James Dewar (1842-1923) is widely known for his pioneering work in cryogenics, of being the first to achieve the liquefaction of hydrogen, by the flask that carries his name, and by his studies about the behaviour of living organisms and materials under conditions of extreme cold. Although he was an excellent experimentalist, he did not leave many significant theoretical contributions.

**Life and career**

James Dewar (Fig. 1) was born on September 20, 1842, in Kinkardine-on-Forth, Scotland, the youngest of seven sons of Thomas Dewar and Ann Eadie Dewar.

When he was ten years old he went skating and fell through ice in a frozen lake and when rescued walked about in his wet clothes until they were dry so that his family would not know about his accident. As a result he contracted rheumatic fever, which crippled him; he had to go on crutches for a couple of years and was left with a damaged heart. During this period he was in much contact with the village carpenter and practiced his hands in making violins. He always regarded the training he thus received as the most important part of his education and the foundation of the great manual dexterity, which he displayed in his work and his lectures.

By the time he was fifteen he had lost both parents and went to live with one of his brothers who owned a drapery shop in Kincardaine. He stayed with him until he was admitted to the Dollar Academy in Clackmannashire. At school he was a very distinguished student and was awarded many prizes, one of them in Peter Guthrie Tait’s (1831-1901) class; with whom he would later do research on high vacuum.

After graduation he went to Edinburgh University where he lived with his brothers Alexander, then nearly through his medical course. Eventually his brother was appointed assistant to professor James Syme (1799-1870), and through him James was probably in full touch with medicine.

He graduated from Edinburgh as a chemist in 1861 and stayed on for almost a decade, first as tutorial assistant to James David (1828-1876) and then as demonstrator for Lyon Playfair (1818-1898), professor of chemistry from 1867 to 1868. Playfair retired in 1868 (to serve in Parliament, he occupied various positions such as Postmaster General and Lord in Waiting of Queen Victoria) and Dewar was appointed assistant to his successor, Alexander Crum Brown (1838-1922). Dewar taught the medical laboratory class.

In 1869 Dewar was appointed Lecturer (1869-1873) and then Professor in the Royal Veterinary College. Between 1873 and 1875 he was appointed...
assistant chemist to the Highland and Agricultural Society of Scotland and delivered district lectures for this body. He was put in charge of analysing manure, foodstuff and fertilizers, lecturing the agricultural association on chemistry and answering any specific inquiries.

During the period 1867-1875, he did research on a variety of subjects in chemistry, biology and physics. He was associated with William Dittmar (1833-1892), Arthur Gamgee (1841-1909) on physiological chemistry; John Gray McKendrick (1841-1929) on the production of vacuum and in experiments on the physiological effect of light on animals; and with Tait on the production of vacuum and in experiments with William Crookes's (1832-1919) newly invented radiometer.

In 1875 he was appointed Jacksonian professor of natural experimental philosophy in the University of Cambridge and became the colleague of George Downing Liveing (1827-1924). Two years later he also became Fullerian professor of chemistry at the Royal Institution, London, replacing John Hall Gladstone (1827-1902).

According to Armstrong, "Dewar was not great as a teacher. His mind was of too original and impatient a type. He never suffered fools gladly and students are too apt to be foolish, even to ape the part of superior beings. His forte lay in directing competent hands, not in forming them. He worked himself and through skilled assistants, not through pupils. He was violently impatient of failure in manipulation, and his work was almost entirely manipulatory. He, therefore, never created a school."

In 1871 Dewar married Helen Rose Banks, the daughter of an Edinburgh printer; they had no children.

James Dewar died on March 23, 1923, while at work, at the Royal Institution on Albemarle Street. He was 82 years old. By his express wish his remains were cremated at Golders Green.

Honours

James Dewar received many honours for his contributions to science and industry. He was awarded many honorary degrees, among them, M.A., Honoris Causa (1875), Cambridge; honorary LL.D. from Glasgow, St. Andrews, Edinburgh and Aberdeen; and honorary D.Sc., Victoria, Oxford, and Dublin. He was nominated Fellow of Peterhouse College, Fellow of the Royal Society of London, of the Royal Society of Edinburgh, of the Institute of Chemistry, of the Chemical Society, and of the Society of Chemical Industry.

He was appointed Director of the Davy Faraday Research Laboratory of the Royal Institution (1896-1923) and was President of the Chemical Society, of the Society of Chemical Industry, and of the British Association.

He was member of the Royal Institution of Great Britain, honorary member of the Institution of Civil Engineers, member of the Institution of Electrical Engineers, and member of the British Association. Dewar was knighted in 1904.

