

GEOGRAPHICAL NOTES

THE new volume (xi.) of the *Geographisches Jahrbuch*, edited by Prof. Hermann Wagner, begins a new series, and assumes a new form. It has been elongated from the small square form with which we have been familiar, into a respectable octavo, containing about 500 pages. Moreover the present volume is entirely devoted to what in former years was only a section: an account of progress in the various departments into which scientific geography is divided. The next volume will no doubt contain memoirs on various subjects of geographical interest. The subject of physical geography (or rather geophysics) is treated by Dr. Hergesell and Dr. Rudolph. Prof. Toula deals with the investigations of the last four years in the geognostic structure of the earth's surface in all parts of the world. The progress of oceanography is of course dealt with by the great authority on the subject, Dr. O. Krümmel, while Dr. Hann does a similar service for geographical meteorology, or climate. Botanical geography is treated by Dr. Oscar Drude, and zoological geography by Dr. L. K. Schmarda. Dr. G. Gerland gives the results of research in ethnology during 1884-86 in the various quarters of the globe. Under Dr. Wagner's sole editorship the *Jahrbuch* is becoming more valuable than ever as a book of reference in scientific geography.

THE Rev. George Grenfell, the explorer of the Mobangi and other important tributaries of the Congo, has arrived in London. Unfortunately his health is by no means satisfactory, and it will be necessary for him to rest for some time, therefore his appearance at the Royal Geographical Society must be delayed. He has brought home with him his original maps, which are admirable specimens of such work. They are on a scale of about 5 inches to a mile, and are evidently plotted with the greatest care; his work is therefore likely to take a high place. Dr. Lenz, who has arrived in Vienna, it is hoped will be in London at the end of this month, and as Dr. Junker may be here about the same time, it is just possible that both these eminent explorers may appear together at the first meeting of the Geographical Society in May.

UNDER Colonel Woodthorpe, the work of surveying our new Burmese territory is proceeding apace. Up to the end of January the out-turn of work amounted to 800 square miles on the $\frac{1}{2}$ -inch, and 260 miles on the $\frac{3}{4}$ -inch scale.

THE narrative of Baron Nordenskjöld's memorable journey into the interior of Greenland in 1883, is now appearing in instalments in the German journal *Globus*, profusely illustrated.

TWO Expeditions are being sent out by the Russian Geographical Society this year: one, under J. P. Kusnetzow, to investigate the flora of the Northern Urals; and another, under Prince Massalsky, to continue his Transcaucasian researches, which include both botany and ethnography.

VALENCY AND RESIDUAL AFFINITY

II.

METALLIC CONDUCTION.—I do not propose in any way to discuss metallic conduction, but merely to call attention to some of the analogies between it and electrolytic conduction.

It is conceivable, and it would appear probable from the fairly regular manner in which the electrical resistance of most pure metals decreases as the temperature falls, the coefficients of change being practically very nearly the same in all cases, that the increase in resistance as temperature rises is mainly due to the increase in molecular inter-distances. As a rule, resistance increases on the passage of a metal from the solid to the liquid state, but there are noteworthy exceptions from which it would appear probable that even in pure metals conductivity to some extent depends on molecular composition: thus the conductivity of bismuth increases at the moment of fusion from 0.43 to 0.73 of that of mercury at 31°, and that of antimony from 0.59 to 0.84 (L. de la Rive, *Compt. rend.*, 1863, lvii., p. 691); it is well known that bismuth contracts considerably on fusion, and this is probably also the case with antimony. Again, according to Bouty and Cailletet (*ibid.*, 1885, c., p. 1188), the resistance of mercury decreases at the point of solidification in the ratio 4.08 : 1; this is a remarkable increase in

¹ Revision and extension of a paper by Prof. H. E. Armstrong, F.R.S., communicated to the Royal Society last year. Continued from p. 572.

conductivity, and it is difficult to believe that it is wholly due to mere contraction of volume.

That the behaviour of alloys is worthy of far more attention than it has hitherto received appears most clearly from the few data at disposal. I would specially call attention to the curve given by Prof. Lodge as representing the specific conductivities of the copper-tin alloys (*Phys. Soc. Proc.*, 1879-80, iii., p. 158). The general resemblance of this curve to that given by F. Kohlrausch for mixtures of sulphuric acid and water appears to me to be in the highest degree suggestive.

