# LII.—*The Inertness of Quicklime.*

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## *Introductory.*

The word "quick" is applied to the substance lime in several European tongues, and in our own it may be taken to represent its living and active nature, especially towards water. But though to this substance, under ordinary circumstances, lime is an active kind of matter, yet to other substances it is relatively, if not completely, inert. Thus, for example, it is a common matter of knowledge that quicklime will not absorb and combine with carbon dioxide gas when dry, and, some years ago (Trans., 1885, **47**, 484) I proved that when dry hydrogen sulphide is passed into quicklime no chemical change ensues.

A short time since, when I was preparing some nitrosulphonic acid by passing sulphur dioxide into concentrated nitric acid, and the nitrous fumes had become intolerable, a glass tower was hastily filled with lime. It was then noticed that, so far as could be judged, all the nitrous fumes passed out as before, and at the exit there was an appreciable odour of sulphur dioxide. But when the lime was moistened with water the absorption, both of nitrous fumes and of sulphur dioxide, appeared to be complete. It seemed, therefore, worthy of interest to examine as to how far the absorptive power of lime for gases, generally regarded to be of an acid nature, was dependent on the mass of water present, more especially as lime is used in manufactures to absorb and retain carbon dioxide, sulphur dioxide, hydrogen sulphide, and chlorine gases, and, on a small scale, as a convenient material for preventing acid fumes from entering the atmosphere of a room. In the present communication it is proposed to deal with carbon and sulphur dioxides only, reserving for further investigation other gaseous substances.

## PART I. LIME AND CARBON DIOXIDE.

### *Historical.*

The conditions of the decomposition of calcium carbonate, as also of the recombination of the basic and acidic oxides, were first studied by Debray (*Compt. rend.*, 1867, **64**, 603); he concludes from his experiments, generally quoted in the manuals of chemistry, that lime does not absorb carbon dioxide below 1040° or thereabouts, and then only on the condition that the tension of the gas is above 520 mm.

It would appear, from the rather meagre description given, that the experiments were conducted on a small scale, the amount of decomposition, on the one hand, and of absorption, on the other, being measured by the reading of a manometer. Birnbaum and Mahn (*Ber.*, **12**, 1547) found that no action takes place at the temperature of melting lead, 326°, but that it begins at the temperature of melting zinc, 415°. In the experiments quoted, the amount of carbon dioxide absorbed per 100 parts of lime varied from 4·1 to 45·7, though the values given do not vary regularly, either according to the duration of the experiment or the mass of material. In the form of apparatus used, the gas passed over, rather than through, the lime, the weight of which never exceeded 1 gram; no details are given of the mass of carbon dioxide passed per unit time. Both these authors and Schulatzenko (*Dingl. polyt. J.*, **205**, 345) observed that calcium carbonate also decomposes at the same temperature, of melting zinc.

Finally, Raoult (*Compt. rend.*, 1881, **92**, 189) noticed that when a rapid stream of pure and dry carbon dioxide is passed over lime at the temperature at which glass begins to soften, the combination is so energetic that the lime becomes vividly incandescent.

## *The Apparatus and Method of Investigation.*

The apparatus used (both for Parts I and II) was made up of a vessel suitable for producing the gas used; this was passed into a wash-bottle containing water to catch spirtings, thence through two wash-bottles of concentrated sulphuric acid, and finally through 1300 mm. of glass tubing packed with pumice and phosphoric oxide, and arranged in a zig-zag form. It was hoped that if the rate of passage were not too rapid, it would be sufficiently dried to come in contact with the lime contained in a small U-tube, fitted with perforated glass stoppers. Next to this was placed a weighed U-tube, filled also with phosphorus pentoxide to catch any water which might be driven off, and, lastly, a small wash-bottle containing sulphuric acid, to prevent any backward passage of moisture. The mass of the gas which passed through the lime was determined either from the volume of water forced out of an aspirator, or by absorption by soda in a tared vessel. The sum of the increase in weight of the lime and the mass of the gas passing through without being absorbed would thus be a measure of the total mass of gas. From these data the percentage of absorption can be calculated, and it appears more rational to refer the increase in weight of the lime to the total mass of gas rather than to the mass of lime. To make each experiment so far alike as possible, a matter of some difficulty in dealing with a solid substance, the same weight approximately of lime was used in each instance, and this was packed within the same length in the U-tube, and, further, in each series of experiments the rate of passage of gas was kept as uniform as possible, being 0·25 gram per hour on the average.

