

# Thomas Carnelley

Jaime Wisniak\*

## ABSTRACT

Thomas Carnelley (1854-1890), in spite of his short life, did fundamental research on the relation between the physical properties of the elements and their compounds, and their position in the Periodic Table (Carnelley's rules). His claims about "hot ice" inspired many famous scientists such as Ramsay and Young, to study in more detail the phase diagram of a pure substance. He did extensive research on the synthesis and properties of tolylphenyl, ditolyl, and their derivatives, discovering many new hydrocarbons in the process.

**KEYWORDS:** atomic weights, Carnelley's rules, ditolyl, hot ice, melting point, phase changes, tolylphenyl, vanadates, ventilation

## Resumen

Thomas Carnelley (1854-1890), a pesar de su corta vida, realizó investigación fundamental sobre la relación entre las propiedades físicas de los elementos y sus compuestos y su posición en la Tabla Periódica (reglas de Carnelley). Sus argumentos acerca de la existencia de "hielo caliente" inspiraron a muchos científicos famosos, como Ramsay y Young, a estudiar a fondo el diagrama de fases de una sustancia pura. Realizó extensa investigación sobre la síntesis y propiedades del tolyl-fenilo y ditolilo, y a través de ese proceso descubrió varios hidrocarburos nuevos.

**Palabras clave:** pesos atómicos, reglas de Carnelley, ditolilo, hielo caliente, punto de fusión, cambios de fase, tolyl-fenilo, vanadatos, ventilación

## Life and career

The only information about the life and career of Thomas Carnelley is contained in the obituary notices published in *Nature* and *Journal of the Chemical Society*, by his mentor Henry Enfield Roscoe (1833-1915) (Roscoe, 1890; Anonymous, 1891). Thomas Carnelley was born in Manchester on October 22nd, 1854, the son of William Carnelley. He received his early education at King's College School, London and after graduation (1868) he entered the Owens College, Manchester, gaining one of the Dalton Entrance Mathematical Exhibitions. He remained at Owens College until 1872. Carnelley's studentship was one of exceptional brilliance, as shown by the record of academic successes, and also by the honors gained at the several examinations for the Bachelorship of Science of the London University, in which University

he matriculated in the year 1870. At his first examination for the Bachelor of Science, in 1871, he was placed third in Third Class honors in Chemistry, and at the final examination, in 1872, obtained the degree, and was placed second in First Class Honors in Chemistry, with marks qualifying for the University Scholarship in Chemistry (Anonymous, 1891).

While preparing for those examinations, Carnelley also found time to devote himself to an investigation on the subject of the vanadates of thallium (Carnelley, 1873), a research for which, in 1872, the Dalton Chemical Scholarship was awarded to him; and in consideration of his success at the final B.Sc. examination, the holding of the Scholarship was extended to a third year (Anonymous, 1891).

During the years 1872-74, Carnelley acted as private assistant to Henry Enfield Roscoe, and began his career as a teacher by giving lectures in connection with the evening classes at the Owens College. The next year he enrolled at the University of Bonn, Germany, to study of chemistry under August Kekulé (1829-1896), Theodor Zincke (1843-1928), and Otto Wallach (1847-1931, 1910 Nobel Prize for Chemistry). While in Germany he conducted research on the reaction of mixed vapors of carbon disulfide and alcohol over red-hot copper (Carnelley, 1875a), and the synthesis and properties of tolylphenyl (Carnelley, 1876b; Anonymous, 1891).

In 1876, Carnelley obtained the degree of Doctor in Science in Chemistry, in the University of London; and from the year 1875 to 1879 he held the appointment of Assistant Lecturer and Demonstrator in Chemistry at the Owens College; during a portion of this period he was also Principal of the North Staffordshire School of Science, at Hanley (Anonymous, 1891).

In 1879, the Firth College at Sheffield was founded and Carnelley was appointed as the first incumbent to the Chair of Chemistry. The three years he spent at Sheffield were actively occupied with the fitting up of the chemical laboratory, and organizing the teaching in his department. In 1872 he was appointed as the Professor of Chemistry first in Dundee,

\*Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.

**Correo electrónico:** wisniak@exchange.bgu.ac.il

**Fecha de recepción:** 22 septiembre de 2011.

**Fecha de aceptación:** 22 de noviembre de 2011.

in the then recently established University College. Here ample means for the building and equipment of the department were placed at his disposal, and he had the satisfaction of superintending the erection of the block of buildings in which are located the chemical laboratories, lecture rooms, etc., arranged in accordance with his own plans and ideas (Anonymous, 1891).

His zeal, untiring energy and unselfish devotion to his work, contributed to make the Chemical Department one of the most important in the new College. Carnelley's first care was the establishment of a School of Chemistry, where he also busied with the establishment of a Dye-house and Technical Museum, which were designed to be an off shoot of the Chemical Department. The material for the latter was presented by Carnelley and his father to the College in 1888. On this occasion, he delivered an inaugural lecture, in which he clearly set forth his views and ideals as a teacher of chemistry: "Let Chemistry be taught in a truly scientific spirit for the real love of it, and its practical applications will follow and indeed accompany it, as certainly as the phenomena of daylight follow the rising or the sun. In no country has chemistry been taught in a more scientific spirit than in Germany, and it is there that some of its most important practical applications have been made" (Roscoe, 1890; Anonymous, 1891).

In addition to his academic and research duties, he did extensive public work in Dundee, among them studies on the chemical and bacteriological quality of the air of dwellings and schools. Such was the interest created by these investigations that he was elected a member of the School Board, and received a special commission from that body to prepare a Report on the Cost and Efficiency of the Various Systems of Heating and Ventilating Schools (Anonymous, 1891).

He had not been settled two years in Aberdeen when he succumbed to a severe and sudden illness, caused by the formation of an internal abscess. He died at his residence, The Cults, Aberdeen, on August 27, 1890, at the comparatively early age of 36 (Anonymous, 1891).

Carnelley was elected fellow of the Chemical Society of London on February 19, 1874, served as Council member of same between 1885 and 1889, and was for many years on the staff of Abstractors for the journal of the Society. Carnelley also assisted in the editing of the *German-English Dictionary of Scientific and Technical Terms*, published by Vieweg and Son (Anonymous, 1891).

