JOSEPH BLACK AND THE IDENTIFICATION OF CARBON DIOXIDE

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THE GREAT Scottish chemist, Joseph Black, identified and studied the chemical properties of carbon dioxide gas. He also observed its toxic properties and employed caustic alkali to absorb it. The classic researches of Joseph Black, published in 1756, form the basis of present day chemical control of carbon dioxide in atmospheres breathed in closed spaces. Before describing these experiments, famous in the annals of science, which influenced the development of pneumatic chemistry and respiratory physiology, it is appropriate to make a brief summary of the life and work of their author.

BRIEF BIOGRAPHY OF JOSEPH BLACK

Joseph Black, born in Bordeaux, France, on April 16, 1728, was the son of a wine merchant from Belfast and the former Margaret Gordon of Aberdeen from whom he received his early education including English. At age 12, he was sent to school in Belfast where he acquired Latin and Greek. On November 14, 1746, he matriculated at the University of Glasgow where he studied languages, philosophy, chemistry, and medicine. About 1751 he transferred to the University of Edinburgh to complete his medical studies. In June, 1754, in fulfillment of the regulations for the degree of Doctor of Medicine, he published his Latin dissertation, "De Humore Acido a Cibis orto, et Magnesia Alba" (1). The first part of this thesis is concerned with acidity of the stomach and the value of *magnesia alba* as an antacid. The second part consists mainly of a detailed account of experiments Black carried out, prior to June 1754, in his examination of *magnesia alba*. No mention of carbon dioxide or fixed air, as Black called the gas, is made in this Latin thesis. An expanded English version of the second part of the thesis was read in June, 1755, to the Philosophical Society of Edinburgh and published in 1756 as "Experiments upon Magnesia Alba, Quicklime, and some other Alcaline Substances" (2). This same year he was called to the University of Glasgow to become professor of anatomy and lecturer in chemistry. Here he performed his fundamental researches on the nature of specific and latent heat, which were of great service to his friend, James Watt, then at Glasgow. During his ten years at Glasgow, in addition to his teaching at the University, he carried on an active medical practice. In 1766, he returned to Edinburgh to become professor of chemistry. His chemistry lectures were well attended and in later years there were as many as 250 students (3). Pupils came not only from the British Isles but from France, Germany, Sweden, Russia, and the United States. His influence was

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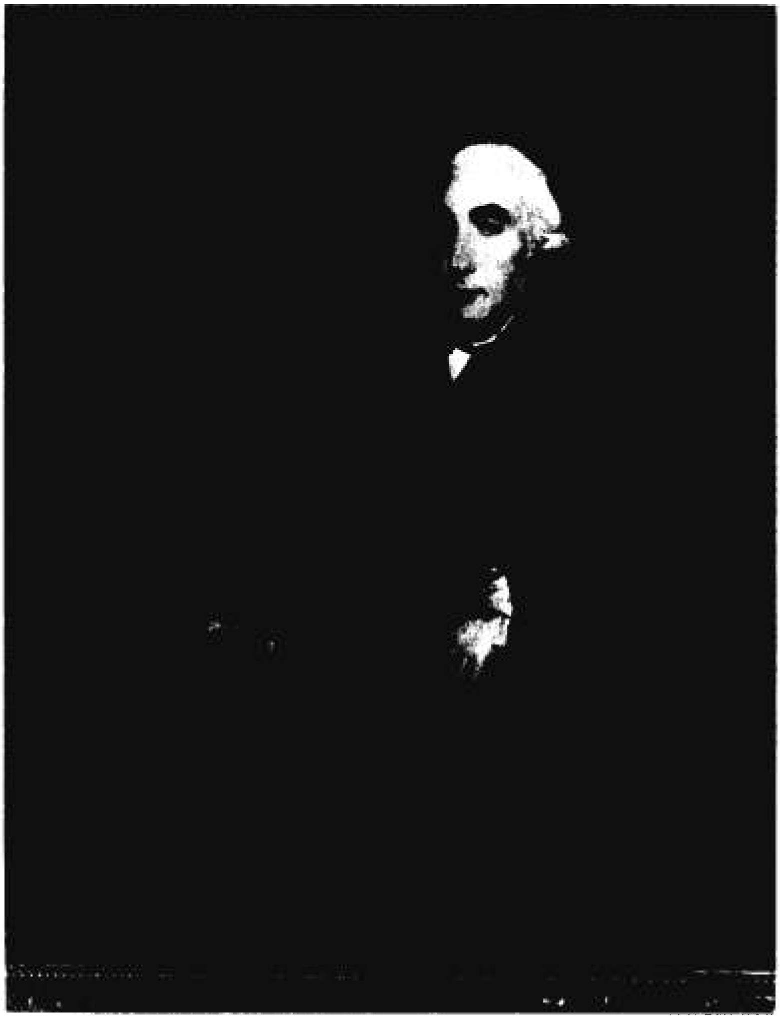