The lime was prepared from the precipitated carbonate; it was free from chlorine and, excepting traces, from ferric oxide, silica, and alumina also.

The portion used for any set of experiments was strongly ignited in a platinum crucible; it was apparently in no case over-burnt, when, as is well known, a cinder-like mass is obtained which cannot be slaked, and would be inactive towards gases. The lime was placed, when still warm, in the experimental U-tube, also warm; it is probable, however, that small traces of water were absorbed in the necessary but rapid transference of the lime from the one vessel into the other. Before commencing experiments, the U-tube and its contents were weighed, filled with air, and, at the conclusion of the first experiment, filled with carbon dioxide; to make the necessary correction, a blank experiment was made once for all, in which the same volume of sand as of lime was placed in the U-tube, and the difference in its weight when filled with air and with carbon dioxide was determined.

### *Effect of Mass of Water present.*

Various series of experiments were conducted at ordinary temperatures with quicklime and lime containing variable proportions of water to compare the absorptive values, and to ascertain if the one is a function of the other.

SERIES I.—*Quicklime*, CaO.

Mean Temperature, 11°.

| Time. | Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| | grams | grams | gram | grams | |
| 4 hours | 10·459 | 10·5058 | 0·0468 | 1·2883 | 3·5 |
| 5¾ ,, | 10·5058 | 10·5103 | 0·0045 | 1·1167 | 0·4 |
| 4½ ,, | 10·5103 | 10·5148 | 0·0045 | 2·2277 | 0·2 |
| 14¼ ,, | — | — | 0·0558 | 4·6327 | 1·16 |

The above experiments confirm, on a more extended scale, previous observations that dry lime does not combine with dry carbon dioxide; for, though a considerable mass of gas was passed, yet the quantity absorbed was extremely small, and that principally in the first experiment, a result probably due to the presence of a small quantity of hydrate. But the water eliminated thereby, though retained by the lime, and doubtless diffused through it, appears not to be enough to continue the chemical combination.

*Hydration of the Oxide.*—In order to add to the lime a known amount of water, under conditions precluding contact with carbon dioxide, a method was adopted which, in a previous investigation (Trans., 1885, **48**, 481), was found to be accurate. I transcribe the passage from the paper quoted:—"A watch-glass containing a weighed sample of the lime was placed at the top of a glass cylinder; over this was inserted another cylinder of rather larger diameter, and the two placed in a beaker containing a hot solution of soda. The apparatus was kept for some time in a warm place." If the lime be exposed to the damp atmosphere for a greater or less time, the quantity of water absorbed is the greater or less; thus, the lime can be made to take up the amount of water desired.

SERIES II.—*Lime with* 3 *per cent. Water.*

Mean Temperature, 14°.

| Time. | Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| | grams | grams | gram | grams | |
| 5 hours . | 10·5388 | 10·5526 | 0·0138 | 1·2974 | 1·05 |
| 4 „ | 10·5526 | 10·5531 | 0·0005 | 1·1129 | nil |

It will be evident from the above results, that the addition of a small proportion of water does not suffice to promote the chemical change, though one might be led to suppose that, as each particle of water was ousted from the hydrate, it would combine with the neighbouring particle, which in its turn would be able to absorb the carbon dioxide. But, when a small mass of water is spread through a large mass of lime, this does not appear to be the case. Accordingly an experiment was conducted with lime containing a greater proportion of water, but incompletely hydrated.

SERIES III.—*Lime with* 11·21 *per cent. Water.*

Time of each Experiment, 4 hours. Mean Temperature, 14°.

| Weight of lime before. | Weight of lime after. | Gain. | Water collected. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| grams | grams | gram | gram | grams | |
| 9·6755 | 9·7408 | 0·0703 | nil | 1·2777 | 4·22 |
| 9·7408 | 9·7473 | 0·0065 | 0·0105 | 2·0841 | 0·81 |
| 9·7473 | 9·7503 | 0·003 | 0·0085 | 1·6307 | 0·51 |
| 9·7503 | 9·753 | 0·0027 | 0·001 | 0·9434 | 0·39 |

In the above series of experiments, the absorption of the gas is still very incomplete, and, when once begun, seems to proceed to a slight degree.

SERIES IV.—*Calcium Hydrate*, $Ca(OH)_2$.

