of sulphuric acid, and will produce sufficient carbon dioxide to aerate 1,000 dozen large bottles of soda water.

A double type of these generators is also made to obviate the necessity of any stoppage of work during re-charging.

From what has been said, it will be gathered that all the Riley generators are adapted to be directly connected with the soda water pump, and that the use of a gasometer is rendered unnecessary, by reason of the special devices to ensure safety in the event of undue pressure being developed.

**The Gasometer.**—With the exception of plant including generators with special devices to prevent explosion, such as those of the Riley Manufacturing Company, a gasometer usually forms part of the machinery of a modern mineral water factory.

The internal arrangement of the gasometer is essentially the



same as in the apparatus in use at the beginning of last century (see p. 124). The gas leaving the generator is preferably passed through a washer or purifying apparatus, and is thence conducted below the surface of the water in the lower part of the gasometer, where it receives further washing before rising into the bell.

The lower vessel is frequently made of oak, while the bell is of sheet copper tinned on the inside ; or, as is the practice in many works, the tank may be constructed of wrought iron and the bell of galvanized iron.

When liquid carbon dioxide is used as the source of the gas, as is now so frequently the case, several tubes are generally grouped round the tank of the gasometer, pipes connected with each being conducted beneath the water. In this way a constant supply of gas to the gasometer is maintained without interruption to couple on a fresh tube.

The water within the tank of the gasometer washes the gas, though this is not so essential as in the case of freshly made gas. The addition of a little potassium permanganate to the water is advantageous, especially when the gas has been derived from breweries, since it keeps the water itself fresh, and oxidises impurities in the gas.

**Continuous Process Machines.**—In its essential working parts the “Bramah” machine has altered but little during the century that has passed since its invention. The frame is of different construction ; but the machine still comprises a pump and a condenser, which contains an agitator to promote the saturation of the liquid by the gas.

The chief development in this type of machine has been the substitution of a much larger condensing cylinder for the original type of cylinder, so as to increase the output of soda water by each machine, without making much more demand upon the space in the factory.

These machines have cylinders of copper or gun metal with a capacity of 12 to 24 gallons, and are designed to be worked either by one or two pumps. In each case the cylinders are either tinned inside, or they may be lined with pure tin

$\frac{3}{16}$  inch thick to prevent metallic contamination. The largest size of these machines, which are made by Messrs. Hayward-Tyler & Co., is represented in Fig. 56. This is fitted with two 3-inch pumps with solid plungers of the type described below, and is provided with a slate solution tank to hold the soda

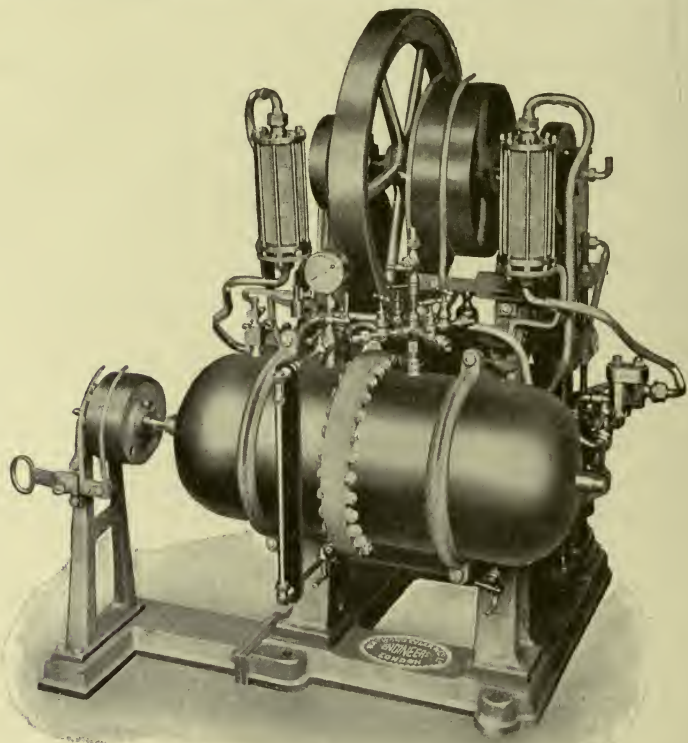


FIG. 56.—Hayward-Tyler's New Pattern AA1 Machine, with Two Pumps.

solution and with two glass saturators, one of which is connected with each pump.

With the larger sizes of these machines about 300 dozens of syphons, or over 2,000 dozens of 10-oz. bottles of soda water, may be produced each day.

**The Pump.**—The soda-water pump of to-day is in all essential

details that which was used in Bramah's first continuous machine (*see* p. 119). Its construction will readily be understood by reference to the accompanying figures (Figs. 57 and 58), which represent one of Hayward-Tyler's "plunger pumps," and a pump with leather buckets.

The advantage of the former is that the use of the solid plunger obviates the wear caused by the friction of the leather

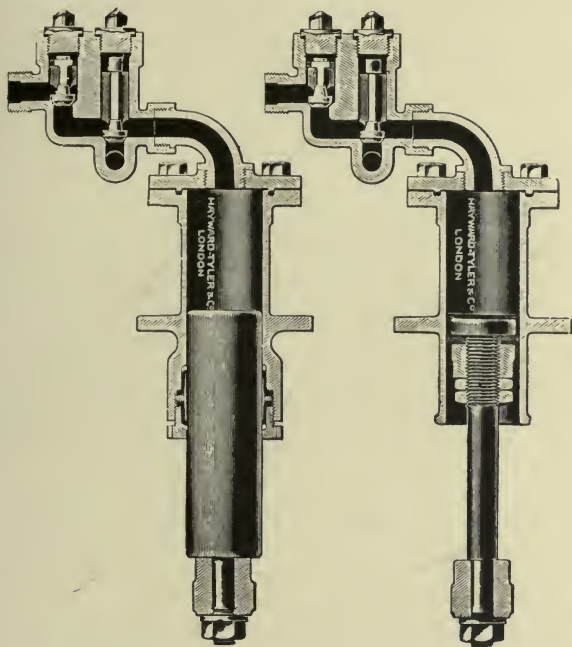


FIG. 57.—Plunger Pump.      FIG. 58.—Bucket Pump.

buckets upon the interior of the pump barrel, which eventually necessitates taking the whole pump to pieces for re-adjustment of the barrel. In the case of the solid plunger pump the wear is practically restricted to the plunger, and it is comparatively a simple matter to remove this and "regulate" without dismantling the entire pump.

Opinions vary as to the relative advantage of having solid valves within the pump, or of having the valves faced with leather or other material. The solid valves are more noisy

than the others, but are, as a rule, much more durable. It may be mentioned, however, that in some pumps, such as those made by the Riley Manufacturing Company, the valves have seats of a particularly durable material.

**Hayward-Tyler's New Pattern Pump.**—The latest pattern of pump manufactured by Messrs. Hayward-Tyler & Co. is shown in Fig. 59.

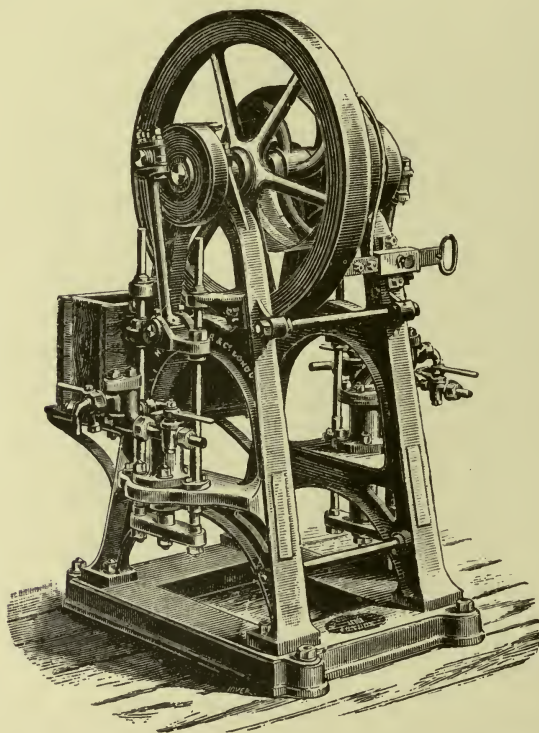


FIG. 59.—Hayward-Tyler's New Pattern Pump.

These pumps are made in three sizes, with diameters ranging from 3 to 4 inches, and being of very solid construction are well adapted for the work of large factories.

Each pump is capable of producing from 1,000 to 2,000 dozen bottles per day, according to the nature of the liquid to be bottled, and all are tested to withstand a pressure of 250 lbs.



A still greater output is obtained by the use of double pumps of this kind fixed in a frame so as to form a separate machine from the saturating cylinder.

Whether single or double, these pumps are intended to be connected with a cylindrical condenser, which may be either vertical or horizontal, and like the pump, forms a separate machine in its own stand.

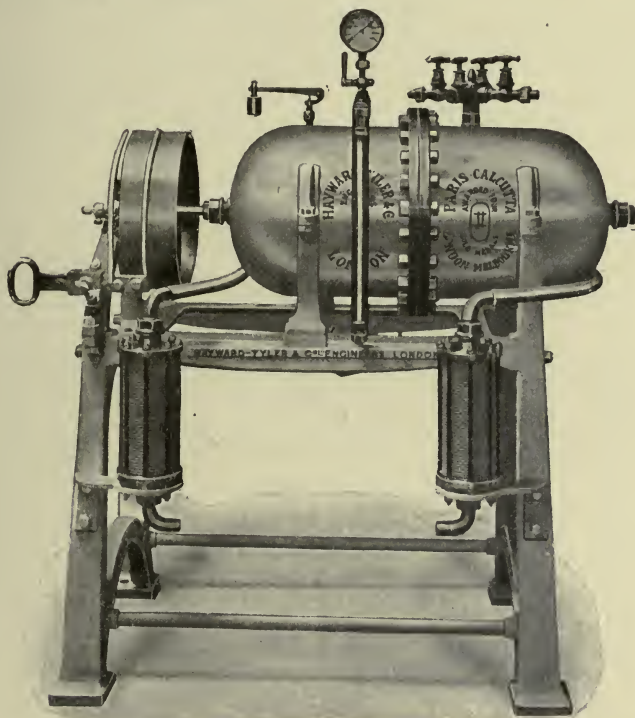


FIG. 60.—Gun Metal Horizontal Cylinder.

Fig. 60 shows one of these horizontal cylinders, which are provided with a central agitator to accelerate the impregnation of the liquid, and with two glass saturators, which promote still further the thorough incorporation of the gas.

**The “Riley” Patent Soda-water Pump and Cylinder.**—In this apparatus thorough admixture of the gas and water is

effected without the use of any agitator in the cylinder, the pumping arrangement being so constructed as to render subsequent agitation quite unnecessary.

The pump is made on the Bramah principle, with a solid plunger working in the reverse manner to a force pump. This

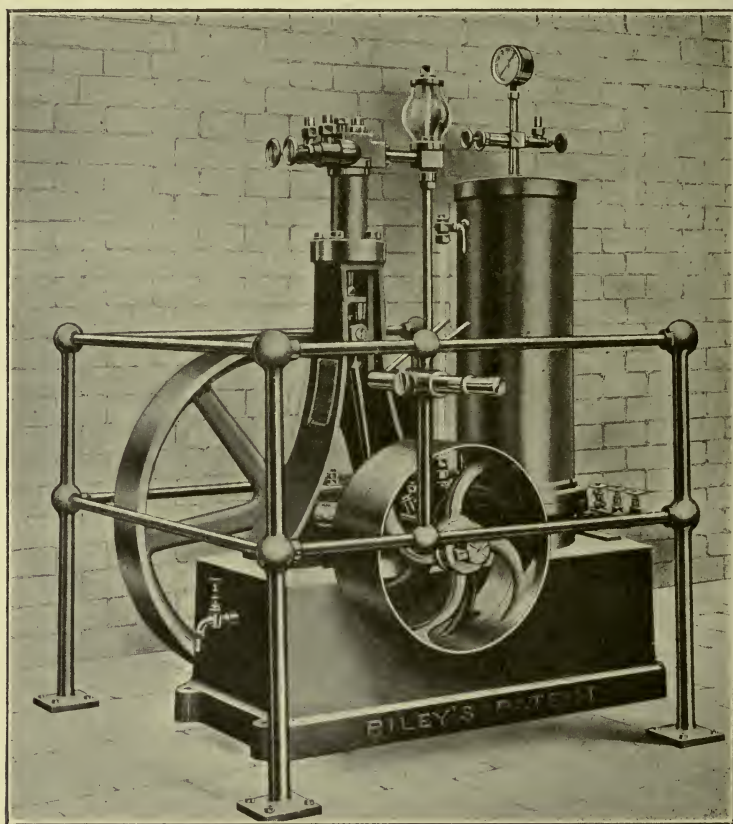


FIG. 61.—The "Riley" Patent Soda Water Pump and Cylinder.

plunger rises very nearly to the top of the barrel, leaving only a very small space, and within this the mixture of gas and liquid is subjected to considerable pressure before it forces back a spring and enters the cylinder.

The silver-plated tube in the connection between the pump and the "super-saturator" is pierced with a number of fine holes, through which the liquid is driven in a fine spray against the walls of the glass globe, thus completing the impregnation of the water by the gas. Thence it passes through a valved tube into the cylinder, and is ready to be drawn off into the bottling machine.

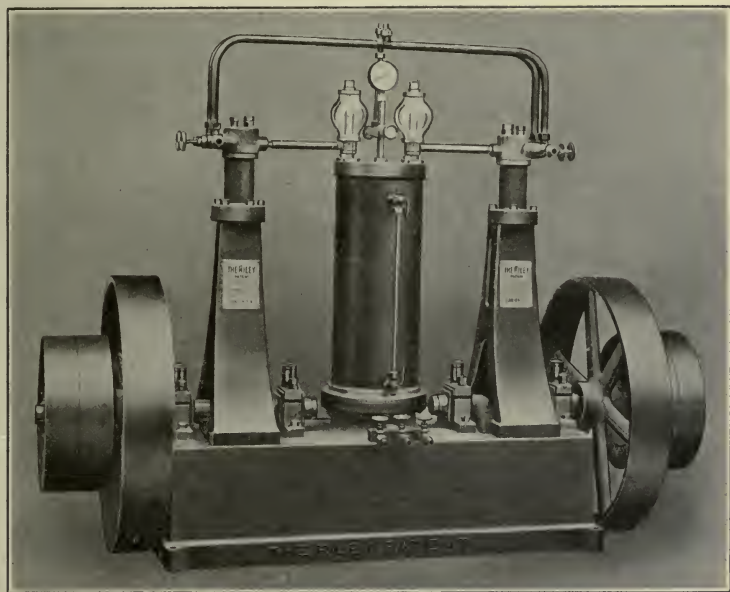


FIG. 62.—The "Riley" Patent Double Soda Water Pump and Cylinder.

The cylinder is constructed of drawn copper, lined with pure tin, and is provided with a retaining valve so that the pump may be disconnected without loss of gas.

The construction of this machine will be understood by reference to the accompanying illustration (Fig. 61), which, proceeding from left to right, shows the pump, super-saturator, and cylinder. The tap shown at the base of the machine is intended for drawing off any water that has been left in the cylinder from a previous day, and thus at the same time enabling the pump to be started more readily.

The size of machine here shown, with a 3-inch pump, is that in most general use, but larger machines with 3½ and 4-inch pumps are also made : while in factories, where the output is very large, machines with one cylinder charged by two pumps have been erected (*see* Fig. 62), effecting a considerable economy in the original cost and a saving in space.

The writer can state, from an experience extending over many years, that the Riley soda-water pump and cylinder gives excellent results in practice, and that the machine rarely requires any repairs.

**The “Aerate-Cool” Machine.**—The production of a well-carbonated soda water, which will retain the gas for a long period after the bottle has been opened, depends to a considerable extent upon the temperature at which the liquid is impregnated with the gas. This point is of essential importance to manufacturers in hot climates, for, as has already been pointed out (p. 46), the amount of gas that water can absorb decreases with the rise in temperature.

Various machines for chilling a liquid by means of the expansion of carbon dioxide have been dealt with in Chapter V. ; but the recently patented “Aerate-Cool” machine of Hayward-Tyler & Co. is more appropriately described in this place, since it combines in one piece of machinery the processes of chilling and carbonating.

In this machine (Fig. 63) the soda-water pump on the left side works independently of the compressor or cooling pump on the right, though both are driven by the same crank shaft. The carbon dioxide used for refrigerating circulates through the compressing pump and coils contained in a circulating tank and in the solution pan at the top. After being compressed by the pump to a pressure of 800 to 850 lbs. it passes through a valve and expands, and entering the coils in the cylinder at the base of the machine chills the temperature of the surrounding water down to about 40° F.

The water thus cooled is carbonated in the usual way by means of the other pump, which obtains its supply of carbon dioxide from an ordinary gas-holder.



About 1,500 dozen bottles of soda water may be charged in a day by means of this machine, and the liquid thus carbonated and bottled at a temperature of 40° F. under a pressure of 70 lbs. in the cylinder will be found to contain much more gas than when bottled at a pressure of 120 lbs. at the ordinary summer temperature.

Another advantage of this machine is that either of the pumps may be used by itself; thus, if desired, the chilling may be omitted, or the compressing pump may be utilised to cool water for other purposes without starting the aerating pump. Thus, for example, it may be utilised in chilling ginger beer to the necessary temperature before the addition of the yeast.

#### Machines for Use with Liquefied Gas.

—The growing use of tubes of liquid carbon dioxide for carbonating soda water by means of the ordinary plant has led to the designing of compact machinery in which the gasometer is eliminated.