### Scientific contribution

In his short life Carnelley published more than 50 papers and several books (Carnelley, 1874, 1885-1887; Carnelley and Haldane, 1887). Here we describe his most important achievements.

### Physics

The significance of Carnelley's contribution in this area is clearly described in the obituary notice published in *Nature* (Roscoe, 1890): "Carnelley, when a student at the Owens

College, appears to have been greatly impressed with Mendeleeff's conceptions, and it was to the study of the physical properties of the elements and their compounds, and to the devising of new methods of obtaining trustworthy determinations of the melting points of metallic salts and the elements that he early devoted his energies. The results of these experiments... (showed) that the fusibility of the elements and of certain of their compounds is a periodic function of their atomic weights. From the relationships discovered by him to exist between the melting points of the chlorides of the elements and the atomic weights of those elements, Carnelley was led to draw conclusions respecting the atomic weight of the element beryllium and to fix its position in the classification of the elements... Other properties have been shown by Carnelley to be related to the atomic weights of the elements, and in a paper read at the Aberdeen meeting of the British Association (Carnelley, 1885) he developed a series of analogies between the elements and various series of hydrocarbons, from which he concluded that the chemical elements may be represented by a formula  $A_n B_{2n + (2 - x)}$ , in which  $n$  is series and  $x$  the group to which the element belongs;  $A = 12$  and  $B = -2$ . In a paper published... last year (Carnelley, 1890), he... states that... he had obtained such an expression, in which the atomic weight is represented as equivalent to the product of a constant,  $c$ , into a factor made up of  $n$ , a member of an arithmetical progression, dependent on the series to which the element belongs, and  $v$ , the maximum valence, or the number of the group of which the element is a member. Thus

$$A = c(m + v^{1/x})$$

The best results are obtained when  $x = 2$ , and  $m$  is 0 for series II,  $2\frac{1}{2}$  for III, 5 for IV,  $8\frac{1}{2}$  for V, 12 for VI,  $15\frac{1}{2}$  for VII, 19 for IX,  $22\frac{1}{2}$  for X, 26 for XI, and  $29\frac{1}{2}$  for XII. The formula thus becomes  $A = c(m + \sqrt{v})$ , and  $m$  is a member of an arithmetical series in which the difference is  $3\frac{1}{2}$ , save in the first two series, when it is  $2\frac{1}{2}$ . By using this equation, the value for  $c$  in the case of 55 elements is found to lie between 6.0 and 7.2, with a mean value of 6.64... The results obtained exhibit very close approximation, the calculated values being, in fact, nearer the experimental numbers than those obtained by the aid of Dulong and Petit's law. The remarkable coincidence that the value 6.6 for the constant  $c$  in the above formula very nearly approximates to the value 6.4, accepted as the atomic heat of the elements, in accordance with Dulong and Petit's law, is noted, and that the specific heats of the elements may consequently be represented as equivalent to  $1/m + \sqrt{v}$ . The specific heats calculated by the aid of this formula are compared with the experimental values, and, in the case of the 55 elements in which a comparison can be instituted, in 45 instances the agreement is very satisfactory, while the other 10 are elements the specific heats of which, according to Dulong and Petit's law, are more or less abnormal (Roscoe, 1890; Carnelley, 1882b).

“Accepting Bettone’s conclusion that the hardness of an element is inversely proportional to its specific volume; it is shown that hardness may be represented in terms of the specific gravity, and the expression,  $6.6(m + \sqrt{v})$  thus

$$\text{Hardness} = 1 / \text{spec. vol} = \text{sp. gr} / \text{at. wt} = \text{sp. gr} / \left[ 6.6(m + \sqrt{v}) \right]$$

...Mendeleeff...in a letter addressed to Henry Roscoe...wrote as follows: “I think it my duty to inform you that the name of Professor Carnelley is deservedly and widely known in every country which interests itself in investigations of the theoretical side of chemical science and especially with reference to the study of the chemical elements. The labors of Carnelley connected with the periodic law of the elements have been so remarkable that the history of the subject would be incomplete if his name were omitted. The connection between the composition of metallic salts and the temperature of their melting points has been determined by the numerous and accurate researches of Carnelley, which have lain bare the internal meaning of this province of empiricism” (Roscoe, 1890).

In his first paper on the subject (Carnelley, 1879) Carnelley stated that he was intent in finding the influence of the atomic weights on the melting and boiling points and heat of formation of the elements, as well as their compounds. He found that the melting points of the elements were a periodic function of the atomic weights, while for compounds the melting and boiling points and heats of formation of the normal halogen compounds were a periodic function of the atomic weights of the constituent elements. The influence of the halogen in these physical properties increased with the number of its atoms in the compound; in any normal halogen compound the influence of either of the elements on the melting or boiling point increased with its own atomic weight, and decreased with the atomic weight of the other element; the melting or boiling point or heat of formation of a bromide was always nearer to that of the corresponding chloride than to that of the corresponding iodide; and that the melting or boiling points of the halogen compounds of the middle member of three consecutive elements of the same group were always nearer to those of the first member, (i.e., the one with least atomic weight), than to those of the last member. The first of these phenomena probably depended on the fact that the atomic weight of bromine is nearer to that of chlorine than to that of iodine, and the second, on the fact that the atomic weight of the middle member of three consecutive elements of the same group is always less than the mean of those of the other two elements (Carnelley, 1879).

