INTRODUCTION.

THE METHOD OF THE INDUCTIVE SCIENCES. OBSERVATION, GENERALISATION AND LAW. HYPOTHESIS AND THEORY.

"*The footsteps of Nature are to be trac'd, not only in her* ordinary course, *but when she seems to be put to her shifts, to make many* doublings *and* turnings, *and to use some kind of art in endeavouring to avoid our discovery.*"

HOOKE, *Micrographia*, 1665.

The scope of the Natural Sciences.

THE object of all the Natural Sciences is the acquisition of knowledge concerning the natural objects surrounding us, as we apprehend them by our senses; of the changes occurring in these objects, together with the laws governing these changes; and of the more proximate or more ultimate causes, to the operation of which are due the individual phenomena and the general laws comprising these. The method now commonly employed for this object is that of proceeding from the observation and the study of the individual phenomena to the detection of uniformities in these, that is, to the law; from that which refers to one to that which refers to many; from the special to the general, by the process termed *Induction*. And the knowledge thus acquired is next utilised in the inverse process, in which from the general laws obtained by induction, inferences are drawn for the purpose of explaining the observed phenomena and of foretelling the occurrence of others. This process, termed *Deduction*, proceeds on the principle that what is asserted to be true of all similar phenomena of a special kind will also be true of any one individually; it argues from the many to the one; from the general to the special. But the inferences thus drawn according to the laws of thought are again checked and verified by appeal to the actual facts, by the study of the phenomena the course of which deduction foretells; and exact coincidence between what actually happens and what had been foretold theoretically, is made the test for the correctness of the inductive and deductive processes by which these inferences had been arrived at.

The province of Chemistry.

Knowledge of the objects surrounding us has been stated to be the common object of all natural sciences. But as knowledge grew, the need for classification and specialisation became evident, and thus there arose a division between the sciences, in which Chemistry has taken for its province one side of the study of the materials of which these objects are composed. Leaving Physics, the science most closely related to it, to investigate the properties common to all kinds of matter and differing only in degree, such as density, power of conducting an electric current, etc., Chemistry deals with the properties which belong to certain kinds of matter and not to others, which characterise one kind of matter and differentiate it from all other matter.

For instance, it is a common property of all kinds of matter to undergo change in volume on the application of heat, but each substance has its own characteristic coefficient of expansion; on the other hand it is a specific property of the solid called red precipitate, that above a certain temperature the further addition of heat transforms it into liquid mercury and gaseous oxygen.

A not uncommon description of Chemistry as "the science dealing with the study of all the different homogeneous kinds of matter met with in nature, and with the permanent changes these can undergo when transformed into other kinds of matter" gives the basis for the usual subdivision of this science into two parts, (I.) descriptive and classificatory, (II.) theoretical. Of these the first has to do with the investigation of the properties peculiar to each of the different kinds of matter, and the classification of all matter according to these properties; that is, the putting together of those kinds of matter which agree in having in common a greater or lesser number of properties, and the separation of these from all the other kinds of matter which do not possess those particular properties. The second is mainly concerned with the facts and laws observed in the study of chemical change, and of the composition of the substances undergoing or resulting from the change.

Thus theoretical chemistry has to deal with two kinds of problems: (i) with those which relate to the changes that matter can undergo, and to the laws regulating these changes; and since change can only be realised by a comparison of the initial and the final condition, (ii) with those referring to its composition. Function and composition are therefore the two kinds of phenomena studied in theoretical chemistry. Mechanical analogies are dangerous, but the comparison of these two aspects of theoretical chemistry to dynamics and statics respectively may be ventured on because it has at any rate become justified by long-established use. To keep these two sets of problems completely separate would be very difficult and unsatisfactory, whatever the form chosen for the presentation of the subject, but when that of the historical development is adopted it becomes practically impossible. And hence, though the subject of this book is professedly the theoretical chemistry of composition, the discussion of dynamical problems cannot and will not be altogether excluded.