Time of each Experiment, 4 hours. Mean Temperature, 14°.

| Weight of lime before. | Weight of lime after. | Gain. | Water collected. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| grams | grams | gram | gram | grams | |
| 9·125 | 9·3045 | 0·1995 | 0·006 | 1·1863 | 14·76 |
| 9·3045 | 9·5595 | 0·255 | 0·0035 | 0·9139 | 22·1 |
| 9·5595 | 9·821 | 0·3615 | 0·0165 | 1·1077 | 25·44 |
| 9·821 | 10·179 | 0·358 | 0·013 | 1·5341 | 24·21 |
| 10·179 | 10·3925 | 0·2135 | 0·003 | 1·914 | 10·15 |

The results given above show that, in the case of the hydrate, the absorption of the gas is, at first, more complete, and, when the hydrate becomes more moist by the water kept back, there is an increase in the combination until the chemical change is nearly completed. To render the effect of the water more manifest, another series was conducted with the hydrate to which 10 per cent. of water was added, and the whole mixture worked up as uniformly and rapidly as possible; the mass was not moist to the touch, and could not be moulded, such being, as is well known, the degree of dampness which gas managers consider best for the absorption both of carbon dioxide and hydrogen sulphide gases.

SERIES V.—*Calcium Hydrate with* 10 *per cent. Water.*

Conditions of Time and Temperature as above.

| Weight of lime before. | Weight of lime after. | Gain. | Water collected. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| grams. | grams. | grams. | gram | grams. | |
| 9·3025 | 11·739 | 2·4365 | 0·015 | 1·174 | 67·48 |
| 11·739 | 11·8275 | 0·0885 | 0·0145 | 1·2242 | 8·41 |

The above results show, in a most marked manner, the effect of the presence of free as distinct from combined water, the percentage of gas absorbed being increased from 14·76 to 67·48 per cent. It would therefore appear that it is necessary for the reaction that both the hydrate and the carbon dioxide should be dissolved in the water, and the change is incomplete when the gas has only the chance of being dissolved in the water which it succeeds in driving out from the hydrate.

### *Effect of Temperature.*

Though lime is inert towards carbon dioxide at ordinary temperatures, yet these substances might combine below the temperature of melting zinc, at which the converse change, namely, the resolution of calcium carbonate into lime and carbon dioxide, takes place. To examine this point, experiments were conducted at temperatures of about 100°, 200°, 300°, 352° (temperature of melting nitre) and 415° (temperature of melting zinc). Previous to conducting the first of each series of experiments the tube with the lime was heated to the same temperature in a current of dried and purified air, in order to drive over any water accidentally introduced. The duration of each experiment was four hours.

### SERIES VI.—*Quicklime.*

Mean Temperature, 104°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 10·1755 | 10·234 | 0·0585 | 1·7324 | 3·38 |
| 10·234 | 10·2498 | 0·0158 | 1·8169 | 0·69 |

At this temperature, there is no appreciable absorption of the gas by the lime.

As an incidental point, the absorptive power of the hydrate at the same temperature was examined in order to study the effect of the liberated steam in promoting the action. The results given below show that the dry hydrate is rather more active under these conditions than the same material at ordinary temperatures, but less active than the damp hydrate.

### SERIES VII.—*Calcium Hydrate*, $Ca(OH)_2$.

Mean Temperature, 102°.

| Weight of lime before. | Weight of lime after. | Gain. | Water collected. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| grams | grams | gram | gram | grams | |
| 10·502 | 11·220 | 0·718 | 0·3535 | 1·896 | 36·95 |
| 11·220 | 11·417 | 0·197 | 0·1765 | 1·0427 | 20·77 |
| 11·417 | 11·6792 | 0·1265 | 0·1265 | 1·2896 | 21·97 |

In the first experiment of the above series, the passage of the gas was somewhat more rapid than in the others; this may account in some degree for the greater percentage absorbed.

### SERIES VIII.—*Quicklime.*

Mean Temperature, 203°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 10·4075 | 10·4628 | 0·0553 | 2·0504 | 2·82 |
| 10·4628 | 10·4918 | 0·029 | 1·8097 | 1·60 |
| 10·4918 | 10·5048 | 0·013 | 1·6385 | 0·80 |

SERIES IX.—*Quicklime.*

Mean Temperature, 290°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | grams | grams | |
| 11·3035 | 11·5387 | 0·2532 | 1·302 | 16·28 |
| 11·5387 | 11·5932 | 0·0542 | Determination lost | 3·0 (approximate) |

SERIES X.—*Quicklime.*

Mean Temperature, 352°. (Temperature of Melting Nitre, Carnelley.)

