# PHOTOGRAPHIC CHEMICALS AND CHEMISTRY

By

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# PREFACE

THOUGH the photographic worker has little need to delve at all deeply into the subject of chemistry, there are many who will be interested to understand the whys and wherefores of the photographic processes with which they are familiar. The present volume sets out to explain this aspect of photography to the reader who is little acquainted with chemistry, and to inform him of the important properties of the chemicals which he employs.

Despite its elementary treatment of the subject, the volume is designed to give the reader a reasonably accurate account of the known facts and the theories that mark the modern science of photographic processes.

The authors wish to acknowledge their indebtedness to the Editor of the *British Journal Photographic Almanac* for permission to reproduce the table of solubilities that will be found at the end of this volume, and to Dr. Laurence Horton for his valued co-operation in correcting the proofs of these pages. They will further be grateful to correspondents drawing attention to errors or inaccuracies that may have eluded detection

In the Third Edition a considerable number of changes have been made in the text in order to bring it fully up to date.

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# AN INTRODUCTION TO CHEMISTRY

## CHAPTER I

## CHEMICAL DECOMPOSITION AND THE ELEMENTS

If a pinch of ordinary white sugar be heated in an old spoon held over a gas flame, the sugar will melt, boil, and eventually catch fire. When the blaze has died down, the spoon and its contents should then be allowed to cool.

On examination, it will be found that the sugar has become converted into a black friable mass, which may be crushed by the fingers into a soft powder very much like charcoal. In fact, essentially it *is* charcoal, since both it and the charcoal are merely slightly different forms of the same substance, carbon.

Our experiment is a typical instance of what is known as a *chemical decomposition*. What has happened is that, by the application of heat, the sugar has been split up—or decomposed—into various other substances, of which carbon is one, the other substances having escaped in the fumes and vapours which arose. We learn, then, that sugar is not a simple substance, but a remarkably intimate combination of several utterly different substances, including carbon.

Now carbon, unlike sugar, cannot be decomposed into any other ponderable substance, either by means of heat or by any of the ordinary methods of chemical decomposition or analysis. It is true that by allowing certain other substances to act on carbon, we can produce fresh kinds of matter which do not resemble carbon in the least degree. But to bring about this effect we have to *add* something to the carbon, although this fact may not be obvious. Thus, when some carbon, freely exposed to the air, is very strongly heated, it burns up into an invisible gas (carbon dioxide). But it only does so because it is able to extract something from the atmosphere; for if the carbon be heated in an absolutely air-tight vessel containing nothing but the carbon, it remains chemically unaltered. On the other hand, sugar is even in these circumstances decomposed quite readily, though it is obvious that there is no opportunity for anything to be added, in the absence of air. Our previous remark as to the relatively undecomposable nature of carbon is thus seen to be justified.

All substances which resist decomposition in a similar manner to that of carbon are known as "elements," meaning simple substances. Not all elements, however, are undecomposable. It has been proved that certain of the rarer elements, including radium, thorium, and uranium, are decomposing of their own accord into other elements, one of which is helium. This decomposition is usually slow; for example, in the case of radium, it takes about 1,600 years for a given quantity of this material to decompose to the extent of one-half its weight; whilst uranium normally decomposes much more slowly. It has been found possible, however, to cause one form of uranium to decompose with explosive rapidity, and this type of reaction is utilized in the atomic bomb. All this goes to prove that the very great stability of most elements in their ordinary state is only an accidental property, although a very useful and important one.*

In the table on pages 123–4 will be found the names of all the elements which the average reader is ever likely knowingly to meet with, together with many more, perhaps, which he is not.

All the common substances, e.g. sand, clay, water, alcohol, coal-gas, etc., which are not mentioned or implied in our list, have been shown by analysis to consist of two or more of the scheduled elements. Sugar, for instance, which we used for our first experiment, has been resolved into carbon and two *gases*, oxygen and hydrogen—a fact

* An element may probably be correctly defined as any substance all the atoms of which have a similar net nuclear electropositive charge. But this definition obviously presumes far too much, in many senses, for it to be conveniently inserted in the text.

which proves that an element may not bear the slightest physical resemblance to the substances from which it may be derived. Oxygen is also an important constituent of the atmosphere. In addition to oxygen, the air contains an even larger proportion of another gas, nitrogen. The oxygen is, however, the most essential ingredient, as it is the only one which actively supports life and combustion.

Chemists have to refer to the elements so very frequently that it has been found necessary to compile a list of abbreviations, which are often used instead of the full names of the elements. The abbreviation, or *symbol* as it is called, of each element, is to be found in the second column of the table of elements. The manner in which these symbols are used will be related in the following chapters. The meaning of the figures in the third column is also held over.