Theoretical Chemistry deals with problems referring to function and composition.

The general remarks made at the outset concerning the method now followed in the building up of the Natural Sciences apply of course in every detail to the special case of theoretical chemistry. But before showing how this method has operated in the development of this particular branch of science, it may be advisable to discuss separately the processes involved, their sequence and interdependence.

The Method of the Natural Sciences.

The beginning is made by the recognition of individual phenomena, leading to what is called the knowledge of facts. This knowledge may be gained either by direct observation of the phenomena occurring in nature, or of those which have been caused by some act undertaken by ourselves for that purpose. "Observation" and "Experiment" are the names given to these two modes of collecting knowledge of facts.

I. The study of facts by observation and experiment.

"When we merely note and record the phenomena which occur around us in the ordinary course of nature we are said to *observe*. When we change the course of nature by the intervention of our will and muscular powers, and thus produce unusual combinations and conditions of phenomena, we are said to *experiment*. Sir John Herschel has justly remarked that we might properly call these two modes of experience 'passive' and 'active' observation—an experiment differs from a mere observation in the fact that we more or less influence the character of the events which we observe." (Jevons, *Principles of Science*.)

The different behaviour of iron, which rusts in air, and of gold, which remains unchanged, had no doubt been observed as a natural occurrence long before experiments were performed in which these metals were exposed to the influence of heat, of water, of acids, etc., and the comparative effect produced on them by these various agents noted. Important and valuable as is the observation of naturally occurring phenomena, yet for the advance of science, experiment is paramount.

"When Galileo let balls of a particular weight, which he had determined himself, roll down an inclined plane; or when Torricelli made the air carry a weight, which he had previously determined to be equal to that of a certain column of water; when at a still later stage Stahl changed metal into calx, and calx back again into metal, by first withdrawing something and then restoring it; then a new light was flashed on all students of nature....Reason, holding in one hand its principles according to which concordant phenomena alone can be admitted as laws of nature, and in the other hand the experiment which it has devised according to those principles, must approach nature for instruction; but not as a pupil, to be taught just what the master pleases, but as a judge, who forces the witnesses to answer the questions he puts to them....Thus after many centuries of groping, the study of nature was first made to walk along the sure path of a science." (Kant's *Critique of Pure Reason*, Second Preface.)

Before they can become material for the building up of a science, it is essential that the occurrences themselves should be correctly apprehended, and that the relation between an effect observed and that which caused it should be ascertained.

"In order that the facts obtained by observation and experiment may be capable of being used in furtherance of our exact and solid knowledge, they must be apprehended and analysed according to some Conceptions which, applied for this purpose, give distinct and definite results, such as can be steadily taken hold of and reasoned from." (Whewell, *Philosophy of the Inductive Sciences*.)

To illustrate the two distinct points involved in the above:

The facts observed must be correct.

We all have heard about the sea-serpent, but should not find anything about such an animal in a treatise on zoology, and that because the tales concerning it cannot be looked upon as trustworthy evidence. No doubt there is a great difference in the number of occurrences reported to the Society for Psychical Research and that used by it as the basis of its work. And to give a chemical example: Regnault had by the action of caustic potash on ethylene chloride (a substance consisting of carbon, hydrogen, and chlorine, and prepared by the direct union of olefiant gas and chlorine) obtained a new substance differing from the parent one in that the elements of hydrochloric acid had been withdrawn, but still containing carbon, hydrogen, and chlorine. This substance was termed vinyl-chloride[1], and at one time it was of the utmost interest to chemists to establish beyond doubt whether another substance having a percentage composition identical with that of Regnault's compound but different properties, did or did not exist. It was maintained by certain chemists that by an altogether different process they had obtained a substance having the percentage composition of vinyl-chloride but entirely different properties[2]. The experiments relating to the production of this substance were repeated by Kekulé and Zincke, who found "that the most remarkable property of this remarkable compound was its non-existence." (Schorlemmer, *Rise and Development of Organic Chemistry.*)

The facts observed must be traced to their causes.

