

height (4.5" - 8"); and one test glass in cylindrical form, (2.5" x 10"). A molecular model kit in a wooden box, with elemental balls of varying size and color and flexible metal connecting bonds, dates from about the period of World War I. Of particular interest is a box of "graphic symbols", consisting of wooden blocks with varying numbers of holes drilled in their edges. Metal clips on the faces of the blocks allow one to attach cardboard labels bearing the symbols of various elements. The blocks can then be connected together with short sections of dowel in order to illustrate the concept of valency (oxidation number). Regrettably both kits are missing the manufacturer's name and patent dates.

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WHATEVER HAPPENED TO THE GROTTA DEL CANE ?

In a recent study Furio Mas *et. al.* found that more than 50% of all 18 year old students think that gases naturally "rise" and that they lack weight or mass, opinions which the authors characterize as "Aristotelian" and as strikingly similar to those held by some chemists prior to the chemical revolution (1). Given this "common sense" view of the behavior of gases, the impact of classic lecture demonstrations in which carbon dioxide is poured "down hill" is understandable, as well as the desirability of continuing to do them in the modern classroom. However, older textbooks not only demonstrated these facts in the classroom and the laboratory, but provided practical everyday examples as well, usually involving the accumulation of carbon dioxide in poorly ventilated mines and caves and its subsequent suffocating action on unsuspecting animals and men.

Perhaps the favorite example of this was the famous *Grotta del Cane*, located at Pozzuoli, near Naples, Italy. Though mentioned in traveler's accounts of the Naples area for centuries, the cave did not find its way into the chemical literature until the end of the 18th century, when carbon dioxide (or fixed air, as it was then called) was finally recognized as a distinct chemical species, largely through the work of Cavendish, Black and Priestley (2). One of the earliest chemical writers to mention the cave was Tiberius Cavallo, who described it in some detail in the 1781 edition of his *Treatise on the Nature and Properties of Air* (3):

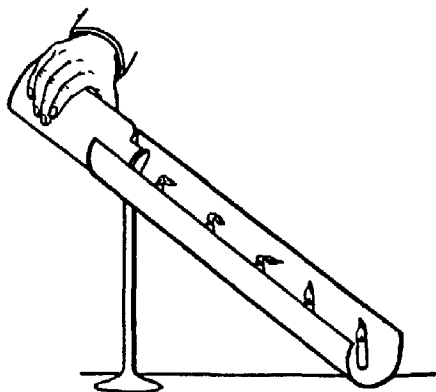
In the kingdom of Naples, and not more than six or seven miles from the capital of that kingdom, is a famous cave, near the foot of a hill, called in the Italian Language *grotta del cane*. This grotto is about fourteen feet long, and near seven feet high at the entrance. On the floor of it, there is always a stratum of that elastic fluid, which constitutes the choke damp. It is continually emitted from the earth, through fissures that may be seen on the ground. The experiments usually shown to the curious, who visit this grotto, are, first, that of bringing a lighted candle or piece of paper near the floor, which is put out as soon as it comes within about 14 inches of the ground, and, secondly, that of keeping a dog with its head near the ground, for about a minute, so as to oblige him to breathe the noxious fluid, which will soon affect his respiration, deprive him of his strength, and would soon kill him, if he was not immediately brought out into the open air, where, if he is not too far gone, he will gradually recover his strength and freedom of respiration. (From this experiment of the dog, the cave derives its name of *grotta del cane*; the Italian word for dog being *cane*.) There is a small lake near this grotto, the water of which is considered as a specific against the effects of the noxious fluid of the grotto, so that the animals apparently killed, or too much affected by that fluid, may be soon recovered by being bathed in that water; but if it is true that those waters at all contribute to restore the animals thus affected, it seems to be merely by the shock they give with the sensation of cold.

Apparently several generations of Italian guides and dogs earned their living by repeating this demonstration for visitors, as Worthington Hooker, writing almost 90 years



Illustrating the mass of carbon dioxide by pouring it downhill (11)

after Cavallo, again mentions the guide and his unhappy canine companion in terms which suggest he had visited the cave himself, the only alterations being the use of a pail of water rather than the nearby lake to revive the dog. Describing the scene in the 1870 edition of his *First Book*



Illustrating the suffocating action of carbon dioxide by pouring it downhill (11).

in *Chemistry for the Use of Schools and Families*, Hooker wrote (4):

A man lives nearby who shows the grotto to visitors, and, in doing this, he takes his dog in, who of course falls down senseless. He brings him out, however, quickly into the fresh air, which, with a dash of cold water, revives the dog, so that the same thing can be shown to the next visitors. But you can see by his leanness and the dullness of his eye [i.e. that of the dog, not the guide, Ed.] that he is dealt with harshly, for this gas, unlike nitrogen, is really poisonous. The dog falls senseless not merely for want of oxygen, but because the gas does him positive harm.

