of the position of the postauricular depression, in both vertical and horizontal direction, as compared with the front of the foramen magnum. That position varies in different races, and is affected by gravitation changes.

10. The position of greatest breadth varies according to the time of life, and as the spaces adjacent to the mesial and lateral roof-ridges are well filled or ill filled ; and an hypothesis is advanced in explanation of this, and of the mesial ridge being prominent in savage skulls, although the ridge on the fœtal skull disappears in childhood.

11. Orthognathism and prognathism are shown to be concrete results of a variety of circumstances, some of them not connected with the anatomy of the face, as, for example, the degree of cranial curvature.   The extent to which the face projects from underneath the skull must be measured by an angle contained between the fore part of the face and the floor of the anterior fossa only of the skull, the curves of the base of the skull further back having really nothing to do with the matter.   This projection of the face is great in French skulls, considerable in Scotch, and small in Irish and German skulls.

12. The facial angle is affected by the height of the ear above the foramen magnum, while prognathism is not.

13. The condyles of the skull become more and more prominent in front from infancy to adult life, and thus tilt the skull more and more backwards.   By this rotation balance is preserved, seeing that the fore part of the head and the face are the parts which proportionally increase in size as growth proceeds, and their increased proportion of weight is made up for by a greater amount being thrown behind the vertebral column.   There is less tilting back in the female head than the male.

14. This principle is shown to be most important in Artistic Anatomy.

15. In the lower animals the cerebral curvature is of very different amount in different species, the most advanced animals having it greatest.

XIX. " Researches on Vanadium."—Part II.   By HENRY E. ROSCOE, B.A., Ph.D., F.R.S.   Received June 16.   Read June 17, 1869.

(Abstract.)

On the Chlorides of Vanadium and Metallic Vanadium

In the first part of these researches ('Bakerian Lecture,' Phil. Trans. 1868, pt. i.) the author stated that the chlorides of vanadium, and probably also the metal itself, could be prepared from the mononitride, the only compound of vanadium not containing oxygen then known.   The process for obtaining the mononitride described in the last communication was that adopted by Berzelius for preparing the substance which he conceived to be metal, but which in reality is mononitride.   This method consists in the action of ammonia on the oxitri-chloride; but it cannot be

employed for the preparation of large quantities of nitride, owing to the violence of the action and consequent loss of material. The author, seeking for a more economical method, found that if the ammonium meta-vanadate (NH_4VO_3) be heated for a sufficiently long time at a white heat in a current of dry ammonia, pure vanadium mononitride remains behind. Analysis of a sample thus prepared gave 79·6 per cent. of vanadium and 20·2 per cent. of nitrogen, theory requiring 78·6 and 21·4 per cent. respectively. The mononitride may likewise be directly prepared by igniting vanadium trioxide (V_2O_3) in a current of ammonia at a white heat in a platinum tube, and also by subjecting the dichloride to the same treatment.

The Chlorides of Vanadium.—Three chlorides of vanadium have been prepared, viz. :—

> Vanadium tetrachloride . . . . VCl_4
> Vanadium trichloride . . . . . . VCl_3
> Vanadium dichloride . . . . . . VCl_2

1. *Vanadium Tetrachloride* VCl_4, molec. wt. $= 193·3$, V.D. $= 96·6$ ($H = 1$).—This chloride is formed as a dark reddish brown volatile liquid, when metallic vanadium or the mononitride is burnt in excess of chlorine. The first method adopted for the preparation of this chloride was to pass dry chlorine over the mononitride heated to redness; the whole of the nitride volatilizes and a reddish-brown liquid comes over. In one operation 44 grammes of the crude tetrachloride was thus prepared ; the liquid is purified by distillation first in a current of chlorine and then in a stream of carbonic acid gas. On fractionating, the liquid was found to boil at 154° C. (corrected) under 760^{mm} of mercury. The second method depends upon a fact already noticed in the preceding communication, that the oxitrichloride ($VOCl_3$), prepared, according to the directions of Berzelius, by passing dry chlorine over a mixture of the trioxide and charcoal, possesses a port-wine colour instead of the canary-yellow tint of the pure substance. This dark colour is due to the formation of the tetrachloride of vanadium, and if the vapours of the oxitrichloride, together with excess of dry chlorine, be passed several times over a column of red-hot charcoal the whole of the oxygen of the oxichloride can be removed, and at last perfectly pure tetrachloride, boiling constantly at 154° is obtained. This reaction, it will be remembered, served first to demonstrate the existence of oxygen in the oxitrichloride. In each distillation of the tetrachloride a peach-blossom-coloured solid residue remained in the bulbs ; this substance is vanadium trichloride, and it slowly burns away in excess of chlorine when heated, forming tetrachloride.