And if caution is required as to what should and what should not be accepted as "facts," it is none the less so as regards the relation between causes and effects. A certain effect undoubtedly does occur, but what has been its real cause? The correct correlation may be a matter of considerable difficulty, because the conditions under which a certain effect is observed to occur are always very complex; a large number of these may be effective at the same time, and it does not follow that those which are most easily apprehended are also those which are really determinant. The correct solution of such a problem, though relating to one fact only, the referring of an effect observed to the real cause producing it, involves the same mental and experimental processes, and the same sequence of these, as does the treatment of a whole collection of facts; and hence a detailed consideration of some such typical cases becomes important. A short account will therefore be given of certain investigations, undertaken with the object of assigning to a phenomenon observed its true cause, from which will be deduced the general method followed in all such cases.

[1] $\underset{\text{ethylene chloride}}{C_2H_4Cl_2} + KOH = \underset{\text{vinyl chloride}}{C_2H_3Cl} + KCl + H_2O$

[2] $\underset{\text{aldehyde + phosgene}}{C_2H_4O + COCl_2} = C_2H_3Cl + CO_2 + HCl$

$\downarrow$ supposed different compound, proved to be a mixture of aldehyde and phosgene.

Illustrations of the method followed in tracing the cause of an experimentally established fact. (*a*) Lavoisier on the change of water to earth.

In 1770, very early in his career, Lavoisier presented to the Académie des Sciences a paper entitled "On the Nature of Water and on the Experiments adduced in Proof of the Possibility of its Change into Earth[1]." This paper exhibits as well as any of his later ones the peculiar characteristics of Lavoisier's method and style, that is, it is marked by the display of extraordinary genius. Lavoisier thus enunciates the object of the investigation:

"I find myself confronted with the task of settling by decisive experiments a question of interest in physics, namely, whether water can be changed into earth, as was thought by the old philosophers, and still is thought by some chemists of the day."

He begins by investigating whether the fact stated is correct, whether earth (solid matter) is really produced in an operation in which, at any rate apparently, water plays the determining part. This fact he finds vouched for historically. Plants had been made to grow, deriving their increase in weight seemingly only from the water supplied to them. Van Helmont had planted a willow weighing 5 lbs. in 200 lbs. of earth thoroughly dried before weighing, then moistened with distilled water, and always fed with such water only. A suitable hood kept out dust, and after five years the willow was found to weigh 169 lbs. and 3 ozs., whilst the earth after again being dried and then weighed, had lost 2 ozs. only. Hence 164 lbs. of willow were assumed to have been produced from water only. Similar experiments seemed very popular and they all led to the same inference. But still more to the point were the observations of Boyle, Becher, Stahl and others, all of whom had found as the result of experiment that water, no matter how often it had been distilled previously,—that is, made to undergo an operation in which the gasifiable water could be separated from any non-volatile solid held by it in solution—yet left on evaporation an earthy residue. But Lavoisier is not content to simply accept the fact; he repeats the experiment and finds that in distilling rain water, a very pure form of water, from a glass vessel, he obtains an earthy residue; and he at once goes further, ascertaining a fact well calculated to throw some light on the cause of the phenomenon investigated. He compares the

[1] *Œuvres*, II. (p. 1).

density of the distillate with that of the original rain water and finds it practically identical:

"I thought that I might infer from this experiment one of two things, either that the earth which I had separated by the distillation was of such a nature that it could be held in solution in the water without increasing its density, or at least without increasing it as much as other substances would do; or else that this earth was not yet in the water when I had determined its density, that it had been formed during distillation, in short that it was a product of the operation. To decide with certainty which of these views I should adopt, no means has seemed to me more suitable than to repeat precisely the same experiment in hermetically sealed vessels, keeping exact count of the weight of the vessel and of that of the water used in the experiment.

