



LXXIV. On the formation of nitric acid in eudiometric combustions of gases mixed with nitrogen

Dr. H. Kolbe

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exists between the particles of the metal which conducts the current: it is as follows:—

“If we make the current of the battery of sixty elements pass through a platina, iron, copper, or any metallic wire, the metal at first reddens, then it melts, and after some instants this fused metallic wire, in which various movements are perceived, breaks at an undetermined place, and the ends formed by the rupture are projected far along the wire; this wire is, after the experiment, terminated, at the spot where it has been broken by the force of the current, by two globules. ‘This phenomenon is not accompanied by any evolution of light or any combustion. The wire neither gains nor loses in weight in this experiment; there is only the ordinary spark which appears at the moment when the repulsion produces its effect, and when the wire is divided into two fragments.’”

Teylerian Museum, Haarlem,

August 20, 1846.

Note. On the subject of this Paper see Mr. Grove's Lecture on the Voltaic Arc at the Royal Institution in February 1845, in the Literary Gazette.—ED.

LXXIV. *On the Formation of Nitric Acid in Eudiometric Combustions of Gases mixed with Nitrogen.* By Dr. H. KOLBE*.

IN an analysis of mixed gases, which contained 90 parts of light carburetted hydrogen and 10 parts of nitrogen, I have often found, that by the combustion in the eudiometer more oxygen disappeared than in accordance with the calculation ought to have disappeared. The explosion caused always such an elevation of temperature, that the mercury sublimed and covered the inside of the eudiometer with a thin, gray, metallic film. After the caustic potash-ball was introduced into the eudiometer for the purpose of absorbing the carbonic acid formed, and the residual volume of gas dried, the diaphanous film of mercury was seen to be covered by innumerable little white crystals, the behaviour of which with water, muriatic acid and caustic potash, showed clearly that they contained protoxide of mercury for their basis.

If these crystals consist of nitrate of protoxide of mercury, as the well-known experiments by Cavendish on the formation of nitric acid render probable, then the before-mentioned diminution of the volume is easily understood.

Therefore, trying at first whether this error was occasioned only by the presence of nitrogen, I mixed a certain volume of pure hydrogen with an excess of oxygen in an eudiometer†

* Communicated by the Chemical Society; having been read May 18, 1846.

† In all these experiments I used an eudiometer which was furnished

over mercury, and after having exploded the mixture, I observed the diminution of the volume of gas.

[The volumes found by observation in this and the following examples were saturated with the vapour of water.]

Experiment I.

	Vol. obs.	Temp.	Barom.	Height of mercury in tube over that in trough.	Corr. vol.
Hydrogen	78.8	11.2°C.	764.7 ^{mm}	366.0 ^{mm}	29.4
After admission of O.	137.6	11.0	...	305.2	59.5
After combustion .	45.6	11.0	...	400.3	15.5

Experiment II.

Hydrogen	145.5	12.0°C.	764.7 ^{mm}	297.9 ^{mm}	63.6
After admission of O.	281.4	11.5	...	162.1	159.9
After combustion .	146.5	11.3	...	296.5	64.4

When we calculate the quantity of the consumed hydrogen from the whole volume of gas which has disappeared by combustion, we find numbers which correspond exactly with the hydrogen used.

	I.	II.
Hydrogen used	29.4	63.6
... calculated	29.4	63.6

By this similarity of the results as found and calculated, it is evident that the mercury cannot become oxidized when pure hydrogen is burnt with an excess of oxygen. Mercury sublimed also in this case; but no trace of the crystals spoken of could be seen, even when the residual gas was dried.

Varying the experiments, I mixed with a similar explosive mixture a small portion of atmospheric air (which is calculated to contain in 100 vols. 20.9 vols. of oxygen); I obtained the following results, very different from the former:—

Experiment III.

	Vol. obs.	Temp.	Barom.	Height of mercury in tube over that in trough.	Corr. vol.
Atmospheric air . .	76.8	8.8°C.	767.9 ^{mm}	367.2 ^{mm}	29.2
After admission of H.	246.0	8.8	768.2	197.0	134.1
After admission of O.	402.9	9.5	768.3	45.8	277.8
After combustion .	225.1	9.6	768.4	218.2	117.8

with a correctly graduated millimetre-scale etched upon the glass, and exactly graduated, on which by employing a mirror it was easy to determine the tenth part of a millimetre. I also took care to observe all the precautions, by which Bunsen has excluded everything that can occasion an error. The mercury was previously purified by digesting for some days with nitric acid, and had all the properties of the pure metal.