FIG. 1. Joseph Black. The original painting by Raeburn is in the possession of Lord Bruntisfield, London.

further extended by the appointment of many of his students to influential positions in the academic and industrial world. Several of the early American Chemistry Chairs were held by former pupils of Black. Thomas Beddoes, a pupil of Black's, set up the Pneumatic Institute for Inhalation Therapy at Bristol to which Black was a financial subscriber (4).

Black's article, "Experiments on Magnesia Alba, Quicklime, and some other Alcaline Substances," was translated in French and published in *Observations sur la Physique* in 1773 (5), probably under Lavoisier's auspices. It was later summarized in his first important book, *Opuscules Physiques et Chimiques* (1774). Lavoisier was influenced by Black's quantitative methods of research as well as by his results and has expressed his debt to Black in his writings and in correspondence with him (6–10). Black's work on carbon dioxide was known to MacBride, Cavendish, Scheele, and Priestley (11–14). In addition to teaching chemistry at Edinburgh, Black carried on his medical practice and acted as a consultant to the developing Scottish chemical industry. His friends in Edinburgh included David Hume, Alexander Carlisle, James Hutton, and Adam Smith. Here he passed thirty years in teaching chemistry and in medical practice until his death in 1799 (10, 15–24).

Early Preparation of Carbon Dioxide

It is known that Black began his first studies on carbon dioxide, or "fixed air," while a medical student at Edinburgh. On January 3, 1754, five months before the publication of his inaugural dissertation he wrote a letter to William Cullen, his first teacher of chemistry at Glasgow (25).

"I fully intended to have wrote last post, but really I happened to be intent upon something else at the proper time, and forgot it. It was, indeed, an experiment I was trying that amused me, in which I had mixed some chalk and vitriolic acid at the bottom of a large cylindrical glass; the strong effervescence produced an air or vapour, which, flowing out at the top of the glass, extinguished a candle that stood close to it; and a piece of burning paper, immersed in it, was put out as effectually as if it had been dipped in water; yet the smell of it was not disagreeable."

Guerlac has recently pointed out that this is the earliest mention of Black's experimental work which resulted in the identification of carbon dioxide as a particular gas (26).

Fixed Air, Caustification Process and Limewater Test

Joseph Black states in his "Experiments on Magnesia Alba, Quicklime and some other Alcaline Substances" (1756) that he began his researches on magnesia in the hope of discovering a new sort of lime and limewater which might be a more powerful solvent of the urinary stone than that commonly used (p. 7).* Although he was disappointed in this expectation, his remarkable researches on magnesium and calcium and other alkaline compounds, besides setting forth the reactions and properties of these compounds, resulted in the identification of fixed air, that is, carbon dioxide as a gas with specific properties which differed from common air. It is all the more remarkable in that at that time common air was considered an element, and as might be expected, the identification of one particular gas led to a succession of discoveries of other gases in the latter third of the eighteenth century.

