THE OBJECTIVE CAUSE OF SENSATION.—

PART. III. THE SENSE OF SMELL.

BY PROF. JOHN BERRY HAYCRAFT.

THE end-organs of the special senses are all built up on the same type. The history of their development from simple ectodermic cells suggests that similar agencies have been at work to produce them. Both sapid and odorous substances, and indeed all gaseous and liquid molecules, are now known to be in constant vibration, and this vibration is more or less characteristic of the substance examined.

The above considerations have led me, for the last five years, to teach that, in all probability, it will be possible to connect *quality* of taste and smell with the *kind* of vibrating stimulus, and that it will be possible to demonstrate, as has already been done in the case of sight and hearing, the truth of this general statement—that quality of sensation will depend (the sensorium being in a normal condition) upon the kind or character of the vibrating stimulus. There is nothing very new in this idea. Without seeking for its germs at an earlier period, we find it clearly enunciated by both Hobbes and Hartley; and in more recent times Mr. Herbert Spencer has lent the weight of his great authority in the same direction. But of experimental proof, without which we cannot rest content, nothing has been advanced. Casual allusions to the probable or possible relationship between the tastes or smells of bodies and their chemical natures, are sometimes though rarely found in the text-books of physiologists, but nothing more. While so much important work has been carried on during the last few years by Helmholtz, Preyer, Maxwell, Rayleigh, and others, in connection with both sound and sight, no one, until quite

recently, has turned his attention to the investigation of either taste or smell.

In a most interesting and suggestive article in 'Nature' (June 22, 1882), Prof. Ramsay brought forward many facts tending to demonstrate the dependence of *smell* upon the vibratory motion of odorous particles. He drew attention to the fact, that many gases and vapours of low specific gravity—their molecules vibrating therefore with great rapidity—are perfectly odourless, and he saw in this an analogy to the rapid vibrations of the ultra-violet rays of the spectrum, and the rapid vibrations of an insect's wing, both incapable of producing any impression on the eye and ear. He also described classes of substances alike in chemical and physical properties, such as the alcohols or fatty acids, as having generic smells; the higher members of the groups producing sensations more powerful and characteristic than those of the lower ones. It will be my endeavour in the present paper to extend more fully this inquiry, and to demonstrate by experimental methods the fact that smell, like sight and hearing, depends for its production on the vibrations of the stimulating medium, the quality of the sensation depending, in all cases, upon the kind of vibration which produces it.

In a paper read before the British Association in 1885, and printed subsequently in the 'Proceedings of the Royal Society of Edinburgh' (1886), I was able clearly to demonstrate these points for the sense of taste. That paper and the present one will be found to run on exactly parallel lines; one is almost a recapitulation of the other, for what is true of taste is also true of smell. In order to avoid unnecessary recapitulation, I have touched lightly on many questions more fully discussed in the other paper, which should therefore be consulted.

An investigation into the odorous properties of substances is to a certain extent limited, as many of them are without smell, especially those found in the inorganic world. In a description of odours one is met with this difficulty, that there is no nomenclature familiar to every one. Hundreds of terms expressing the well-known colours of familiar objects, enable one to describe by a single term almost any tint and shade. We have cardinal, rose, magenta, maroon, carmine, crimson

scarlet, and a dozen other shades of red alone, and all of these can be expressed by words. The smells, however, and especially those of the chemist's museum, are so unfamiliar, and often so peculiar, that we are forced to speak of them simply as the odours of the substances which produce them, or to say that they are like, though seldom identical, with that of some other and better known substance.

No two observers quite agree in their descriptions of a given odour, and the information readily at hand in the text-books, but culled from a hundred sources, is therefore not reliable. I have, for this reason, availed myself freely of the kindness of Prof. Tilden and my friend Prof. Ramsay, who have placed at my disposal their private collections of chemical compounds. In almost every case the description of a smell given in this paper is derived from personal observation.

In the first place, let us study those few substances found among inorganic compounds which have distinct smells. It is well known that many substances, like arsenic, chlorine, sulphur, bromine, and their compounds, have characteristic odours. Can we associate the odours of these substances with any chemical or physical properties they may possess, and show that when similar odours are produced by two or more substances, then we have some similar chemical or physical property present at the same time?

