

2d. Non-metallic elements present in a metallic mass may change their relation to the metallic atoms; and

3d. The atoms in the molecule of a solid metal or alloy may be redistributed or rearranged, and this is called *polymerization*.

These molecular changes are almost always accompanied by the evolution or absorption of heat, and can, therefore, be studied by the aid of thermal measurement.

The photographic records have thrown much light on all these cases of molecular change, but for the purpose of minute investigation, another mode of experimenting may be adopted.

Suppose that the spot of light from the galvanometer (Figs. 6 or 7), with which the thermo-couple is connected, does not fall through a slit on to a sensitized plate, but on to a screen placed at some distance from the galvanometer. This screen may be forty feet long, and may be suitably divided into degrees. The room must, of course, be darkened, so that the spot of light may be readily visible. The screen is fixed, and, therefore, the spot of light will traverse it horizontally, and the freezing of a metallic mass would simply be indicated by a more or less prolonged arrest of the spot of light during the solidification of the metal. Suppose, however, that it is not a question of studying the behavior of a freezing metal, but of one which, though it may be strongly heated, is still solid. Take, for instance, the case of a piece of steel of somewhat low carburization which is being slowly cooled. Here the molecular behavior is very complicated. M. Osmond and myself, and, recently, other experimenters, have studied this behavior minutely. There will be at least two arrest points, and probably three, as the pieces of steel cool from bright redness. One of these will occur at a temperature which varies slightly, but is somewhere close to 650° C., and is caused by a change in the relations between the carbon and the iron. An ordinary photographic record obtained on a plate about ten by six inches would simply show a bend in the curve of about the form and amplitude shown in the sketch (Fig. 12). If, however, it is wished to



FIG. 12.

study this particular change more fully, the following plan may be adopted: Assume that, in indicating temperatures up to a white heat, the path of the spot of light along the screen is some forty feet, then it is easy so to arrange the experiment that the spot of light may be received (at the critical part of its path which it is desired to study) on a second but smaller screen, say four feet square, which may be moved upward at a slow but uniform rate of, say, an inch a second. The spot of light from the galvanometer may be divided by the images of cross wires, and, as the point of intersection of these wires is clearly visible on the moving screen, its position at any given moment may be recorded, by hand, with a pencil mark. The result is, that the portion of the cooling curve which represents the "recalcence" of iron, instead of being a small sinuous line, shown in Fig. 12, becomes a loop four feet across, of the form shown in Fig. 13. The

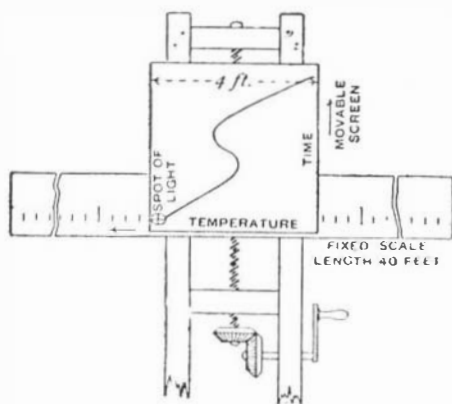


FIG. 13.

same degree of magnification may be applied at any period during the cooling of the steel, and it enables the molecular change in the iron which occurs at 855°, that is at a higher temperature than recalcence, to be submitted to a very rigorous investigation. For the purposes of lecture demonstration, it is only necessary to fix a screen of paper on a light frame, and place it like a canvas on an artist's easel, which is provided with a vertical screw for elevating the screen, but it will be evident that for purposes of delicate research some method of uniformly moving the screen could readily be devised.

It is now possible to study the behavior of alloys at high temperatures and to obtain photographic records of the molecular changes by the aid of a simple and trustworthy appliance, which is considered to afford "incontestable" results by so distinguished a pioneer in molecular research as M. Raoult.

#### THE PURIFICATION OF WATER BY PRECIPITATION AND SEDIMENTATION.

By Dr. PERCY FRANKLAND, F.R.S.