A horizontal machine of this type is shown in Fig. 64. This was made for H.M.S. *Powerful* by Messrs. Hayward-Tyler & Co.,

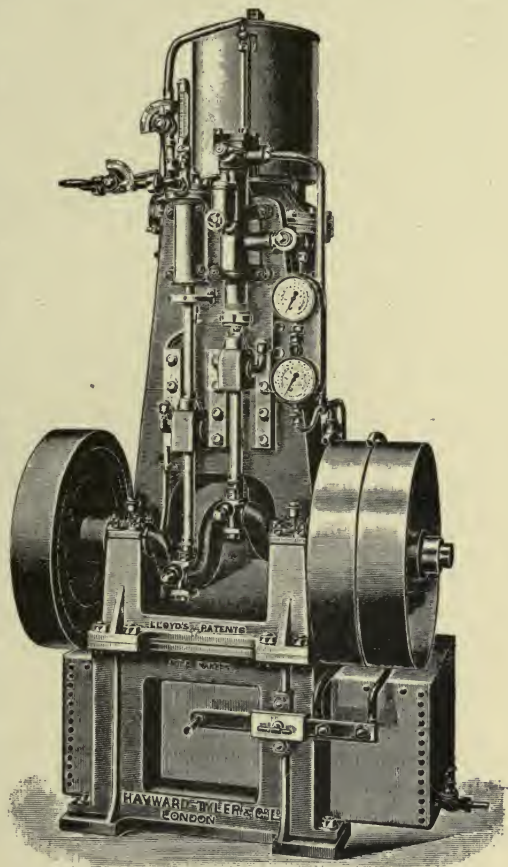


FIG. 63.—Hayward-Tyler's "Aerate-Cool" Machine.

and is especially suitable for the manufacture of soda water for hospitals and small establishments.

The gas tube is connected with the cylinder by means of a pipe, upon which is an automatic reducing valve to regulate the supply of gas, while water is pumped into the cylinder by means of the pump at the bottom. The agitation of the liquid and gas is effected by an agitator, which is worked at the same time as the pump by turning the handle.

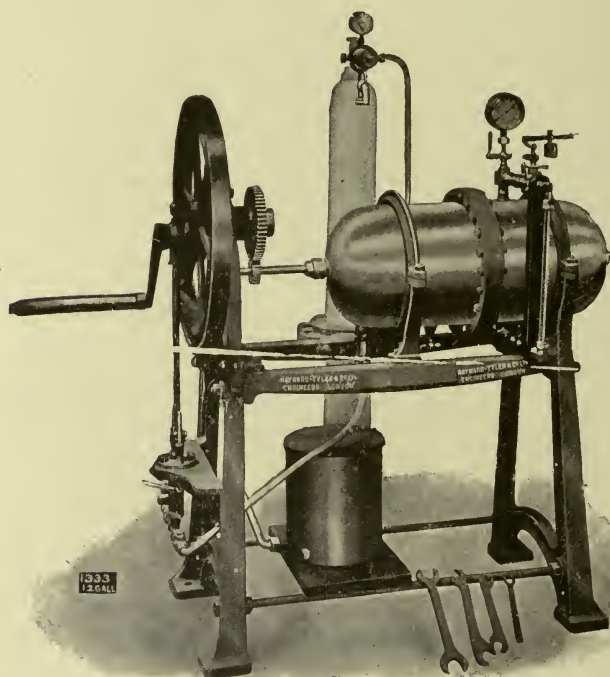


FIG. 64.—Horizontal Machine for Use with Tubes of Liquefied Gas.

Any form of bottling machine may be connected with the cylinder, and about 35 dozen bottles of soda water can be produced in an hour by the machine.

The “Combined Vertical” machine of the same firm is still more compact than the preceding one. It comprises a vertical copper cylinder and saturator, together with an automatic

reducing valve, with pressure gauge between the gas tube and the cylinder (Fig. 65).

As in the case of the horizontal machine, the water is pumped into the cylinder by turning the fly-wheel, but the use of the saturator renders agitation unnecessary. The machine may be fitted with a Turnover Bottling Machine for charging Codd's bottles (p. 154), or with a syphon-filling machine, or with both as shown in the illustration.

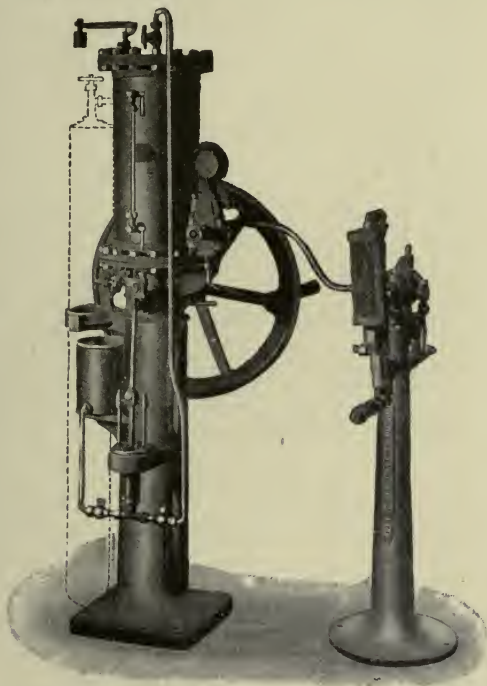


FIG. 65.—Vertical Machine for Use with Liquefied Gas.

The process of manufacture is continuous, the output being about 22 dozen bottles of soda water per hour.

The method of using portable soda-water fountains charged by means of tube gas is described on another page (*see* p. 171).

Care must be taken to ensure the purity of the gas supplied in the tubes, since even if there is only a small proportion of air present it is impossible to produce a satisfactory soda water.

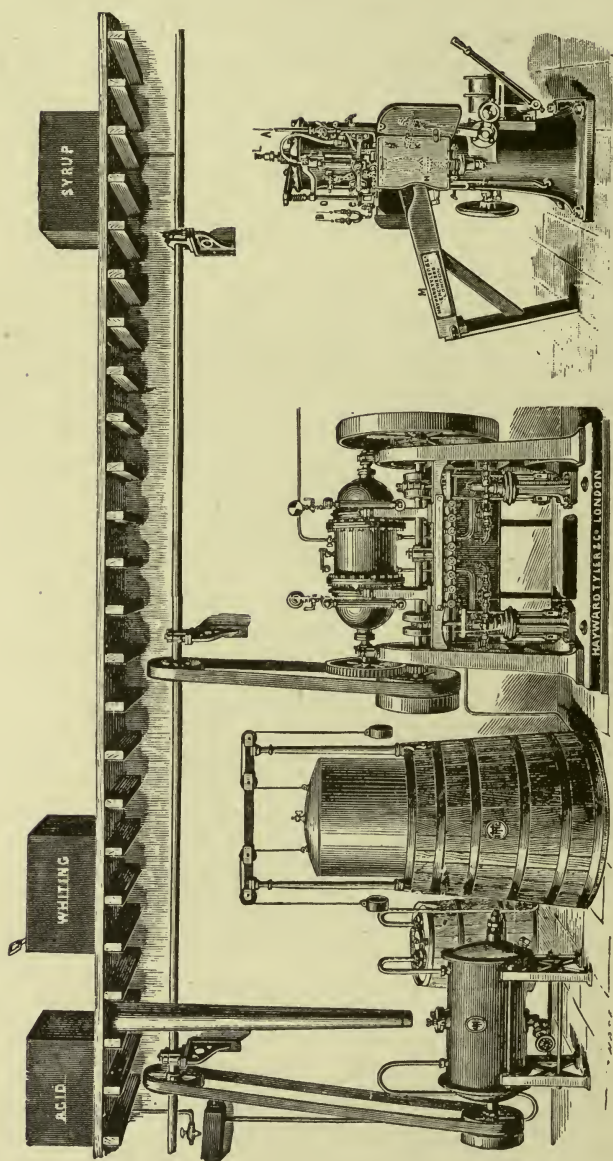


FIG. 66.—General Arrangement of Mineral Water Factory.

**Arrangement of a Mineral Water Factory.**—In a modern factory the syrup tanks and the tank for the soda solution



are placed on a floor above the bottling machines, with which they are connected by means of pipes of tin or of glass.

The generator for the gas (or the gasometer with the gas tubes) and the pumps are usually put in a separate room opening into the bottling factory, so as to keep the processes distinct, and another series of pipes connects the soda-water machines with the bottling machines.

The general arrangement is thus somewhat upon the lines shown in the accompanying diagram (Fig. 66).

In the case of soda water a concentrated solution of sodium carbonate is made in a slate tank with a closely fitting cover, and measured quantities of this are drawn off into each bottle through the one tube, while aerated water from the soda-water machine enters the bottle through another tube.

In like manner lemonade, ginger ale, or other sweetened goods are prepared by a regulated quantity of filtered lemon syrup, and so on, being introduced into the bottle with the aerated water.

The process of introducing the sodium carbonate solution or the syrup is known as "syruping" the bottle, even when, as in the case of soda water, no sugar is present.

## CHAPTER IX

### BOTTLES AND BOTTLING MACHINERY

**Bottling Machinery.**—In all the early machines the bottles were filled from the carbonating cylinder by hand, and considerable skill and practice were necessary to prevent a great loss in the pressure. Even in the hands of the most experienced men, however, the method of “hand-and-knee bottling,” as it was subsequently termed, involved some loss, the amount of which depended on the speed of working and the initial pressure.

The bottles with their corks loosely inserted in their necks were placed to the right of the bottler, who sat upon a low stool in front of the tap, with his knees covered with a leather apron, on which rested a board, and his hands and arms protected by gloves. Each bottle was brought in turn beneath the leather fitting of the tap, and was held in position by the pressure of the knee, while the cylinder tap was turned. The aerated liquid rushed into the bottle, and the air in the latter was then expelled by lowering the knee a little and thus easing the neck slightly from the leather fitting of the tap, so as to allow the filling to be completed. The cock was now shut off, the bottle rapidly withdrawn, and its cork skilfully inserted and driven home by the blow of a wooden mallet, after which it was immediately wired down by a second workman.

It is obvious that with a process of this kind there was inevitably a want of uniformity of pressure within the bottles, and that there was a great difference between the results obtained by a skilled and an inexperienced bottler.

A demand thus arose for a machine that could be worked by a relatively inexperienced person, and that would minimise the loss of pressure involved in bottling by hand

**Briggs' Bottling Machine.**—The first bottling machine made in this country was invented about 1830 by John Briggs, manager to Hayward-Tyler & Co. In this machine, an illustration of which is given in Fig. 67, the cork was inserted into a conical holder, *d*, which became narrower towards the bottom, so that the cork became compressed on its passage downwards.

The bottle, *h*, was placed on a wooden support, *l*, beneath the cork holder, and could be raised or lowered as desired by the pressure of the foot upon the treadle, *h*, at the base. A screw-valve at the side, connected with the pipe from the carbonating cylinder, was opened to admit the soda water into the bottle, the neck of which could subsequently be eased by means of the treadle. The cork was then forced down by the action of the rack, *E*, which was moved up or down by turning the handle.

A few years later Hayward-Tyler & Co. introduced a modification of this machine, the improvement in which was that a weighted lever, adjusted to the desired pressure, was employed to press the bottle upwards into the mouthpiece. Atmospheric air was thus automatically expelled, and an equal pressure obtained within each bottle before the cork was driven in by the lever at the top. This lever was also provided with a weight to raise the handle again, and bring the plunger out of the cork holder, while a handle in front of the machine held the bottle steady during corking, and also served to raise the bottom weight and release the bottle (Fig. 68).

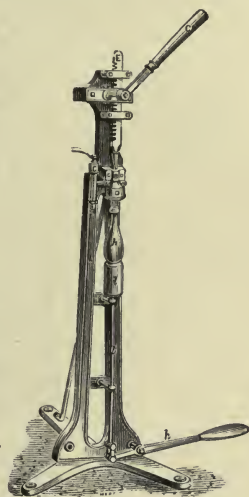


FIG. 67.—Briggs' Bottling Machine. 1830.

The bottling machine claimed on behalf of Savaresse in Berry's patent (English Patent, No. 7,899 of 1838) is shown in the accompanying figure (Fig. 69). It was connected by means of two leaden pipes with the carbonating apparatus described on a previous page (*see p. 112*).

The end of one of these pipes was attached to the cock of

the saturating cylinder, and the other end to the cock, *v*, of the bottling machine. The other tube formed a connection between the cock, *w*, and another cock in the upper part of the cylinder. The bottle was raised and pressed against

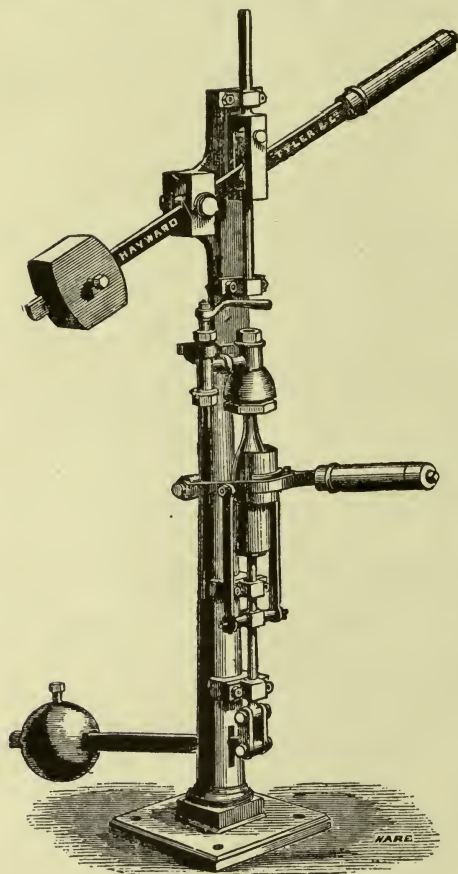


FIG. 68.—Hayward-Tyler's Early Bottling Machine.

a rubber or cork washer by the action of the foot, and a cork was inserted in the holder, *x*. Then by turning the tap, *w*, the pressure within the bottle was made equal to that within the cylinder, and on now opening the tap, *v*, the liquid ran into the bottle, expelling the air through the cock, *w*, and a valve in the cylinder, in the upper part of which it collected.

When the bottle was filled the cork was driven down by the action of the lever, *y*, and was immediately tied down with string or wire.

**Macdonell's Automatic Corking Machine.** — In this machine, which is worked by steam power, the corks are subjected to considerable lateral

pressure, by means of the special device illustrated (Fig. 70), before being driven into the bottle by the plunger.

By this arrangement a larger and longer cork than usual may be employed without risk of its being crushed or broken, and



this greatly reduces the chance of bottles technically known as "leakers" being sent out.

The position of the bottle during filling and of its supporting mechanism behind the screen is shown by the dotted lines in the illustration.

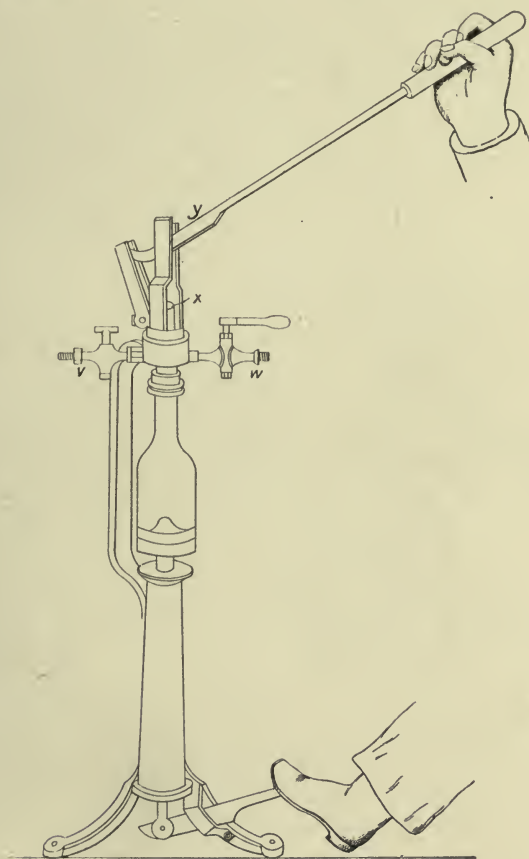


FIG. 69.—Savaresse's Bottling Machine. 1838.

To prevent loss of syrup and gas during bottling a special automatic device is provided, by means of which the air is expelled by carbon dioxide before charging, or is drawn off into a vacuum vessel. Any accumulation of cork dust is prevented by an arrangement which automatically washes

it away. This machine may be regulated to take any size of bottle.

**The Wiring of Corks.**—When ordinary corks are used for closing bottles of aerated waters, some method of wiring is required to prevent the cork being driven out of the bottle. In the case of ginger beer put into stone bottles and left to ferment spontaneously, a much lower pressure is developed than that of artificially carbonated waters, which show a pressure of over 60 lbs., so that string is usually sufficiently strong to keep the corks in their place.

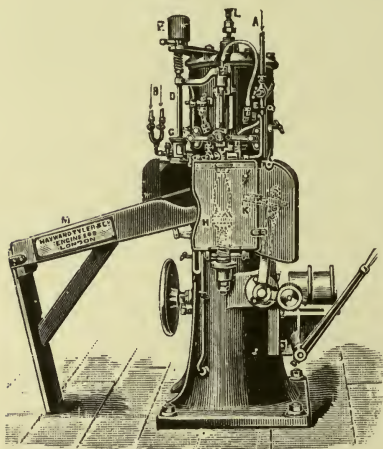


FIG. 70.—Macdonell's Automatic Corking Machine.

During the wiring of the corks a simple stand is conveniently employed to hold the bottle, while the cork is meanwhile pressed down by the action of a lever controlled by a treadle at the base of the stand. With the assistance afforded by one of these devices, the corked bottles are very rapidly wired by hand.

#### Howard's Wiring Machine.

—A great saving of labour is effected by the use of Howard's wiring machine, an illustration of which is shown

in Fig. 71. The wire is carried in the four spools at the bottom of the machine, and is drawn from these by turning the handle on the right, or by means of a belt connecting the wheel at the top with a source of power, a convenient form of which is an electric motor.