Valency—Chemical Change.—Notwithstanding the fierce controversy which has been waged between the advocates of the doctrine of fixed valency, our views on the subject are still in an unfortunate degree unsatisfactory and indefinite. Even those—and they probably form a large majority—who regard valency as a variable, dependent both upon the nature of the associated radicles and the conditions—especially as to temperature—under which these are placed, often hesitate to attribute a valency sufficiently high to account for every case of combination; in fact, both parties agree in distinguishing “atomic” from “molecular” compounds, and differ only as to where the line shall be drawn.

It is difficult to over-estimate the importance of the theory of valency: its application has led to an enormous extension of our knowledge of carbon compounds especially, and it has furnished us with a simple and consistent system of classifying the mighty host of these bodies; but, on the other hand, it may be questioned whether it has not led us away from the search into the nature of chemical change, and even if the introduction of the terms saturated and unsaturated has not had a directly pernicious effect. The almost universal disregard of molecular composition as an important factor in chemical change in the case of solids and liquids, and the popular tendency to overlook the fact that our formulæ of such bodies are purely empirical expressions, has undoubtedly exercised a prejudicial influence.

No known compounds are saturated: if any were, such would be incapable, I imagine, of directly taking part in any interaction, and in their case decomposition would necessarily be a precedent change. The paraffins are apparently, of all bodies, the most inert and the most nearly saturated,¹ and next to them comes hydrogen—the unsaturated character of which is displayed in interactions such as occur at atmospheric temperatures between it and platinum and palladium, and when it displaces silver from silver nitrate or certain of the platinum metals from their salts. One of the most striking instances, perhaps, of popular error in this respect is water, which is always regarded as a saturated compound, although its entire behaviour, and especially its physical properties, characterise the molecule H₂O, I think, as that of an eminently unsaturated compound: I fail to see how, otherwise, we are to explain the high surface-tension and high specific heat of liquid water, its high heat of vapourisation, and its imperfectly gaseous behaviour up to temperatures considerably above its boiling-point, let alone its great solvent power and its tendency to form hydrates with a multitude of compounds—especially oxygenated compounds, be it added.

The theory was brought most prominently under the notice of chemists by Helmholtz in the last Faraday Lecture, that electricity, like matter, is, as it were, atomic, and that each unit of affinity or valency in our compounds is associated with an equivalent of electricity—positive or negative; that the atoms cling to their electric charges, and that these charges cling to each other. Thus barely stated, this theory does not appear to take into account the fact that the *fundamental* molecules, even of so-called atomic compounds, are never saturated, but more or less readily unite with other molecules to form molecular compounds—molecular aggregates; and unless the application of the theory to explain the existence of such compounds can be made clear, chemists must, I think, decline to accept it. The impression which the facts make upon the mind of the chemist certainly is (1) that no two different atoms have equivalent affinities; and (2) that affinity is a variable depending on the nature of the associated elements: but, owing to the recognised complexity of nearly all cases of chemical change, it is difficult to draw any very definite conclusion on this point.

If, however, the nature and properties of so-called molecular compounds generally be considered, and if an attempt be made to form any conception of their constitution, one striking fact is

² It is probably more correct to place nitrogen first in the list, as being the most inert substance known.

noticeable, viz. that the *metals* in them apparently retain the properties which they exhibited in the parent atomic compounds. Everyone knows the marked difference in properties of ferrous as contrasted with ferric salts: they differ not only in chemical behaviour, but also in their physical properties, and are readily distinguishable by their colour. The properties of the ferrous molecular compounds, however, are those of the simple ferrous compounds: ferrous potassium chloride, for example, $\text{Fe}_2\text{Cl}_4 \cdot \text{Cl}_2\text{K}_2$, is a green salt much like ferrous sulphate. Facts such as these have led me to suggest that in such cases the formation of the molecular compound is due to the attraction of the negative element of the one "atomic" compound by the negative element of the other, the metal having no influence except that the amount of affinity of which the negative element is possessed depends on the nature of the metal with which it is associated. It would in fact appear that hydrogen and the metals generally may be regarded as the analogues of the $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-7}$ hydrocarbon radicles, and that their compounds with negative elements may be likened to unsaturated hydrocarbons of the form $\text{C}_n\text{H}_{2n+1} \cdot \text{CH} \cdot \text{CH}_2$. We know that whenever such a compound enters into combination, the $\text{C}_n\text{H}_{2n+1}$ radicle takes no part in the change, combination of whatever kind being effected by means of the unsaturated radicle, $\text{CH} \cdot \text{CH}_2$, with which it is associated. I do not mean to contend that the metals are fully neutralised in their compounds, but merely that as a rule they behave as though they were saturated, just as do the $\text{C}_n\text{H}_{2n-7}$ radicles derived from the benzenes. There can be little doubt that an absolute distinction must be drawn between hydrogen and the metals on the one hand, and the non-metals on the other. Regarding the facts in the light of our knowledge of carbon compounds, it is difficult to resist the conclusion that the differences observed are due to differences in structure of the stuffs of which the elements as we know them are composed, the which differences condition perhaps a different distribution of the electric charge or its equivalent, in the case of each element.