In recent years a remarkable discovery of Newlands has opened up a fresh point of departure in the science of chemico-physics. His observations led him to formulate a law which he termed the law of octaves. Lothar Meyer, Mendelejeff, and Carnelley, extending his work, have shown that the "periodic-law," as it is now called, is one of vast application and importance. The nature of this periodic-law is now so well known, thanks to the many recent publications of Professor Carnelley, that it would be superfluous to attempt more than roughly to sketch out its main features. If we arrange the elements in the order of their atomic weights, beginning with that which has the lowest, and passing to that which has the highest, we shall find a periodic recurrence of property or function in the series. The first element is a monad, the second a dyad, the third a triad, and the fourth a

tetrad. Then we find the fifth a triad, the sixth a dyad, and the seventh once more a monad. Then follows a second series of seven elements, showing the same variation in atomicity; this repeats itself right through the list of elements. This periodic recurrence of function is seen not only in the case of atomicity, but it may also be observed in the atomic volumes, the fusibility and the electrical and other properties of the elements. There is then a general resemblance in physical properties between the first, eighth, fifteenth, &c., and between the second, ninth, and sixteenth elements. Mendelejeff has arranged the elements in the convenient tabular form given on the opposite page, which indicates these and some other important facts.

Those elements which resemble one another, and which we can pick out by taking every eighth one from that other from which we elect to start, form what he calls a "group," and are arranged vertically. The sets of seven elements each, arranged horizontally, form twelve "series."

There is yet another point of importance. The elements of a "group," which are in an even "series," are especially related to one another; so in like manner elements in an old series of the same group are similarly allied. Thus Li, Na, K, Cu, Rb, Ag, Cs, Au, have all these properties in common; but in this group Na, Cu, Ag, Au are most alike, and Li, K, Rb, and Cs, in like manner, are most closely related.

In the paper to which I have already alluded, I was able to demonstrate the fact, that elements in the same group are capable of producing similar or related tastes. The power of producing a given taste is then a property which, like the ordinary physical qualities of the elements, follows the periodic law. As will now be shown, the same obtains for smell.

In studying the facts of the case, let us start with Group VI. We find here, in odd series, three well-known substances whose compounds have strong and characteristic odours. Sulphuretted, seleniatted, and telluretted hydrogen have all a disagreeable odour, like that of rotten eggs. The compounds

TABLE OF NATURAL CLASSIFICATION OF ELEMENTS—*After Mendeleeff.*

Groups.	I.	II.	III.	IV.	V.	VI.	VII.	Group VIII.
Series.	Monads.	Dyads.	Triads.	Tetrads.	Triads or Pentads.	Dyads or Hexads.	Monads or Heptads.	
1.	H = 1	...	...	...	...	...	...	Fe=56. Co=59. Ni=59. Ru=104. Rh=104. Pd=106. Os=193. Ir=193. Pt=195.
2.	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19	
3.	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4.	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 53	Mn = 55	
5.	Cu = 63	Zn = 65	Ga = 69	...	As = 75	Se = 79	Br = 80	
6.	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96	...	
7.	Ag = 108	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 125	I = 127	
8.	Cs = 133	Ba = 137	La = 139	Ce = 142	Di = 147	...	...	
9.	..	...	...	...	Er = 166	...	...	
10.	...	...	Yb = 173	...	Ta = 182	W = 184	...	
11.	Au = 197	Hg = 200	Tl = 204	Pb = 207	Bi = 210	...	...	
12.	...	...	...	Th = 234	...	U = 240	...	

of the elements of this group with methyl and ethyl are disagreeable and alliaceous. In Group VII. chlorine, bromine, and iodine have very similar smells, and so have the acids they form with hydrogen, and their compounds with methyl, ethyl, ethylene, &c. Although similar in all cases, yet they are not the same. One can distinguish the odour of iodine from that of bromine or chlorine. It may be described as having more flavour, and not so chlorous. Bromine is like them both, having an odour intermediate between the two in quality. From a study of the above substances, this is seen to hold good in all cases, the odour uniformly changing, often to a slight degree, as we pass from the lowest to the highest member of a group. A very marked change is seen in the formyle compounds of Group VII. Chloroform has a fragrant and characteristic smell. So has bromoform, but it has something else in addition, which is recognised as being the odour of iodoform. Bromoform thus connects chloroform and iodoform, these latter substances being very unlike one another.