Joseph Black was familiar with the work of Stephen Hales on airs and in the first part of his paper which concerns magnesia alba states "for Dr. Hales has clearly proved, that alkaline salts contain a large quantity of fixed air, which they emit in great abundance when joined to a pure acid" (p. 17).* Up to the time of Black, however, the term fixed air was used in a generic sense, that is, air which became fixed in

* All page numbers refer to Black's work, "Experiments on *Magnesia Alba*, Quicklime, and some other Alcaline Substances" (1756) as reprinted in the Alembic Club Reprint, No. 1, Edinburgh, 1910.

a substance but did not have identifiable or specific properties of its own.

His experiments on magnesia suggested to him an explanation of the nature and properties of lime itself (p. 22),* and he devotes the second part of his paper to his suppositions and his experiments on lime. In the course of these experiments, he recognized that the so-called "calcareous earths" in their native state contain a large quantity of fixed air, that "the relations between fixed air and alkaline substances was somewhat similar to the relation between these and acids" (p. 22); * that "when we mix an acid with an alkali or with an absorbent earth, that the air is then set at liberty and breaks out with violence; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time" (p. 22).* When limewater was exposed to the open air, he states that,

"the particles of quick-lime which are nearest the surface gradually attract the particles of fixed air which float in the atmosphere. But at the same time that a particle of lime is thus saturated with air, it is also restored to its native state of mildness and insolubility . . . (p. 24).*

As a corollary to this observation, he reasoned that since slaked lime "is an uniform compound of lime and water: it followed, that, as part of it can be dissolved in water, the whole of it is also capable of being dissolved" (p. 26).* To test this proposition he prepared limewater and after removing a small amount of sediment, found that "the water tasted strongly of the lime, had all the qualities of limewater and yielded twelve grams of precipitate upon the addition of salt of tartar [K_2CO_3]." He had expected a much larger quantity of sediment because of the air which water constantly contains. To determine if limewater contains air he subjected equal quantities of limewater and common water to an air pump and obtained equal amounts of air from each. In conclusion he stated,

"from whence it is evident, that the air which quick-lime attracts, is of a different kind from that which is mixed with the water. . . . Quick-lime therefore does not attract air when in its most ordinary form, but is capable of being joined in one particular species only, which is dispersed thro' the atmosphere, either in the shape of an exceedingly subtile powder or more properly in that of an elastic fluid. To this I have given the name of fixed air, and perhaps very improperly; but I thought it better to use a word already familiar in philosophy, than to invent a new name, before we be more fully acquainted with the nature and properties of this substance. . . ."

As part of his researches on lime, he also explained the caustification process. The caustification process as a chemical reaction is stated as follows:

$$Ca(OH)_2 + K_2CO_3 \longrightarrow 2KOH + CaCO_3\downarrow$$

Slaked lime + mild alkali ⟶ caustic alkali + lime

Or:

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3\downarrow$$

Slaked lime + mild alkali ⟶ caustic alkali + lime

In order to obtain the caustic alkali, he mixed slaked lime ($Ca(OH)_2$) with a fixed alkaline salt solution (K_2CO_3), allowing the precipitate ($CaCO_3$) to settle and pouring off as much of the clear solution (KOH) as possible. Then he made various tests to show that the clear solution had the chemical properties of caustic alkali and was free from the lime which had been originally used (pp. 31–32).* When he made tests on the precipitated sediment, he found that "It was similar in every trial to a fine powder of ordinary chalk, ($CaCO_3$) and was therefore saturated with air which must have been furnished by the alkali" (pp. 28–29).* In summarizing his explanation of the caustification process, he says,

"If quick-lime be mixed with a dissolved alkali, it likeways shews an attraction for fixed air superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself, while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony . . ." (p. 25).

In his examination of caustic alkali solution he found that it "gave only a faint milky hue to lime water; because the caustic alkali wants [lacks] that air by which salt of tartar [K_2CO_3] precipitates the lime" (p. 32).* This is the present limewater test for the presence of carbon dioxide.