From there, Carnelley went on to describe a process for calculating unknown melting and boiling points for halogen compounds, which gave very good results when applied to known melting and boiling points; the average error for all known boiling points being  $\pm 4.5^\circ\text{C}$ , or 0.8%, and for all melting points  $\pm 15^\circ\text{C}$  or 3%. In his first paper about melting points (Carnelley, 1876c) Carnelley stated that with the exception of a few compounds melting at a comparatively low tempera-

ture, the melting point of the different metallic salts, and even of the high melting alloys, had not been determined and represented numerically, and was described in vague terms, such as “the salt in question melted just below red heat, at a dull red heat, or at a full red heat”, etc., while any possible connection between this physical property and others such as the chemical composition and properties, was even less known. It appeared then that it would be useful to have a method by which the fusion point of the different metallic salts could be determined, if not with the accuracy attainable in other cases, yet at the very least with some approach to the correct number. He then proceeded to describe the experimental method he had developed for this purpose, which was particularly applicable when only a small quantity of the salt was available (a few centigrams were enough). The procedure consisted in introducing a small quantity of the salt in a weighed platinum crucible heated with a Bunsen burner. As soon as the salt appeared to melt, the crucible was dropped into a known weight of water of known temperature. The initial melting temperature was then calculated by a heat balance (Carnelley named the procedure “specific heat method”). Using this procedure Carnelley measured the melting point of 28 different salts, ranging from silver nitrate, the most fusible, to sodium sulfate, the most difficult to fuse. A similar procedure was used to determine the solidification point. The results indicated that the difference between the two points varied between  $6^\circ$  and  $21^\circ\text{C}$ , a result which Carnelley considered satisfactory, considering the difficulty of registering high temperatures.

In a following publication (Carnelley, 1876c; 1877a) Carnelley described an additional procedure for determining the fusion point, which depended on the following principle: If three metallic salts, *A*, *B*, and *C*, which fuse at different temperatures, such that *A* fuses before *B*, and *B* before *C*, be arranged on a cold block of smooth iron, and this is placed in a muffle kept at a constant high temperature, and if *x* be the number of seconds which elapse between the melting of *A* and *B*, and *y* the number of seconds between the melting of *A* and *C*, then the ratio *y/x* is approximately constant for the same three salts, whatever be the temperature of the muffle, provided only it is considerably higher than that at which *C* fuses. Carnelley then went on to describe a new method he called “time method” to determine high melting points. The method was not perfectly independent but presupposed knowing the melting points of a small number of salts. These salts, which he called “standard salts”, were sulfur, silver nitrate, potassium nitrate, potassium chlorate, thallium (I) chloride, lead (II) chloride, potassium iodide, potassium chloride, and potassium carbonate. The melting point of the standard salts was determined using the specific heat process.

The first step was the determination of the time values of the nine standard salts. By this term he meant the time, which elapsed between the fusing of that salt and sulfur, when under the same conditions ten seconds elapsed between the melting of sulfur and silver nitrate (a table is given listing

the melting point of the standard salts and the pertinent time values). Carnelley then described the time method to determine high melting points and provided a table comparing the melting points obtained by the two different methods he had developed. The table showed that almost the same mean melting points were obtained. Anyhow, he stated that the method of the specific heat should be especially preferred because it is entirely independent of any fixed melting points, whereas in the time methods, the melting points of the standard salts have to be assumed, so that the results which it yields are not wholly independent (Carnelley, 1877a).

In another paper Carnelley pointed out that the specific method for determining high melting points gave results, which for temperature up to 400°-500°C were somewhat high. In this paper he investigated the causes of this error, took the necessary steps to reduce them to their minimum and then proceeded to use the specific heat method to determine the melting point of 62 salts (Carnelley, 1878c, 1880a).

In conducting a research on certain high boiling hydrocarbons Carnelley and William Carleton-Williams strongly felt the need of some method for determining with ease and enough accuracy, the boiling points of substances that volatilize at temperatures too high to be measured with a mercury thermometer. The method they developed consists in noticing whether certain salts melt on exposure to the vapor of the boiling substance. Since Carnelley had already measured the boiling point of a large number of metallic salts, it was possible to ascertain within certain limits, the boiling point of the substance in question (Carnelley and Williams, 1878).

For temperatures below 500°C the substance was boiled in an ordinary distillation flask provided with a perforated cork, through which pass several capillary tubes containing salts which melt at known temperatures (Carnelley and Williams, 1879). The method developed previously (Carnelley and Williams, 1878) was slightly modified to determine the boiling points of several elementary and compound bodies. The salts or metals used in the determinations were exposed to the potassium or sodium vapor in long capillary tubes of hard glass, which were externally corroded by the metallic vapors, though not to such an extent as to eat through the glass. When the temperature of the boiling substance was above 1000°C, glass capillary tubes could no longer be used for containing the metals to be exposed to its vapor, in which case the metals employed in measuring the boiling point were enclosed in a small thin iron cylinder, the open end of which was closed with a tight fitting plug of the same metal. The tube was lowered into the boiling liquid or vapor by an iron wire, where it was allowed to remain for five minutes.

It was well-known that none of the pyrometers which had been proposed at various times for measuring high temperature were of simple construction, or admit of such ready manipulation as to be extremely employed in the arts, whilst in those cases where these conditions were fulfilled, the results were not so exact or so constant as could be wished. Carnelley and Thomas Burton developed a new pyrometer, which

although it had several drawbacks, it overcame most of the difficulties attached to the older pyrometers (Carnelley and Burton, 1884). It was extremely simple in its construction and arrangement, it was cheap, did not readily get out of order, and required little manipulation except the reading two of thermometers and a reference to a table. It consists basically of a copper coil (five turns) of internal diameter 6-mm and total height about 8-cm, located inside the space whose temperature is being measured. A constant stream of water flows through the coil; the circuit is provided with two temperatures, one measuring the inlet and the other the outlet temperature of the water. For the purposes of graduation, the pyrometer is placed inside a cylindrical oven heated in a small coke furnace. The oven is heated to the highest temperature attainable under the circumstances and then allowed to cool slowly. During the cooling process the temperature of the out and in-flowing water is read off periodically, and the actual temperature of the oven estimated simultaneously by exposing therein metallic salts of known melting points enclosed in capillary tubes, or for temperatures below 300°C with an ordinary thermometer. A series of calibration curves is constructed showing the relation between the temperature of the oven and the increase in temperature of the effluent water.