For if it should be a case of the fire matter passing through the glass and combining with the water, there must needs occur after many distillations an increase in the total weight of the matter, that is to say, in the combined weight of the water, the earth and the vessel. The same thing should not occur if the earth had been formed at the expense of the water or of the vessel; but if so, there must needs also be found a diminution in the weight of one or the other of these two substances, and this diminution must be exactly equal to the quantity of earth separated."

Here then we find Lavoisier enumerating the various possible causes for the formation of the earth, and in each case drawing the inference as to what would be the influence of the operation of this particular cause on the weights of the whole system and of its component parts. The paragraph just quoted, when cast into tabular form, would present itself thus:

Earth is formed by the repeated distillation of water in a hermetically sealed glass vessel

cause:	the earth has its origin in something external to the vessel and its contents	the earth has its origin in the vessel and its contents themselves
inference:	as the earth forms, the weight of the vessel and its contents should increase.	as the earth forms, the weight of the vessel and its contents should remain the same.

cause:	the earth comes from the vessel	the earth comes from the water	the earth comes from the vessel and the water
inference:	the vessel loses weight, and this loss is exactly equal to the weight of earth formed.	the weight of the vessel remains the same.	the vessel loses weight, but not to the extent of the weight of earth formed.

It is evident then what quantities must be determined experimentally, in order to settle to which of these theoretical inferences the actually occurring phenomenon corresponds, and hence what is the cause sought for.

A special glass vessel termed a pelican, the use of which for repeated distillation goes back to alchemical times, was employed.

"A pelican is a flask devised for the circulation, the rising and falling back, of liquids, and therefore adapted for distillation, for which purpose it is provided with handle-like tubes reaching almost to the top, and curving back into the sides, like a pelican plucking at its own breast. The lower bulb is the larger of the two, and communicates with the neck, which terminates in a small top with an opening. But of this vessel also there are very many different varieties[1]."

John French in *The Art of Distillation*, 1650, gives this illustration: Form of a Pelican.

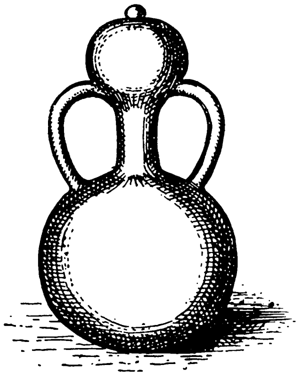

Fig. 1.

"The matter must be put in at the top, which afterwards must be closed up."

The pelican was weighed empty in a balance specially constructed for the purpose, and surpassing in sensitiveness the instruments of that time. A certain amount of water purified by repeated distillation was introduced into the pelican, the whole heated gently on a sand-bath, and the stopper closing the vessel lifted from time to time to allow the air to escape. As soon as it could be assumed that all the air had been expelled, the stopper was fixed in securely and the pelican with the water contained in it weighed. The whole apparatus was then surrounded by sand, and heating was begun on October 24th, 1768; for 25 days no change was noticed, on December 20th solid particles were observed floating about, the quantity of these was seen to increase until on February 1st, 1769, the experiment was stopped, lest by some accident the results of this long operation should be lost. The whole apparatus was then weighed again. The values obtained in the different weighings were:

[1] "Pelecanus est ampulla circulatoria, ascensui descensuiq.; atque ita vario discursui spirituum apta, cuius gratia ansata est canalibus, prope caput productis, et in latus reflexis, instar pelicani pectus suum fodientis. Venter inferius grandior est; inde quasi in collum coit, cui caput paruum cum foramine impositum est, quamquam etiam in hac vase mira sit varietas." (Libavius, *Alchymia*, 1595.)