The composition of the tetrachloride was established by six well-agreeing analyses, made from several different preparations. The mean result is :—

	Calculated.	Found.
V = 51·3	26·54	26·87
Cl_4=142·0	73·46	73·02
193·3	100·00	99·89

Owing to the facility with which the tetrachloride splits up into trichloride and chlorine a solid residue was left in the vapour-density bulb, and the density of the vapour (at 219°) was found by Dumas's method to be 99·06 (or 6·86) instead of 96·6 (or 6·69). By volatilising the liquid in a small bulb, and allowing the vapours to pass into a large bulb already heated above the boiling-point of the liquid this deposition of trichloride was avoided, and the density was found to be 96·6 or 6·69 at 205°, and 93·3 or 6·48 at 215°, the last determination indicating that a partial decomposition into VCl_3 and Cl had occurred. The specific gravity of the liquid tetrachloride at 0° is 1·8584 ; it does not solidify at −18°, nor does it at this or any higher temperature undergo change of properties on treatment with chlorine. It not only undergoes decomposition on boiling, but at the ordinary atmospheric temperatures it splits up into VCl_3 and Cl. Tubes in which the liquid tetrachloride had been sealed up have burst by the pressure of the evolved chlorine. Thrown into water, the tetrachloride is at once decomposed, yielding a blue solution identical in colour with the liquid obtained by the action of sulphurous or sulphydric acids on vanadic acid in solution, and containing a *vanadous* salt, derived from the tetroxide V_2O_4. In order to prove that a vanadous salt is formed when the tetrachloride is thrown into water, the solution thus obtained was oxidized to vanadic acid by a standard permanganate solution. The calculated percentage of oxygen thus needed according to the formula $2VCl_4 + O + 4H_2O = V_2O_5 + 8HCl$ is 4·14 ; the percentage of oxygen found by experiment was 4·11.

The solution of the tetrachloride in water does not bleach ; but if the vapour be led into water a liquid is obtained which bleaches litmus. Vanadium tetrachloride acts violently on dry alcohol and ether, forming deep-coloured liquids. The author is engaged upon the examination of this reaction.

Bromine and vanadium tetrachloride, sealed up and heated together, do not combine ; on the contrary, trichloride is deposited. Hence it is clear that vanadium does not readily form a pentad compound with the chlorous elements.

2. *Vanadium Trichloride.*—VCl_3=157·8. The trichloride is a solid body, crystallizing in splendid peach-blossom-coloured shining tables, closely resembling in appearance the crystal of chromium sesquichloride. It is non-volatile in hydrogen, and, when heated in the air, it decomposes, glowing with absorption of oxygen, and forming the pentoxide. Heated in hydrogen the trichloride first loses one atom of chlorine, forming the dichloride (VCl_2), and afterwards, on exposure to a higher temperature, loses all its chlorine, leaving metallic vanadium as a grey lustrous powder.

The trichloride is extremely hygroscopic, deliquescing on exposure to air to a brown liquid. The trichloride is best prepared by the quick decomposition of the tetrachloride at its boiling point, or by its slow decomposition at the ordinary temperature of the air. The crystalline powder obtained by either of these methods only requires freeing from adhering tetrachloride by drying in carbon dioxide at 160° in order to yield good analytical results.

		Calculated.	Mean of 4 analyses.
V =	51·3	32·5	32·57
Cl_3 =	106·5	67·5	67·42
	157·8	100·0	99·99

The trichloride thrown into water does not at once dissolve; but, as soon as the crystals get moistened, a brown solution is formed, which becomes green on addition of a drop of hydrochloric acid, and contains a *hypovanadic* salt in solution. This green tint is identical with that got by reducing a solution of vanadic acid in presence of magnesium. According to the equation $2VCl_3 + O_2 + 3H_2O = V_2O_5 + 6HCl$ the solution of the trichloride requires 10·14 per cent. of oxygen to bring it up to vanadic acid, whilst analysis showed that 10·1 per cent. was necessary. The specific gravity of the trichloride at 18° is 3·00.

3. *Vanadium Dichloride* $VCl_2 = 122·3$.—The dichloride is a solid crystallizing in fine bright apple-green micacious plates. It is prepared by passing the vapour of vanadium tetrachloride mixed with hydrogen through a glass tube heated to dull redness. If the heat be pushed further a blackish crystalline powder, consisting of a mixture of lower chloride and metal, is obtained. The dichloride, when strongly heated in hydrogen, loses all its chlorine, leaving vanadium in the metallic state in grey crystalline grains. Analysis gave :—

		Calculated.	Mean of 2 analyses.
VCl =	51·3	41·95	42·16
Cl_2 =	71·0	58·05	57·88
	122·3	100·00	100·00

Vanadium dichloride is extremely hygroscopic; when thrown into water a violet-coloured solution is formed, identical in tint with the liquid containing a *hypovanadous* salt obtained by reducing vanadic acid in solution in presence of zinc- or sodium-amalgam ; and like this latter liquid, the solution of dichloride in water bleaches strongly by reduction.

Oxidized by permanganate this liquid required 18·78 per cent. of oxygen (on the dichloride taken) to bring it up to vanadic acid, whereas the equation $2VCl_2 + O_3 + 2H_2O = V_2O_5 + 4HCl$ requires 19·6 per cent. The specific gravity of vanadium dichloride at 18° is 3·23.