The bottle is placed upon the rest seen in the front of the machine, and is raised, so that its neck enters the wiring head, by pressing down the treadle with the foot. The four wires are here guided over the cork, and are finished off by a single loop upon the neck of the bottle. By untwisting this with the finger

and thumb, the whole of the wire is removed from the cork—a great advantage over the older method, in which the wire required cutting, and a piece was invariably left upon the neck of the bottle.

From 50 to 70 dozen bottles per hour can be wired by this machine, and by the use of a slight modification it can also be made to take ginger-beer bottles.

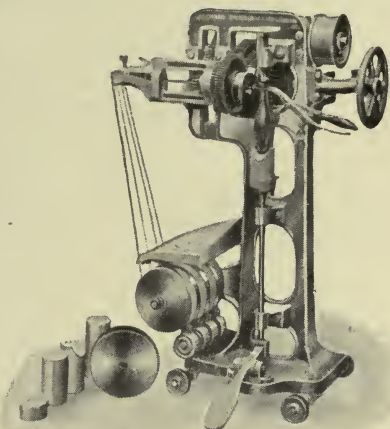


FIG. 71.—Howard's Patent Wiring Machine.

**Bottles with Patent Stoppers.**—The use of corks for closing the bottles of mineral waters

was practically universal during the first fifty years of the industry. Corks are still employed to a large extent for certain classes of goods, and there is much to be said in their favour, even from a hygienic point of view. The objections to their use are that the uncorking is not always a simple matter, and that when once a bottle is opened its contents must be drunk immediately, since it is not practicable to re-cork the bottle and reserve it for another time.

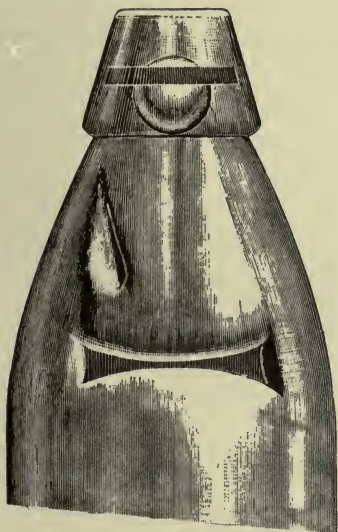


FIG. 72.—Codd's Patent Bottle Stopper.

Numerous patents have been taken out for special stoppers and bottles to overcome these drawbacks, and while some of these have been still-born or have had only a short commercial life,

others have met with a general approval which shows no signs of waning.

Of the special bottles the most generally known, perhaps, is that commonly described as "Codd's Patent" (Fig. 72). This is a bottle of strong glass, either with a flat bottom or conical in form. In the neck of this is a groove of a particular shape

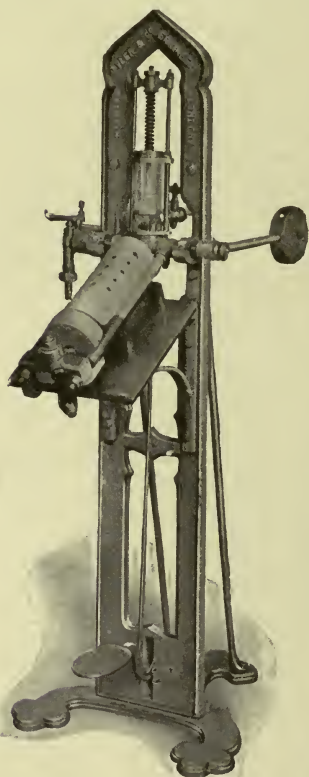


FIG. 73.—Swing-Filling Machine for Codd's Bottles.

constricted towards the base, and within this small chamber lies a movable glass marble, which is prevented from falling into the empty bottle by the constriction at the base. When the bottle is charged with aerated water the marble is forced by the pressure of the gas to the top of the bottle, and being held tightly against the inside of the mouth, where the glass is constricted prevents either liquid or gas from escaping. The bottle is opened by pressing the ball stopper downwards with sufficient force to overcome the internal pressure, and the marble, falling into the chamber in the neck, allows the liquid to pass.

At one time these bottles were very widely employed, but at the present day are only found in country districts; for in towns they have been practically superseded by bottles with patent screw stoppers.

Various machines have been devised for rapidly filling Codd's bottles. In the case of some of these, such as Hayward-Tyler's Swing-filling Machine shown in Fig. 73, the bottle is first charged with syrup or soda solution on the slanting table, and then swung round into a vertical position so that the marble drops down into the neck.



There are also several machines that are automatic in their action, and that charge the bottles entirely in an upright position. These work by steam power up to a speed of over 80 dozen bottles per hour, as in the case of the automatic machine of Hayward-Tyler & Co. which is shown in Fig. 74.

This machine, when once regulated, charges the bottles with liquid and gas, and if by accident a bottle is not placed in position, there is no waste of solution.

**Lamont's Patent Bottle.**—The principle of keeping the stopper in position by means of internal pressure was also used for other patent bottles and stoppers. Thus Lamont's stoppers (Fig. 75), which were made of wood, ebonite or glass, had double elongated ends, which could pass through an opening in the mouth of the bottle, but were held in position by the central disc, which was somewhat wider in diameter than a glass ridge blown within the neck of the bottle. These bottles lacked the simplicity of Codd's patent bottles, and in the case of the wooden stoppers, at all events, were objectionable from the point of view of cleanliness.

Special machines were devised for filling these bottles, which could readily be done at the rate of 40 to 60 dozen per hour.

A modification of this form of stopper is still used, the ebonite base being surrounded by a rubber ring, which makes a tight joint in the neck of the bottle.

The objection to this principle is that since the stopper

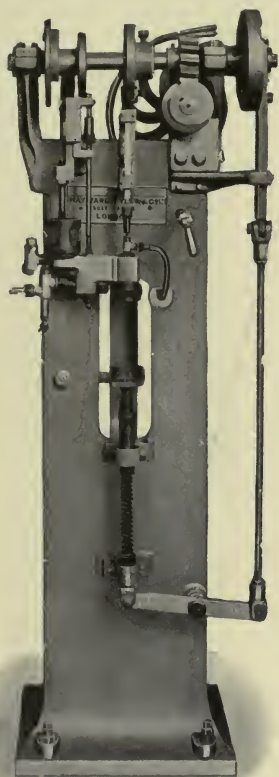


FIG. 74.—Power Filling Machine for Codd's Bottles.

remains inside the bottle, the rubber ring can only be removed and renewed by the use of a special instrument, and owing to the time required for this it will seldom be done. Hence the stopper is much more likely to be a cause of bacteriological impurity, than in the case of ordinary corks or screw stoppers.

**Screw Stoppers.**—The invention by Barrett of the now well-known screw stoppers for bottles was welcomed both by brewers and mineral-water makers, since it solved the problem of preventing the contents of an opened bottle becoming flat. In these stoppers, which are made of vulcanite, wood, or other hard material, the base is in the form of a screw, which is adapted to fit into a corresponding screw groove in the neck of the bottle, while the top is round with a milled edge, and is slightly larger than the mouth of the bottle.



FIG. 75.—Lamont's Patent Bottle and Stopper.

A rubber ring fits tightly over the top of the screw part of the stopper, so that when the latter is screwed tightly down the bottle is closed hermetically. It is thus possible

to use part of its contents and reserve the remainder while still retaining a large proportion of the gas in the liquid. This type of stopper is extensively used for light carbonated beers, and is also the usual form of stopper for ginger beer when sent out in glass bottles.

**The "Riley" Patent Stopper.**—A screw stopper based upon a similar principle to that just described has been patented by the Riley Manufacturing Company, and is now in more general use than any other form of stopper (Fig. 76). It is made of vulcanite, and has a screw which fits into a corresponding groove

in the neck of the bottle, where it forms a tight joint by means of the rubber ring, which is kept in place by a projection on the stopper.

The upper portion of the stopper, outside the bottle, is elongated and has a depression on each side, so that it may be easily held between the finger and thumb, or unscrewed with the assistance of a holder adapted for the purpose.



FIG. 76.—Riley's Patent Screw Stopper.

As in the case of most stoppers of the kind the rings are made of red rubber, and contain antimony, the possible action of which upon the contents of the bottle is discussed on a later page. The question of their bearing upon the bacteriological purity of soda water is also considered in Chapter XI.

**Riley's Machine for Screw Stoppers.**—A machine, worked by steam power, was invented by the Riley Manufacturing Company for rapidly charging the bottles and automatically closing them with their patent stoppers. This machine was largely employed by mineral-water manufacturers, and may still be found in many factories, although during the last three years its place has gradually been taken by the rotary counter-pressure machine described on p. 162.

In the machine which this is superseding there is a cam plate driven by friction, and the action of the machine is controlled by a lever at the left-hand side. The stopper is first screwed down into the bottle, and the latter placed on to the seat with its stopper passing into a slot of a twisting device above. This unscrews the stopper and allows a measured quantity of syrup or soda solution to be thrown into the bottle, after which the bottle is charged with carbonated water from the soda-water machine. The air in the bottle is meanwhile expelled through a sniffling valve controlled by a tap on the right, and in this process there is an inevitable waste of liquid and gas. The twisting device now descends again, screws the stopper tightly



down, and releases the bottle, which is then removed with the left hand and replaced by another with the right hand. From 50 to 60 dozen bottles per hour may be filled with this machine by a practised worker.

During the filling of each bottle a screw automatically closes in front of the bottle as a safeguard against accidents if a bottle should burst, and the worker is further protected from injury by wire masks over the face and gauntlets on the arms, the use of which is strictly enforced. The accompanying illustration,

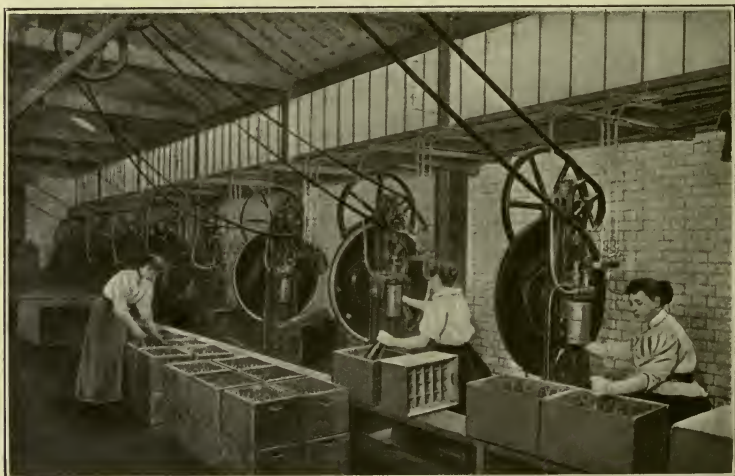


FIG. 77.—Riley's Screw-Stopper Machines at Work.

which shows the way in which a number of these machines could be connected with a single shafting, represents part of the interior of Messrs. Beaufoy & Co.'s works as it was about six years ago (Fig. 77).

For the purpose of the photograph the girls discarded their masks and gauntlets, which was never done under the conditions of actual work.

The drawback of these and similar machines by other makers is the "sniffting," or drawing off the air during the filling, since this entails a simultaneous loss of carbon dioxide and, in the case of sweetened goods, of syrup.



**The "Crown Cork" System.**—A novel method of closing bottles of aerated water was devised some years ago and described by this name. It is still extensively employed by many manufacturers, as it is both hygienic in principle and cheap to use.

Essentially it consists of a cap of tinned steel or of aluminium with a corrugated edge. Within the cap is fitted a disc of prepared paper and a thin disc of cork, which has previously been sterilised.

The neck of the bottle is made with a special ridge, into which the corrugated edges of the steel cap are pressed, thus forming

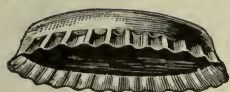


FIG. 78.—"Crown Cork."

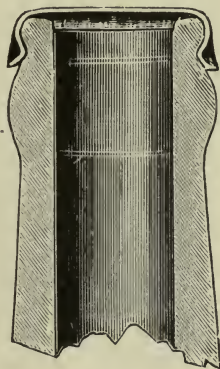


FIG. 79A.  
"Crown Cork" in position on the Bottle.

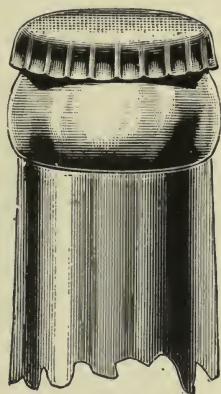
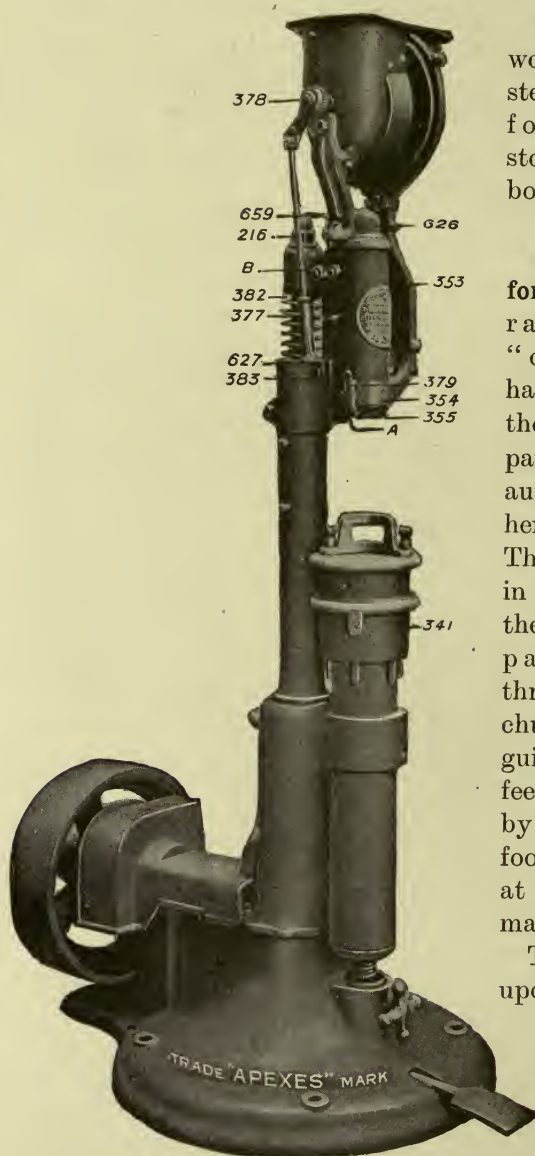


FIG. 79B.

a joint that is sufficient to resist the internal pressure of the carbonated liquid, while the cork disc, being held tightly against the mouth of the bottle, prevents the escape of any gas.

The construction of the "Crown cork" and the method of affixing it to the bottle are shown in the accompanying figures (Figs. 78 and 79). The same system may also be employed for securing ordinary corks in place of the usual method of wiring.

The contents of bottles closed by means of the sterilised discs are less liable to bacterial infection from the stopper than those in bottles corked in the usual way, or closed with screw stoppers.



Various machines, worked by hand or steam power, are made for fixing these stoppers to the special bottles.

**Automatic Machine for Crown Corks.**—A rapid method of "crowning" bottles has been devised by the Crown Cork Company, one of whose automatic machines is here shown (Fig. 80). The crowns are placed in the hopper, 378, at the top, whence they pass downwards through the feeding chute, 353, into the guide cup, 354, the feed being controlled by pressing with the foot upon the treadle at the base of the machine.

The bottle is placed upon the rubber bed of the rest, 341, which is so adjusted that the neck comes about a quarter of an inch below the guide cup.

FIG. 80.—Automatic Machine for "Crown Corks."

The single pressure upon the treadle then releases one

crown from the chute, and locks it upon the bottle by a downward stroke of the head of the machine.

The cylinder below the bottle rest is arranged so that it will offer sufficient resistance to the stroke of the head to allow the crown to be properly locked, while at the same time it is compensated to such a degree as to prevent the bottle being broken in the process.

The machine may be driven by a belt from the main shaft, and it is essential that it should revolve at the correct speed of 100 to 110 revolutions per minute. The bottles intended to be crowned in this machine must be made to a standard size and shape, and gauges for testing them and for ascertaining that the locking rib is properly formed are supplied by the makers of the machine.

**Clasp Stoppers.**—Stoppers which fit closely into the mouth of the bottle, where they are kept in position by a strong clasp of wire, are extensively used for bottling sterilised milk, and have also met with some favour for mineral waters.

Various forms of these clasps are employed, some being permanently attached both to the stopper and the bottle, while in the case of others the clasp is removable.

The most suitable application of the patent clasp (Fig. 81) is as a substitute for wiring down the corks of soda-water bottles. The clasp is fixed to the neck of the bottle, and is intended to stay there after the bottle has been emptied and is ready for use again. The wire is pulled over the top of the cork when the bottle is charged, and holds it in more securely than the ordinary method of wiring, in addition to the process being more rapid and more economical. To open the bottle all that is necessary is to push the clasp aside from the cork.

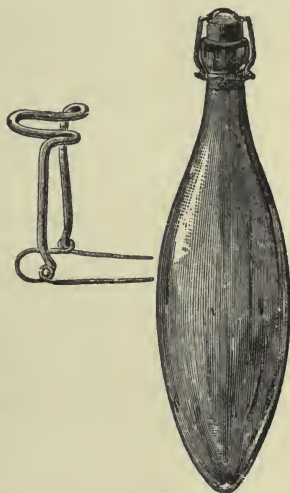


FIG. 81.—Clasp Stopper.