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 8·142 | 8·66 | 0·518 | 1·0973 | 32·06 |
| 8·66 | 8·7682 | 0·1082 | 0·8998 | 9·06 |

The results given in the above tables would seem to indicate that, under the conditions of experiment, the lime and carbon dioxide enter into combination to a slight extent at 290° and to a greater extent at 352°; a further set of experiments were accordingly conducted at the temperature of melting zinc.

SERIES XI.—*Quicklime.*

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | grams | grams | |
| 9·516 | 10·75 | 1·234 | 1·2512 | 49·69 |
| 10·75 | 10·6405 | 0·8905 | 1·3015 | 40·85 |
| 11·6405 | 11·9655 | 0·325 | 1·2525 | 21·19 |
| 11·9655 | 12·4483 | 0·4825 | 0·8392 | 37·28 |

The absorption of the carbon dioxide by the lime at this temperature is very considerable, though there can be no doubt that the actual temperature at which combination commences is influenced by the porosity of the lime, this, in its turn being conditioned by the degree of ignition to which the material had been subjected. It is further to be noted that the absorption is the more complete at that temperature at which, according to previous observers, calcium carbonate, when heated in a current of an inert gas, begins to decompose; my own results, for which dry hydrogen was used, were confirmatory on this point.

## PART II.—LIME AND SULPHUR DIOXIDE.

### *Historical.*

It is a familiar lecture experiment to show that sulphur dioxide gas, even when dried without any particular care, does not affect dry litmus paper. Schott (*Dingl. Polyt. J.*, **202**, 52) observed that dry calcium oxide and sulphur dioxide react at a temperature which is above that of boiling water, but below a red heat; a sufficiently wide range!

Birnbaum and Wittich (*Ber.*, **13**, 651) showed that no combination took place below 400°; at the melting point of zinc there was a very rapid absorption of gas, and equally at 500°, but at this temperature the product decomposed into calcium sulphate and sulphide. These authors do not, however, give any details of a single quantitative experiment.

### *Experimental Work.*

Accordingly experiments were conducted in greater detail by the methods and apparatus described. The sulphur dioxide was prepared in the usual manner from copper and concentrated sulphuric acid, and that portion of it which passed through the lime without absorption was collected in a small weighed glass vessel containing a strong solution of soda. For obvious reasons, the current of the gas could not be regulated to such a degree of nicety as in the case of the carbon dioxide; the duration of each experiment was four hours.

### SERIES XII.—*Quicklime*, CaO.

Temperature, 12—13°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 8·7915 | 8·8769 | 0·0854 | 7·3335 | 1·15 |
| 8·8769 | 8·8769 | nil | 4·088 | nil |

### SERIES XIII.—(A Repetition of XII.)

Temperature, 14—14·5°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 7·673 | 7·7397 | 0·0667 | 2·427 | 2·69 |
| 7·7397 | 7·7447 | 0·005 | 3·515 | 0·14 |
| 7·7447 | 7·7499 | 0·0052 | 5·1945 | 0·1 |

The results given above show that at ordinary temperatures quicklime does not combine with sulphur dioxide; the slight absorption in the first experiment of each series can be explained, as shown above, by the slight hydration of the lime in the processes of manipulation.

By way of comparison, the experiments were repeated under the same conditions with a sample of the hydrate.

### SERIES XIV.—*Calcium Hydrate*, $Ca(OH)_2$.

Temperature, 18—20°.

| Weight of lime before. | Weight of lime after. | Gain. | Water collected. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|---|
| grams | grams | gram | gram | grams | |
| 8·567 | 9·6525 | 1·0845 | 0·0943 | 4·568 | 20·5 |
| 9·6525 | 9·919 | 0·2665 | nil | 1·043 | 20·34 |
| 9·919 | 10·6805 | 0·7615 | nil | 1·942 | 28·13 |

In the second experiment of the above series, the passage of the gas was, by accident, rather slow, though the absorption was equal in amount to that in the first experiment. These results show that the absorptive power of the hydrate is, under the same conditions, 200 times as great as that of the oxide.

### *Effect of Temperature.*

Further series of experiments were conducted in order to ascertain the temperature at which these anhydrous oxides enter into combination; the results are given in the tables below.