In this paper of Black's, in summary, are found three main propositions relative to fixed air: (1) Fixed air, that is, carbon dioxide, is different from common air and of one particular species with certain properties. (2) Caustic properties resulting from the caustification process depend upon the transfer of fixed air (CO_2) from alkali carbonate to slaked lime ($Ca(OH)_2$). (3) Limewater may be used to determine the presence of fixed air in a solution.

Toxicity of Carbon Dioxide

Notes taken in Black's lectures were available to subsequent students and could be bought just as text books are obtainable today. Such notes are important from an historical standpoint in presenting the status of scientific thought at a particular time. According to notes made of his lectures of 1767–68, Black said (27),

". . . the air which is contained or attracted by quick-lime, is not the same with common air. This air is of that kind which is remarkable for being poisonous and extinguishing flames. The common air which we breathe is incapable of serving the same purpose for a considerable time, something either being taken from it or something added to it. So if we put an animal under a small glass, the [animal] at first hearty will soon grow convulsive and die: or if we suddenly take it out before it is dead, will soon recover, which shews no fault in the animal. Therefore it [the air] has undergone a change and is no longer fit for the animal. If we put a glass bell over a candle, the air immediately has such an effect as to extinguish the candle and in both of these two cases the air has received the same change. The elastic matter that arises from vegetables during fermentation as in wort, wine, etc. is very pernicious and has struck a man senseless. If we dip a small animal into the vessel, it is killed in a moment. This air therefore seems to be like the former and this sort of air is attracted by the alkaline substances; and in proof of this (I) shew some experiments.

"I. If that air be the same which is attracted by alkaline substances that kills an animal? In a glass tube of this form [U-shaped] put in a small quantity of lime-water. If we draw the external air in [at one end], the water will be quite pure, but if we expel the air or blow out at [the other end], the water will immediately turn turbid and be rendered to its mild state."

Other experiments in this series of lectures were concerned with testing the fumes of burning charcoal with limewater, comparing the weight of fixed air with that of common air, observing its effect on lighted candles and animals, and transferring the fixed air to caustic alkali after adding strong acid to chalk. These procedures required manipulation of the gas in an apparatus.

Further Chemical and Physiological Properties

Daniel Rutherford, the discoverer of nitrogen gas and an uncle of Sir Walter Scott, was a student of Joseph Black. He summarized Black's work on carbon dioxide up to the year 1772 in his inaugural dissertation entitled, "Aere Fixo Dicto, aut Mephitico" (28, 29, 30).

"By mephitic air, which some call fixed air, I understand with the distinguished Professor Black, that singular species of air which is fatal to animals which extinguishes fire and flame, and which is attracted with great avidity by quick-lime and alkaline salts. . . .

"Further, it arises from the lungs of animals, for air, however wholesome to begin with, becomes to some extent mephitic by repeated respiration (Dr. Black's lectures).

"But the chief difference between pure air, or any other species of air, and this mephitic air is to be found in that conspicuous sympathy and attraction with which it unites with lime, with alkaline salts, and with any other bodies of the same nature. It is caught in their embrace and joined in so stable a union that it, so to say, becomes solid with them, yet not without a great change in their nature."

Applying his chemical knowledge of the union of carbon dioxide with caustic alkali, he placed a small animal in a confined amount of air until it died. The carbon dioxide produced was removed by absorption with caustic alkali. The noxious gas (nitrogen) which remained would support neither life nor flame.

After Black's death his manuscripts and notes were compiled and published by Professor John Robison (31). The following remarks on carbon dioxide taken from these lectures of Joseph Black are of interest (32).

"In the same year, however, in which my first account of these experiments was published, namely 1757,† I had discovered that this particular kind of air, attracted by alkaline substances, is deadly to all animals that breathe it by the mouth and nostrils together; but that if the nostrils were kept shut, I was led to think that it might be breathed with safety. I found, for example, that when sparrows died in it in ten or eleven seconds, they would live in it for three or four minutes when the nostrils were shut by melted suet. And I convinced myself, that the change produced on wholesome air by breathing it, consisted chiefly, if not solely, in the conversion of part of it into fixed air. For I found, that by blowing through a pipe into lime-water, or a solution of caustic alkali, the lime was precipitated, and the alkali was rendered mild. I was partly led to these experiments by some observations of Dr. Hales', in which he says that breathing through diaphragms of cloth dipped in alkaline solution, made the air last longer for the purposes of life.