ADDENDUM, April 1887.—I will now venture to call attention to the points which after a year's further consideration of the subject appear to me of special importance.

We are as far as we ever were from being able to define a "simple electrolyte" in the chemical sense—that is to say, to define the class or classes of compounds to which simple electrolytes belong. The investigation of the electrical behaviour of *pure* compounds is therefore of the highest importance; it is essential, however, to bear in mind that not only must pure compounds be studied, but scrupulous care must be taken to guard against a possible decomposition of the substance under examination, either by heat alone, or by contact with the electrodes or the containing vessel. I believe that the conclusions which Clark based on his most interesting observations on the electrolysis of mercuric salts are vitiated by some such effect having been overlooked. The experimental difficulties surrounding the problem are therefore very great; and the more hopeful method of attacking it in many cases would appear to be that adopted in Kohlrausch's experiments on the specific resistance of water: in other words, to determine the influence of impurities.

A similar problem relates to the possibility of basing a definition of a non-metal as distinct from a metal on electrical properties. It is well known that no consistent definition can be given, and that we are at present obliged to base our division of the elements into metals and non-metals on general considerations. Now, although metals differ enormously in specific resistance, the metals as a class oppose a comparatively feeble resistance to the passage of electricity, and moreover resistance always increases as the temperature of a metal rises; it is therefore noteworthy that not only is the specific resistance of non-metals, such as carbon, phosphorus, selenium and sulphur, enormously great in comparison with that of metals, but that it diminishes as temperature rises: non-metals therefore behave in this respect as electrolytes, and as no special precautions have hitherto been taken to obtain pure non-metals for the purpose it is well worth while to ascertain if the specific resistance offered by non-metals be not the greater the nearer the approximation to purity.

To determine the valency or atom-fixing power of an element, according to present views, it is necessary to determine the number of atoms which can enter into direct association with an atom of the element considered; and this necessarily involves a discussion of the nature of "atomic" as distinct from "mole-

cular" compounds. The electrical hypothesis that an atom of unit valency carries unit charge, a dyad two such charges, a triad three, involves the more specific determination of the number of charges which are associated with any particular atom; but, again, on this hypothesis we have to determine whether any real distinction can be drawn between atomic and molecular compounds, and whether an atom having, say, unit charge, has the power of combining with more than a single atom. My own view certainly is that atomic and molecular compounds are specifically distinct; and that in the latter the number of atoms associated with what may be regarded as the grouping element or elements in the compound is in excess of the number of unit charges which the particular element or elements of necessity carry. Taking nitrogen as an example, it appears to me that the whole of the evidence to be derived from the study of nitrogen compounds is compatible with the assumption that nitrogen carries at most three charges: that it is a triad, in fact; and I am inclined to regard the ammonium compounds of the type $\text{NH}_3 \cdot \text{HX}^1$ as molecular compounds in which the residual affinities of N and X^1 serve to unite H_3N with X^1H . The more I study the question the more I incline to the belief that sooner or later we must accept Kekulé's ruling, unfashionable as this has become of late years.