**Automatic Bottling Machines.**—The last five years have witnessed the general adoption of automatic bottling machines into mineral-water factories, and it is in this direction that the

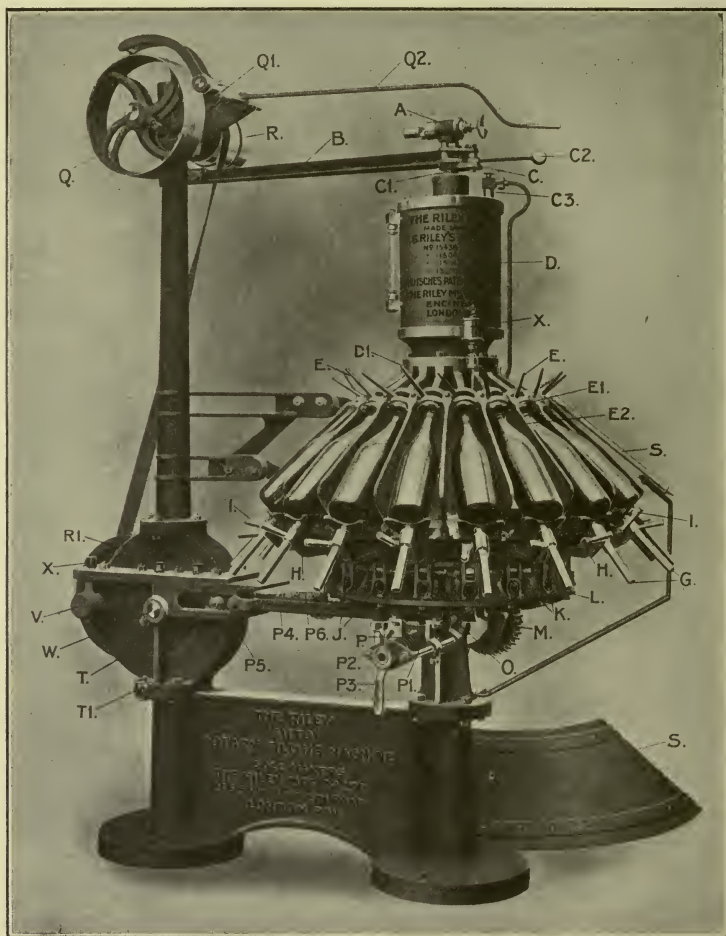


FIG. 82.—The "Riley" Automatic Rotary Filling Machine.

chief advance of recent times has been made in soda-water machinery.

There are several machines of the kind on the market.



One that has met with a large measure of success is the patent "Auto" Rotary Filling Machine, made by the Riley Manufacturing Company, one of the patterns of which is shown in Fig. 82.

The principle upon which this machine is based is that of charging the upper cylinder with the carbonated liquid, and filling the bottles automatically in turn, after creating a counter-pressure. Under these conditions the liquid flows quietly into the bottles, which are filled without the necessity of "sniffling," with its inevitable loss of gas and syrup.

Since the gas is already thoroughly incorporated with the liquid in the cylinder, the loss of pressure in transferring it to the bottles is relatively small, and soda water showing a pressure of, say, 70 lbs. within the cylinder will show a pressure of about 50 lbs. within the bottle.

The carbonated liquid coming from the soda-water machine enters the cylinder, D, through the valve, A, and flows into the bottles through a valve connecting with a series of tubes, the handles of which, E, are seen at the bottom of the cylinder. Each bottle is placed on a seat, C, carried on a pan, beneath which is a gear wheel, which is worked through a ratchet, a wheel, M, connected with a slide block, rod and pawl, receiving their motion from a cam plate, the shaft of which is at X.

The forward stroke of the rod compresses the spring, P, and this, when its tension is released, at the end of the stroke, drives the rod back again, for the process to be repeated. With each stroke of the machine the whole of the bottles are moved a stage forward in their circuit round the cylinder, while the bottle immediately in front of the bottling valve is pushed forward by the action of the corresponding lever slide, J, which is put in motion by mechanism also connected with the cam plate. The bottle fits tightly into the bell-mouth, E, during the filling, the air expelled by the carbon dioxide escaping through the valve, C<sub>3</sub>, at the top of the cylinder.

Each bottle, when charged with the liquid, is removed by hand and its stopper or cork inserted—all this without material loss of pressure.

The rotation of the bottles is contingent upon the regular

supply being maintained, the omission of a single bottle through carelessness bringing them all to a standstill at once. At the same time, this stoppage does not cause the bottle in process of filling to overflow, the supply of liquid being automatically cut off at a definite level.

This machine is made in three sizes, to take nine, twelve or eighteen bottles. With the smallest size about 60 dozen bottles per hour may be charged, while the larger sizes will give an output of 100 to 140 dozen bottles per hour, according to the nature of the liquid being bottled.

A screen, S, is put over the bottles while the machine is working, and in the event of one of the bottles breaking, the supply of liquid to the cylinder may be cut off at once, by means of the handle, C<sub>2</sub>.

The air expelled from the bottles, prior to filling, collects above the liquid in the feeding cylinder, and when a certain pressure is reached it is automatically discharged through a valve, C<sub>3</sub>, at the top. The amount of gas simultaneously blown off with this air is negligible, and the saving in gas over machines in which the air is removed from the bottles by "sniffing" works out in practice at about 25 per cent.

Every description of bottle may be charged upon this machine, including the various patent varieties, such as Codd's bottles (p. 154), and those stoppered by the "Crown Cork" system (p. 159).

The method of lubrication has been simplified to a remarkable degree, the whole of the machinery being oiled by pouring oil into the two lubricators, X, whence it is distributed to the respective parts beneath, while solid grease lubricators are provided for the crank and pawl.

**The "Thistle" Filler.**—Another type of machine which rapidly charges the bottles without the necessity of "sniffing" is the "Thistle" Filler, various forms of which are made by Messrs. Hayward-Tyler & Co.

The principle upon which this machine is based is that of putting the bottles, before filling, in connection with "air-chambers," from which the air has been previously exhausted.

The air in the bottles is drawn off into this vacuum, so that on then introducing the carbonated liquid coming from the soda-water machine the bottles are filled quietly, without loss of either gas or syrup.

One of these machines, adapted for charging twelve bottles, is shown in Fig. 83. The air cylinders, which are shown at the top of the machine, are first screwed into their places, and the bottles placed in the filling heads. The machine revolves, and as the bottles pass a certain point a filling valve is opened and the carbonated liquid is introduced to a height previously arranged. As soon as the full number of bottles has been placed in the machine, the first bottle is fully charged, and is ready to be withdrawn to be corked or stoppered, while its place is taken by another bottle.

As in the case of the Riley machine previously described, the

loss in pressure during the process of corking is negligible, and excellent results may be obtained by working at a pressure of about 80 lbs.

The height to which the bottles are filled is regulated by means of handles attached to the air cylinders, these being raised or lowered according to the size of the bottles to be filled and the final pressure desired.

In the smaller machines, worked by hand, the bottles are

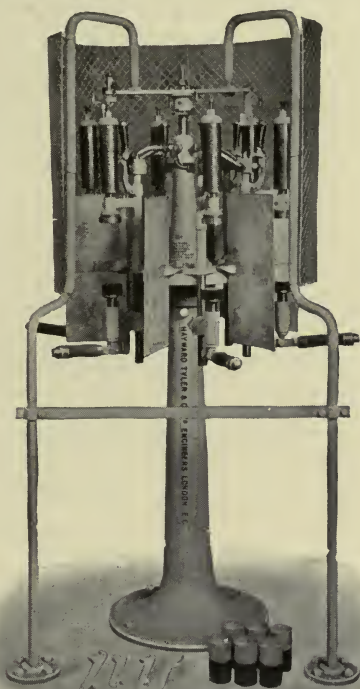


FIG. 83.—Scott's Patent "Thistle" Filler.

brought into position by pressing down handles in front of each filling head, but in the power machines this is done automatically.

With the aid of these machines, which when worked by two operators will charge about 120 dozen bottles per hour, the soda water will show more perfect aeration than in the case of products carbonated at much higher pressures by the older types of machines.

On applying a pressure gauge to a freshly carbonated bottle from either this machine or Riley's machine (p. 162), working at a pressure of about 80 lbs., the needle upon the dial will at first indicate but little pressure, but on shaking the bottle to liberate the dissolved gas the needle will immediately rush upwards, until a pressure of over 60 lbs. is shown.

This may be taken as representing the average pressure of the liquid within the bottles.

**The Syphon.**—The idea of the syphon now universally employed for mineral waters appears to have originated with Deleuze and Dutilleul, who in 1829 took out a patent in France for a device for emptying ordinary corked bottles. A tube terminating at one end in a point was passed through the cork nearly to the bottom of the bottle. This tube was closed by a valve provided with a lever, and by inverting the bottle and pressing upon the lever, the valve was opened and the liquid was expelled by the pressure of the gas.

Then, in 1837, Savaresse patented a syphon, the head of which was affixed to the neck of the bottle instead of being connected with a cork. The syphon of Savaresse, which he named "Perpigna," was soon imitated and improved upon in detail by numerous inventors, but the principle underlying all these forms of bottles was practically the same. In each case the aerated liquid was kept in the bottle by the action of a valve, and on releasing this by pressing upon a lever outside, the liquid was expelled by the force of the gas.

The main differences in the various modifications lay in the mechanism by means of which the valve was opened and automatically closed again on removing the pressure from the lever.



**Savaresse's Syphon.**—The special form of "vase" described in the patent taken out in 1838 by Miles Berry on behalf of Savaresse deserves special description. In its essential details this was the syphon as we know it to-day. It consisted of a vessel of metal, earthenware, or glass, into the neck of which was fitted and secured by sealing-wax a spout of the construction shown in Fig. 84. By pressing the lever, *b*, the two teeth inside, which fitted into corresponding teeth, raised a piston, *c*, that was otherwise pressed down by the coiled spring at the top, capable of being tightened by the screw, *d*. This allowed the liquid to escape from the tap, *a*, so long as pressure was applied to the lever.

In charging this vessel all that was necessary was to apply the tap to the nozzle of a conical tube communicating with the cylinder (*see* p. 149) and to depress the lever, in the same way as for emptying the syphon (Fig. 85). The atm-

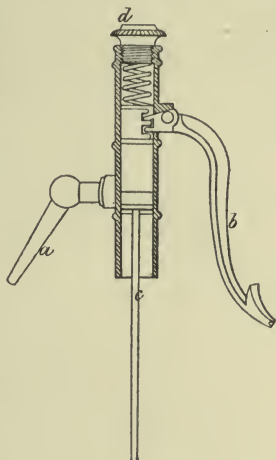


FIG. 84.—Savaresse's Syphon Tube. 1838.

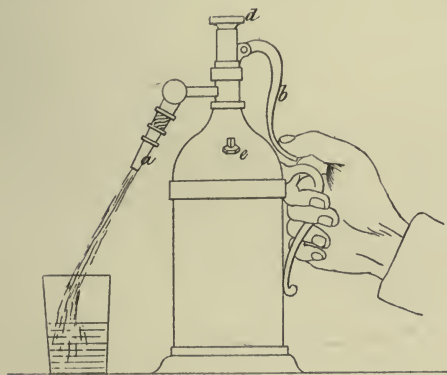


FIG. 85.—Savaresse's Syphon.

spheric air in the bottle was expelled during filling through a small opening, *e*, near the top, which was afterwards secured by a screw stopper. This opening was also used for the introduction of syrups, as in the modern method of making lemonade.

**Modern Syphons.**—The mechanism of two forms of syphon are shown in the accompanying figures, which represent long-handled and short-handled apparatus.

In the first of these (Fig. 86) the pressure applied to the lever, C, raises the piston-valve, overcoming the force of the spring above. This opens the communication between the

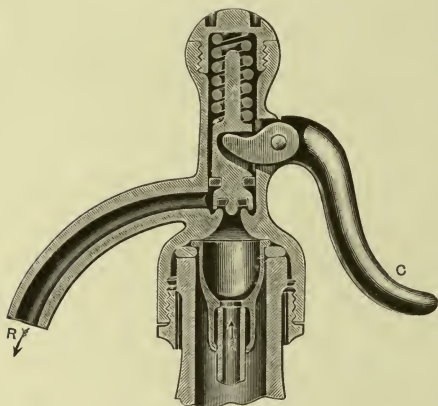


FIG. 86.—Mechanism of Syphon with Long Lever.

chamber, and the outlet tube, R, so that the soda water is forced out by its own pressure. But as soon as the hand is removed from the lever the valve is forced back into position by the action of the spring, an air-tight joint being ensured by rubber-fittings, and the flow instantly stops. Rubber joints are also provided to prevent the soda water gaining access to the mechanism.

In the other type of syphon (Fig. 87) the action of the short lever, C, forces down a valve which is mounted on a rod and meanwhile compresses the spring. The soda water can then pass through the chamber and the openings above it into the tube, R. As soon as the pressure is withdrawn from C the rod and the valve rise at once, and the supply of liquid is cut off, at the points where rubber joints are fitted.

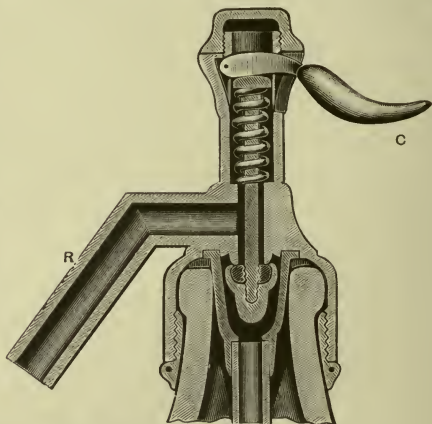


FIG. 87.—Mechanism of Syphon with Short Lever.

It will be seen from this description that the term "syphon" is a misnomer, the liquid being expelled not by the action of a siphon tube, but by the pressure of the dissolved gas.

the pressure of

**Syphon-Filling Machines.**—An early machine devised by Hayward-Tyler & Co. for charging syphons is shown in Fig. 88. By the action of the treadle at the bottom, the syphon, which was put into the machine upside down, was raised until its nozzle was pressed against a nipple, through which the soda water was introduced from the carbonating apparatus. The handle of the syphon was next pressed up by means of the lever on the left of the machine, and on then turning the handle on the right the liquid rushed into the bottle, while the air escaped through a valve by the side of the nipple, and the pressure within the bottle was thus also regulated. An iron guard with a wire grating was latched in front of the syphon during the filling, as a protection against possible explosions.

**Hayward-Tyler's Syphon-Filling Machine.**—The latest pattern of this machine is shown in Fig. 89. The syphon is put with its head resting on the support, *a*, and is kept in position by pressure of the foot on the treadle, *A*.

The supply of syrup is controlled by the handle, *C*, of the syrup pump, while the pin, *D*, regulates the stroke of this pump, and consequently the amount of syrup introduced. The lever of the syphon rests upon the end of the lever, *B*, and by lowering the handle of this the valve of the syphon is opened. The soda water is admitted through the pipe, *G*, the valve of which is controlled by the handle *E*. The same handle is also used to work the snift valves to expel the air from the syphons. The syrup pump is connected with the syrup tank by means of the pipe. *F*.

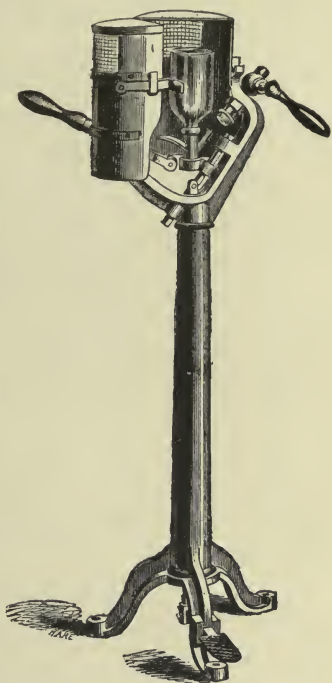


FIG. 88.—Early Syphon-Filling Machine.

Syphons can be charged by this machine at the rate of about 20 dozen per hour.

**Ferguson's Double Syphon Filler.**—From 40 to 45 dozen syphons per hour may be charged by means of this machine, which is worked by hand (Fig. 90).

An empty syphon is placed in the right-hand filler at B, where it is kept in position by raising the handle, A, which simultaneously opens the valve admitting the aerated water. Meanwhile a second syphon is placed in the left-hand filler, and as soon as it is in position the right-hand syphon is ready for snifting. This is done by moving the handle, F, down to the horizontal position shown by the dotted lines, G, and immediately raising it again.

The process thus continues alternately, each syphon being removed as soon as it is charged, and replaced by another empty one.

During the filling a guard, E, falls automatically and covers the syphon as is shown at H. The pipe bringing the aerated water from the cylinder is indicated by C, while J K show the duplicate arrangements for holding the syphons in position and opening the supply-valve connected with

the pipe, C, these being controlled by the lever, L.

To prevent loss of gas during snifting a special snifting chamber is provided, so that the syphons may be charged at a low pressure. A saving of 25 to 30 per cent. of gas is thus effected.

**Counter-Pressure Chamber for Syphons.**—The principle of creating a back pressure in the bottles, and thus enabling the charging to be done at low pressures, has been adopted in various bottling machines described on the preceding pages, such as, for instance, Riley's "Auto" Rotary Machine.

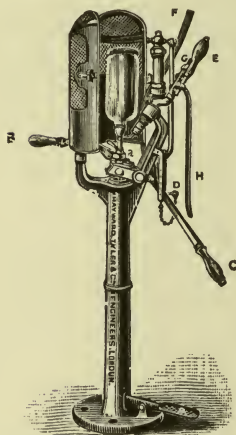


FIG. 89.—Hayward-Tyler's Syphon-Filling Machine.



These machines are only suitable for filling ordinary bottles, while for charging syphons a special machine must be used.

Some of the latter have, as an essential part, a special snifting chamber, as was mentioned in the case of Ferguson's Syphon Bottling Machine described on the preceding page.

In order to convert any ordinary hand or power syphon-filling machine into a counter-pressure machine, and thus prevent the loss of gas that ordinarily takes place, a special snifting chamber, such as is shown in Fig. 91, is fixed either upon the machine, or upon a separate stand connected with the machine by means of tubes.

**The Portable Cylinder or Fountain.**—Although not so popular in this country as in America and South Africa, the portable cylinder is frequently used here as a convenient method of distributing aerated liquids.

The methods of charging these cylinders directly by generators, by the soda-water machine or by tube gas have already been described (Chapter VIII.), and the way in which they are used will be seen by reference to the accompanying illustration (Fig. 92), which shows one of Hayward-Tyler's cylinders attached to a draught column on a counter.