In a previous publication (Carnelley, 1882a) Carnelley showed that the solubility and fusibility of a substance were very closely related to one another, so that of two or more isomeric bodies, the one that dissolves the most easily has the lowest melting point and the least symmetrical atomic arrangement. At that time the investigation had included only a small number (58) of compounds, and involved no original experiments. The present paper (Carnelley and Thomson, 1888) extended the results of the previous so as to include all isomeric sets of carbon compounds whatever. The data was obtained from the literature and from their own determinations. Carnelley and Andrew Thomson reported their experimental method for measuring solubility and listed the solubility of *m*- and *p*-nitro aniline in 13 different solvents at 20°C, and of solubility of mixtures of sodium nitrate and potassium nitrate in water at the same temperature. Raoul Pictet (1846-1929) had shown that the lower the melting point of a solid the larger the oscillations of its molecules, and that the melting points of solids corresponded to equal lengths of oscillations (Pictet, 1879). Of two isomeric bodies, therefore, the one with the lower melting point will, at any given temperature below the melting point, have its molecules moving with oscillations of greater amplitude than the one with the higher melting point. The molecular weights being equal, the force of restitution will be less in the case of the more fusible compound, and hence its molecules will be in a less stable condition, and be the more readily separable from their fellows than those of the less fusible compound. Now in order that a solid may dissolve in any liquid it is necessary that its molecules undergo a sort of unloosening process, hence we can infer that of two isomeric compounds, the one that will dissolve more easily is the one in which the attraction or the

force of restitution to the mean position of oscillation was the smallest, that is, the one which is the more easily fusible. This argument shows: (1) that for any series of isomeric organic compounds the order of solubility is the same as the order of fusibility, that is, the most fusible compound is likewise the most soluble (Carnelley and Thomson took the data for 1778 compounds and found that the rule was satisfied for 1755 of them), and (2) In any series of isomeric acids, not only is the order of solubility of the acids themselves the same as the order of fusibility, but the same order of solubility extends to all the salts of the several acids, so that the salts of the more soluble and more fusible acids are also more easily soluble than the corresponding salts of the less fusible and less soluble acids. Application of the rule to 143 cases showed that it was satisfied for 138 of them. In total there were only 28 exceptions to the 1921 cases examined. Carnelley and Thomson looked in detail at the exceptions and found that 12 of them referred to only five sets of isomers.

The next item to be examined was the influence of the nature of the solvent. Carnelley and Thomson stated that if it is true that the more fusible compound is also the more soluble, then the following additional rules may be stated: (3) For a series of isomeric compounds the order of solubility is the same, no matter what may be the nature of solvent. They applied this rule to 666 cases and found no exception to it; (4) the ratio of the solubilities of the two isomers in any given solvent is nearly constant, and is therefore independent of the nature of the solvent.

### Hot ice

In 1881 Carnelley published a paper in which he claimed that under certain conditions it was possible for ice and other bodies to exist in the solid state at temperatures far above their ordinary melting points (Carnelley, 1880-1881). According to Carnelley when the applied pressure was maintained below a certain point, which he called (unfortunately) critical pressure, it was impossible to melt ice, mercuric chloride, and probably other bodies, no matter how much heat is applied. Above these pressures they melted when heated. The following year Carnelley published another paper, repeating the experiments he had done with mercuric chloride and giving a very detailed description of the experimental method and the pertinent calculations. The latter required measuring the specific heat of the solid salt between its melting point and the ordinary temperature of the air. For mercuric chloride he obtained 0.06404 cal/g.°C in petroleum and 0.06898 in turpentine, very similar to the ones reported by Kopp and Regnault under the same conditions. Carnelley's results indicated that when mercuric chloride was in the form of a compact powder, it could be heated 21°C, and sometimes 50°C above the normal melting point (277°C) without melting. When the salt was in the form of a resolidified cylinder, the temperature rose by 15°C above the melting point (Carnelley, 1882a).

After the publication of these papers, a number of scien-

tists repeated Carnelley's experiments and verified the first proposition, but were unable to observe any rise in temperature of the ice and mercuric chloride above their ordinary melting points under the circumstances indicated. In 1880 Sidney Young (1857-1937) demonstrated Carnelley's discovery that at sufficiently low pressures ice sublimates and cannot be liquefied by the application of heat (Young, 1883).

In a letter to the editor, James Ballantyne Hannay (1855-1890) (Hannay 1891a) reported that he had repeated Carnelley's experiments on hot ice, but using a Torricellian vacuum system, which produced a clear continuous piece of ice around the thermometer, instead of the flaky one obtained by Carnelley using a Sprengel pump vacuum system, which Hannay thought would lead to serious errors because part of the stem remained bare. Repeated experimentation showed that the ice cannot be raised above 0°C under any circumstances and that the pressure determining the volatilizing or boiling point of both solids and liquids is determined by the pressure. In a second letter to the editor, Hannay added (Hannay, 1891b) that although he had shown hot ice to be an impossible commodity, perhaps the existence of solid mercuric chloride above its boiling point might still hold. He repeated Carnelley's experiments and found that the problem was related with the deposition of a porous plug of solid mercuric chloride around the stem of the thermometer, thus vitiating the readings. After many experiments he concluded that the idea of being able to raise solids in vacuum to a temperature above their ordinary boiling points should be dismissed as inadmissible, except perhaps in some rare case of allotropy.

The phenomenon was also discussed by William Ramsay (1852-1916) and Young in a series of papers devoted to analyze the possibility that solids have definite volatilizing points under different pressures, as liquids have definite boiling points, and whether these pressures are identical with their vapor pressure at the temperatures in question (Ramsay and Young, 1884abc). In their review of the state of the art, Ramsay and Young wrote that already in 1873 James Thomson (1822-1892) had analyzed the behavior of a pure substance in the  $P$ - $T$  domain (Thomson, 1873). Here the three phase change curves, solid-gas, solid-liquid, and liquid-gas, were represented by three continuous curves which seemed to meet at one common point, which Thomson named *triple point*. Thomas Andrews (1813-1885) (Andrews, 1869, 1876) had already demonstrated that the liquid-gas separating boundary came to an end at a point, which he named called the *critical point*, and that the transition from any liquid state to any gaseous state could be gradually affected by an infinite variety of courses *passing round* the extreme end of the boiling line. Thomson then proceeded to demonstrate that the triple point corresponds to a discontinuity in the curves of phase change and the sublimation curve reaches the triple point with a slope *larger* than that of the vaporization curve. With most pure substances (normal substances) the three boundary curves had a positive slope, but for a few ones like

water, the boundary curve for the solid-liquid equilibrium had a negative slope (anormal substances), that is to say, the melting point decreases as the pressure is increased (at some time, this result was used to explain ice skating).