Awards

The Royal Society awarded to Dewar its three most prestigious medals: Rumford (1894), Davy (1909), and Copley (1916). He received the first Hodgkins Gold Medal of the Smithsonian Institution (1899); the Gunning Victoria Jubilee Prize of the Royal Society of Edinburgh (1904); the first Lavoisier Gold Medal of the French Academy of Sciences (1904); the Matteucci Medal of the Societa Italiana delle Scienze (1906); the Albert Medal of the Royal Society of Arts (1908); the Medal of the Society of Chemical Industry (1918); and the Franklin Institute Medal (1919).

Scientific activities

Dewar is widely known for his pioneering work in cryogenics, the first to achieve the liquefaction of hydrogen, by the flask that carries his name, and his studies about the behaviour of living organisms and materials under conditions of extreme cold. Although he was an excellent experimentalist, he did not distinguish with theoretical contributions. He left us with more than 265 scientific papers in the many areas he was active.

Here are described some of his most important contributions.

The structure of benzene

One of the first incursions of Dewar into organic chemistry was related to the oxidation of unsaturated hydrocarbons. He was aware that a common method for determining the structure of a compound was by oxidation and analysis of the products. In the case of benzene derivatives, although the synthesis and analysis of its derivatives confirmed each other, the structure of the principal nucleus remained unexplained. For many years Agustin Kekule (1829-1896) had tried to solve the riddle and in 1865 he had suggested that benzene consisted of a ring of six carbon atoms decorated with six peripheral hydrogen atoms; the carbon atoms were arranged in a closed chain with the carbon bonds bound two and one...
separately. Now, if the formula was examined graphically, it became evident that benzene had to have three symmetrical groupings, \( C_2H_2 \) (acetylene). Dewar reasoned\(^3\) that if Kekulé’s model was correct then oxidation would separate the carbon atoms in pairs and yield the corresponding oxidized product, \( C_2H_2O_4 \), oxalic acid. He tried oxidizing benzene with potassium permanganate in a sealed tube at 150°C, but no reaction occurred; addition of aqueous potassium permanganate to an aqueous solution of phenyl alcohol (phenol) resulted in immediate decomposition, the solution became alkaline and manganese peroxide precipitated. Acidulation of the liquid phase and addition of calcium acetate precipitated calcium oxalate. Dewar believed that by controlled oxidation of phenol several substances might be produced, such as oxalic and fumaric acids. He added that if the resisting nucleus in benzene was \( C_4H_2 \), then he would expect that mellitic (\( C_4H_2O_4 \)) acid would be formed.

In this publication\(^3\) Dewar did not present any significant experimental results that helped nail down the chemical structure of benzene. But his paper has an especial feature that illustrated his understanding of the problem as well as his manual skills. He described the construction a simple mechanical arrangement adapted to illustrate the structure in non-saturated hydrocarbons. His device consisted of a series of narrow thin bars of brass of equal length, where it was possible to join every two of the bars in the centre by a nut. This primary structure represented a single carbon atom with its four places of attachment. In order to make the combination look like an atom, Dewar added a thin round disk of blackened brass under the central nut. When a number of carbon atoms were now joined together, all the joints and arms were moveable and it was easy to show saturation in a closed or open chain and the many arrangements corresponding to the same formula.

Dewar illustrated the use of his device showing seven different ways of associating six carbon atoms, among them being the well-known arrangement often referred to as Dewar’s benzene formula, although he did not single it out in particular (Fig. 2).

Professor Playfair was so impressed by Dewar’s ingenuity that he sent a copy of the paper to Kekulé at the University of Ghent; Kekulé responded by inviting Dewar to spend with him the summer of 1867.

The chemical action of light

Dewar did work on the chemical action of light on plants and its physiological effects on the retina and the optical nerve\(^4\).\(^5\).

According to him, the chemical actions generally induced by light were of the trigger or relay description; they were not necessarily related to the power evolved by the transformation. Plants, for example, stored large amounts of energy in the form of combustible matter under the influence of solar light. It was not yet possible to show that there existed an accurate equivalent proportion between the power of energy of the solar rays, which was absorbed by the green leaves of the plants, and the energy which was stored up in the form of chemical force in the interior of plants. It was known that under the influence of solar energy a square foot of land producing corn or trees was able to manufacture 0.036 lb of carbon per year. Burning of an equivalent amount of carbon
allowed heating 291 lb of water by 1°C. Since the total amount of solar energy reaching the earth could heat by 430,000 lb of water by 1°C the numerical relation between these two phenomena was so high that it was impossible to determine the quantity of solar heat so accurately so as to be able to detect the loss of such a small fraction as absorbed by the plants. Anyhow, Dewar’s first estimate of the mean agricultural efficiency of a given piece of land cultivated as forest was about 1/600 of the total energy of sunlight.