The cylinder, which has a capacity of 8 gallons, is made of copper lined on the inside with pure tin, and is constructed in two parts, bolted together so that it may easily be opened and cleaned.

This ought to be done at regular intervals, to see that the

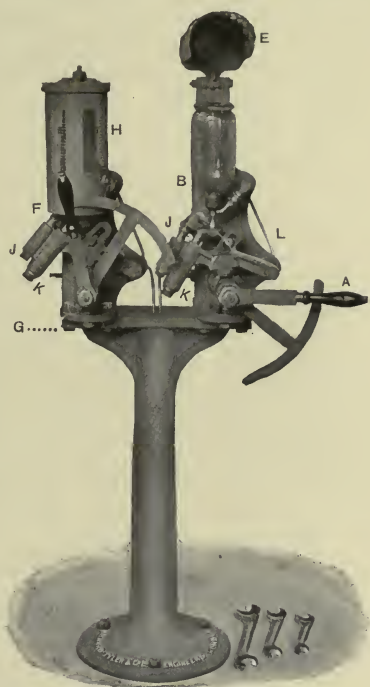


FIG. 90.—Ferguson's Double Syphon Filler.

tin lining of the cylinder is sound, and that the whole of the inside (as well as the connecting pipes) is absolutely clean.

The soda water passes upwards into the column through a coil of tin pipe surrounded by ice in the ice tank, and enters the glass globe, E, at the top. The air is expelled by a snifting valve, and the soda water may then be drawn off quietly through the tap, F.



FIG. 91.—Counter-Pressure Chamber.

**The Sparklet System.**—The main objection to the use of gasogenes in which water is aerated by the interaction of tartaric acid and sodium carbonate is that the liquid remains charged with salt (sodium tartrate), which in the case of certain individuals has a bad effect upon the digestion.

The difficulty of aerating a liquid so as to introduce nothing but carbon dioxide has been overcome in a very ingenious manner in the Sparklet system.

A protected syphon of special construction is used, having upon its head at the side an opening on to which can be screwed a compressor.

The liquefied gas is supplied in small pear-shaped receptacles, each of which contains the right quantity to aerate the liquid in the syphon.

One of these is placed in the bed of the compressor, which is then screwed down hard, and by its action brings the cap, at the narrow end of the gas bomb, in contact with a hollow needle fitted by means of a rubber washer into the side opening. The cap is pierced, and the carbon dioxide, expanding, is forced through the hollow needle into the syphon, the compressor which has been screwed down meanwhile forming a tight joint at the side opening.

It then only remains to shake the syphon to complete the aeration, and the carbonated liquid may then be drawn off by pressing on the lever as in the case of ordinary syphons.

**Bottle-Washing Machinery.**—The method of cleaning the returned empty bottles is of great importance, since upon its efficiency largely depends the purity and keeping qualities of the mineral waters subsequently placed in them.

Much of the contamination and resulting bacteriological impurity of certain bottles of soda water has been traced, not to any want of purity in the water itself, but to the paste from the old labels, which have been soaked off in the washing tank. If the bottles have not been rinsed in an effective manner, traces of this paste, upon which bacteria readily develop, may remain and infect the soda water.

For this reason the preliminary soaking of the bottles in hot water ought to be done in a tank that is kept quite distinct from the actual washing of the bottles. After having had their old labels removed, the bottles are transferred to the washing tanks. Several types of these are on the market, but the general principle followed is to soak the bottles in partitioned trays, which are made to revolve slowly through the tank, then to brush them inside by means of revolving brushes, and finally to place them mouth downwards in metal supports, and to rinse them by injecting a powerful jet of water, the final rinsing being given by water of known purity, the same as is used in the manufacture of the soda water itself.



FIG. 92.—Portable Cylinder or "Fountain."

A washing machine specially constructed for Messrs. Beaufoy & Co., by Messrs. Wickham & Sons, of Ware, is shown in the accompanying figure (Fig. 93).



FIG. 93.—Wickham's Washing Machine.

The body of the tanks is made of wood, but is completely lined with sheet copper as a safeguard against bacterial infection from the wood.

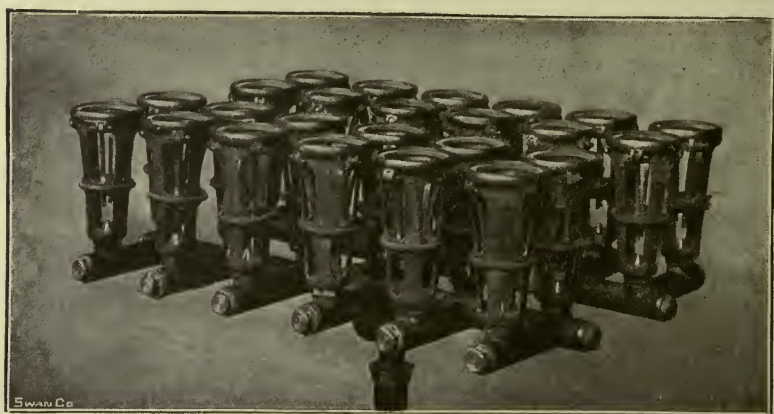


FIG. 94.—Wickham's Patent Revolving Rinser.



The revolving wire trays in which the bottles are placed are seen projecting above the two tanks, the revolving brushes and the rinsers for the first rinsing are fixed between the two tanks, while after the bottles have passed through clean water in the second tank, they are given their final rinsing immediately before being filled again, with a strong jet of water



FIG. 95.—Wickham's Patent Rinser with Bottle in Position.



FIG. 96.—Old-fashioned Type of Rinser.

drawn straight from the rising main of an artesian well which yields a perfectly pure supply.

The bottle rinsers are shown on a larger scale in Fig. 94, and the method in which the bottles are supported in the gun-metal guides will be understood by reference to Fig. 95. The bottles are held in a perfectly upright position, and the water from the jet is therefore distributed evenly over the whole of

the interior, ensuring a thorough rinsing. In the old-fashioned type of rinser (Fig. 96) the spiggot nearly closed the mouth of the bottle and prevented particles of cork or dirt from being washed out.

Another form of washing machine is shown in Fig. 97, which represents one of Messrs. Hayward-Tyler & Co.'s "Automatic" Upright Machines.

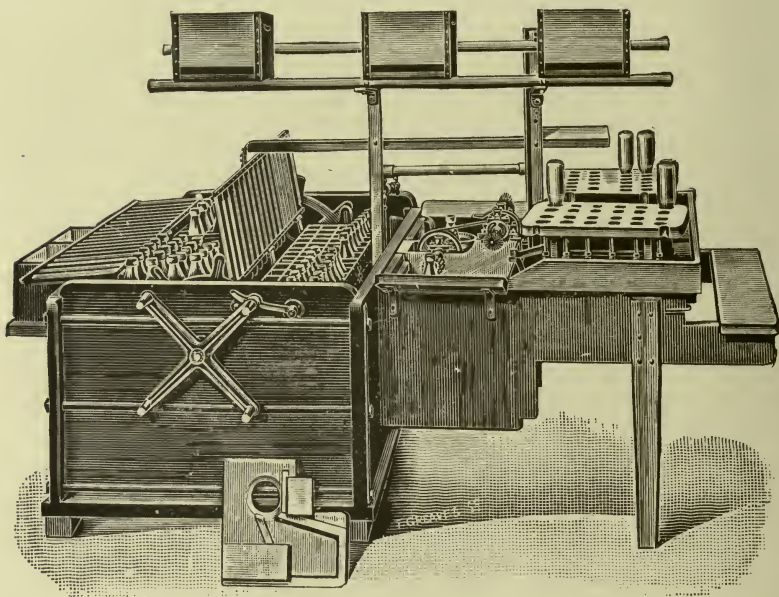


FIG. 97.—Hayward-Tyler's "Automatic" Upright Washing Machine.

The bottles are placed in the trays, which revolve in the tank on the left, and there receive a soaking, which effects a preliminary cleansing and removes the labels, the latter being retained by means of a guard.

The bottles are then applied to the revolving brushes by two persons, one working on each side of the machine, and are finally given a thorough rinsing on the rinsers on the right. The rack above is an overhead slide, upon which the boxes are placed after emptying, so that by merely pushing them

along to the other end they are ready to be taken down and re-filled with rinsed bottles.

By means of this machine, the tank of which is of wood or of metal, bottles are cleaned inside and out and rinsed at the rate of 100 to 150 dozen per hour, according to the kind of bottle. The objection to its use in this way is that no means are provided for the preliminary soaking of the bottles to remove the labels, and that the rinsing given is, therefore, not sufficient to prevent all risk of bacterial infection from the old paste.

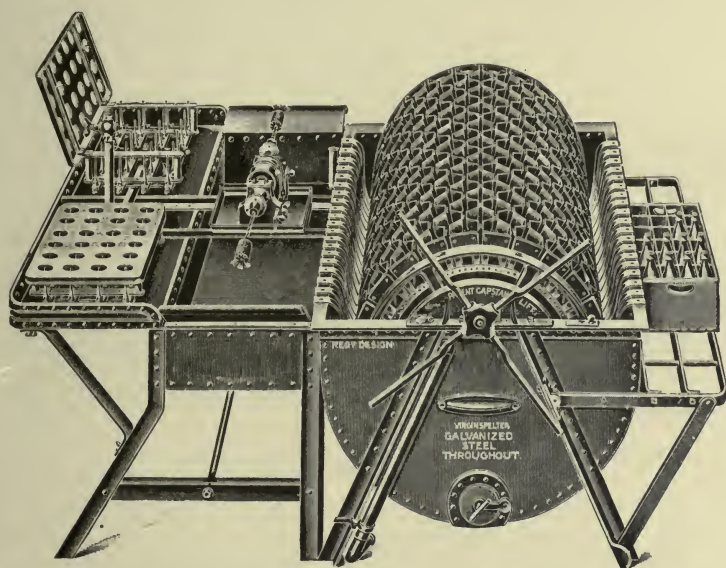


FIG. 98.—Riley's "Wheel" Washing Machine.

It ought, therefore, to be used in conjunction with another tank. For the same reason the wooden tank is objectionable, and only the form with a tank of metal is really suitable for the mineral-water factory.

**"Wheel" Washers.**—Several forms of wheel washers are made by the manufacturers of mineral-water machinery, and one of these, made by the Riley Manufacturing Company, is represented in Fig. 98.

The bottles to be cleaned are placed in the cells, and their



weight causes a slow revolution of the wheel, the bottles being meanwhile held in position by a grid. From 36 to 84 dozen bottles may thus be soaked at one charge, according to size of the wheel, and the period of soaking is longer than is possible with horizontal trays.

After soaking, the bottles are put upon the brushes, and then transferred to the rinsers. As in the case of the last machine described, this washer ought always to be used in conjunction with a tank in which the bottles have had a preliminary washing to remove the old labels and stale paste.

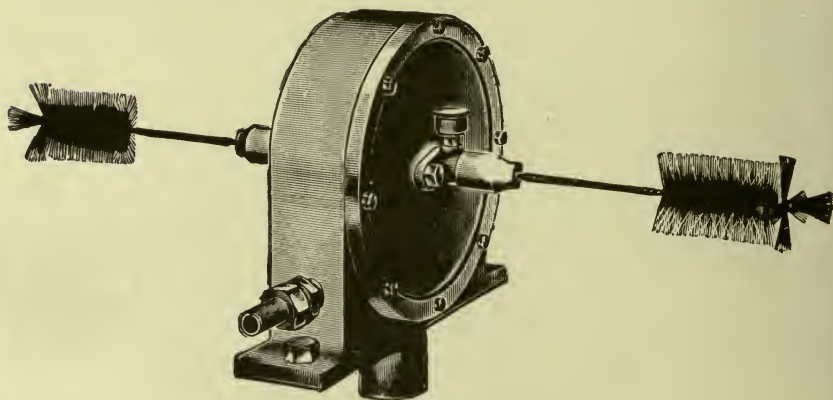


FIG. 99.—Riley's Turbine Brusher.

**Riley's Turbine Brusher.**—A convenient type of brusher is made by the Riley Manufacturing Company, the special advantages of which are that it runs silently, may be driven either by steam or water, and can be bolted down over any washing tank (Fig. 99).

For cleaning Codd's bottles a special form of brush, revolving in a stationary tube, is used to prevent jamming by the movable marble.



## CHAPTER X

### THE MAKING OF GINGER BEER

BREWED ginger beer, which at first was one of the products of the housewife, who prepared it from her old family recipe, has now become an important article of manufacture in the mineral-water factory.

The real "home-brewed" ginger beer, which may still be met with in country houses, is usually a somewhat acid liquid containing a high percentage of spirit, since no method is used to check the combined alcoholic and acetic fermentations. To be really palatable it must be drunk soon after brewing and while it still contains unfermented sugar.

From time to time attempts have been made by mineral-water manufacturers to produce a ginger beer without fermentation, by aerating a solution containing sugar, tartaric acid, and a decoction of ginger, but none of these preparations has the flavour of the brewed beer they are intended to imitate.

Hence during the last three-quarters of a century the brewing of ginger beer has gradually become a separate branch of the industry, and special plant has been devised so as to obtain constant results and produce a beer that will keep well for a considerable time after bottling.

**Outline of Process of Manufacture.**—Briefly outlined, the process of manufacturing ginger beer is to make an infusion of crushed ginger with boiling water, to add sugar and tartaric acid, and to cause the liquid to ferment either by exposure to the atmosphere or by the addition of a suitable yeast. After standing for some hours the ginger beer is bottled and kept for a fortnight or more to mature before being sent out into the trade.

The general arrangement of the plant used for the purpose is shown in Fig. 100.

The ginger after being bruised between rollers is placed in the infusion tank, where it is extracted for several hours with two or three charges of boiling water, from the hot-water tank above. The infusions are drawn off through strainers in this tank into another large wooden tank, where they are sweetened with the weighed quantity of sugar, after which the solution is passed through a refrigerator, which cools it down to a temperature of between 60° and 70° F.

The fermenting vessels in which the inoculation with yeast

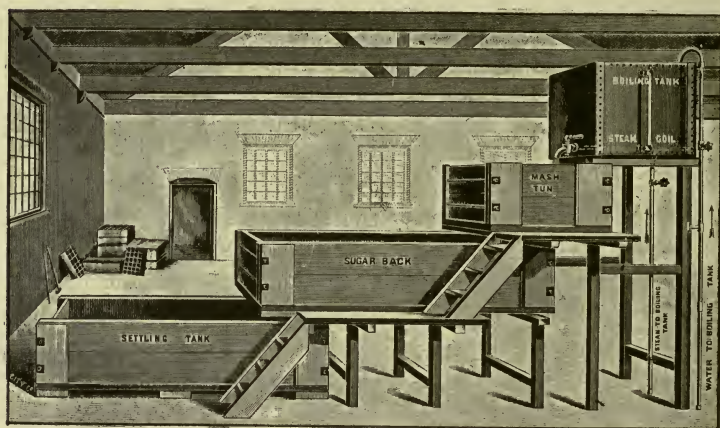


FIG. 100.—Riley's Ginger Beer Brewing Plant.

takes place are frequently made of wood, but slate is much to be preferred for the purpose, as it can be kept absolutely clean more easily, and does not, as in the case of wooden vessels, form "nests" (due to initial decay of the wood fibre), which can harbour bacteria or undesirable wild yeasts.

**Fermentation.**—In many factories the fermentation of the beer is started by the action of one or more species of the yeasts floating in the air; but the method is unreliable, and while it may give satisfactory results for months at a time,

trouble is certain to occur sooner or later, through the action of some of the objectionable wild yeasts.

The particular wild yeast, which normally selects a sweetened infusion of ginger as a suitable medium for its growth, occurs in a formation popularly known as the "ginger-beer plant," from the fact of its forming a gelatinous envelope analogous to that produced by acetic bacteria and the organisms that cause the so-called "mucinous fermentation."

This "plant" affords a remarkable example of the association of two micro-organisms working upon the same medium and mutually assisting in each other's growth and vitality—or, to use the technical term, they stand towards each other in symbiotic relationship.

The yeast is a pear-shaped organism termed *Saccharomyces pyriformis*, while its accompanying bacterium is *B. vermiforme*, which owes its name to a curious worm-shaped envelope surrounding the cells.

Ward succeeded in artificially reconstructing the ginger-beer plant from its two component organisms, and found that it formed a curious horn-like mass when dried, in which state it could be stored without losing its vitality.

The main products formed during the fermentation are carbon dioxide, lactic acid, and alcohol, with traces of acetic acid.

From what has been said above it is obvious that it is better to select a yeast for the fermentation rather than to trust to luck, and for this purpose a selected distiller's yeast will often be found suitable. It is necessary to choose one that does not ferment the sugar too briskly and that does not increase too rapidly.

In the first case the proportion of alcohol formed may exceed the amount permitted by the Excise authorities, while in the second case the deposit of yeast cells at the bottom of the bottle is excessive and complaints may arise. This is particularly the case with the ginger beer sent out in clear glass bottles, which, unlike the old-fashioned stone bottles, allow the amount of deposit to be seen.

The proportion of yeast to be added is also a matter of

importance, and the quantity must be varied according to the time of the year, the weather, and the length of time that the beer is likely to be kept before consumption.

As a rule, from about half an ounce to four ounces of yeast is required for "pitching" a brew of about 300 gallons, the proportion being settled from experience of results obtained both during summer and winter with the yeast in question.

Usually the amount of alcohol produced during the limited fermentation is less than 2 per cent. of proof spirit, and to this proportion no exception is taken by the Excise. Sometimes, however, when a suitable yeast has not been used, the fermentation proceeds far beyond this point, and the "non-alcoholic" ginger beer may then contain more alcohol than an ordinary beer.

For example, in certain bottles of ginger beer examined by the writer the whole of the sugar has been fermented and the liquid has contained from 10 to 12 per cent. of proof spirit.