In 1884 (Ramsay and Young, 1884ab) demonstrated that the pressures corresponding to the temperatures of volatilization coincided with the vapor pressure of the solid at the same temperature, that solids have definite temperatures of volatilization, as liquids have definite boiling points, depending on the pressure to which they are subjected, and these are sensibly coincident with those of their vapor pressures (Ramsay and Young, 1884b). Their experiments with ice at low pressures clearly showed that during freezing the phenomenon of supersaturation was nearly always observed. The temperature fell occasionally as low as  $-11^{\circ}\text{C}$ , while the water was still liquid. A sudden formation of ice then occurred and the temperature rose to  $0^{\circ}\text{C}$ .

## Inorganic chemistry

### (a) Vanadates

Carnelley's research on metal vanadates brought him the Dalton Chemical Scholarship and also his first scientific publication (Carnelley, 1873). The alkaline vanadates had been shown to differ in their chemical behavior from the corresponding phosphates in-as-much as in the formed series the meta- and pyro-salts were found to be more stable than the ortho ones, while in the phosphates the stability order was the opposite. From the high atomic mass of thallium, Carnelley thought that an examination of its vanadates would help clarify the differences between phosphorus and vanadium. Thallium and alkaline phosphates were known to possess similar physical and chemical characteristics, forming ortho-, pyro-, and meta-salts, several of which contained basic hydrogen; in addition, they were soluble in water and had a similar order of stability. The results of Carnelley's experiments showed that thallium vanadates behaved different from the alkaline ones; the latter were soluble in water but the corresponding thallium salts were insoluble, behaving more like the silver and lead vanadates. The tendency of the vanadates to form anhydrous salts containing a greater portion of vanadium than corresponded to the ortho compounds was, as expected, even more strikingly exhibited by the thallium vanadates than by those of the alkaline metals. It was not possible to prepare thallium ortho-vanadate by precipitation of sodium sulfate and orthosodium vanadates; at room temperature a yellow precipitate of pyrovanadate  $\text{Tl}_4\text{V}_2\text{O}_7$  precipitated immediately and the solution became strongly alkaline.

Carnelley's paper contains a description of the properties and mode of preparation of the thallious vanadates, together with an examination of the reactions that lead to the formation of thallium orthovanadate  $\text{Tl}_3\text{VO}_4$  or the tetravanadate  $\text{Tl}_{12}\text{V}_4\text{O}_{16}$ ; thallium pyrovanadate  $\text{Tl}_4\text{V}_2\text{O}_7$  or the hexavanadate  $\text{Tl}_{12}\text{V}_6\text{O}_{21}$ ;  $\beta$ -thallium vanadates or the octovanadate  $\text{Tl}_{12}\text{V}_8\text{O}_{26}$ ;  $\gamma$ -thallium vanadates or the decavanadate

$\text{Tl}_{12}\text{V}_{10}\text{O}_{31}$ ; thallium metavanadate  $\text{TlVO}_3$  or the dodecavanadate  $\text{Tl}_{12}\text{V}_{12}\text{O}_{36}$ ;  $\delta$ -thallium vanadate or the tetradecavanadate  $\text{Tl}_{12}\text{V}_{14}\text{O}_{41}$ ;  $\beta$ -sodium vanadate or the octovanadate  $\text{Na}_{12}\text{V}_8\text{O}_{26}$ ; and  $\beta$ -silver vanadates or the octovanadate  $\text{Ag}_{12}\text{V}_8\text{O}_{26}$  (Carnelley, 1873).

### (b) Analytical chemistry

As mentioned before, Carnelley was very interested in health problems related to the community. In 1876 he had developed an accurate method for the calorimetric estimation of very small amounts of copper present in aqueous solutions, using an aqueous solution of one part of potassium ferrocyanide in 25 parts of water, which gives a purple-brown color with very dilute solutions of copper (Carnelley, 1876d). Copper metal was used in many domestic and industrial applications; several culinary artifacts as well as pipes and cisterns for conveying and storing water were manufactured from this metal. In addition, there was little information on the corrosive action which different waters containing ammoniacal salts and chlorides had on the brass fittings of machinery, on brass taps, etc. As copper exerts on the human system a very poisonous effect, Carnelley thought important to know what solvent action did different waters have on this metal, and decided to apply his method to investigate fully the action of distilled water and aqueous saline solution on copper metal. His results indicated that distilled water as well as the aqueous solutions of salts, dissolved a distinct amount of copper on standing in contact with the metal even for one hour only. For example, with distilled water, the amount of dissolved copper increased slowly with time and with the amount of surface exposed per unit volume of water, and it decreased with the temperature of the water. He tested many salts, like the nitrates of sodium, potassium and ammonia, the sulfates of calcium, potassium, ammonia, and magnesium, the carbonates of sodium and potassium, and the chlorides of potassium, sodium, and ammonia. He found that with the exception of the ammonia salts, the action of the salt depended chiefly on the nature of its radical and little on the nature of the base; the influence increasing in the order nitrate, sulfate, carbonate, and chloride. A general conclusion was that waters contaminated by sewage, and therefore containing large quantities of ammonia salts and chlorides in solution, were harmful for household purposes on account of their actual composition; they also were detrimental for copper pipes, vessels, etc., and for use in generating steam, etc., where brass taps and machinery fittings were exposed to their action (Carnelley, 1876a).

Upon learning about Carnelley's experiences, F. T. Bond, from the Sanitary Association of Gloucester, suggested that since copper sulfide was very insoluble, perhaps it would be possible to protect the copper surface by treating it with a solution of an alkaline sulfide. Shaw and Carnelley tested this hypothesis using ammonium sulfide (Shaw and Carnelley, 1877). Clean pieces of copper foil were dipped in diluted am-

monium sulfide until they were entirely covered by a thin film of copper sulfide, and then washed with distilled water. The experiments of the previous paper were repeated, once with clean copper, once with copper sulfide. The results indicated that previous washing with copper sulfide did not lessen the action on copper of cold or hot distilled water, but on the contrary it increased it. Another set of runs were done using closed flasks at ordinary temperature, in order to test the possibility that the copper sulfide in contact with air became oxidized to sulfate, which would then dissolve. The experiments proved this hypothesis true; this time the copper sulfide coating diminished the action of water. Pretreatment with ammonium sulfide lessened the action of saline solutions on the metal, even when air had free access (Shaw and Carnelley, 1877).