There may then be so little difference in the odours of compounds of the same group of elements that they may with difficulty be distinguished. On the other hand, the differences may be great, there being intermediate sensations produced by intermediate members of the group. One is forcibly reminded of the changes in sensation experienced in allowing the eye to traverse the spectrum from one end towards the other. In a drawn-out spectrum, only a part of which is visible, one passes, say, from orange into yellow, and these colours are recognised as being different, and at the same time alike. In a shorter spectrum the eye may pass from the yellow into the red. The two sensations are quite different, but the orange is seen to connect them. The importance of the above statements—and they may be verified in the case of the few odorous compounds in Group V.—will become apparent when they are placed in juxtaposition with identical facts mentioned in the previous paper on taste, and some recent observations of Professor Carnelley.

In those groups of elements whose compounds are sapid, we find that the same change in taste sensation is apparent as we pass from lower to higher members of the group. Let us take

as an example Group VII., which furnishes us both with sapid and odorous bodies.

GROUP VII.

Element.	Potassium Compound.	Formyle Compound.
F	Salt and <i>saline</i> .	...
Cl	Salt, <i>saline</i> , <i>bitter</i> .	Characteristic odour of chloroform.
Br	Salt, <i>saline</i> , and <i>bitter</i> .	Intermediate odour.
I	<i>Saline</i> , <i>bitter</i> .	Characteristic odour of iodoform.

Potassium fluoride is salt—like common salt in taste. In addition it is slightly saline—like nitre. Chloride of potassium has a suspicion of a bitter taste as well, and so has potassium bromide. Potassium iodide has lost the taste of common salt, being a saline, and bitter.

So far, then, we have seen that the power of producing taste is a property or function of elements. Our knowledge of matter is derived from its power of producing sensation within us. In the case of sight and hearing we have associated quality in sensation with the kind or character of the vibrating stimulus. If it can be shown that elements belonging to the same "group" are capable of vibrating in a way which is similar or related to one another, then we have grounds upon which to draw an analogy between smell, taste, sight, and hearing.

On account of our incomplete knowledge of the ultra-red and ultra-violet regions of the spectrum, a final answer to this question cannot perhaps be given. Only rough indications are to hand, but these point in the same direction.

The chlorides of the alkaline earths have spectra which are nearly related. The spectra of Group I. are not dissimilar, especially potassium and rubidium, with the five groups of lines. Then, again, the chlorides, bromides, and iodides of calcium and barium are similar, *the lines shifting towards the red end of the spectrum* in a way which is nearly proportional to the increase of atomic weight.

The colour of a substance is an index to the pitch of the vibrations of its molecules. In a paper on the colour of

chemical compounds recently published in the 'Philosophical Magazine' (July 1864), Professor Carnelley demonstrated the existence of a relationship between the salts of the same group of elements in respect to colour. The salts, say the chlorides, of a group of metals may not be of the same colour, but we find that, in passing to higher members of the group from the lower ones, a uniform *change* in colour is to be observed. This change is produced by a gradual shifting of the absorption towards the red end of the spectrum, the molecules vibrating more and more slowly with increase of atomic weight. This can be illustrated by the following diagram, taken from his paper :—

Metal.	Cl	I	Metal.	CrO ₄	AsO ₄
Na	White	White	Mg	Lemon yellow	White
Cu	White	Cream	Zn	Yellow	White
Ag	White	Light yellow	Cd	Orange yellow	White
Au	Yellow white	Golden yellow	Hg	Red	Yellow

It is probable, then, that metals of the same group vibrate in a similar way. This vibration we know is complex, consisting of many wave-lengths of different pitch. When a metal vibrates, any one of its vibrations falls within the scale of the visible spectrum, we shall find the corresponding wave of another member of the same group in the neighbourhood. If a higher member of the group, it will absorb the light nearer the red end; if a lower, nearer the blue end of the spectrum. Together with this alteration of pitch, we have corresponding alterations in the sensations produced, whether they be of sight, taste, or smell. Whatever reason we have for associating quality of colour with the pitch of vibration, we shall likewise have for associating quality of smell and taste with the same physical cause.¹

Amongst organic substances many are so closely allied that

¹ If a curve be constructed in which the ordinates represent the atomic weights of the positive elements, and the abscissæ a chromatic scale arising from blue, green, &c., to black, we shall obtain a curve indicating that the colours of the compounds are a periodic function of the elements arranged in atomic series. This is well seen in the case of the normal iodides (Carnelley).

they fall into distinct classes or groups. Thus we have the fatty acids, alcohols, &c. If these be arranged in homologous series, commencing with that which has the lowest, and passing to that which has the highest molecular weight, a uniform change will be observed in many physical properties on ascending the series. Thus the lower ones may be gaseous, the middle ones liquid, and the higher ones solid.