The foregoing may appear to many to be but a restatement of the tenets of the advocates of the doctrine of fixed valency. It appears to me, however, that in the hypothesis of a definite unit charge—in other words, of a definite unit valency—we have a conception which for the first time enables us to frame a consistent doctrine of valency: a given atom may be assumed to carry under all circumstances a certain definite charge, and the problem which the chemist has to determine is, firstly, the number of unit charges associated with any particular atom, and, secondly, the manner in which the charge is, as it were, distributed when the atom is brought into association with other atoms. The following illustration will perhaps serve to make my meaning clear. Let unit charge or unit valency be regarded as a unit "line of affinity" passing through the atom, and let it be supposed that the atom moves upon this line of affinity with a degree of freedom depending on its nature; then it may be supposed that combination between two atoms consists in the overlapping of the lines of affinity. If each atom move out to the end of its line of affinity, no part of the line will overhang; the molecule will consequently be saturated; there will be no residual affinity. On this view the stability of a molecule will depend on the extent to which the lines of affinity of the constituent atoms *overlap*, and its tendency to associate with other molecules will depend on the extent to which the lines of affinity of the constituent atoms *overhang*. For example, it may be supposed that in ordinary chlorine the two atoms of which the molecule consists have moved out near to the end of the lines of affinity, so that there is but little overhang: the molecule is therefore of considerable stability, but forms unstable combinations with other molecules; in iodine, on the other hand, it may be supposed that the atoms are closer together, the lines of affinity overlapping less than those of chlorine; consequently the molecule is less stable than that of chlorine, but may form more stable molecular compounds as the lines of affinity overhang to a greater extent than do those of chlorine. It is possible in this way to understand that an atom which carries but unit charge—a monad, in fact—may enter into association with two distinct atoms. Adhering to the above symbolic language, it may even be suggested that perhaps the difference between a non-metal and a metal may be that the structure of the non-metals is such that they move with difficulty upon their lines of affinity, and probably in a very limited number of directions, and with unequal freedom in different directions; and that the structure of metals is such that they move with comparative freedom upon their lines of affinity, in some cases even with complete freedom, and almost equally so in several directions.

Speculations such as these are of value only if they serve as a guide to further inquiry. I venture to put them forward in the hope of inducing chemists to devote more attention to the study of molecular compounds, for it is in this direction that we are likely to gather most important information as to the valency of elements other than carbon and hydrogen. Of late years such inquiries have been but rarely pursued, and no doubt they are less attractive than those which result in some new synthesis or the determination of the constitution of an organic product; but their future value will be great, and the number of workers is

now so large that our sense of proportion demands that attention should no longer be directed almost exclusively to the study of carbon compounds.

There is one other problem to which I would direct attention—the study of liquid diffusion. No interpretation of the remarkable results obtained by Graham has yet been given, and they appear in many cases to be quite at variance with the results of chemical inquiries. But there is a striking parallelism to be observed between Graham's results and those obtained on determining the electrical conductivity of solutions. Applying the view which I hold regarding the electrolysis of composite electrolytes to liquid diffusion, it appears to me not improbable that diffusion may be to a large extent the outcome not so much of the proper motion of the molecules of the dissolved substance as of a propulsive action exercised by the molecules of the solvent. The molecules in a mass of water we know may be assumed to be moving in every direction, and this being the case they would tend to carry other molecules along with them: the extent to which this action would take place would, however, largely depend on the attraction which exists between the molecules of water and those of the dissolved substance. From this point of view it appears of considerable importance to extend the study of liquid diffusion to dilute solutions. It may be added that this hypothesis would probably account for the behaviour of colloids, as these are known to be chemically neutral substances; in fact, they are compounds almost destitute of residual affinity.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE

KING'S COLLEGE, LONDON.—Prof. W. Grylls Adams, F.R.S., will deliver a course of lectures on Electro-Magnetism, Magneto-Electricity, the Testing of Motors and Dynamos, Electric Lighting, and Transmission of Power, during the present Term.

A course of practical work in Electrical Testing and Measurement with especial reference to Electrical Engineering will also be carried on under his direction in the Wheatstone Laboratory.

The lectures will be given once a week—on Mondays, at 2 p.m.,—and the Wheatstone Laboratory is open daily from 1 to 4, except on Saturdays.

SOCIETIES AND ACADEMIES

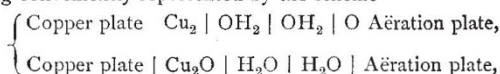
LONDON

Royal Society, March 31.—“Note on the Development of Voltaic Electricity by Atmospheric Oxidation.” By C. R. Alder Wright, D.Sc., F.R.S., Lecturer on Chemistry and Physics, and C. Thompson, F.C.S., Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

Whilst investigating processes for the manufacture of cuprammonium hydroxide (now used commercially on a considerable scale) we noticed that if the air supply be greatly in deficiency relatively to the bulk of the copper, under certain conditions the solution is but little coloured, containing copper dissolved principally as cuprous, and not as cupric, oxide. This might, perhaps, be anticipated *a priori*, inasmuch as it is well known that blue cupric solution in ammonia, when digested with metallic copper in the absence of air, takes up a second equivalent of copper, becoming colourless cuprous solution; but further experiments seem to indicate that the production of cuprous oxide under the oxidising influence of a limited supply of air is the primary action, and not merely a secondary result.