Metallic Vanadium $V = 51·3$.—Although from what we now know of the characters of vanadium it appeared unlikely that any compound con-

taining oxygen would yield the metal by direct reduction, the author has
repeated the experiments of other chemists on this subject, but without
success. There is no doubt that the metal cannot be obtained by any
of the processes described in the books. The only methods which pro-
mised possible results were :—

 1. The reduction of a vanadium chloride (free from oxygen) in hydro-
  gen gas, either with or without sodium.

 2. The reduction of the mononitride at a white heat in hydrogen.

The first of these methods has proved to be successful, whilst the
second does not appear to yield metal, inasmuch as the nitride exposed for
$3\frac{1}{2}$ hours in a platinum tube to the action of hydrogen at a white heat,
lost only 8 per cent., whereas it must lose 21·4 per cent. on conversion
into metal.

Notwithstanding the apparent simplicity of the method, the author has
found it exceedingly difficult to obtain the metal perfectly free from oxy-
gen. This arises from the fact that whilst vanadium is quite stable at the
ordinary temperature, it absorbs oxygen with the greatest avidity at a red
heat, and that therefore every trace of air and moisture must be excluded
during the reduction. Another difficulty consists in the preparation of the
solid chlorides in large quantity and free from oxygen or moisture, as also
in the length of time needed to reduce these chlorides in hydogen, during
which time unavoidable diffusion occurs and traces of oxygen enter the
tube. Again, the reduction can only be effected in platinum boats placed
in a porcelain tube, as the metal acts violently on glass and porcelain, and
tubes of platinum are porous at a red heat.

A description of the apparatus employed is then given, the main points
being to guard against diffusion, and to introduce the powdered dichloride
into the platinum boat in such a way that it shall not for an instant be
exposed to moist air. After all precautions are taken the tube is heated to
redness, torrents of hydrochloric acid come off, and the evolution of this gas
continues for from 40 to 80 hours, according to the quantity of dichloride
taken. After the evolution of any trace of hydrochloric acid has ceased to
be perceptible, the tube is allowed to cool, and the boat is found to contain
a light whitish grey-coloured powder, perfectly free from chlorine.

Metallic vanadium thus prepared examined under the microscope re-
flects light powerfully, and is seen to consist of a brilliant shining crystal-
line metallic mass possessing a bright silver-white lustre. Vanadium does
not oxidize or even tarnish in the air at the ordinary temperature ; nor
does it absorb oxygen when heated in the air to 100°. It does not de-
compose water even at 100°, and may be moistened with water and dried
in vacuo without gaining weight. The metal is not fusible or volatile
at a bright red heat in hydrogen ; the powdered metal thrown into a
flame burns with the most brilliant scintillations. Heated quickly in
oxygen it burns vividly, forming the pentoxide ; but slowly ignited in air
it first glows to form a brown oxide (possibly V_2O), and then again ab-

sorbs oxygen and glows with formation of the black trioxide and blue tetroxide till it at last attains its maximum degree of oxidation. The specific gravity of metallic vanadium at $15°$ is $5\cdot5$. It is not soluble in either hot or cold hydrochloric acid ; strong sulphuric acid dissolves it on heating, giving a yellow solution ; hydrofluoric acid dissolves it slowly with evolution of hydrogen ; nitric acid of all strengths acts violently on the metal, evolving red nitrous fumes and yielding a blue solution ; fused with sodium hydroxide the metal dissolves with evolution of hydrogen, a vanadate being formed.

One sample yielded on oxidation a percentage increase of $77\cdot94$, whereas that calculated from metal to pentoxide is $77\cdot98$. Another preparation gave a percentage increase of $70\cdot8$, showing the presence of a small quantity of oxide. On treatment in a current of chlorine metallic vanadium burns and forms the reddish black tetrachloride ; heated in a current of pure nitrogen the mononitride is formed.

The properties of the compounds of vanadium with silicon and platinum are then described in the memoir.

XX. " On *Palæocoryne,* a genus of the Tubularine Hydrozoa from the Carboniferous formation." By Dr. G. MARTIN DUNCAN, F.R.S., Sec. Geol. Soc., and H. M. JENKINS, Esq., F.G.S. Received June 14, 1869.

(Abstract.)

Palæocoryne is a new genus containing two species, and belongs to a new family of the Tubularidæ. The forms described were discovered in the lower shales of the Ayrshire and Lanarkshire coal-field, and an examination of their structure determined them to belong to the Hydrozoa, and to be parasitic upon Fenestellæ. The genus has some characters in common with *Bimeria* (St. Wright), and the polypary is hard and ornamented. The discovery of the trophosome, and probably part of the gonosome of a tubularine Hydrozoon in the Palæozoic strata brings the order into geological relation with the doubtful Sertularian Graptolites of the Silurian formation, and with the rare medusoids of the Solenhofen stones.

XXI. BAKERIAN LECTURE.—" On the Continuity of the Gaseous and Liquid States of Matter." By THOMAS ANDREWS, M.D., F.R.S., &c. Received June 14, 1869.

(Abstract.)

In 1863 the author announced, in a communication which Dr. Miller had the kindness to publish in the third edition of his ' Chemical Physics,' that on partially liquefying carbonic acid by pressure, and gradually raising at the same time the temperature to about $88°$ Fahr., the surface of de-