Professor Ramsay examined several of these groups, and came to the following conclusions:—In the first case, that the smell of a group was generic; and, in the second case, that the smell became more distinct, and gained in flavour in ascending from the lower to the higher members. My observations are not quite in accordance with the first statement, for I do not believe any uninitiated person would find any resemblance, say, between the odours of ethyl alcohol and octyl alcohol, or of acetic and valeric acids, which would prompt him in any way to class them together. I find that in ascending the organic series, as in ascending one of Mendeleeff's groups, the odour changes. This change may be slight, so that it may be said with truth that there is a generic smell belonging to the series; or, more frequently, the change is so great that it is only by a study of intermediate members that any continuity of sensation can be made out.

These statements may be verified by a study of the following tables. They are not as complete as I could have wished, owing to my inability to obtain some of the rarer acids and alcohols.

Monatomic Alcohols.

$\text{CH}_3\text{.OH}$	Methyl alcohol	=	Faint alcoholic odour.
$\text{C}_2\text{H}_5\text{.OH}$	Ethyl	" =	Alcoholic odour.
$\text{C}_3\text{H}_7\text{.OH}$	Propyl	" =	Alcoholic odour with flavour.
$\text{C}_4\text{H}_9\text{.OH}$	Isobutyl	" =	Flavour becomes more marked, and the alcoholic odour less and less.
$\text{C}_5\text{A}_{11}\text{.OH}$	Amyl	" =	
$\text{C}_8\text{H}_{17}\text{.OH}$	Octyl	" =	

The term "flavour" expresses very badly what is meant. It is only possible by experiment to become acquainted with the nature of a smell.

Among the fatty acids another flavour equally characteristic

gradually supersedes the acetic odour of the first two members of the group.

Fatty Acids.

CHO.OH Formic acid	=	Acetic odour.
$\text{C}_2\text{H}_3\text{O.OH}$ Acetic "	=	Acetic odour.
$\text{C}_3\text{H}_5\text{O.OH}$ Propionic "	=	Acetic, together with a flavour.
$\text{C}_4\text{H}_7\text{O.OH}$ Butyric "	=	{ Slightly acetic, with a well-marked flavour.
$\text{C}_5\text{H}_9\text{O.OH}$ Valeric "	=	{ No longer acetic, the flavour alone is present.

In this case the smell has altogether changed in character. The same holds good with the following series.

Acetates.

$\text{C}_2\text{H}_5.\text{C}_2\text{H}_3\text{O}_2$ Ethyl acetate	=	Acetic and ethereal smell.
$\text{C}_3\text{H}_7.\text{C}_2\text{H}_3\text{O}_2$ Propyl "	=	Acetic ethereal, with a flavour.
$\text{C}_4\text{H}_9.\text{C}_2\text{H}_3\text{O}_2$ Butyl "	=	{ Slightly acetic, with a pine-apple flavour.
$\text{C}_5\text{H}_{11}.\text{C}_2\text{H}_3\text{O}_2$ Amyl "	=	Pine-apple flavour and not acetic.

If we pass to quite another group, the hydrocarbons, and starting with benzene, replace first one, then two, and finally three atoms, with methyl, the ethereal aromatic odour will be found progressively to change in a manner which it is impossible to describe, but which can readily be demonstrated.

Hydrocarbons.

C_6H_6 Benzene	} Have a progressing and aromatic and ethereal odour.
$\text{CH}_3.\text{C}_6\text{H}_5$ Methyl benzene	
$2(\text{CH}_3).\text{C}_6\text{H}_4$ Dimethyl benzene	
$3(\text{CH}_3).\text{C}_6\text{H}_3$ Trimethyl benzene	

The way in which the sensation changes, analogous to that observed in studying Mendelejeff's groups, can in a similar way be explained on the vibration hypothesis.