"In the same year I found that fixed air is the chief part of the elastic matter which is formed in liquids in the vinous fermentation. Van Helmont had indeed said this, and it was to this that he first gave the name *gas silvestre*. It could not long be unknown to those occupied in brewing or making wines. But it was at random that he said it was the same with that of the Gratto del Cane in Italy, (but he supposed the identity, because both are deadly); for he had examined neither of them chemically, nor did he know that it was the air disengaged in the effervescence of alkaline substances with acids. I convinced myself of the fact by going to a brew-house with two phials, one filled with distilled water, and the other with lime-water. I emptied the first into a vat of wort fermenting briskly, holding the mouth of the phial close

† An error for 1756.

to the surface of the wort. I then poured some of this lime-water into it, shut it with my finger, and shook it. The lime-water became turbid immediately. Van Helmont says, that the dunste, or deadly vapor of burning charcoal, is the same gas silvestre; but this was also a random conjecture. He does not even say that it extinguishes flame, yet this was known to the chemists of his day. I had now the certain means of deciding the question, since, if the same, it must be fixed air. I made several indistinct experiments as soon as the conjecture occurred to my thoughts; but they were with little contrivance or accuracy. In the evening of the same day that I discoverd that it was fixed air that escaped from fermenting liquors, I made an experiment which satisfied me. Unfixing the nozzle of a pair of chamber-bellows, I put a bit of charcoal, just red hot, into the wide end of it, and then quickly putting it into its place again, I plunged the pipe to the bottom of the phial, and forced the air very slowly through the charcoal, so as to maintain its combustion but not produce a heat too suddenly for the phial to bear. When I judged that the air of the phial was completely vitiated, I poured lime-water into it, and had the pleasure of seeing it become milky in a moment.''

Thus in the year 1756, Black had established by a chemical test that the air produced in respiration, vinous fermentation, and the burning of charcoal was identical with the fixed air liberated from chalk by acids or heat. Fixed air was also a part of the atmosphere. He had described the toxic properties of fixed air and knew that it was absorbed by caustic alkali and slaked lime. In his investigations of the production of fixed air in respiration, he performed the following experiment (33):

''In the winter of 1764–5, Dr. Black rendered a considerable quantity of caustic fossil alkali [NaOH] mild and crystalline, by causing it to filtre slowly by rags in an apparatus which was placed above one of the spiracles in the ceiling of a church, in which a congregation of more than 1500 persons had continued near ten hours.''

Black lived in Glasgow in the winter of 1764–65. At this period the College residents worshipped in the Blackfriars Kirk, which may have been the scene of the experiment.‡ Further details of this magnificent large scale experiment on the absorption of carbon dioxide by means of caustic alkali, are so far lacking.

Summary

Joseph Black identified carbon dioxide as a specific gas with certain properties which differed from common air. He ascertained its effects on animals, its production by respiration and fermentation and by the burning of charcoal and inferred its presence in small amounts in the atmosphere in 1756. Fixed air or carbon dioxide behaved as an acid and was absorbed by slaked lime and the caustic alkalis to form carbonates. During his research on lime using quantitative methods he showed that the caustification process was due to the transfer of carbon dioxide from alkali carbonates to calcium hydroxide resulting in the formation of alkali hydroxide and calcium carbonate. He used the present limewater test to determine the presence of carbon dioxide and as part of his experiments precipitated limewater by breathing through it. The researches of Joseph Black form the basis of our present day methods for the absorption of carbon dioxide in anesthesia practice, metabolism testing, mine rescue work, and underwater and high altitude operations.

‡ Personal communication to author from A. Kent, Glasgow, June 11, 1955.

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