	Livres	Onces	Gros	Grains[1]
Weight before heating on Oct. 24, 1768, of the empty pelican	1	10	7	21·50
Weight before heating on Oct. 24, 1768, of the pelican and water	5	9	4	41·50
∴ Weight of the water	3	14	5	20·00
Weight after heating from Oct. 24 to Feb. 1st, of the pelican, water and earth	5	9	4	41·75
∴ Change in weight	0	0	0	0·25

"The weight at the end differs only by one quarter of a grain[2] from that determined before the operation; but so trifling a difference can be neglected because the accuracy of the balance is not great enough to allow me to answer for so small a quantity.......From the fact that no increase had been found in the total weight of the matter, it was natural to conclude that it was not fire matter, nor any other extraneous body, that had penetrated the substance of the glass and combined with the water to form the earth. It remained to determine whether the earth owed its origin to a destruction of a portion of the water, or of the glass; and nothing was easier. With the precautions I had taken it was only a case of determining whether it was the weight of the vessel or that of the water contained in it that had suffered diminution."

The pelican was next unstoppered, a process attended with difficulty, and thereby affording conclusive proof that the vessel had been securely closed, no air having been able to leak in. It was emptied, and the water, together with the solid suspended in it, carefully preserved in a glass vessel. The empty pelican was weighed with the following results:

	Livres	Onces	Gros	Grains
Weight of the vessel in which water had been distilled 100 days	1	10	7	4·12
Original weight of the vessel	1	10	7	21·50
∴ Loss of weight sustained by the vessel ...	0	0	0	17·38

"Therefore it was clearly shown that it was the substance of the glass itself which had supplied the earth separated from the water during the digestion, that what had happened was merely a solution of the glass; but in order to completely accomplish my object, it still remained for me to compare the weight of the earth which had separated from the water during the digestion, with the diminution in weight sustained by the pelican. These two quantities should of course be equal, and if there had been found a considerable excess in the earth, it would have become necessary to conclude from it that it had not been furnished by the glass alone."

[1] Old French measures: 1 livre = 16 onces à 8 gros à 72 grains;
1 livre = 489·5058 grams; 1 once = 30·59 grams; 1 grain = 0·053 gram.

[2] 1 quarter grain = ·013 gram.

The weight of this earth was ascertained by adding together the weight of the solid actually suspended in the water, and that obtained from the water by evaporating it in another glass vessel.

Weight of earth	20·40 grains
Loss of weight of the pelican	17·38 „
Difference	3 „

"But the diminution in weight of the pelican was only $17\frac{4}{10}$ grains, and hence there is an excess of three grains in the weight of the earth which cannot be attributed to the solution of the particles of the pelican. A little reflection on the conditions of the operation will however make it easy to see what is the origin of this excess, and how indeed it was a necessity of the case. It will have been noted that on removal from the pelican, the water had been poured into a glass vessel, and that it had afterwards been transferred for evaporation to a glass retort. But these different operations could not have been accomplished without solution of a small portion of the substance of these two vessels."

He concludes, "It follows from the experiments described in this memoir that the greater part, possibly the whole, of the earth separated from rain water by evaporation, is due to the solution of the vessels in which it has been collected and evaporated."

(b) Davy on the acid and alkali produced in the electrolysis of water.

In the Bakerian Lecture given by Sir H. Davy before the Royal Society in 1806, the subject of which was, "On Some Chemical Agencies of Electricity[1]," is found an investigation concerning the products of the electrolysis of water. Besides hydrogen and oxygen there are also formed acid and alkali. Davy states this as a fact:

"The appearance of acid and alkaline matter in water acted on by a current of electricity at the opposite electrified metallic surfaces, was observed in the first chemical experiments made with the column of Volta."

The fact itself was therefore well established; it had been observed by Davy himself, as well as by other investigators. The problem requiring solution was, to ascertain whether the acid and alkali were derived from the water, and if they were not, whence they came. In pre-Lavoisierean times the action of the electric current itself might have been looked upon as a possible generating cause, but the day for such interpretations had gone. Davy, in his attempt to settle this question, had to make other plausible hypotheses for explaining the fact observed. He had to pass in review all the possible guesses as to the cause of the

[1] London, *Phil. Trans. R. Soc.* 1807 (p. 1).