Experiment IV.

	Vol. obs.	Temp.	Barom.	Height of mercury in tube over that in trough.	Corr.vol.
Atmospheric air . .	79·2	8·4°C.	773·0 ^{mm}	364·2 ^{mm}	30·7
After admission of H.	250·4	8·5	773·7	192·4	139·1
After admission of O.	391·7	8·5	773·7	55·8	269·4
After combustion .	200·3	8·6	773·4	241·9	101·5

	III.	IV.
Hydrogen used . . .	104·9	108·4
... calculated .	106·8	111·9

According to these experiments, it appears impossible to determine accurately in the usual way, by combustion with oxygen, the quantity of a combustible gas when nitrogen is present, on account of the simultaneous oxidation of the nitrogen producing from 2 to 3 per cent. more hydrogen, as shown by the last two experiments, and which under more unfavourable circumstances is liable to be still increased. Notwithstanding the dilution with atmospheric air, the elevation of the temperature on combustion was so great, that the inner surface of the eudiometer was covered with sublimed mercury, upon which was deposited a number of microscopic crystals; they made their appearance as soon as the remaining gas was dried by means of chloride of calcium.

One of the conditions which in the above case appears to be absolutely necessary for the formation of nitric acid, is the great elevation of temperature of the gas during combustion. The lowering the temperature to a certain point is sufficient entirely to prevent the oxidation of the nitrogen. This is best accomplished by diluting the combustible gas with 1, 2 or 3 volumes of atmospheric air, by which means the accuracy of the analysis is not in the least affected. The following analysis, where hydrogen was deflagrated with twice its volume of atmospheric air mixed with the requisite quantity of oxygen, will justify this assertion, besides which I have been able to confirm it by a series of other experiments.

	Vol. obs.	Temp.	Barom.	Height of mercury in tube over that in trough.	Corr.vol.
Atmospheric air . .	212·3	14·2°C.	756·9 ^{mm}	244·8 ^{mm}	100·9
After admission of H.	282·7	15·1	757·4	175·3	152·5
After admission of O.	321·6	15·4	758·3	137·3	185·1
After combustion .	221·7	14·7	758·5	234·0	107·7

	Used.	Calculated.
Hydrogen . . .	51·6	51·6

Professor Bunsen has been so kind as to communicate to me the following very interesting series of experiments relating to this subject, proving clearly that the formation of nitric acid is diminished in the combustion of explosive mixtures according to the dilution with atmospheric air. He mixed a constant quantity of atmospheric air with a decreasing quantity of pure explosive gas formed by decomposing water by means of electricity, and obtained the following results on combustion:—

Vol.			Vol.		Vol.
100	atmospheric air	gave after combustion with	259·70	explosive gas	86·15
100	226·80	...	88·56
100	84·98	...	99·19
100	63·21	...	99·97
100	48·98	...	99·99
100	40·	...	100·10
100	36·39	...	100·36
100	21·20	...	100·79
100 air mixed with 11 vols. of explosive gas did not ignite.					

By this it is proved that the ignition of combustible gases containing nitrogen must not be attempted at too far a limit from the point at which the mixed gases are combustible. This point may be ascertained with an unknown mixture by previous experiment, as the gas before its separation from the carbonic acid, &c. may be mixed with nearly double its volume of oxygen gas (which quantity is sufficient even if it consisted of pure light carburetted hydrogen), and small portions added by degrees to a known volume of atmospheric air in an eudiometer until ignition by means of the electric spark took place. For example, if it is found that 50 volumes of such a mixture with 100 volumes of atmospheric air will just ignite, then, according to the foregoing experiments, treble the quantity of the former mixture may be ignited without the formation of nitric acid. Therefore, in an eudiometrical analysis, the gas to be examined may be mixed with twice its volume of atmospheric air, besides the requisite quantity of oxygen gas. In this manner it is ascertained whether the gas to be analysed requires still a dilution with atmospheric air.

LXXV. On Tribasic Boracic Æther.

By J. E. BOWMAN, Esq.*

A FEW months ago M. Ebelmen published an account of two compounds of silicic acid and æther, and announced that by subjecting them to the gradual action of moist air, he

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