IN an interesting article on "Recent Improvements in the Manufacture of Aerated Waters," published in *Industries and Iron* on the 27th October last, reference is made to some experiments which I made some years ago\* on the remarkable bacterial purification which may be procured by agitating a water with certain substances in a fine state of division, and allowing subsidence to take place. In this manner I found for the first time that bacteria are carried down

together with the coarser suspended particles in the water. The substances I used were spongy iron, chalk, animal charcoal, vegetable charcoal, coke and other materials, the coke being especially effective, for after agitating the water for fifteen minutes with one-fiftieth of its weight of this material in a finely divided condition and allowing it to subside for forty-eight hours, the supernatant water was on one occasion absolutely sterile or did not contain a single organism.

It may interest your readers to know that I have quite recently been examining the processes and value of sedimentation, as it takes place on the large scale in waterworks reservoirs, used for the storage of more or less turbid water before submitting it to sand filtration. As these are so far the only experiments which have been made on the large or practical scale, they are of especial interest in bearing out the results which I obtained previously on a small scale in the laboratory.

The object of these reservoirs is, as every one knows, to enable some of the coarser particles in suspension to subside before running the water onto the several filter beds, so that the latter may be taxed with the minimum amount of suspended matter. Although such reservoirs have been constructed without any view to the bacterial purification of the water, this actually takes place to a very remarkable extent, as the following investigations carried out at the works of the London Water Companies show very clearly. Thus, in the first instance, the water in a large cemented reservoir belonging to the Grand Junction Company was examined. The water in this reservoir had been obtained from the Thames at Hampton, and the greater part of it had been stored for six months. Now, I have repeatedly shown in the course of the periodical examinations which I made of the London water supply for the Local Government Board, that this raw, untreated water contains sometimes as many as 92,000 bacteria in one c. c. of water, while the smallest number I have ever found is over 1,000. This reservoir water taken from two different ends of the basin contained, however, only 464 and 368 micro-organisms per c. c., showing that a most remarkable bacterial purification had taken place during the storage of this water.

The value of this process of sedimentation was even more strikingly brought out by the following investigations made at the West Middlesex and New River Companies' works respectively. The Thames water is run successively into two reservoirs at the West Middlesex works, where it remains for some time before being run onto the filter beds. The raw river water running into the reservoir on this occasion contained 1,437 bacteria per c. c.; in the water running out of this reservoir only 318 were found, while after passing through the second reservoir only 177 were present. In the case of the New River Company's water I obtained equally striking results, for, while this water (a mixture of river with spring and deep well water) contained 677 as running into the first reservoir, in that flowing out of this reservoir 560 were present, while after remaining in the second reservoir only 183 micro-organisms were found per c. c.

The hygienic importance of these results is obvious, for, should pathogenic bacteria be present at any time in the raw, untreated water, while some diminution in their numbers will take place already in the course of a river's flow, on collecting the water in these reservoirs there is additional opportunity afforded for their removal by the natural processes of sedimentation which I have shown take place to such a remarkable extent.

It is, therefore, of great importance that in the purification of all water for hygienic purposes the maximum amount of sedimentation should be allowed to take place before the processes of sand filtration or other methods of purification are resorted to.—*Industries*.

#### PLANT CHEMISTRY AND BACTERIOLOGY.

By HENRY WURTZ, Ph.D.

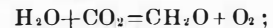
AMONG the many wondrous chemical laboratories in which Dame Nature employs herself without ceasing, those which occupy the cells of plants are in a high degree the most mysterious, inscrutable and astonishing in the results they present to us. Although some few animals secrete or excrete materials of peculiar and exceptional characters and qualities, yet the great majority of their products are very closely similar, in the main, in composition and character, when from animals under normal conditions. Their principal plastic constituents also are usually much the same. But in the vegetable kingdom we find that almost every family has its peculiar and characteristic product or products, found often in no other. Moreover, ordinary plants deal with the simplest compounds of the chemical elements of matter, and are constantly occupied in building up from these more elaborate compounds of the greatest variety and complexity, endowed with potential chemical energies great in amount and variety. These the animal, under normal conditions, is continually occupied in consuming and destroying, and reducing back again to the simplest compounds, which the plant immediately proceeds again to build up into complexity, and endow with energy, for the animal again to use up. The plant is always building beautiful structures, temples and palaces of molecules, merely that the animal may destroy and tumble them into ruins again. The plant process is one of deoxidation or decomposition, while the animal process is always one of oxidation or combustion. The plant, however, does not accomplish this decomposition and accumulation of potential energy in the products thereof, by virtue of any inherent power of its own. Plant life, in some wondrous way, directs, controls, and condenses the energies brought by the heat rays and chemical rays from the sun. With some strange exceptions, of which further on, the plant races are children of the sun.