### Organic chemistry

In 1858 Marcelin Berthelot (1827-1907) reported the synthesis of methane by passing a vapor mixture of water and carbon disulfide or hydrogen sulfide, over red-hot copper (Berthelot, 1858). On this basis, Carnelley studied the possibility of synthesizing *n*-pentane by passing a mixture of carbon disulfide and alcohol vapors over red-hot copper (Carnelley, 1875a). Although the results were negative, he found that the reaction produced large amounts of carbon oxisulfide (carbonyl sulfide). The gas issued from the tube had a very unpleasant and strong pungent smell; it was inflammable and burned with a blue sulfur flame, giving off large amounts of sulfur dioxide. It did not precipitate an acid solution of cupric sulfate or mercuric chloride but with an ammonia solution of silver nitrate it gave a black precipitate proved to be silver sulfide. Analysis of all the gas phase indicated the presence of acetaldehyde, carbonyl sulfide, ethyne, ethylene, methane, and hydrogen, while the copper superficially converted into sulfide and amorphous carbon deposited, no hydrogen sulfide or sulfur dioxide were produced. According to Carnelley, the pertinent reaction was  $\text{CS}_2 + \text{C}_2\text{H}_6\text{O} + \text{Cu} = \text{COS} + \text{CuS} + \text{C}_2\text{H}_6$ , followed by decomposition of ethane into methane, ethylene, etc.

Kekulé suggested to Carnelley to study the synthesis of tolylphenyl, or phenyl-methylbenzene, the hydrocarbon between diphenyl and ditolyl, having three possible isomers. Carnelley prepared the *para* isomer (Carnelley, 1876b) by adding sodium to an equimolar mixture of bromobenzene and *p*-bromotoluene, dissolved in ether. He found that purified *p*-tolyl-phenyl was a colorless refractive liquid having a pleasant aromatic odor, a density of 1.015 at 27°C, boiling in the range 263°–267°C, and solidifying into a mass of pretty large colorless crystals, melting in the range –2° to –3°C.

Carnelley studied the oxidation of the new hydrocarbon with diluted nitric acid and also by dissolving it in glacial acetic acid and adding chromic acid. Elemental analysis of the oxidized material corresponded to the formula  $\text{C}_{13}\text{H}_{10}\text{O}_3$ , that is, diphenyl carbonic acid,  $\text{C}_6\text{H}_5\text{—C}_6\text{H}_4\text{—COOH}$ . Oxidation with an excess of chromic acid, followed by dilution with

water, led to precipitation of a greenish-white precipitate, which after purification produced a white powder, very insoluble in water, very soluble in alcohol and ether, and sublimating at high temperature without decomposition. The elementary analysis corresponded to  $\text{C}_8\text{H}_6\text{O}_4$ , that is, terephthalic acid. Carnelley also prepared and studied the properties of some substitution products of the hydrocarbon, such as the  $\alpha$ - and  $\beta$ -mononitro, the  $\alpha$ -monoamido compounds, and the dinitro derivatives.

Later, Carnelley used his procedure to prepare ditolyl by reacting sodium with *p*-bromotoluene. Oxidation of the product produced two isomeric ditolyls, *p-p*- and *o-p*-ditolyl (Carnelley, 1877b, 1887).

In a following memoir Carnelley reported that *p*-tolylphenyl and its homologue ditolyl could be obtained cheaper and in much larger yields, by reacting an equimolar mixture of benzene and toluene on a red-hot tube, a reaction similar to that by which diphenyl was obtained from benzene (Carnelley, 1880b). He collected and analyzed the different fractions that emerged from the hot tube, as the temperature was increased up to about 420°C, finding that they included naphthalene, diphenyl, *p*-tolylphenyl, *o-p*-ditolyl,  $\gamma$ -methylene-diphenylene,  $\delta$ -methylene-diphenylene, diphenylbenzene, and phenanthrene. Carnelley reported the properties of the two new hydrocarbons  $\gamma$ -methylene-diphenylene and  $\delta$ -methylene-diphenylene.  $\gamma$ -methylene-diphenylene was obtained from the fraction boiling between 293° and 305°C. Pure it crystallized in small pearly plates, melting at 118°C, resolidifying at 116°C and boiling at 295°C. It was moderately soluble in hot alcohol and hot glacial acetic acid, but only sparingly soluble in cold alcohol or in cold glacial acetic acid. Its alcoholic and acetic acid solutions showed a faint blue fluorescence. Carnelley prepared the picrate, quinone, and dibromo derivatives of the compound.  $\delta$ -methylene-diphenylene was present in the fraction boiling between 305° and 339°C and was separated by repeated crystallization from alcohol. It crystallized in small pearly plates, which were only sparingly soluble in cold, but more easily in hot alcohol. It melted at 208°C and boiled at about 320°C. According to Carnelley, the hydrocarbon was probably identical with benzyhydrolene,  $\text{C}_{13}\text{H}_{10}$ , which is obtained by the distillation of the succinate or benzoate of diphenylmethanol.

Carnelley summarized his findings as follows: (1) passing a vapor mixture of benzene and toluene through a red-hot tube, generates naphthalene, diphenyl, *p*-tolylphenyl, *o-p*-ditolyl,  $\gamma$ -methylene-diphenylene,  $\delta$ -methylene-diphenylene, phenanthrene, anthracene, *p*-diphenylbenzene, a hydrocarbon having the composition  $\text{C}_{32}\text{H}_{28}$ , a liquid hydrocarbon boiling at 293°–316°C and melting at 13°C, two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359°–383°C and 404°–427°C, respectively, and solid black bitumen, (2) two new methylene-diphenylenes and some few of their derivatives are described, (3) of the six possible methylene-diphenylenes three and probably four are known.