I am not aware of any odorous organic series possessing at the same time colour, although some of them have very weak absorption bands. From a study of these latter, and from inferences drawn from a study of other coloured series, it is possible to obtain an insight into the state of vibrational activity of the substances in the tables above. Dr. W. J. Russell has investigated the absorption bands of ammonia,

alcohol, &c. These substances absorb light, but to so slight an extent that long columns of the liquids have to be examined before the bands are distinctly seen. Under these conditions, ammonia gives several distinct and characteristic bands. If now an atom of hydrogen of the ammonia be replaced by methyl, the ammonia bands are still visible, but they are shifted somewhat towards the red end of the spectrum. Replacing the hydrogen by the larger molecule of ethyl, the bands are seen to pass still nearer to the end of the spectrum.

NH_3 , Ammonia	} Produce bands which shift to red end of spectrum in ascending the series.
CH_3NH_2 , Methylamine	
$\text{C}_2\text{H}_5\text{NH}_2$, Ethylamine	

In the same way, we find that common alcohol possesses absorption bands, seen also in higher members of the group, but shifting towards the red end of the spectrum in ascending the group.

$\text{C}_2\text{H}_5\text{OH}$ Alcohol	} Produce bands which shift to the red end of the spectrum in ascending the series.
$\text{C}_3\text{H}_7\text{OH}$ Propyl alcohol	
$\text{C}_4\text{H}_9\text{OH}$ Butyl alcohol	

In the case of coloured acids, such as chromic and picric acids, the salts too are coloured. If the bands of these acids be examined, and if they be then converted into salts, the absorption will shift towards the red end of the spectrum. It seems that the molecule, having a certain vibrational character depending upon its structure, is weighted by the added metal, the vibrations of which do not probably appear at all in the visible spectrum, and, in consequence, its pitch is lowered. If an odorous substance like acetic acid be combined with another odorous substance, it is generally possible to detect the two intermingled sensations in the compound. Ethyl acetate is ethereal and acetous at the same time. Allyl sulphide is like allyl alcohol, and has the odour of a sulphur compound as well. In this case, it is probable that those vibrations in each substance which produce smell are not so much lowered in pitch by the new substance with which they are combined as to change the character of the sensations they are each capable of producing. The ammonia vibrations are shifted towards the red end of the spectrum in methylamine,

but not enough to produce another sensation. In other compounds of two odorous substances it may not be possible to distinguish the original odours, and for the reason that the pitch has shifted, as we have seen it often does, so as to produce quite a different sensation.

It may be urged as an objection to some of these conclusions that the same odours are often produced by substances, chemically speaking, quite unlike each other. Thus benzoic aldehyde smells very much like nitrobenzene. In the case of taste, too, there are many examples of totally dissimilar bodies having indistinguishable acid or sweet tastes. In answer to this objection one has only to remember, that there are instances, equally numerous, of very different substances which produce the same colour sensations. One may produce exactly the same tint with either a chromate, a picrate, or an aniline dye. It would be strange, indeed, if among the complex vibrations of a compound, or even of an element, some tones were not of the same pitch, as some of the vibrations of substances quite dissimilar in general properties. When these tones fall within the scale of the visible spectrum, the scale of taste, or smell sensations, we have, according to the vibration theory, a similar sensation produced.

In this paper I have endeavoured to avoid all questions which are matters of speculation. I have dealt only with already ascertained facts, or those which can readily be verified. I do not attempt to offer any hypothesis to account for the action of vibrating matter on the olfactory end-organs. It may or may not be a mechanical or chemical action. This question is not raised. We know next to nothing as to how it is that ether vibrations stimulate the cones of the retina, still less can we guess at the action of vibrating atoms and molecules of ordinary matter on the sensitive end-organs of the nose. My aim has been to establish the fact that, just as we have reason to connect differences in colour sensations with differences in the vibration of the ether, so, in like manner we have reason to connect differences in smells with differences in the vibrations which call them into existence. This analogy is established upon the following grounds:—

(1) In passing from the lower to the higher members of one

of Mendelejeff's groups, such molecular vibrations as have been investigated tend to become lower in pitch. At the same time the colour, taste, and smell sensations alter in character when present.

(2) In passing from the lower to the higher members of an organic series, such as the alcohols, such molecular vibrations as have been investigated tend to become lower in pitch. When present, the colour, taste, and smell sensations alter in the manner I have described.