The present writer wrote as follows on this subject in 1877: "Within the leaf of the plant resides the inscrutable vital influence which is able, with the assistance of the heat of the solar ray, to set up the most mysterious of chemical laboratories, wherein such substances as cellulose and starch (and though these sugars), with still more complex proteid bodies, are elaborated from the simple compounds, carbonic acid and water. Generations may pass away at the present

rate of progress of chemical investigation before any real insight will be gained into the chemistry of the plant leaf."

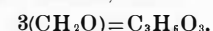
Nevertheless, the writer was not optimistic enough here. But a few years subsequent to this date, an important insight was actually gained into the way in which these plastic constituents of plants are chemically built up in the leaf cells. A German chemist, Baeyer, discovered that the process consists of two successive steps: First, and essentially, in the formation in the leaf, from the moisture and carbon dioxide of the air, of the compound *oxymethylene*,  $\text{CH}_2\text{O}$ , also called *formic aldehyde*. This is accomplished by the operation above referred to, simply by the deoxidation (or dissociation) by the energy of the solar rays of the carbon and oxygen of the carbon dioxide, commonly, but inaccurately, called "carbonic acid," of the atmosphere, under the influence of this mysterious vital influence of the plant.

The latter is thus able to transfer the energy of the sun rays to the carbon of the oxymethylene—which comes from the decomposed carbon dioxide—in the form of chemical potential energy, which would be given out again if the oxymethylene were set on fire and burned. The chemical equation of this primary transformation is thus:



free oxygen passing into the atmosphere, as we know is constantly the case, from the growing leaf. It will be seen that the other product besides the free oxygen, that is, oxymethylene, may be looked upon as virtually a compound of carbon and water,  $\text{H}_2\text{O}$ . As it is a gaseous body, which is largely soluble in water, such a solution may be looked upon as in effect a solution of carbon in water. This body, oxymethylene, considered to be formic aldehyde, thus continually being formed in the plant leaf by a natural process, may be produced artificially by passing a mixture of vapor of wood alcohol and air over a red hot helix of copper or platinum wire contained in a glass tube. Such helix may be heated by an electric current.

Second.—Like other aldehydes (with many other organic bodies) this formic aldehyde has a fashion of forming *polymeres*, so called. In this case, just as with common or acetic aldehyde, three molecules combine together into one, thus:



This triplicated molecule constituting now a *solid* body instead of a gas. Such solidification of the gaseous compound takes place spontaneously in a concentrated watery solution. Now it happens (or rather results, for nothing can be rightly said to happen in chemical transformations, all being subject to fixed laws) that by carrying this polymerization twice as far as above, which the leaf knows how to do, though we cannot yet do it, there results  $\text{C}_6\text{H}_{12}\text{O}_6$ , which is *glucose*, or fruit sugar. Then by separating from this a molecule of water,  $\text{H}_2\text{O}$  we get  $\text{C}_6\text{H}_{10}\text{O}_5$ , which is *starch*. By a second doubling up of glucose, and taking out a molecule of water, we get  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , which is *cane sugar*. By taking out another molecule of water, we get  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$ , which is *cellulose*, the main component of wood and of all plants. It may be observed that in all these cases the resulting polymere may still be regarded as a compound of carbon and water, and the energy that has come from the sun is locked up solely in the carbon atoms, which all come from the carbon dioxide gas of the air. There is no more beautiful development of chemical science than the one we have here been following up.

It is desirable here to emphasize the fact that these are developments mainly of *chemical* science. The botanists, biologists, and microscopists have, until of late, had the great fields of investigation of plant structure, with the transformations and metamorphoses that proceed in plant cells, almost wholly to themselves. The time has fully come, however, when chemistry must step in, and do what man has been endowed with the power to do, namely, to subdue this kingdom of nature. The laboratory and the microscope have indeed already begun to co-operate in earnest, and will jointly achieve discoveries which neither alone could hope to approach. At last summer's meeting of the British Association for the Advancement of Science, several papers were read by chemists of distinction relative to this subject. So many facts of interest and importance demonstrative of the necessity of applying chemical knowledge and laboratory methods to the study of microscopic and microbe vegetation, and their relations to health and disease, to life and death, that a strong impression was produced. The project was started and urged of the immediate "establishment of an institute for research where chemists, biologists and pathologists could mutually assist one another."