When the fermentation has not proceeded to this excessive degree only a relatively small pressure is developed within the bottles. As a rule, a pressure gauge passed through the cork after the ginger beer has matured for about a fortnight will show a pressure of 8 to 10 lbs. to the square inch; but where the fermentation has not stopped at the desired point, a much higher pressure, in some instances exceeding 50 lbs., is produced within the bottle.

This affords the explanation of the cracking of the stoneware bottles, which gives trouble to the manufacturer who does not take into consideration the factors described. It is particularly liable to happen in the case of ginger beer made to ferment spontaneously.

**Wild Yeasts.**—The so-called "wild yeasts" are given their name to distinguish them from the cultivated species used in the breweries, the separation of which in a pure form originated with Dr. E. C. Hansen, of Copenhagen. These wild yeasts are widely distributed and appear to develop normally upon the outside of fruit where they produce the bloom, while at other



times they remain quiescent in the soil until blown by the wind or carried by insects on to a suitable culture medium.

It is now thirty years since Hansen traced the turbidity and the bitter flavour produced in certain beer to the action of definite species of these wild yeasts, and showed that when efficient precautions had been taken to prevent the access and growth of these, and the wort had been fermented with pure cultures of a normal yeast, there was no further difficulty.

Among these organ-



*S. anomalous*, film.  $\times 1,000$   
FIG. 101.



*S. apiculatus* (Schweitz).  $\times 1,000$ .  
FIG. 102.

isms, which are now known to be undesirable visitors to the fermenting vats, may be mentioned Hansen's *Saccharomyces ellipsoideus* II., which causes a turbidity, and *Saccharomyces Pastorianus* I., to the action of which bitter flavours are frequently due. Two other species which cause trouble by producing a fruity odour and taste in the beer, are known as *S. anomalous* (Fig. 101) and *S. apiculatus* (Figs. 102, 103).<sup>1</sup>

<sup>1</sup> These photographs of wild yeasts are reproduced here by the kind permission of Mr. A. C. Chapman.

The first of these produces spores of a peculiar shape, while the second may be recognised by the characteristic ovoid form of its cells, which appear like a number of connected lemons. Budding takes place at the pointed end of the cell, and for some time the new cell retains the appearance of an ordinary yeast cell.

Since ginger beer resembles beer in being made by the action of yeast, it too is liable to be infected by wild yeasts, and to acquire an undesirable flavour.

Thus, within the author's experience, successive brews of

ginger beer, which had a perfectly normal flavour when freshly brewed, gradually acquired a pronounced apple flavour when kept for some time in the bottles.

Ginger beer brewed by the method of spontaneous fermentation is particularly liable to be infected in this way, since it is entirely a matter of chance as to which yeast grows first on exposure of the infusion to the air.



*S. apiculatus* (Schweitz).  $\times 1,000$   
FIG. 103.

The use of a cultivated yeast which has been proved to give satisfactory results is in itself a safeguard against the invasion of wild yeasts, since, when the liquid is briskly fermenting, the latter cannot easily gain any foothold, and the chance of their surviving and doing their work later on is greatly reduced.

In the case of infection of ginger beer mentioned above, the trouble was cured by thoroughly cleansing and disinfecting the brewing plant with sulphurous acid, sterilising the ginger wort, rapidly cooling it, and fermenting with a very active distiller's yeast. Although the ginger beer thus produced had somewhat of a "yeasty" flavour, the odour and taste of apples

which had rendered the other beer unsaleable had been completely checked.

In a paper read by Mr. Chapman before the Institute of Brewing,<sup>1</sup> an interesting account is given of a case of infection in a brewery by *S. apiculatus* during the winter. As the whole of the plant had been thoroughly cleansed and disinfected there could have been no possibility of any decaying woodwork having formed a spot where the wild yeast could lodge from brew to brew, and it appeared probable that the cells had been borne by the wind into the brewery earlier in the year, and had lodged upon the window-sills, whence from time to time they had been blown into the fermenting tuns.

Many of the precautions suggested by Mr. Chapman (*loc. cit.*) against infection of beer by wild yeasts, might with advantage also be taken in the brewing of ginger beer. For example, a cultivation of pure yeast in sufficient quantity should be used for the fermentation so as to oust any wild yeast that may put in an appearance. All soft parts in the woodwork of the fermenting should be removed since they are liable to form centres of infection which resist the actions of disinfecting agents. This is one of the reasons why slate is preferable to wood, as the material for the fermenting vessels.

The use of a refrigerator (*vide infra*) for cooling the infusion of ginger beer is a great safeguard against infection by airborne wild yeasts, since it so greatly reduces the period of standing before introduction of the proper yeast. It is the exception, however, for this method of cooling to be employed, and in most instances the beer is left exposed to the air in the fermenting vessel until it has spontaneously cooled sufficiently for fermentation.

**Infusion Tanks.**—The crushed ginger is infused with three successive quantities of boiling water which is heated in a separate tank and then run on to the ginger. Or, in another method, the mixture of ginger and hot water is heated in a vat by means of a steam coil in the infusion tank itself. The arrangement of the steam coil used for this purpose will be

<sup>1</sup> *Journ. Inst. Brewing*, 1904, X., p. 382.

understood by reference to Fig. 104, a space being left underneath so that the vat may be easily cleaned.

To prevent metallic contamination the tubes, which are of drawn copper, are tinned on the outside.

In the other method, in which the water is heated entirely

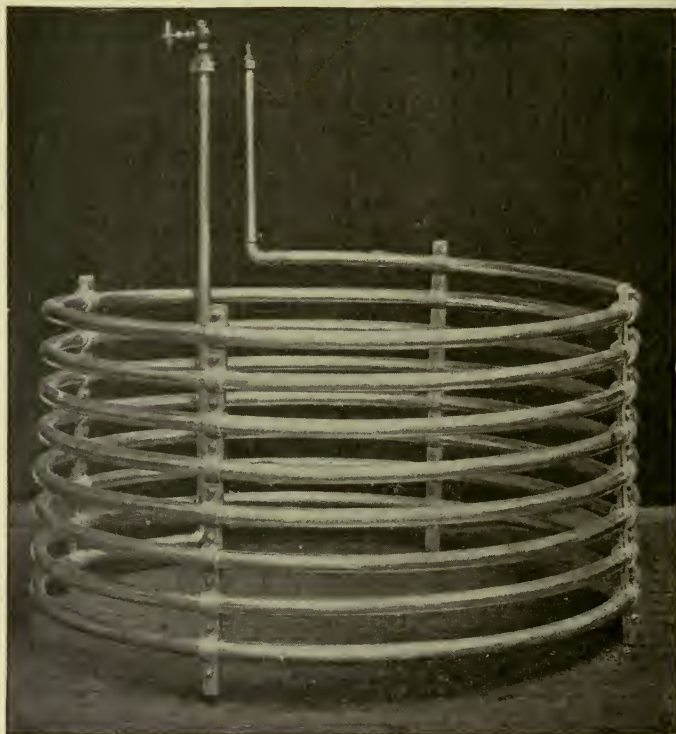


FIG. 104.—Steam Coil in Ginger Beer Infusion Tank.

apart from the ginger, a tank of galvanised iron is ordinarily used, and a jet of naked steam may be blown into the water.

The infusion tanks are generally made of wood either in the form of vats, or more conveniently as shallow squares, which may be ranged at different levels above each other. The cocks and other fittings are made of gun-metal, which is practically unaffected by any organic acids. The hot infusion of ginger



is strained off into the vat below, while the residual ginger receives a second and third treatment with boiling water, after which it is spent.

The united extracts are now sweetened with the calculated amount of sugar, and when a refrigerator is not used, the tartaric acid is also added at this stage.

**The Refrigerator.**—The apparatus used for cooling beer rapidly, before introduction of the yeast, was devised some forty years ago.

The refrigerators of to-day are essentially the same in principle, the chief modifications that have been made having

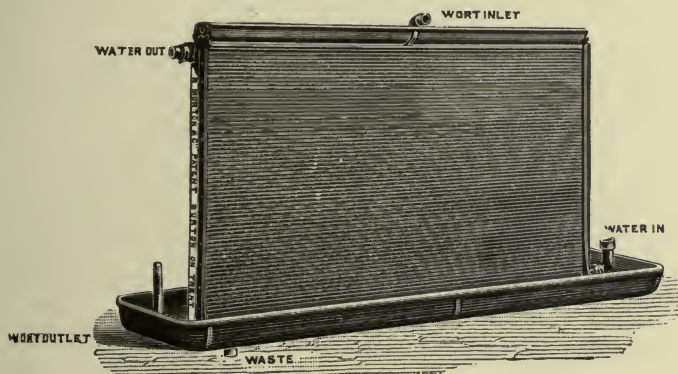


FIG. 105.—Vertical Refrigerator.

had for their object the provision of a greater cooling surface, and the facilitating of the cleaning of the inside.

In its simplest form the refrigerator consists of a series of copper tubes arranged above one another in a vertical frame, and having on the lower side of each tube a metal attachment, which is sometimes cut in the form of a saw, to secure even distribution of the liquid falling over them. Cold water enters the lowermost of these tubes, and passing successively through those above it, leaves the top tube by a waste-pipe.

Above this series of tubes is a perforated trough into which the hot ginger beer flows in a steady stream. Thence it trickles through the holes and falls upon the top cooling tube

and so on from tube to tube until it reaches the bottom where it is received in another trough with an outlet pipe connected with the fermenting vessel.

The degree of cooling it receives varies with the temperature of the water within the pipes, and of the speed at which it is made to trickle over them. But speaking generally there is usually a difference of about 70° F. between the temperatures of the ginger beer in the upper and lower troughs.

In modern forms of the refrigerator the cooling tubes are a flattened oval instead of round, so as to give a greater surface for cooling, and caps are fitted to the ends of the tubes, which enable them to be cleaned inside from time to time to remove any deposit of salts from hard water.

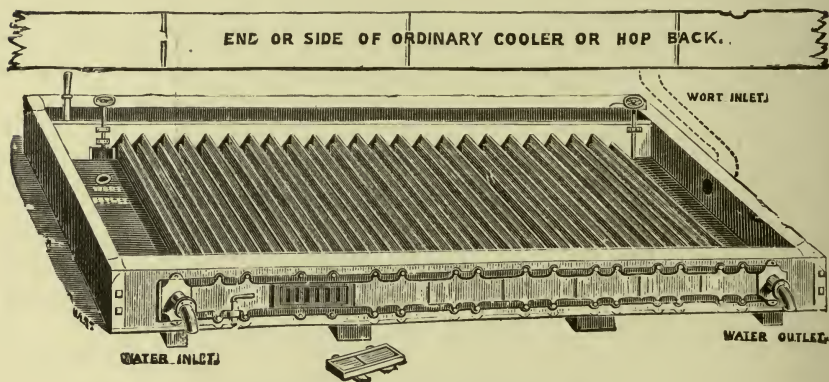


FIG. 106.—Horizontal Refrigerator.

In another pattern of refrigerators the cooling tubes are arranged horizontally instead of vertically, the liquid to be cooled passing through a succession of compartments in a trough.

This type of apparatus has the advantage of occupying very little space, and of needing only a drop of about a foot from the bottom of the infusion vessel. On the other hand, it uses more water than the vertical form of apparatus. This, however, is not an important point, where the water, which leaves the refrigerator quite hot, can be conducted to the tanks used for washing the bottles instead of being run to waste.

As in the case of the vertical apparatus these horizontal refrigerators are fitted with caps at the ends of the tubes so that the inside can be periodically examined and cleaned.

In yet another pattern of refrigerator the cooling tubes are arranged in a circle so that in section the apparatus has the form of a cylinder.



FIG. 107.—Apparatus for Filling Casks with Ginger Beer.

**Fermentation Tanks.**—These are constructed either of wood or of slate, the latter being preferable (see p. 180), and are provided with a draw-off cock made of gun-metal. This is fixed in the side a little distance from the bottom to prevent the yeast that has subsided being drawn off with the clear beer.

When wooden tanks are used it is essential that the wood should be free from resinous matter which could be extracted by the beer and impart an unpleasant flavour. For this purpose the Riley Manufacturing Company use only kauri pine for the sweetening and fermentation vats, since this wood contains very little resin.

When a refrigerator is employed for chilling the beer it is



usually placed beneath the sweetening tank and above the fermentation tank, and the tartaric acid is added to the cooled solution in the latter to prevent the metal fittings of the refrigerator being attacked.

After fermentation, either spontaneous or produced by the addition of yeast, the ginger beer is allowed to stand for twelve hours or more before being drawn off into small casks or bottles. Sufficient sedimentation of the yeast is an essential process in the production of a beer that will mature properly and keep well.

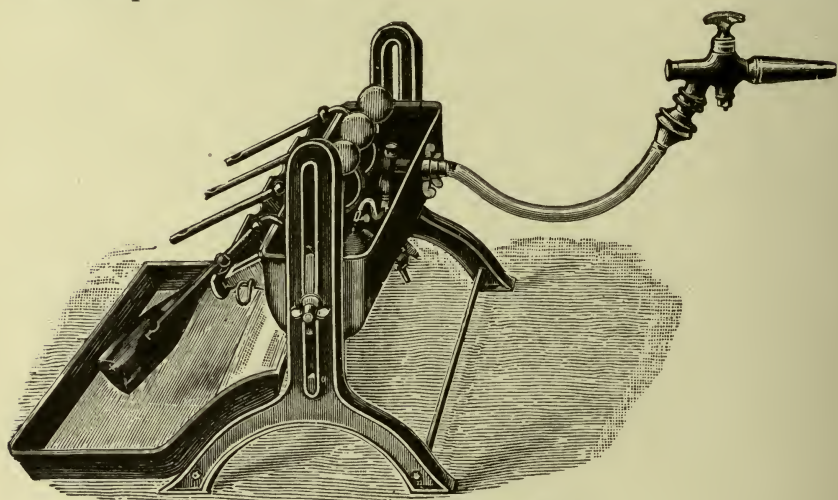


FIG. 108.—Riley's Filling Machine.

**Bottling Machinery.**—The clear beer that is drawn off from the fermentation tank is put up in casks or is bottled in the well-known earthenware or “stone” bottles, or in glass bottles with screw stoppers.

In either case a filling apparatus is used to simplify the process and render it more speedy. A convenient machine for charging casks without the inconvenience otherwise caused by the froth or “fob” is that made by Messrs. Hayward-Tyler & Co. (see Fig. 107).

The beer coming from the fermentation vat through the pipe A, enters the measuring vessels, F,F,F, by way of the



cocks, B,B,B, which are turned off as soon as the froth reaches the holes, F, at the top. The outlets are then opened by pulling the chains, C, and the beer runs into the casks through the

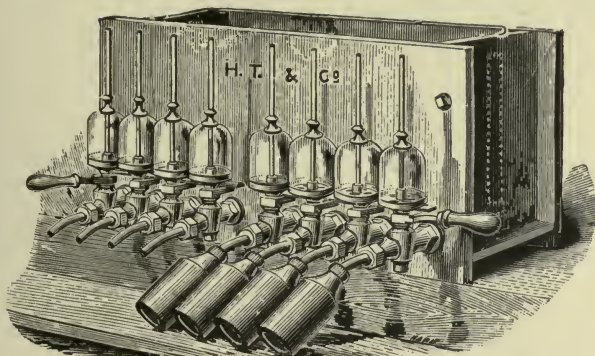


FIG. 109.—Hayward-Tyler's Filling Machine.

movable arms and hose, D. The process is carried on continuously the place of each cask when filled being taken by another.



FIG. 110. --Filling the Bottles.

Any beer overflowing or spilt falls into the trough, H, while an upper trough, E, receives what may be carried over with the froth through the holes at the top.

For filling bottles machines acting upon the siphon principle are in common use, the beer passing from the fermentation vat into a trough in which are a number of syphons controlled by automatic ball valves. One of these machines, made by the Riley Manufacturing Company, is here illustrated (Fig. 108).

This has a broad enamelled trough which can be raised or lowered as required, and is fitted with special check valves to prevent the ginger beer overflowing. From two to eight bottles may thus be filled simultaneously, the place of each one as filled being taken by another empty bottle.

As fast as they are filled the bottles are removed and handed to another attendant, who drives in the cork and ties it down with string.

Another machine made by Messrs. Hayward-Tyler & Co., is shown in Fig. 109.

The process of filling the bottles is shown in the accompanying illustration of this part of the factory of Messrs. Beaufoy & Co.

## CHAPTER XI

### EXAMINATION OF MINERAL WATERS : GENERAL CHARACTERISTICS — THE PRESSURE — METALLIC CONTAMINATION — BACTERIOSCOPIC EXAMINATION — INJURIOUS FERMENTATIONS — ROPINESS — PRESERVATIVES AND COLOURING MATTERS

THE general characteristics to be looked for in well-made soda-water are that it should be quite clear and free from sediment or deposits on the inside of the bottle ; that it should open without violence ; and that it should continue to give off bubbles of gas for at least five minutes after being turned out of the bottle.

The almost explosive manner in which badly-made soda-water leaves the bottle indicates the presence of air in the water. Although such water effervesces very vigorously at first in the glass, the evolution of the gas soon stops, and the water becomes flat long before that in which no air is present.

The occurrence of a deposit, or of sediment, in the bottle is usually due to bacterial changes and its presence generally indicates that the bottle or the stopper has not been properly cleaned. In properly regulated factories special precautions are taken to prevent any dirty bottles or stoppers accidentally slipping into a batch. Not only is an elaborate system of cleaning employed, but every bottle is subsequently " sighted " as a safeguard against any of them having been overlooked. This is the more necessary, owing to the fact that empty mineral-water bottles are frequently used as convenient receptacles for paraffin oil, turpentine and so on before being returned to the dealer.

**Measurement of the Pressure.**—Small pressure gauges have been devised for the measurement of the pressure of the gas inside the bottles—a point of importance in ascertaining whether they are uniformly charged.

The adaptation of these test gauges is very simple. Thus, the instrument for corked bottles has a loosely fitting point attached to a hollow corkscrew with a tap and screw at the end. When this is screwed into the bottle and through the cork the movable point falls from its socket, and on now screwing the gauge on to the end and opening the tap the gas is brought in contact with the recording mechanism (see p. 62), and the pressure may be read upon the dial.