CHAPTER II

# CHEMICAL COMBINATION

We commenced the preceding chapter by giving an example of chemical decomposition. We will now begin this chapter with an instance of *chemical combination.*

When a length of magnesium ribbon is burned in air for the purpose of taking a photograph by the intense light thus afforded, the ribbon becomes converted into a white ash. Where it is possible to collect and weigh all this ash, the weight is found to be considerably *greater* than that of the original piece of ribbon. It is clear, then, that during the process of combustion something is introduced into the ribbon which transforms it into the white ash already referred to. This something is chiefly oxygen, obtained from the air.

Essentially, therefore, what occurs is that the element magnesium (symbol Mg) combines with the element oxygen (O) to form a white ash consisting of another substance, *magnesium oxide.* Magnesium oxide is a typical example of that very extensive class of substances which are known as *compounds*, because they are essentially combinations of those other simpler forms of matter, the elements.

One of the first things we learn from our observations on the combustion of magnesium is that a chemical compound need not have the same physical properties as the elements of which it is composed. Thus, magnesium is a metal, and oxygen a gas; but there is nothing metallic looking about magnesium oxide, nor does it ever display any gaseous characteristics. When different elements become so very closely associated that their properties are thus completely altered, they are said to be in a state of *chemical combination.* Elements which tend to unite in this way are said to have a *chemical affinity* for one another. The actual process of combination is termed a *chemical reaction.*

Now the chemist's brief way of expressing the reaction which occurs when magnesium is burned in air, using the symbols previously referred to, is as follows—

$$Mg + O = MgO$$

This is known as a chemical *equation*, and means simply that in the particular circumstances of the case, magnesium and oxygen together give magnesium oxide. Hence, it may be inferred that, when the symbols of elements are written separately with the sign + in between, this indicates that at the moment the elements alluded to are *not* in a state of combination, (although they may become combined immediately afterwards). On the other hand, when symbols are written one after the other with nothing in between (for instance, MgO, KI, NaOH, etc.), this indicates that the elements are combined into a compound. Such a repetition of unseparated symbols is termed the *formula* of a compound, because it points out the elements of which the compound is made up. Formulæ, then, stand for compounds, just as the separate symbols denote elements. The sign = in the above equation means that, when the substances on the left react with one another, the substance (or substances) on the right are produced.

Our example is one of chemical combination: but exactly analogous means would be used to indicate a process of decomposition. When the compound mercuric oxide is heated, it breaks up into the elements mercury and oxygen. As the formula of mercuric oxide is HgO, the equation signifying decomposition would be written thus—

$$\underset{\textit{Mercuric oxide}}{HgO} = \underset{\textit{Mercury}}{Hg} + \underset{\textit{Oxygen}}{O}$$

Could anything be simpler?

To return to the properties of compounds; it will be remembered that we said that these might be very different from the properties of the constituent elements. This is one of the chief features which distinguish a mere physical *mixture* of elements from a definite chemical compound of them.

If we mix about four parts by weight of copper filings with one part of "flowers" of sulphur, we obtain not a chemical compound but only a mixture, which has decided resemblances to both of its ingredients. Thus, the mixture, as we should expect, is of a brownish-yellow colour. Moreover, the particles of copper can often be actually seen, in amongst the usually finer particles of sulphur. By sieving, it is occasionally possible to re-separate these elements. If not, then separation may be effected by pouring over the mixture some bisulphide of carbon, a liquid which will dissolve out the sulphur and leave the copper behind.

If, however, our mixture is strongly heated, as we heated the sugar in our first experiment, in an old spoon over a gas flame, chemical reaction sets in, the copper combining with the sulphur to form another substance, cuprous sulphide. Now cuprous sulphide so prepared does not resemble either copper or sulphur; for it is a black powder. Moreover, separate particles of copper and sulphur cannot be distinguished in it, when pure, even with the aid of a most powerful microscope. We cannot separate the elements by any amount of sieving, nor does bisulphide of carbon dissolve out any sulphur.

Thus, we learn that in a chemical compound the elements are united infinitely more closely than they ever are in a purely physical admixture, however intimate the latter may be.

CHAPTER III

## COMBINING WEIGHTS

Referring again to our table of elements we find that in addition to the columns giving the names and symbols, there is another column giving the *combining weights* (or atomic weights) of the elements. In explanation of this term we may say that, ***whenever elements combine to form a compound, each element does so either in the simple proportion of its combining weight, or in some whole multiple of that proportion.*** We will first consider an instance where elements unite in the simple proportions of their combining weights as given in the aforesaid table—which latter incidentally embodies the results of the experiments and researches of innumerable chemists for a great many years past.