The work of the microscope, which has laid the foundation for the great structure of plant chemistry that is now soon to arise, has not been confined merely to the morphology, or study of the forms and minute structure, of such plants as we see around us, without microscopic aid—or rather only with that conferred on us by the Creator—the microscope and telescope combined, which gives us our limited *natural* insight into his illimitable creation. The microscope has further developed to us the existence of generations of plants, whose number baffles human speech to convey and the human mind to conceive, and whose importance to the present welfare and future destiny of the human race is greater than that of any other agency in the scheme of nature. These are the so-called bacteria.

At this last meeting referred to of the British Association, the eminent chemist, Frankland, stated that microscopic manipulations and methods had largely failed in the fundamental matter of recognition and identification, with the needed certainty, of some of the more important forms of bacterian life. This, even when aided by the chemical method, now in universal use, of staining the internal structure of these organisms by soaking them with brilliant dyes. Even in the case of the cholera bacillus or spirillum he said that much difference had been found "between different specimens as between this spirillum and totally different species."

\* "The Removal of Micro-organisms from Water." *Proc. Roy. Soc.*, 1885. *Transactions Institution Civil Engineers*, 1886.

\* "Johnson's Universal Cyclopedia," vol. 4, p. 1117. Under "Chemistry of the Vegetative Process."

He added that "morphological tests have consequently been obliged to give way to chemical and physiological tests." The chemical tests are just now undergoing investigation, some being not yet sufficiently familiar to be fully relied on. We may be sure, however, that an immense number of new tests of this class will be discovered when these subjects of investigation obtain a fair lodgment in the laboratory of the skilled chemist.

Frankland mentioned some examples already known. The cholera bacillus gives a characteristic reaction with the compound called *indol*, with which the typhoid bacillus gives none. The latter, however, coagulates milk, but will not cause the fermentation of glucose. Frankland makes the important though obvious statement that an essential to success in the chemical tests between these pathogenic fungoids is *pure culture*, that is, the culture of each germ by itself, without admixture with the others. The special ptomaines, ferments, or bases to animal vitality, which some of them engender, will doubtless each be found to have its characteristic chemical reactions, when obtained free from others. Experiment has shown also that the culture of the same bacterium, when alone, in differing media, will in many cases give identical products. There are classes which contain species identical under the microscope, and which can only be distinguished now by determining which of them is the morbid one, through actual experiments on animals. Further knowledge will give us chemical means of detecting which of these produces the deadly ferment. One of this kind is the *anthrax* bacillus, the cause of terrible diseases. Frankland also lays stress upon what he calls "educational culture"—modifications of the nature of the baneful fungoids, by culture in special media, so that they no longer produce the poison, just as we know that other plants may be essentially modified, in color, odor, taste, magnitude, and even in animal digestibility, by special cultivation. One point is especially important, if confirmed further; namely, that while the poisonous bacilli may be made harmless by cultural variations, none of the harmless ones have been yet found to become poisonous. Frankland discussed also the effects of sunlight, peroxide of hydrogen and other bactericidal agents; and the necessity that bacteriologists should acquire a profound knowledge of chemistry and of laboratory methods, while the chemist should, *vice versa*, become also a botanist and a biologist.

At this same meeting a most important paper was read by another distinguished British chemist, Warrington, mainly on an important branch of the same subject, possessing special interest, and to which a number of chemists have already given extensive research. This is now beginning to bear fruit. It relates to the property known to be possessed by the most abundant bacteria, of producing directly from decaying nitrogenous materials the dioxide and trioxide of nitrogen, the essential components of the nitrites and nitrates.

All the *ptomaines*, or corpsealkaloids, so far as known, all the *toxalbumens*, as a matter of course, and furthermore, in all probability, the serpent poisons, and blood poisons generally, are nitrogen compounds.