Afterwards, Dewar used the experimental results of Jean-Baptiste Boussingault’s (1802-1877) on the amount of carbon dioxide recomposed by a given area of green leaf and Edward Frankland’s (1825-1899) determination of the thermal value of grape sugar to improve his estimate of the efficiency conserved putting it now at 1/238 of the total incident energy of sunlight.

Dewar worked with McKendrick in measuring the effect of light on the electromotive force of the retina and the optic nerve. Their results indicated that the alteration was 3 to 10 percent of the total amount of the natural current, the action on the compound eye of the crustacean being the same as that on the simple eye. The change of the electrical effect with luminous intensity was found to vary according to Gustav Theodor Fechner’s (1801-1887) law that the difference in sensation was proportional to the logarithm of the luminous intensities by which they were provoked. Dewar also showed that yellow light, which was known to have the greatest luminous effect, was also the most effective in producing the electrical alteration. Warm and cold-blooded animals were shown to behave alike.

**Effect of low temperature on vital phenomena**

Low temperature research is of extreme importance for the study of vital phenomena. Warm-blooded animals will die when subjected to extreme cold. Samples of blood, meat, and milk, sealed in glass tubes, will undergo putrefaction after prolonged immersion in liquid oxygen. The power of resistance, however, increases with simplicity of organization, and bacteria are able to survive an indefinite amount and degree of freezing. The germinating power of seeds is also not impaired by subjection to high cold. Macfadyen and Dewar studying the effect of very low temperatures on a typical series of bacteria possessing various degrees of resistance to external agents. They were first simultaneously exposed to –190°C for twenty-four hours without any noticeable impairment of their growth or functional activity. Phosphorescent microorganisms supplied a striking illustration of the alternate suspension and renewal of vital processes by freezing and thawing. Under normal conditions their cells emitted light as a result of chemical processes of intra cellular oxidation, and the phenomenon ceased with the cessation of their activity. Surprisingly, when cooled down in liquid air they became non-luminous, but the intracellular oxidation producing the phosphorescence recommenced with full vigour when the temperature was raised. The sudden cessation and rapid renewal of the shining faculty of the cells, despite extreme changes of temperature, were very instructive. The same results were observed when the microorganisms were exposed to the temperature of liquid hydrogen. On the basis of these results, Macfadyen remarked “that the fact that life can continue to exist at a temperature at which, according to our present conception, molecular activities with which we are acquainted, either cease or enter on an entirely new phase, affords new ground for reflection as to whether life, after all, is dependent for its continuance on chemical reactions.”

**Liquefaction of gases**

At the end of 1877 the scientific community learned that Louis Cailletet (1832-1913) in France and Raoul Pictet (1846-1929) in Geneva had independently and simultaneously achieved what was believed impossible: the liquefaction of oxygen. On hearing this news Dewar promptly obtained a Cailletet expansion apparatus, quickly set to work and developed his own appliances. Simultaneously, two Polish scientists, Zygmunt von Wroblewski (1845-1888) and Karol Olszewski (1846-1915) also set about to modify Cailletet’s apparatus and within two months they were able to produce a reasonably amount of liquid oxygen. To do so they resorted to cooling Cailletet’s thick walled glass tube down to lower than –130°C using pumped ethylene rather than ethylene at atmospheric pressure. Obtention of a significant amount of liquid oxygen by Wroblewski and Olszewski was considered to be a major scientific achievement. It demolished the concept of a permanent gas and established that the concept of critical isotherm developed by Thomas Andrews (1813-1885) for carbon dioxide was applicable to all gases.

In 1878 Dewar succeeded in producing liquid oxygen in England for the first time. He performed
many experiments with the liquid and in 1891 he showed that it was magnetic. He was the first person to obtain solid oxygen.

He constantly improved his equipment until he was able to produce routinely large quantities of liquid oxygen and liquid air materials, which would be a major help factor in his following achievements. His next major goal was to try to liquefy hydrogen. The difficulty of the problem can be appreciated from the fact that the critical temperature of hydrogen is 33.3 K whereas the lowest temperature obtainable by pumping liquid air (the coolest medium available at that time) is in the neighbourhood of 70 K. Dewar’s experiments on the liquefaction of hydrogen were performed at the Royal Institution in London. On May 10, 1898, after several runs, which were hampered by the presence on impurities in the air and in the equipment, he finally succeeded in liquefying hydrogen. According to his Laboratory Notebooks: “Shortly after starting the nozzle plugged but it got free by good luck and almost immediately drops of liquid began to fall...and soon accumulated 20 cc. The hydrogen was a clear transparent liquid well-defined meniscus ...” When Dewar immersed a sealed tube contained helium into the liquid hydrogen he “could see liquid formed. This tube gave nothing when placed in liquid air.” He repeated the experiment several days later and found liquid hydrogen appear “more brilliant than liquid air”.