Carnelley with James Schleselman studied the synthesis of

aminodiphenyl sulfonic acid and azo dyes from diphenyl (Carnelley and Schleselman, 1880) and with Thomson (Carnelley and Thomson, 1885) the preparation of the brominated derivatives of diphenyl, tolylbenzene, and ditolyl, and the physical properties of tribromodiphenyl, dibromodiphenyl, *p*-bromotolylbenzene, dibromotolylbenzene, dibromophenylbenzoic acid, bromoditolyl (isomers), bromodiphenic acids, and dibromoditolyl. In a following publication (Carnelley and Thomson, 1887) Carnelley and Thomson described the preparation of another monobromotolylbenzene, the separation of the dibromo compounds and the formation of new oxidation products from these, such as monobromo-1,4-tolylbenzene [ $\alpha$ -bromotolylbenzene (1,2 or 3,4')],  $\beta$ -bromotolylbenzene (1',4' or 1,4), dibromotolylbenzenes, C<sub>13</sub>H<sub>10</sub>Br<sub>2</sub> [ $\alpha$ -dibromotolylbenzene (1',4', 1,2, or 3,4)], and  $\beta$ -dibromotolylbenzene (1',4', 1,3, or 2,4).

### Miscellaneous

In addition to his multiple activities in the areas mentioned above, Carnelley and his collaborators were also involved in matters of public hygiene. For example, in 1887 Carnelley and John Scott Haldane made an extensive examination of the air of houses and schools in Dundee (Carnelley et al., 1888). Owing to the complaints that had been made of bad smells in the House of Commons, a Select Committee was appointed in 1886 to inquire into the ventilation of the House, and Carnelley and Haldane were instructed by the Committee to make a series of analysis of the air in the sewers under the House of Parliament, and gather information of their sources and on the conditions affecting their dissemination. Their results indicated (1) that the air in the sewers was much better than expected, (2) that the CO<sub>2</sub> was about twice, and the organic matter rather over three times as great as in outside air at the same time, whereas the number of microorganisms was less, (3) that in reference to the quantity of the three constituents named, the air of the sewers was in a very much better condition than that of naturally ventilated schools, and that with the notable exception of organic matter it had likewise the advantage of mechanically ventilated schools, (4) that the sewer contained a much smaller number of microorganism than any class of home. The CO<sub>2</sub> was rather greater than in the air of houses of four rooms and upwards but less than in two- and one-roomed houses (Carnelley and Haldane, 1887ab).

An interesting off-shoot is the following. The chemistry laboratory was the first building to be purpose-built for the new University College. It opened in 1883 under the name *Carnelley building*, honoring Thomas Carnelley. Carnelley itself took active part in its design, and one of the most notable features of the building was its ground-breaking use of an air purification system, something taken for granted in modern buildings but which was almost entirely unknown at this time, all the air in the building was filtered, warmed and humidified. Carnelley's invention wasn't entirely successful, however, the fans were not strong enough to drive

the air right along the ducts going out of the building, and various punctures acquired over time meant that the various noxious vapors were merely distributed from one lab to another.

Carnelley and Wilson developed a modification to Hesse's method for the bacterioscopic analysis of air in which Hesse's conical flask (like an Erlenmeyer) was substituted for a tube (Carnelley and Wilson, 1888). The latter was provided with two-holed rubber stopper through which passed two glass tubes, one for introducing the air and the other for letting it out. Comparison of the new equipment with the standard Hesse's one showed that they gave essentially the same result. The new method had the following advantages: (1) it possessed in common with Hesse's system, the advantages of a solid nutrient medium, (2) it gave accurate results, as shown by comparative tests, (3) there was no risk of aerial contamination, either during the preparation of the flasks previous to use, or subsequently during the growth of the colonies, (4) it was much cheaper than Hesse's method, (5) the flasks being of thin glass rarely broke during sterilization, whereas this was a serious source of annoyance and expense in the case of Hesse's tubes, (6) there was no chance of leakage during sterilization, as sometimes occurred with Hesse's tubes, and (7) there was a great saving in jelly.

Carnelley and William Frew studied the influence of atomic arrangement on the antiseptic properties of isomeric organic compounds, particularly of di-derivatives of benzene (Carnelley and Frew, 1890). The compounds tested were sodium *o*-, *m*-, *p*-hydroxybenzoates, *o*-, *p*-sodium phthalates, *o*-, *p*-nitrotoluenes, *o*-, *m*-, *p*-sodium nitrobenzoates, sodium *o*-, *m*-, *p*-dihydroxybenzenes, *o*-, *p*-amidotoluenes, *m*-, *p*-nitroanilines, *o*-, *p*-nitrobenzaldehydes, *o*-, *m*-, *p*-sodium nitrophenol, *o*-, *p*-potassium nitrophenol, sodium  $\alpha$ -naphthol, sodium  $\beta$ -naphthol, methyl oxalate, sodium mesaconate, and sodium itaconate. The results, expressed as weight of the respective compound per liter of jelly required to prevent the appearance of colonies of microorganisms during 6 days at temperatures from 16° to 18°C, indicated that the *para* derivatives are usually more powerful antiseptics than the corresponding ortho and meta compounds, exception made of the hydroxybenzoates.

### References

- Andrews T., On the Continuity of the Gaseous and Liquid States of Matter, *Phil Trans*, **159**, 575-590, 1869.
- Andrews T., On the Gaseous State of Matter, *Phil Trans*, **166**, 421-449, 1876.
- Anonymous, Thomas Carnelley, Obituary Notice, *J. Chem. Soc. Trans.*, **59**, 452-467, 1891.
- Berthelot, M., Sur la Synthèse des Carbures d'Hydrogène, *Compt. Rendus*, **46**, 1102-1105, 1858.
- Carnelley, T., On the Vanadates of Thallium, *J. Chem. Soc.*, **26**, 323-339, 1873.
- Carnelley, T., *On a Colorimetric Method of Determining Iron in Water*, Harrison and Sons, London, 1874.