### SERIES XV.—*Calcium Oxide.*

Temperature, 100—102°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 7·7499 | 7·7593 | 0·0093 | 1·87 | 0·5 |
| 7·7593 | 7·7798 | 0·0205 | 4·569 | 0·45 |

### SERIES XVI.—*Calcium Oxide.*

Temperature, 200—204°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | grams | grams | |
| 9·987 | 10·1317 | 0·1447 | 2·762 | 5·24 |
| 10·1317 | 10·1597 | 0 028 | 1·6395 | 1·55 |
| 10·1597 | 10·1692 | 0·0295 | 1·8325 | 1·51 |

### SERIES XVII.—*Calcium Oxide.*

Temperature, 290—300°.

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | grams | |
| 10·1692 | 10·3912 | 0·222 | 1·5825 | 12·3 |
| 10·3912 | 10·5045 | 0·1135 | 2·1755 | 4·98 |
| 10·5045 | 10·556 | 0·515 | 4·479 | 1·11 |

### SERIES XVIII.—*Calcium Oxide.*

Temperature, 352°. (Melting point of Nitre.)

| Weight of lime before. | Weight of lime after. | Gain. | Gas passed unabsorbed. | Percentage absorbed. |
|---|---|---|---|---|
| grams | grams | gram | gram | |
| 8·609 | 9·1005 | 0·4915 | 0·675 | 42·11 |

The results detailed above show that there is practically no combination between the oxides below a temperature of 300°, but that it commences to a slight extent at that point and is fairly complete at 350°. In the last experiment it was observed that a small quantity of sulphur had sublimed on the cooler part of the tube. An experiment was conducted at the melting point of zinc, but under these conditions a considerable quantity of sulphur was formed, so that any weighing would not give accurately the amount of gas which had been absorbed. The lime at the end of the experiment contained both sulphide and sulphate, an observation in accordance with that of Birnbaum and Wittich (see above). The calcium sulphate formed, doubtless, decomposes initially, according to the equation

$$4CaSO_3 = 3CaSO_4 + CaS,$$

and the sulphur dioxide acting on the sulphide produces the sulphur. Under these circumstances it was not thought necessary to repeat the experiment or to examine the extent of the absorption at any higher temperature.

### *Discussion of Results.*

In these and numerous other investigations, it has been shown that the presence of a trace of water produces an effect precisely similar to that of heat energy in inducing the combination of substances which, under otherwise similar conditions, are practically inert towards one another. The general effect of heat energy is the resolution of more into less complex combinations, and ultimately into the constituent atoms. Within recent years the hypothesis has been brought forward by a certain school of writers that substances in dilute solution are similarly resolved or dissociated into their constituent atoms or ions, as the case may be. If the hypothesis be of any validity, it might follow as a deduction that the presence of a trace of water causes one or both the reacting substances to enter into solution, and thereby become resolved into constituent atoms; chemical change is induced either by the combination of all or any of the substances present. The production of calcium carbonate would therefore result, not from the combination of lime and carbon dioxide, but from the elementary substances calcium, carbon, and oxygen.

Further, it has been shown that the presence of a trace of water, sufficient to start the action, is insufficient to carry it on to its ultimate limit, even though water may be formed as a product of such a change, metallic oxides and hydrogen sulphide, for example. But if the reacting substances were decomposed into their constituents, it would follow that the less the relative mass of water the more concentrated the solution and the less, therefore, the dissociation and, consequently, the less the amount of chemical combination.

It may, however, be questioned whether the analogy of the effects of heat and traces of water is not apparent rather than real. The phenomena can be explained equally by an association or hydrate as by a dissociation hypothesis, that, for example, sulphur dioxide combines with water to form its hydrate or sulphurous acid, and lime equally to form its hydrate, and by the interaction of these substances calcium sulphite is formed, and subsequently precipitated from solution, leaving the water again to combine with the substances. After a time the water becomes more spread through the mass and thus becomes ineffectual.

### *Conclusions.*

I. Carbon dioxide does not combine with dry lime to an appreciable extent below a temperature of 350°, nor at ordinary temperatures with incompletely hydrated lime; under the latter conditions, the addition of 10 per cent. water to the hydrate greatly increases the absorptive power.

II. Sulphur dioxide does not combine with dry lime to an appreciable extent below a temperature of 350°, at which point there is an incipient decomposition of the sulphite formed.

There is a great similarity of behaviour between these two gases as regards the amount of them absorbed by lime at the same temperature.

III. Incidentally, it is noted that ordinary quicklime does not absorb nitrous fumes.

It is proposed to continue these investigations in the case of chlorine and gases of an acidic character.

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