If the two elementary gases, hydrogen (H) and chlorine (Cl) be mixed together in a closed glass vessel, it will be found that the mixture will be of a slightly greenish colour, owing to the chlorine, which is naturally of a faint yellowish-green appearance.

If the two gases have been mixed in the proportion of their combining weights, that is, 1·008 parts by weight of hydrogen, and 35·46 parts of chlorine (it need hardly be said that, although they are very light, even gases have weight and can be weighed with suitable apparatus), no chemical reaction takes place until the mixture is exposed to light—ordinary diffused daylight is best: strong sunlight may cause an explosion. When thus exposed the mixture gradually loses all its colour, through the hydrogen and chlorine combining to form another colourless gas, hydrogen chloride (HCl).

If the proportion of chlorine be very much greater than as stated above, the green colour will be reduced on exposure to light, but will not entirely disappear, because some of the chlorine will remain in its original uncombined condition. If, on the other hand, the proportion of hydrogen be excessive, the colour will vanish completely, showing that all the chlorine has been combined; but there will now remain an excess of uncombined hydrogen, the presence of which can be detected by means which do not concern us here.

Hydrogen chloride may be produced in many other roundabout ways, besides the direct combination of the elements such as is described. But however prepared, all normal samples of pure hydrogen chloride are found on analysis to contain just 1·008 parts of hydrogen and 35·46 parts of chlorine. Hence, when hydrogen and chlorine combine to form hydrogen chloride, they do so in the simple and direct proportion of their combining weights.

The combination of hydrogen and chlorine is of course easily expressed by means of symbols: H + Cl = HCl. We know that this equation means that hydrogen and chlorine unite to form hydrogen chloride; but to a trained chemist it also signifies a great deal more. *For whenever a symbol is used, in the absence of any indication to the contrary it is always to be associated with the combining weight of the element referred to.* Thus, in our equation the symbol H stands not only for hydrogen, but for exactly 1·008 parts by weight of hydrogen, this being the combining weight. In an analogous way, the symbol Cl stands for 35·46 parts of chlorine.

When elements combine to form a compound, they usually lose many of their characteristic properties; *but they do not lose weight.* So that when the above relative weights of hydrogen and chlorine are taken and combined, the relative weight of hydrogen chloride which is produced is 1·008 plus 35·46, that is, 36·468 parts. Of course, these "parts" may be of any weight imaginable, from tons to fractions of a grain. It is not the actual magnitude of the weights that is important, but the relative proportions in which the elements are present.

The full meaning of our equation may now be set out as follows—

| H | + | Cl | = | HCl |
|---|---|---|---|---|
| *Hydrogen* | | *Chlorine* | | *Hydrogen chloride* |
| (1·008 parts) | | (35·46 parts) | | (36·468 parts) |

We will now consider an instance where hydrogen combines not in the simple proportion of its combining weight, but in a multiple of that proportion.

When hydrogen and oxygen are mixed together in a strong glass vessel they do not combine until the mixture is fired (as by an electric spark), when there is a slight explosion, drops of liquid afterwards condensing on the walls of the container. This liquid is water, which is thus shown to be a compound of hydrogen and oxygen. Now it is found that, when the two gases are mixed in the proportion of their combining weights, (H 1·008) and (O 16), there is always some oxygen which remains uncombined. On the other hand, when we take just a double proportion of hydrogen, that is 1·008 × 2 or 2·016 parts, and the usual 16 parts of oxygen, complete combination occurs, the whole of both gases being converted into water. When any other proportion but this is used, there is always an excess of uncombined gas. Hydrogen, therefore, combines directly with oxygen, not in the simple proportion of its combining weight, 1·008, but in the proportion of a multiple of this, that is 2·016.

As a symbol is, in the absence of any indication to the contrary, always to be associated with the combining weight, when we seek to express the above by means of an equation we place the figure 2 in front of the symbol H representing hydrogen, in order to show that a proportion equal to double the combining weight has to be taken to produce a complete combination. Thus—

| 2H | + | O | = | $H_2O$ |
|---|---|---|---|---|
| *Hydrogen* | | *Oxygen* | | *Water* |
| (2·016 parts) | | (16 parts) | | (18·016 parts) |

It will be noticed that in the formula for water the figure indicating the double proportion of hydrogen is placed after (and a little below) the symbol H, instead of in front of it. We do this because when a figure is placed in front of a symbol it affects *all* the symbols which immediately follow it, so that 2HO would mean a double combining weight of hydrogen and a double combining weight of oxygen. This would not be correct, so the figure is