Bacteria, therefore, those at least of the non-morbid kinds (which of course make up the great mass of them, most of the morbid or pathogenic species being comparatively rare) are actual scavengers, and do good work in destroying the corpses of animals, which would otherwise, in time, have encumbered the earth. It is because the germs of these organisms are diffused in almost infinite numbers throughout all soils that corpses buried in the earth so rapidly decay and become inoffensive.

It has recently been discovered also, that although sea water is almost destitute of bacterian germs, yet the floor of the ocean is loaded with them. Russel found in mud from the Mediterranean, at 164 feet depth, 245,000 microbes in a cubic centimeter, and in mud from Buzzard's Bay, Mass., 30,000 per cubic centimeter.\* Also large numbers in mud from the Gulf Stream, 100 miles from shore and 600 feet depth.

Warrington states that to bring the nitrogen of dead animal matter fully up to the point of complete oxidation to nitrogen trioxide, requires the successive agencies of more than one distinct tribe of bacteria. The process of nitrification, so far as yet known, begins with ammonia, though it seems probable that even this will yet be found to be itself a product of a special bacterium. One class of microbes has the property of oxidizing the nitrogen of such ammonia to nitrites, or dioxide compounds, but cannot carry it any further. Another class now takes the task in hand and converts the nitrites into nitrates. Neither of these can perform the function of the other.

The nitrate-making bacterium can make nitrates only from nitrites and not from ammonia directly, and the nitrite-making organism cannot make nitrates, either from nitrites or from ammonia. As the germs of both of these tribes usually occur together in soils and waters, nitrites seldom appear, nitrates being usually found.

Warrington announces, moreover, on the authority of another bacteriologist, Winogradsky, a most extraordinary new fact, if fact it be. Namely, that the latter has found a bacterium which engenders nitrates from the nitrogen of the air. This, he says, will grow and accumulate nitrogen in a solution of pure sugar, with phosphates and sulphates of lime and magnesia, without any nitrogenous pabulum. The sugar is converted into butyric acid. This would confirm the assertions of Ville and others, who have claimed that plants get nitrogen from the atmosphere in some way.

#### ARTIFICIAL INDIGO.

TAKING a retrospect of the general position of the industry which uses as its primary materials benzol and other aromatic hydrocarbons, and builds up from these more complex compounds which find their principal use either in the form of intermediary products or as coloring matters or medicinal preparations, we may consider the results as, on the whole, satisfactory. Manufacturers of coal tar derivatives have been fully employed. The demand has been constantly increasing, and the introduction of new products and the cheapening of the methods used in the production of

already established articles have fully compensated for lower prices, and it is certainly most satisfactory to note that this country has participated, if only yet to a modest extent, in the development of this important industry. A large number of patents has again been applied for during the past twelve months, of which the greater part deals with improvements on old or substitutes for existing colors, but there is nothing of an exceptional character to report. I cannot, however, pass from this subject without calling attention to the continued efforts which have been and are being made by chemists to further improve the methods for the production of artificial indigo, which so far possessed only a scientific value, for the reason that this country has a twofold interest in this question. In the first place, we are the principal producers of natural indigo, the annual outturn of which represents a value of about four millions sterling; and, secondly, we are one of the largest, if not the largest, consumers of this coloring matter.

It is now several years since Prof. Bayer made the startling discovery of the synthetical production of one of the most important coloring matters hitherto solely supplied by the agency of nature. The first patent taken out in the name of the professor for the production of artificial indigo was in 1880, then followed a number of patents in rapid succession from 1880 to 1884, having as their primary material either orthocinnamic acid or its homologues or products of substitution. Considerable sums were spent during these years with the object of perfecting the technical methods, and reducing the cost of the necessary intermediate products, but all these efforts were in vain, and artificial indigo remained so far more a chemical curiosity than anything else, except perhaps the very limited use of the orthonitrophenylpropionic acid.

Little was heard of it by the outside world for some time until attention was again directed to it by Prof. Heuman's beautiful discovery in 1890, which I had an opportunity of illustrating by experiment shortly after, on the occasion of addressing the chemical students at the opening of the session of the Manchester Technical School. Heuman's discovery in the production of artificial indigo proceeded on different lines from those first followed by Bayer, and afterward by others. Heuman heats phenylglycine with caustic alkalis at about 260° C., when indigo white is the result, which may then readily be oxidized to indigo blue. Here again, unfortunately, notwithstanding the great simplicity of the process, the large destruction of the principal raw material made this process also too expensive for trade purposes.