In his description of the toxicity of carbon dioxide, Hooker, in common with many other 19th century textbook writers, seems to have confused its properties with those of carbon monoxide, a confusion which, in conjunction with a knowledge of the grotto, once worked to the advantage of the famous British chemist, Lyon Playfair. In his memoirs, Playfair relates how, as a young chemist serving as "Honorary Professor of Chemistry" at the Manchester Royal Institution, he was given a poorly ventilated cellar for use as a teaching laboratory. One day he and his pupils were doing some routine combustion analyses using open charcoal furnaces, when Playfair became ill and had to go home. However, he was soon summoned back to the laboratory, where he found to his dismay (5):

... two of the pupils lying insensible in the area outside, and [I] at once saw they had been poisoned by the fumes of charcoal, as indeed I had been. Recalling that the guide at the *Grotta del Cane* uses his dog continuously by dragging the insensible body out of the cave, which contains carbonic acid in its lower layer, and immersing it in cold water, I instantly dashed a pail of water over each of my prostrate pupils, and

to my joy found that they revived. This was a practical lesson in ventilation which I never forgot.

In fact, Hooker was so taken with the grotto as a popular teaching device, that he actually designed a lecture demonstration using the grotto motif in which a pasteboard model of the cave was partially filled with carbon dioxide and a candle was lowered into the gas through a hole in the roof.

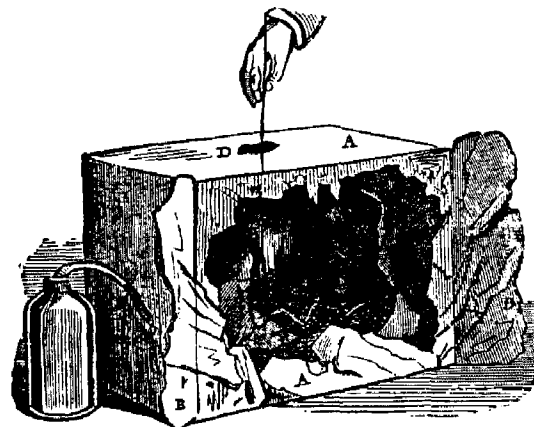
The grotto continued to be a favorite textbook example, not only throughout the 19th century, but well into the second and third decades of this century. It is mentioned in the popular texts of this period by Findlay (6), Partington (7), and Mellor (8). Indeed, the latter author provides additional details, stating that the carbon dioxide layer had a relatively constant depth of 18 inches and that analysis showed it to be 70.3% CO_2 , 23.7% N_2 , and 6.0% O_2 . Only in the 1940's and 50's, with the increasing emphasis on theory, does the grotto finally disappear from the textbooks.

The *Grotta del Cane*, however, was not the only striking example available to the 19th century textbook writer. Later in the century it was joined by the even more exotic *Valley of Death*, located at Lake Laach in Java. This site was apparently much less well documented and the textbook descriptions were consequently more exaggerated. Thus, in his 1886 text, Paul Bert reported that (9):

In the island of Java there is said to be a valley in which the soil emits such quantities [of carbon dioxide] that nothing can live within its bounds, and the very birds that venture to fly through it fall down overpowered and die.

Mellor, likewise, states that (8):

... one traveler says the whole bottom is strewn with the



Hooker's pasteboard model of the grotto (4).



Paul Bert's (1886) version of the guide at the grotto and his recumbent dog (9).

skeletons of human beings, animals, and birds which have been asphyxiated in an atmosphere overloaded with carbon dioxide.

Like the *Grotta del Cane*, the *Valley of Death* seems to have disappeared from the textbook literature in the 1940's and 50's.

Should one wish to revive these interesting examples, the modern textbook writer would have yet a third to add to them - an example even more striking than the *Valley of Death* and certainly much better documented. This is, of course, the massive release of trapped carbon dioxide from the bottom of Lake Nios in Northwest Cameroon in late August of 1986 (10). The spreading blanket of dense carbon dioxide suffocated close to 2,000 people and as many animals, a set of statistics which leaves Hooker's generations of dull-eyed Italian canines far behind.

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2. Mellor (8) claims that van Helmont, who imperfectly anticipated the discovery of carbon dioxide in the 17th century in the form of his so-called *gas sylvestre*, also identified it with the gas in the *Grotta del Cane*, but he does not provide a citation for this reference.
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7. J. R. Partington, *A Textbook of Inorganic Chemistry*, Macmillan, London, 1939, p. 676.
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11. R. P. Williams, *Elements of Chemistry*, Ginn, Boston, MA, 1897, pp. 172-173.

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QUESTIONS AND QUERIES

The following item appeared in the 21 May 1881 issue of "The Chemical News". Since no one apparently answered Duckworth's original query, we thought we would resubmit it to our present day readers:

Sirs - Without doubting for a moment that Priestley discovered oxygen on 1 August 1774, I should be glad if you or some other historical chemist would enlighten me as to the following statement which I have culled from an old work on Chemistry:

"Klaproth, 'On the Knowledge of the Chemistry of the Chinese in the Eighth Century', infers that the Chinese were then acquainted with oxygen and the composition of water. The following is interesting:

There are many circumstances that purify it (referring to the atmosphere), and which can rob it of part of its *yne*; the chief of these are those things which are modifications of the *yann*, such as the metals, sulphur (*lieou-hhouann*), and *tane*, or carbon. These ingredients, when burnt, amalgamate the *yann* of the air, and form with it new combinations of two fundamental bases. The *ky-yune*, or *yne* of the air, is always pure; but by the aid of fire it can be extracted from *tchine-che*, a black stone found in the marshes. It enters also into the composition of water, in which it is so closely united with the *yann* that its decomposition becomes extremely difficult. Gold never amalgamates with the *yne* of the air, and is always found native.' - *Memories de l'Academie*