- Carnelley, T., Note on the Effect of Passing the Mixed Vapours of Carbon Disulphide and Alcohol over Red Hot Copper, *J. Chem. Soc.*, **28**, 523-526, 1875a.
- Carnelley, T., On the Action of Water and of Various Saline Solutions on Copper, *J. Chem. Soc.*, **30**, 1-12, 1876a.
- Carnelley, T., On Tollyl-phenyl, a New Hydrocarbon, *J. Chem. Soc.*, **29**, 13-23, 1876b.
- Carnelley, T., On High Melting Points, with Special Reference to those of Metallic Salts, *J. Chem. Soc.*, **29**, 489-509, 1876c.
- Carnelley, T., On a Colorimetric Method for Determining Small Quantities of Copper, *Lit. Phil. Soc. Manchester, Proc.*, **15**, 24-30, 1876d.
- Carnelley, T., On High Melting Points, with Special Reference to those of Metallic Salts. Part II., *J. Chem. Soc.*, **31**, 365-388, 1877a.
- Carnelley, T., On the Oxidation of Ditolyl, *J. Chem. Soc.*, **32**, 653-660, 1877b.
- Carnelley, T., On the Determination of High Boiling Points, *J. Chem. Soc.*, **33**, 281-284, 1878c.
- Carnelley, T., Relations Between the Atomic Weights and Certain Physical Properties (Melting and Boiling Points and Heats of Formation), *Proc. Roy. Soc.*, **29**, 190-192, 1879.
- Carnelley, T., The Melting and Boiling of Certain Inorganic Compounds, *J. Chem. Soc.*, **37**, 125-127, 1880a.
- Carnelley, T., Action of Heat on the Mixed Vapours of Benzene and Toluene. Two New Methylene-Diphenylenes, *J. Chem. Soc.*, **37**, 701-720, 1880b.
- Carnelley, T., Preliminary Note on the Existence of Ice and other Bodies in the Solid State at Temperatures far Above their Ordinary Melting Points, *Proc. Roy. Soc.*, **31**, 284-291, 1880-1881.
- Carnelley, T., Action of Heat on Mercuric Chloride under Low Pressures, *J. Chem. Soc. Trans.*, **41**, 317-323, 1882a.
- Carnelley, T., Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds, *Phil. Mag.*, **13**, 112-130, 1882b.
- Carnelley, T., Suggestions as to the Cause of the Periodic Law and the Nature of the Chemical Elements, *Brit. Assoc. Adv. Sci.*, Report of the 55th Meeting, 969-970, Aberdeen, Sept. 1885.
- Carnelley, T., *Physico-Chemical Constants. Melting and Boiling Point Tables*, Harrison and Sons, London, 1885-1887.
- Carnelley, T., Derivatives of Tollylbenzene, *J. Chem. Soc.*, **51**, 87-91, 1887.
- Carnelley, T., An Approximate Algebraic Expression of the Periodic Law of Chemical Elements, *Phil. Mag.*, **29**, 97-113, 1890.
- Carnelley, T., Burton, T., A New Form of Pyrometer, *J. Chem. Soc. Trans.*, **45**, 237-241, 1884.
- Carnelley, T., Frew, W., The Relative Antiseptic Powers of Isomeric Organic Compounds, *Chem. Soc., Trans.*, **57**, 636-639, 1890.
- Carnelley, T., Haldane, J. S., The Air of Sewers, *Proc. Roy. Soc.*, **42**, 501-522, 1887a.
- Carnelley, T., Haldane, J. S., *The Air of Sewers*. Harrison and Sons, London, 1887b.
- Carnelley, T., Haldane, J. S., Anderson, A. M., The Carbonic Acid, Organic Matter, and Micro-organisms in Air, More Especially of Dwellings and Schools [1886], *Phil. Trans. (B)*, **178**, 61-111, 1888.
- Carnelley, T., Schleselman, J., Amidodiphenylsulphonic Acid and Azo-dyes from Diphenyl, *J. Chem. Soc.*, **49**, 380-383, 1880.
- Carnelley, T., Thomson, A., Brominated Derivatives of Diphenyl, Tollylbenzene, and Ditolyl, *J. Chem. Soc. Trans.*, **47**, 586-593, 1885.
- Carnelley, T., Thomson, A., Derivatives of Tollylbenzene, and Ditolyl, *J. Chem. Soc. Trans.*, **51** 87-91, 1887.
- Carnelley, T., Thomson, A., The Solubility of Isomeric Compounds and of Mixtures of Sodium and Potassium Nitrates, and the Relation of Solubility and Fusibility, *J. Chem. Soc.*, **53**, 782-802, 1888.
- Carnelley, T., Williams, W. C., High Melting Points, Part IV., *J. Chem. Soc.*, **33**, 273-281, 1878.
- Carnelley, T., Williams, W. C., On the Boiling Points of Certain Metals and Metallic Salts, *J. Chem. Soc.*, **35**, 563-567, 1879.
- Carnelley, T., Wilson, T., A New Method of Determining the Number of Microorganisms in Air, *Proc. Roy. Soc.*, **44**, 455-464, 1888.
- Hannay, J. B., Dr. Carnelley's Experiment with Hot Ice, *Nature*, **23**, 505-506, 1891a.
- Hannay, J. B., Dr. Carnelley's Experiment with Mercuric Chloride, *Nature*, **24**, 77-78, 1891b.
- Pictet, R., Demonstration Théorique et Expérimentale de la Définition Suivante de la Température: La Température est Représentée par le Longueur de l'Oscillation Calorifique des Molécules d'un Corps, *Compt. Rendus*, **88**, 855-857, 1879.
- Ramsay, W., Young, S., On the Vapour Pressure of a Substance in the Solid and Liquid States at the Same Temperature, *Brit. Assoc. Rep.*, 675-676, 1884a.
- Ramsay, W., Young, S., The Influence of Pressure on the Temperature of Volatilisation of Solids, *Phil Trans.*, **175**, 37-48, 1884b.
- Ramsay, W., Young, S., Influence of Change of Condition From the Liquid to the Solid State, *Phil Trans.*, **175**, 461-478, 1884c.
- Roscoe, H. E., Thomas Carnelley, *Nature*, **42**, 522-523, 1890.
- Shaw, F. W., Carnelley, T., On the Influence Exerted by Ammonium Sulphide in Preventing the Action of Various Solutions on Copper, *J. Chem. Soc.*, **31**, 642-644, 1877.
- Thomson, J., A Quantitative Investigation of Certain Relations Between the Gaseous, the Liquid, and the Solid States of Water-Substance, *Proc. Roy. Soc.*, **22**, 27-36, 1873.
- Young, S., Ice Under Low Pressures, *Chemical News*, 104-105, 1883.