With all these negative results, so far as the profitability of the various processes is concerned, chemists have persevered in their efforts to solve the great problem which offers so great a prize, and I will now illustrate a process which might almost be called an extension of Heuman's discovery. In December, 1890, the Farbenfabriken, of Elberfeld, discovered that when phenylglycine is treated with anhydrous sulphuric acid, an oxidation accompanied by an evolution of sulphurous acid takes place, converting almost instantaneously phenylglycine into indigo sulpho-acid or indigo carmine. I have here some phenylglycine (produced by the action of mono-chloroacetic acid on aniline) which has been ground up with twenty times its weight of sand in order to moderate the reaction. I now put some of this into a large excess of 70 per cent. anhydrous sulphuric acid. You will notice a yellow coloration, which already indicates the formation of artificial indigo, but in order to make the real color appear it will be necessary to remove the anhydrous acid (SO<sub>3</sub>) by absorbing it in a large quantity of ordinary sulphuric acid, when you will notice an intense blue coloring matter. I am now pouring this blue acid solution on a block of ice, when the characteristic color of indigo carmine will be more easily perceptible to the eye and we will dye some woollen cloth with this solution after first neutralizing the excess of acid contained therein.

In the year 1882 the Badische Anilin und Soda Fabrik patented a process for manufacturing artificial indigo by treating the solution of ortho-nitrobenzaldehyde in acetone with alkali. Bayer and Drewsen in the same year further investigated this reaction, and they found that when nitrobenzaldehyde in presence of acetone is treated with very diluted alkali that first a product of condensation is formed, viz., the orthonitrophenyllactoketone, which on further treatment with alkali is instantly converted into indigo. I have here some orthonitrobenzaldehyde, and am now dissolving it in acetone. We will add to it some water, and put to it a few drops of a caustic soda solution: the ketone is first formed, which you will see will be almost immediately converted into artificial indigo on adding a little more of the alkali solution. This reaction, simple as it appears in its execution, was also doomed to failure, on account of its costliness, notwithstanding Eugene Fischer's process, patented in 1888, for a cheaper method of producing orthonitrobenzaldehyde from orthonitrobenzyl-chloride.

It was, moreover, impracticable to apply the ketone direct to yarn or cloth and then develop the indigo blue direct on the fiber, on account of its comparatively small solubility in water. Some of these difficulties in the way of the practical application of Bayer and Drewsen's discovery have now been overcome by Kalle & Co., of Biebrich, and though their process may not so far be cheap enough to produce indigo direct, the development of indigo in the fiber appears to me likely to find some application in the arts, on account of the superiority of the shades produced, and the greater resistance to light of the lighter shades, and for the reason that new effects can be obtained by it in printing which would be difficult to produce by following the old process, always provided that means be found to reduce the strength of the caustic soda solution which the patentees specify as being necessary for developing the indigo, as a solution of 21° Be., as recommended by the patentees, mercerizes the cotton.

A few months ago Messrs. Kalle & Co. found that when Bayer and Drewsen's ketone is treated with bisulphite of soda, the bisulphite compound of the ketone is formed, viz., the orthonitrophenyllactoketone bisulphite, and this compound has the great advantage over Bayer and Drewsen's of being easily soluble in water, and hence can readily be applied to the fiber;

moreover, to obtain the ketone in a pure state by Bayer and Drewsen's method is more costly. I have here the bisulphite ketone; we will dissolve some of it in water, when you will at once observe its conversion into indigo on the addition of a diluted caustic solution. I will now illustrate the application of this compound to the production of indigo shades on the fiber.

This hank of cotton yarn we will pass several times through a solution of the ketone; squeeze it and then take it through a caustic soda solution, when it will be dyed a deep indigo blue. I have also here some cloth that has been prepared by printing upon it a solution of the ketone thickened with dextrin. We will now pass it through caustic soda, when the cloth which was previously practically colorless will be colored indigo blue in all parts which had been impregnated with the ketone.—Ivan Levinstein, in *Journal Society Chemical Industry*.

#### THE

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