When a sheet of copper is kept out of direct contact with air by being immersed in ammonia solution, oxidation of the metal is gradually effected by virtue of the dissolving of oxygen from the air at the surface of the fluid, and diffusion of the oxygen solution to the vicinity of the copper. This action is an extremely slow one if the copper be covered by some depth of fluid, and if the setting up of convection currents through heating or evaporation be prevented by keeping the vessel perfectly at rest and at an equable temperature, and well closed to prevent escape of ammonia; but if these precautions be neglected it goes on much more rapidly, and the liquid comparatively soon becomes blue; it can, however, be also materially accelerated by arranging horizontally on the surface of the fluid a plate of platinum or other electrically conducting material not chemically acted upon by the fluid, and connecting this by means of a wire, &c., with the copper plate. The upper conductor, or *aération*

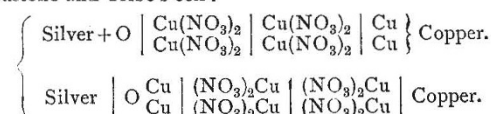
plate as it may be conveniently termed, being simultaneously in contact with the atmosphere and fluid, attracts to its surface a film or aura of condensed gases, the oxygen of which becomes gradually transferred to the copper, a voltaic current circulating through the fluid and connecting wire. Cuprous, and not cupric, oxide thus results, dissolved in the ammonia solution in contact with the copper plate, the mechanism of the reaction being conveniently represented by the scheme—



water being represented as the electrolyte for simplicity's sake. The air film on the aération plate being constantly renewed by absorption from the atmosphere, the process goes on continuously as long as the two plates are connected together by the wire. This wire may be lengthened at will so as to make the current which passes through it whilst the action goes on relatively stronger or weaker according to the amount of resistance introduced into the circuit; and by including a galvanometer or silver voltameter in the circuit the ordinary phenomena due to the passage of currents are readily recognisable.

The maximum E.M.F. thus capable of development varies considerably with the strength of the ammoniacal solution, being the less the weaker the fluid; addition of common salt or of sal ammoniac to the liquid notably increases the E.M.F. and diminishes the internal resistance of the cell. Spongy platinum in a thin layer as the aération plate gives higher values than thin platinum foil; the highest numbers thus obtained, using pretty concentrated ammoniacal brine, fell but little short of 0.8 volt; or somewhat less than the E.M.F. corresponding with the heat of formation of cuprous oxide,¹ since, according to Julius Thomsen, $\text{Cu}_2\text{O} = 40,810 = \text{about } 0.88 \text{ volt}$.

It is obvious that this copper atmospheric oxidation cell has a close connexion with the “air-battery” described in 1873 by Gladstone and Tribe (Roy. Soc. Proc., vol. xxi. p. 247) in which what is virtually an “aération plate,” consisting of a tray full of crystals of silver is used, opposed to a copper plate immersed in a solution of copper nitrate. Cuprous oxide is formed in both cases, in virtue of the indirect combination brought about between the oxygen of the air and the copper: but there is this great difference between the two (apart from the cuprous oxide being deposited as such in Gladstone and Tribe's arrangement, and being kept in solution in ours), that in the one the cuprous oxide is formed *at the surface of the copper plate* itself, and in the other *at the surface of the aération plate*. This essential difference is embodied in the above depicted scheme as compared with the following one which represents the action in Gladstone and Tribe's cell:—



One result of this difference is that the surface of the aération plate in the ammonia cell is kept constantly the same, whereas in the nitrate cell it is continually changing its character through deposition of solid cuprous oxide on the silver: in consequence of this deposition, whilst the E.M.F. of the ammonia cell, *ceteris paribus*, is constant, that of the nitrate cell is continually varying. Gladstone and Tribe, moreover, only obtained an E.M.F. of $\frac{8}{10}$ to $\frac{11}{10}$ of a Daniell, or about 0.104 to 0.143 volt, even under the most favourable conditions, viz. when the cell was connected with an electrometer; whilst four or five times this amount is indicated by the cells examined by us.

Following up the ideas suggested by the above observations, we are making a number of experiments with a variety of analogous combinations, in which atmospheric oxidation constitutes the essential chemical action taking place; by varying the nature of the aération plates, the metals dissolved, and the liquids employed (as also by substituting other gases, e.g. chlorine, for air), a large number of combinations are obviously obtainable. Some of those which we have so far examined present points of considerable interest, the oxidising action exerted under favourable conditions being strongly marked: so much so that certain metals, e.g. mercury and silver, not ordin-

¹ The actual chemical change going on in the cell is the synthesis of cuproso-ammonium hydroxide, so that the (unknown) heat of solution of cuprous oxide in ammonia should be added to this to obtain the total heat development.