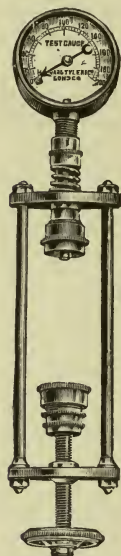


FIG. 111.—Testing Gauge for Syphons.

A similar instrument is used for testing the pressure in syphons, the mouth of the latter being brought into connection with the tube of the gauge, which is meanwhile kept in position by means of two stays and a screw that is turned down until it grips the head of the syphon (see Fig. 111).

Testing gauges are also made to be used with screw-stoppered bottles, and Codd's or ball-stoppered bottles (Fig. 112).

As has already been mentioned, there is an inevitable loss of pressure in charging a bottle with an aerated liquid. With the older types of bottling-machines it is necessary to use a pressure of upwards of 120 lbs. to the square inch for filling ordinary bottles and a much higher pressure for syphons, and this inevitably results in a considerable loss of gas.

By the use of the counter-pressure methods of bottling (pp. 162, 170) much lower pressures may be used with better results. A pressure of 50 to 60 lbs. to the square inch is quite sufficient for the liquid in the bottle, and if, as has already been pointed out all air has been

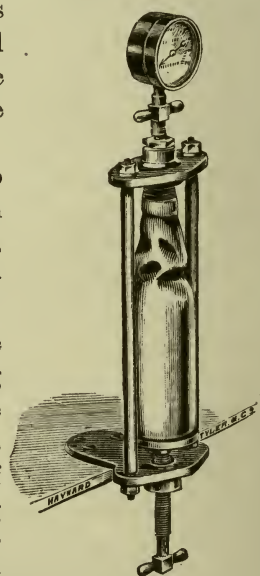


FIG. 112.—Testing Gauge for Codd's Bottles.



previously expelled, soda-water showing a pressure of about 70 lbs. when taken from the carbonating cylinder and bottled in a counter-pressure machine will leave the bottle without splashing over the glass and continue to sparkle for a long time.

**Examination of Sediment.**—Any sedimentary deposit in bottles of aerated water should be examined chemically and under the microscope. Occasionally, in the case of dark-coloured goods, it is due to some of the colouring matter having been thrown out of solution—a change that is promoted by the bottle having been exposed to strong sunlight.

A white powdery sediment adhering loosely to the bottom of the bottle is usually of an organised nature, and appears to be derived from impurities introduced with the sugar or from imperfectly cleansed vessels. To the same causes may also be attributed the floating flocculent particles, which are sometimes seen in bottles of lemonade.

A crystalline deposit on the sides and bottom of the bottle is generally mainly due to calcium tartrate, which is formed by the interaction of the tartaric acid (used in the lemonade syrup) with the calcium salts in a hard water. The formation of the calcium tartrate takes place very gradually, and is of no importance from the hygienic point of view, though it spoils the appearance of the lemonade.

If much trouble is caused in this way the remedy is to use a soft or a distilled water in the manufacture of any aerated drink containing tartaric acid.

**Metallic Contamination.**—The metals, traces of which are of most frequent occurrence in mineral waters, are iron, copper and lead, while tin, arsenic and zinc are occasionally present.

Iron, the presence of which in the minute quantity in which it occurs is probably of no physiological importance, usually finds its way into soda-water from contact of the soda with some iron object, such as a wet scale pan, or it may be derived from rust from the water pipes that feed the solution tank.

The chief objection to its being present is that it causes

discolouration if the soda-water subsequently comes in contact with any liquid containing tannin, such as for example spirits that have been kept for some time in oak casks. A mere trace of tannin is sufficient to cause the darkening of soda-water containing iron as impurity; and tannin thus forms a good re-agent for the metal. It is not difficult to prevent the contamination of mineral waters with iron by carefully noting all the possible sources.

**Antimony in Rubber Rings.**—The red rubber composing the rings fixed round screw stoppers to make an air-tight joint with the bottle contain a large proportion of antimony sulphide, to which they owe their colour.

Some years ago a medical man writing in a daily paper asserted that this antimony was a source of danger, since it was liable to be dissolved by carbonated mineral waters, especially those which, like lemonade, contained free citric acid. There was a further risk, it was urged, in the possibility of small particles of the rubber rings becoming separated by friction, and being subsequently swallowed and dissolved by the gastric juice.

In order to ascertain the degree of truth in these statements a series of experiments was made by the present writer. No trace of antimony could be found in any bottles of soda-water, even when a rubber ring had been cut up and left in the bottle so as to give a much greater chance of contamination than is possible under normal conditions, in which only a relatively small surface of the rubber can come in contact with the liquid.

Treatment of the rubber rings with hot hydrochloric acid of five per cent strength also failed to extract any antimony from the rubber, and since this degree of acidity was many times greater than that of the gastric juice it was evident that there was no risk of antimony poisoning, even in the unlikely event of actual particles of the rubber being swallowed.

The only way in which the metal could be extracted was by treatment with alkali; and since the usual product of the mineral water manufacturer are always acid, the chance of

any antimony being found in soda-water or lemonade may be dismissed as infinitesimal.

Antimony is also employed as an alloy to harden the tin used for the heads of syphons, but metallic antimony is not soluble in a solution of carbon dioxide, and contamination of the soda-water with antimony from this source is out of the question.

**Copper.**—Some years ago copper was a very common impurity in soda-water, into which it found its way through the action of the dissolved carbon dioxide upon the copper of the soda-water machines and pumps. The recognition of this fact has led to precautions being taken to exclude copper, and at the present time, all parts of any machinery liable to come in contact with carbonated liquids are either lined with pure block-tin or are given a thick wash of that metal. Hence copper is now much less frequently present in mineral waters though it may still be found occasionally, especially in cases where the tinning of the inside of a carbonating cylinder has worn away in places. The copper is then dissolved very readily, possibly owing to some galvanic action being set up between the two metals.

Apparently the copper is first oxidised by the oxygen contained in the water, and the oxide converted into carbonate, which dissolves in water containing an excess of the gas.

In the light of recent experiments upon the effect of copper upon the human system, and in view of the facts that metallic copper and copper sulphate are extensively used in America for the sterilisation of water, it is questionable whether traces of copper such as sometimes occur in mineral waters could have any injurious effect upon the system. At the same time, as there is a doubt on this point, manufacturers rightly endeavour to prevent their customers from being the subjects of experiments.

**Lead.**—A saturated solution of carbon dioxide readily dissolves lead in the presence of oxygen, an oxide or hydroxide being probably formed first before the lead is converted into a carbonate.

When lead occurs in soda-water it is usually derived from the solder forming the joints of the tin-pipes, or from the metal in the heads of syphons ; but increasing care is given nowadays by the makers of mineral-water machinery to prevent contamination from either of these sources.

Another possible source of lead contamination, to which attention was called in 1894 by Budden and Hardy, lies in the glazing of stoneware bottles and of earthenware pans which are sometimes used in the preparation of the syrup. In fact, these chemists definitely assert that mineral waters have sometimes taken up lead in this way.

The dangerous extent to which soda-water in the past was liable to become charged with lead through contact with the metal in the course of manufacture may best be illustrated by quotation of the following passage, written in 1856 by Payen<sup>1</sup>.—“ During the early days of the manufacture, waters aerated with carbonic acid were accidentally changed in composition by prolonged contact with tubes or fittings of lead or of an alloy containing 10 to 18 per cent. of that metal. A small quantity of the oxide of lead formed under the influence of the oxygen in the air was then converted into carbonate which passed partly into solution and was partly precipitated. This poisonous compound would have been able to have caused serious accidents, especially if it were taken over a long period. Fortunately, however, the authorities, warned in time, prohibited the use of alloys containing lead. Pure tin is now employed and all danger has passed. It is therefore advisable to distrust all old apparatus, and to see, by means of a simple test with sulphuretted hydrogen, that the aerated water does not contain any trace of compounds of lead. Otherwise all the fittings and all the lead tubes in the machinery ought to be replaced by other of pure tin.”

Lemonade is much more liable than soda-water to contain traces of lead, owing to the fact that the citric or tartaric acid used in the preparation of the syrup is very frequently contaminated with a minute quantity of lead derived from the leaden pans used in their manufacture.

<sup>1</sup> *Traité des Substances Alimentaires.*



In fact, it is not an easy matter to obtain a commercial sample of either of these acids that does not give a faint reaction in the test for lead.

Before attention had been directed to the point the amounts of lead in commercial citric and tartaric acids were much greater than the traces found at the present time, and the proportions detected in lemonade and other sweetened aerated drinks were also correspondingly larger.

For instance, Mr. Stokes<sup>1</sup> found in a sample of ginger beer (of which tartaric acid is one of the ingredients) the serious quantity of  $4\frac{1}{2}$  grains of lead per gallon.

It is probable that this was an exceptionally bad case, but it illustrates the want of thought then given to the manufacture of these acids and the need that there was of reform in this direction.

Samples of citric acid, tartaric acid and cream of tartar more recently examined by Mr. R. Tatlock,<sup>2</sup> President of the Society of Public Analysts, were never found to be quite free from that metal, and even a sample of citric acid, bought with a guarantee of its being free from lead, contained 0.0015 per cent.

A standard was recommended by Dr. MacFadden in a report to the Local Government Board in 1907, of 0.002 per cent. as a maximum permissible quantity, but in Mr. Tatlock's opinion, such a limit is unnecessarily stringent as regards the manufacturer. In the case of numerous commercial samples of tartaric acid he found amounts up to 0.012 per cent., while the highest amount detected in citric acid was 0.010 per cent. These results indicated that some standard for lead in these products was certainly required, but taking into consideration the physiological factor Mr. Tatlock considered that a somewhat higher proportion than the 0.002 per cent. of Dr. MacFadden's standard might safely be permitted.

On this point it may be mentioned that the standard of 0.002 per cent. of lead as a limit has been found practicable in the case of cream of tartar, and that there should be no insu-

<sup>1</sup> *Analyst*, 1894, XIX., p. 174.

<sup>2</sup> *Analyst*, 1908, XXXIII., p. 173.

perable difficulty in producing citric and tartaric acid of an equal degree of purity.

In any case the mineral-water manufacturer would do well to have a test made from time to time to ascertain that the acids used by him do not contain appreciably more than this amount, and in this way he would ensure that the still smaller proportion of lead in the finished lemonade would be entirely negligible.

**Arsenic.**—The principal direction in which precautions must be taken to guard against the introduction of arsenic into mineral waters is the preparation of the syrups for sweetened goods.

It will be remembered that in the remarkable epidemic of arsenical poisoning by beer some years ago the origin of the poison was traced to the glucose from which the beer had been partially brewed, and that this glucose had derived it from having been made from a sulphuric acid prepared from arsenical pyrites.

Since glucose is frequently used in mineral-water factories there is a possibility of arsenic gaining access to the mineral water from this source, though such care is now taken in the manufacture that it is rare to meet with glucose giving a reaction for as much as one part of arsenic in a million.

Arsenic may also be present in citric and tartaric acids, being introduced by the mineral acids used in their manufacture. Thus, in the case of several samples of Spanish tartaric acid examined by Dr. MacFadden, notable quantities of arsenic were present, although the majority of the samples examined were either quite free from the impurity or contained not more than 0.00014 per cent. ( $\frac{1}{100}$  grain per pound) which was the permissible limit fixed by the Arsenic Commission.

There is no reason why both these and other raw materials used by the mineral water maker should not answer to the requirements of this standard, and the manufacturers of citric acid and glucose will usually give guarantees that their products will comply with the test.

There is a possibility that the use of arsenical sulphuric acid

in a generator might give rise to the formation of volatile arsenic compounds which could be carried forward with the gas and thus be dissolved in the mineral-water. This suggests the advisability of using, for this purpose, only oil of vitriol that is practically free from arsenic.

**Pharmacopœia Method.**—A committee of the General Medical Council has recently (June, 1912) issued a Supplementary Report dealing with the most suitable method of testing for arsenic in official drugs and fixing limits for the permissible quantities in these substances.

The apparatus, a diagram of which it is intended to publish in the next edition of the Pharmacopœia, consists of a wide-mouthed bottle of about 120 c.c. capacity, closed by a rubber stopper through which passes a glass tube constricted at one end and having a small opening about 2 mm. in diameter at B (Fig. 113).

Both ends of this tube are open, the top being covered with a strip of mercuric chloride paper, which is kept in position by means of a rubber cap. This test paper is prepared by soaking white filter paper in a saturated solution of mercuric chloride and then drying it. When the paper is

exposed to arseniuretted hydrogen a yellow stain is produced, the intensity of which is proportional to the amount of arsenic, and by comparing the stain with that given by a standard solution of arsenious oxide (1 c.c. = 0.00001 gramme) an estimation of the quantity of arsenic may be made. For this purpose a "standard stain" is freshly prepared under the same conditions as the material under examination. Within the tube, at D, is placed a roll of lead acetate paper. Each of the reagents, including the acid and zinc for the production of the gas is tested for arsenic in the apparatus under specified conditions to ensure that they

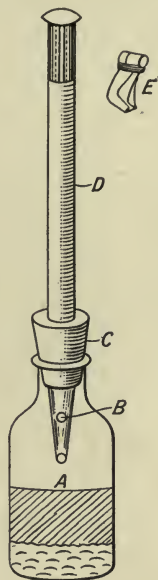


FIG. 113.—Apparatus for Arsenic Tests.

are sufficiently pure for the purpose. Thus, in the case of hydrochloric acid containing stannous chloride the stain produced on the mercuric chloride paper in a period of 30 to 40 minutes must not indicate more than 0.1 part of arsenic per million ; while 10 grammes of zinc should give no visible stain in an hour when tested with the stannated hydrochloric acid.

Special directions are given for the application of the test to the different drugs of the Pharmacopœia, and the maximum permissible quantity of arsenic in each case is also fixed.

As the following substances in the Pharmacopœia are used by the mineral-water manufacturer the limit of arsenic allowed in the Report may be quoted here :—

	Parts per Million.		Parts per Million.
Citric acid .. ..	2	Potassium carbonate ..	2
Glucose .. ..	2	Salicylic acid .. ..	2
Hydrochloric acid ..	5	Sodium bicarbonate ..	2
Lithium carbonate ..	5	Sodium carbonate ..	2
Magnesia .. ..	5	Sodium sulphite .. ..	5
Phosphoric acid ..	5	Sulphuric acid .. ..	5
Potassium bicarbonate ..	5	Tartaric acid .. ..	2

**Tin.**—In a communication by Budden and Hardy to the Society of Public Analysts<sup>1</sup> upon the estimation of minute traces of metals it is stated that the predominating metallic impurity in mineral waters is tin. This statement is at variance with the experience of other chemists<sup>2</sup> who have found that pure tin was not affected by a solution of carbon dioxide and that only a doubtful reaction could be obtained in the experiments with that metal.

The discrepancy is probably due to the fact that an impure tin will dissolve more readily than the pure metal, possibly owing to electrolytic action, and that twenty years ago the same care was not taken as at present to ensure that the carbonating cylinders and other parts of the plant were lined with tin free from impurities. The tin now used by the best makers of mineral-water machinery for this purpose contains

<sup>1</sup> *Analyst*, 1894, XIX., 169.

<sup>2</sup> *Cf. The Lancet*, 1893.



not less than 99·90 per cent. of the pure metal. In the present writer's experience no trace of tin can be detected in soda-water prepared in modern apparatus, although in the case of lemonade a trace of tin may sometimes be found if the syrup pipes have not been washed absolutely clean at the end of the day.

**Bacterioscopic Examination.**—As far back as the middle of the eighteenth century, long before the real nature of putrefaction was discovered, the use of fixed air was advocated by MacBride (see p. 67) as a means of preventing putrefactive changes. And subsequently, after the part played by micro-organisms in fermentation and decay had become known, it was still generally accepted that carbon dioxide was an efficient antiseptic agent, and that the process of carbonating a liquid involved its simultaneous sterilisation.

It came therefore, as a great surprise to scientific men in general as well as those connected with the industry, when in the course of an investigation made some four years ago by the Medical Officer for the City of London, it was discovered that from a bacteriological point of view a considerable proportion of the soda-water then being sold was far from pure.

A very large number of samples representing those of all the leading London manufacturers had been examined by Dr. Klein and while many of these contained only one or two micro-organisms per c.c. and were practically free from *B. coli communis*, in others the number of micro-organisms exceeded 500 to 1,000 per c.c., and the *Bacillus coli communis* could be isolated from one c.c. of the liquid.

The publication of these results was held back for six months, pending the taking of steps by the mineral-water manufacturers to insure the production of a pure product.

A meeting was held at which Dr. Collingridge described the precautions which, in his opinion, were necessary. These included the use of a water the bacteriological purity of which was controlled by periodical tests; preparation of the soda solution in slate tanks with covers of slate or of metal (not wood); the removal of old labels in a separate tank and sub-

sequent cleansing of the bottles in a series of metal tanks, the final rinsing being given by a powerful jet of the same water, as used in the manufacture of the soda-water; and finally a periodical test of the bacteriological purity of the finished product.

These precautions were accepted by the mineral-water manufacturers, and their association now issues a certificate annually to those firms whose products comply with these regulations, and a subsequent examination by Dr. Klein of the soda-water upon the market showed that the changes had effected a great improvement in the quality of the aerated mineral waters sold in London.

While there can be no question as to the public advantage of enforcing precautions to prevent bacterial contamination, and to ensure the utmost cleanliness in the factory, it is doubtful to what extent a bacterioscopic examination of a bottle of soda-water, taken at random, ought to be regarded as a fair test of the degree of purity attained by a particular manufacturer.

Experiments made by the writer have shown that, although for a time the number of bacteria increases in a bottle of soda-water, the contents do, eventually, after the lapse of some months, become sterile; and the factor of the time that has elapsed after bottling ought, therefore, to be taken into account. Otherwise it might very easily happen that an originally impure soda-water, which had been in the shop for a year, would give a much better result than one bottled under the most sanitary conditions.

Apart from that, in the examination of a sample bought at random there is always the chance that the stopper may have been accidentally contaminated by the hand of the worker, and several bottles known to have been bottled fairly recently ought, therefore, to be examined before drawing a conclusion adverse to the methods used in a particular factory.

The use of distilled water in the preparation of mineral waters has the advantage of obviating the deposit of any of the salts contained in hard waters, but it by no means follows

that soda-water prepared from it is any purer bacteriologically than that prepared from ordinary hard waters.

The water after distillation is of necessity more or less exposed to the air and soon ceases to be sterile. Moreover, unless distilled water is also used for washing and rinsing the bottles, the chances of bacterial infection are very strong.

In fact, bacterioscopic examinations of soda-water made from distilled water, have, in some cases, given worse results than those obtained with soda-water made from ordinary tap water.

In the case of mineral waters prepared from the London water supply, which is constantly examined by the Metropolitan Water Board, it seems hardly reasonable to demand, in the finished soda-water, a greater degree of purity than that of the original water, over the management of which the manufacturer has no control.

This, of course, does not apply to those whose mineral waters are made from private artesian wells as is frequently the case in the London area. The purity of such waters ought obviously to be placed beyond doubt, both by chemical and bacteriological examination.

As to the standard of bacteriological purity it is not easy for the reasons to be given to fix any definite limit as to the permissible number of bacteria in 1 c.c. of the liquid. However, as the writer has suggested elsewhere,<sup>1</sup> a soda-water examined after bottling ought certainly not to show more than 100 micro-organisms per c.c. at 20° C.

In any case, a system of inspection of the factories, carried out at irregular intervals, would be a much more efficient safeguard of purity than even a frequent examination of samples bought at random.

**Mucinous Fermentation.**—It not infrequently happens that a bottle of lemonade becomes gum-like and viscous—sometimes to such an extent that it can hardly be poured out.

This so-called “ropiness” is due to the action of certain bacteria upon the sugar, which they convert into a mucinous mass, to which the name of *viscose* has been applied.

<sup>1</sup> Article on Aerated Waters in Thorpe's “Dictionary of Applied Chemistry” 1911.



Several species of bacteria possess this power of acting upon sugar, and one of these, *Bacillus viscosus sacchari*, will transform beet-sugar into a viscid mass in about 48 hours.

Another species, *B. gelatinosum betæ*, discovered in beet juice, that had become gelatinous, differed from the preceding one in its conditions of culture and in the fact of its being motile.

A micro-organism that is particularly troublesome in cane-sugar factories is known as *Leuconostoc mesenteroides*.

Under favourable conditions this bacterium inverts the sugar, while it meanwhile becomes converted itself into a gelatinous mass or zooglœal condition. It has the power of resisting a high temperature, which accounts for its development in the hot sugar juice in the factories.

Some of these organisms act upon sugar much more readily when air is excluded, and this probably explains their rapid growth in sweetened aerated drinks from which all air has been expelled by the carbonic acid gas.

The main source of this trouble in the mineral-water factory is beetroot sugar, in which, as is explained above, these bacteria occur normally. Owing to the formation of their protective mucinous covering they are able to resist both heat and long-continued drying. For instance, in one experiment, a certain species was found to be alive after being heated for five minutes by dry heat at 212° F., and then exposed for three and a half years to the air.

The spores are still more resistant to heat, and probably remain in the sugar ready to develop under suitable conditions. Hence the greater the degree of purification to which beet-sugar has been subjected the less liable it will be to become "ropy" from this cause; and this is why it is often economical, without taking into consideration the sweetening power, to use only thoroughly purified sugar in the preparation of the syrups for lemonade, ginger ale and the like, and to see that the syrups have been thoroughly sterilised before filtration.

When only an occasional bottle of lemonade becomes viscous the contamination may be regarded as accidental and probably due to insufficient cleansing of the bottle, but when, as has been



known to happen, a whole batch of goods becomes ropy, the cause must be sought in the sugar, or in wholesale infection of the syrup filters or pans.

**Acetic Fermentation.**—Ordinary bottled mineral waters are not liable to be affected by acetic bacteria, since these require a supply of oxygen for their development and specific fermentation. In the case of ginger beer, however, conditions favourable to the growth of these bacteria frequently are present, and it is not rare for souring in cask beer to take place owing to conversion of part of the alcohol into acetic acid.

The micro-organisms that cause this curious fermentation are bacilli, several species of which have been described. One of these, which normally forms long chain-like forms, is shown in Fig. 114.

If only a small quantity of air is supplied, as may happen in a ginger beer bottle with a defective cork, the bacteria transform themselves into a compact tripe-like mass, scientifically described as the zooglœal condition, but more popularly known as *mother-of-vinegar*.

In this form they are able to survive much longer in the absence of a sufficient supply of oxygen. Acetic bacteria thrive best at a high temperature, and in vinegar factories work well at temperatures about 100° F. For this reason ginger beer is more liable to turn sour in the course of a hot summer than in the autumn or winter, and storing the casks or bottles in a cool place will reduce the chance of the beer deteriorating in this way, even when air can gain access to it.

So long as the ginger beer is being quietly fermented by the yeast there is little risk of its turning sour, for the alcoholic fermentation prevents the action of the acetifying bacteria.

The chemical action effected by the latter appears to be a complex one, although its main results may be expressed by the formula—

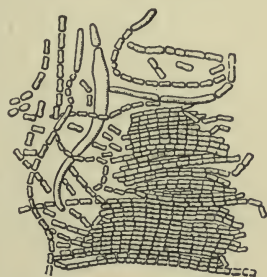
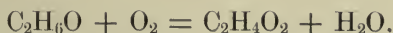


FIG. 114 —Acetic Bacteria (Hansen).

That is to say the alcóhol is eventually transformed into acetic acid, though aldehyde and other compounds are formed as intermediate products.

Apparently the acetic bacteria act merely as conveyers of the oxygen from the air to the alcohol, and do not seem to be changed in the oxidation process, which will continue so long as air and alcohol are present.

In the course of the oxidation heat is spontaneously produced, and under the most favourable conditions for acetification the temperature will rise to above  $110^{\circ}$  F., as was mentioned above.

It is interesting to note that this is a striking example of gradual acclimatisation of a living organism to its surroundings ; for according to the text-books of Continental authorities, the bacteria die at a lower temperature than this.

Since the germs of the bacteria are present in the air it is essential that the bungs should not be left out of casks of ginger beer during use, for under these conditions even the best products are liable to become sour.

**Preservatives in Mineral Waters.**—The question of the permissibility of using preservative agents is not so urgent as in the case of other non-alcoholic drinks, such as lime-juice cordial, since, with a few exceptions, they are not necessary.

Soda-water, for instance, if prepared from pure materials and properly carbonated in clean bottles ought to keep indefinitely, while the occurrence of fermentation in sweetened goods, such as lemonade and ginger ale, is quite exceptional, and is generally caused by the use of an impure or insufficiently sterilised sugar.

In one class of goods, however, the so called winter syrups, the use of some preservative agent appears to be unavoidable, since they contain a very large amount of sugar and fruit juice and are only used gradually after the bottle is opened.

They could, of course, be sterilised in the bottle by heat, but this would only be effective while the bottle was closed, and when once its contents had been exposed to the air they would be liable to rapid fermentation ; and the customer would refuse

to have any further supplies of the kind. Apart from this, there is the objection that fruit syrups thus sterilised lose much of their freshness of flavour, and are not equal to those in which the preservation is ensured by the addition of a chemical agent.

A further difficulty that the manufacturer has to meet is that in the event of accidental fermentation of any of his products he is liable to prosecution by the Excise authorities for selling spirits without a license, whereas if he add an antiseptic agent proceedings may be taken against him under the Food and Drugs Act.

The chaotic state of the law upon the subject is shown by the fact that every county and borough authority forms its own opinion upon the question. In some districts the use of salicylic acid in non-alcoholic drinks is tacitly permitted, while in others prosecutions frequently take place.

Nor is there any agreement upon the point among public analysts, who have frequently discussed the subject but without coming to any definite decision upon the point.

The medical officers of health also hold different views on the preservative question, and not long ago there was witnessed the curious spectacle of the medical authority of a borough giving evidence in a prosecution that the use of salicylic acid as a preservative in non-alcoholic drinks was objectionable, while the medical officer of an adjoining county was called as a witness as to its being harmless. The case was dismissed, but as the law stands there is no finality in such matters, and the same manufacturers might have been summoned again for the same offence in the same court.

A case strongly defended as this one was, is generally dismissed, but it is absurd that a matter of so much importance both to the public and the manufacturer, should be left to the caprice of individual magistrates who have not the necessary knowledge to decide a question upon which there is a profound difference of opinion among leading medical men.

The only fair method of settling this dispute between those who have to supply an article that will keep and those who say it must not be done in the only way in which practically it can be done, is to have a Board of reference upon which are repre-



sentatives both of the public health authorities and of the manufacturers, and for this Board to decide whether preservatives shall be used, and if so, to what extent.

Any regulations made by such a Board would need to be very rigidly enforced, and not administered in the present haphazard fashion. Otherwise a manufacturer who tried to comply with the law would be unable to compete with a more unscrupulous rival who risked an occasional prosecution, secure in the knowledge that he could pay any fine out of the profits of his goods that escaped detection.

Readers interested in the general aspects of this subject may be referred to the Report of the Royal Commission of 1901 upon Preservatives and Colouring Matters in foods. The recommendations of that body, which are largely based upon the very conflicting views of the medical witnesses, are sometimes quoted in prosecutions, but, with few exceptions, they have never been given legal force and the condition of affairs is very little different from what it was before it began its lengthy enquiry.

With regard to the preservatives actually used in mineral waters the only ones of common occurrence are salicylic acid and sulphites, the former being used in the sweetened goods, especially during periods of very hot weather. Sulphites or bisulphites are extensively employed in breweries in cleansing the plant, and are sometimes used for the same purpose in mineral-water factories. In this way small quantities of the preservative may find their way into mineral waters, apart from their being intentionally added, but as the sulphurous acid is soon oxidised to sulphate, the presence of such traces is of no practical importance.

**Artificial Colouring Matters in Mineral Waters.**—The presence of artificial colouring matters in the products of the mineral-water manufacturer is not of such importance as the presence of preservatives. In the majority of the articles made, the aim is to exclude colour as far as possible; and even in the case of lemonade, objection is taken to a slight yellow tint, and a perfectly colourless liquid must be bottled.



In the darker goods, such as kola and ginger ale, an addition of a specially prepared caramel is often made while in other cases an aniline dyestuff is employed. Caramel has the advantage of being above reproach from the hygienic point of view, but is open to the objection that unless special means are taken in its preparation, it is liable to deposit in the bottles under the influence of the carbonic acid gas.

Since it is not always easy to obtain a supply of caramel of a uniform character in this respect, an aniline dyestuff is much more frequently used for colouring ginger ale and the like.

Suitable colouring matters sometimes of vegetable origin are also used for colouring concentrated fruit syrups, since the natural colour of the fruit itself is regarded by the public as too pale for the purpose.

So much attention has been drawn to this subject, that really poisonous dyes such as Martius Yellow are now rarely used for the purpose of colouring food. In any case the proportion used in any aerated water is extremely small, and the following conclusion of the Departmental Committee on Preservatives and Colouring Matters in Foods applies also to mineral waters :—" In regard to the colouring matters of modern origin, while we are of opinion that articles of food are very much preferable in their natural colours, we are unable to deduce from the evidence received that any injurious results have been traced to their consumption.

Undoubtedly some of the substances used to colour confectionery and sweetmeats are highly poisonous in themselves ; but they are used in infinitesimal proportions, and before any individual had taken enough of colouring matter to injure him his digestion would probably have been seriously disturbed by the substance which they were employed to adorn."

It is an easy matter to distinguish between caramel and aniline dyestuffs in the examination of mineral waters, advantage being taken of the dyeing properties of the latter in tests with silk or woollen fibre.

**Use of Mineral Acids.**—The acidity of the lemon being due

to citric acid it is preferable to use this acid in the preparation of the syrups for lemonade.

In practice, however, tartaric acid made from wine lees, is also commonly used, and there is very little difference in flavour between the lemonades prepared with either acid, although, when compared side by side, tartaric acid is slightly rougher to the taste.

In addition to these fruit acids, preparations of mineral acids, usually phosphoric acid, are sold as substitutes for obtaining the desired acidity. These phosphoric acid syrups are advertised under attractive titles and give a much greater degree of acidity than the citric acid bought for the same sum.

The flavour of the lemonade prepared with them is somewhat similar to that containing citric or tartaric acid, but there is a harshness in the phosphoric acid preparations that is lacking in those made from fruit acids. Phosphoric acid is as liable as tartaric acid to contain traces of lead and arsenic, and some of the preparations have also been found to contain a notable proportion of free sulphuric acid.

An advantage claimed for its use is that it acts as a preservative and checks fermentation. This is probably true, but the drawbacks cited more than outweigh this.

**Alkalinity of Soda-Water.**—A point of considerable importance in the examination of soda-water is the estimation of the amount of sodium bicarbonate in solution.

Prior to the publication of the current "British Pharmacopœia" in 1898, soda-water was an official drug, and had to contain exactly 30 grains of sodium bicarbonate per pint. As this proportion of the salt was often too large to suit the public taste, soda-water containing much less sodium carbonate than the prescribed quantity was widely sold, with the result of prosecutions under the Food and Drugs Act for the sale of an article "not of the substance and quality demanded."

In the eyes of the general public, however, it was usually good aeration that was required, not a certain proportion of sodium bicarbonate, and thus even plain aerated water had come to be

known as "soda-water." It was not a question of economy on the part of the manufacturer, since the cost of the amount of sodium bicarbonate officially prescribed was infinitesimal, but of supplying an article for which there was a better sale.

The position of affairs was thus very similar to the development in France, where *Eau de Seltz*, which had originally been introduced as a medicinal preparation in imitation of the natural *Selterswasser*, had gradually become a popular drink.

The mineral salts were then gradually reduced, until finally the name *Eau de Seltz* has come to connote nothing more than ordinary carbonated water.

The suggestion was frequently made in this country that a distinction should be made between plain "aerated-water" and "soda water," but changes in trade names of this kind are not easily made, except under compulsion applied to all the manufacturers.

The omission of soda-water from the current "British Pharmacopœia" has put the matter upon a different basis. Now that the preparation is no longer regarded as a drug, there is no official standard for the amount of sodium bicarbonate it shall contain, and the usual practice of the manufacturer at the present time is to introduce as much of the salt as he can without rendering the soda-water too unpalatable and stopping his trade.

Since the name "soda-water" is still retained, a substantial proportion of sodium bicarbonate ought to be present, and in the majority of the varieties now upon the market this is the case.

In some of these the amount of bicarbonate ranges from about 5 to 10 grains per pint, and it is only exceptionally that the bottle contains only ordinary water aerated.

The composition of potash- and lithia-water stands upon a different footing from that of soda-water. They have never, as in the case of soda-water, become popular drinks, but have been taken only medicinally. Hence, anyone buying lithia-water, for example, does so in the anticipation of getting a definite dose of lithium carbonate in a form that is pleasant to take.

In the "British Pharmacopœia" of 1885, both potash-water and lithia-water were recognised as official drugs, and it was prescribed that the former should contain 30 grains of potassium bicarbonate and the latter 10 grains of lithium carbonate per pint, and be bottled under a pressure of about 4 atmospheres.

Although both potash- and lithia-waters have shared the fate of soda-water and are no longer recognised officially as drugs by the "Pharmacopœia," the proportions of the carbonates formerly prescribed are still generally taken in preparing these mineral waters.

**Saccharin in Mineral Waters.**—The substitution of a large proportion of the sugar in sweetened mineral waters is a very general practice in the industry. It offers the advantages of cheapness and, when added in not too large an excess, of giving a drink that is sweet without being heavy. On the other hand, if saccharin is used by itself, or if too little sugar is employed, the product will have a cloying effect upon the palate. Another point claimed for saccharin by its manufacturers is that it possesses antiseptic properties, and thus acts as a preservative and tends to check fermentation.

The corporation that controls the sale of saccharin in this country issued a pamphlet setting forth its advantages for the mineral water manufacturer and citing the opinions of well-known medical men as to its harmless nature. On the other hand, there have been communications to foreign scientific papers in support of the view that saccharin may be injurious. No exception, however, has ever been taken to its use in mineral waters in this country, and considering the fact that it is now so widely used, any isolated action, unsupported by the Local Government Board, would probably fail.

**Saponine.**—The popular demand for sweetened aerated drinks, that will froth when poured from the bottle and retain a certain degree of foaminess in the glass, has led to the introduction of a class of preparations known as "foam headings" and so on. A small quantity of one of these added to the syrup produces the desired result in the aerated liquid.



The addition is not made to soda-water, while ginger beer, if allowed to mature for a short time, produces its own " heading " by the action of the yeast during the fermentation. It is in such products as lemonade, lime-ade, kola and ginger ale, that artificial frothing may be anticipated.

The basis of most, if not all, of these " foam " preparations is quillaia bark, which contains an active principle, saponine, that has the property of frothing like soap with water.

Researches made a few years ago by Bourcet and Chevalier<sup>1</sup> showed that ordinary commercial saponine usually consisted of a mixture of acid saponines with a poisonous neutral saponine. The latter is very toxic when injected into the system, but is less poisonous when taken internally. In the latter case it is liable to produce inflammation of the mucous membrane. It must be borne in mind, however, that the experiments were made with the pure substance, and not with the commercial mixture containing the toxine, and that no cases of poisoning by mineral waters containing saponine have been reported over a period of many years.

At the same time the addition is not really a necessity, and, as was pointed out above, has grown as the result of a demand for a product possessing artificial properties.

<sup>1</sup> *Bull. Sci. Pharm.*, 1905, VII., p. 262.



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