Dewar presented his results to the Royal Society on May 12, 1898, and asserted that he was able to liquefy both hydrogen and helium; only by mid-June did he stop mentioning the liquefaction of helium after he understood that what he took to be condensed helium were traces of impurities.

Liquefaction of hydrogen was regarded at the time as a major technological achievement and was fraught with dangerous experimentation, as can be appreciated by the fact that during the course of this liquefaction study two of Dewar’s assistants, J. W. Heath and Robert Lennox, both lost an eye, as a result of explosions.

Some authors claim that Dewar never gave a detailed account of his apparatus, although it was based on the Joule-Thomson effect. Gravrogolu has pointed out that although this claim is nominally correct, the full details of his equipment do appear in Dewar’s Laboratory Notebooks.

Dewar, after succeeding in liquefying hydrogen, did much research studying its properties, as well as the behaviour of substances at this new low-temperature level. One year after being able to liquefy hydrogen he succeeded in achieving its solidification. His first attempts at obtaining the solid phase, made by pumping hydrogen vapour over the liquid, failed and he immediately realized that the stray heat influx into his cryostat was too large to be counterbalanced by the cold he could obtain in evaporating the liquid. This finding lead to further improvements in the design and building of what would eventually become known as the Dewar flask, for storing liquefied gases (see below).

At about that time it was realized that helium, which had recently been found (1884) to also exist in the earth, had an even lower boiling point. This discovery set the three personalities, Dewar, Olszewski and Heike Kamerlingh Onnes (1853-1926) on independent programs to achieve the liquefaction of the gas having the lowest boiling point.

After Kamerlingh Onnes succeeded in liquefying helium in 1908, Dewar lost interest in low temperature research and this topic became neglected in England for many years.

Fluorine

Dewar collaborated with Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) in achieving the liquefaction and solidification of fluorine and studying the properties of the element in these two states. For this purpose Moissan travelled to England and took with him his apparatus for producing fluorine.

The liquefaction of fluorine was realized one year before that of hydrogen and was achieved initially at about -185°C using liquid oxygen as the cooling medium, and afterwards at -190°C using liquid air.

Moissan and Dewar proceeded then to determine the physical and chemical properties of liquid fluorine. They reported that it was a clear yellow liquid of great mobility, boiling in open vessels at -187°C and refusing to solidify at -210°C. It was soluble in liquid air and oxygen, had a density 1.14 times that of water and a capillarity smaller than that of liquid hydrogen; examined with the spectroscope through a thickness of about 0.5 cm showed no specific absorption bands in the visible spectrum and put between the poles of a powerful electromagnet did not show any magnetic phenomena. The energetic chemical affinities characteristics of the gas were almost entirely suppressed by the extreme cold needed for its condensation. The liquid could be
stored harmlessly in glass bulbs and did not react with oxygen and water. There was no reaction either when silicon, selenium, boron, carbon, sulphur, red phosphorus, arsenic, iodides, and reduced iron were first cooled in liquid oxygen and then put in an atmosphere of fluorine. It did though react with hydrogen and hydrocarbons with incandescence. Turpentine in the solid state was attacked by liquid fluorine; combination took place with explosive force, a brilliant flash of light and deposition of carbon. It would thus seem that the powerful affinity of fluorine for hydrogen was the last to disappear.

If a current of liquid oxygen was directed to the surface of liquid oxygen at about −190°C, the fluorine dissolved in all proportions, imparting a yellowish colour, giving the liquid a graded tint from the upper to the lower part. If on the contrary, fluorine gas was introduced at the bottom of liquid oxygen, the yellow colour was produced at the bottom and diffused slowly to the upper layers. This phenomenon indicated that the densities of liquid fluorine and oxygen are very near each other.

Liquefication of fluorine was now followed by achievement of its solidification using liquid hydrogen. The yellow liquid was converted into a white solid (solid chlorine is also solid, bromine becomes somewhat paler in colour) melting at about 40 K, a temperature a little below that at which solid oxygen melts. When the point of a tube containing solid fluorine plunged in liquid hydrogen was broken off by means of steel pincers a violent explosion took place.

**The use of charcoal in the production of high vacuum**

Tait and Dewar were the first to realize that charcoal had a strong power for retaining gases even under very low pressures: “The method we have devised to absorb traces of gases is based on the remarkable power of absorption of cocoa-nut charcoal for gaseous bodies generally... We need hardly say that this easy means of obtaining vacua will be of importance in spectroscopy observations...”

The method developed by Tait and Dewar consisted of heating charcoal to low red heat in a tube during exhaustion with a mercury pump and then sealing the vessel when it was completed. When the charcoal was cold the vacuum was found to be so complete that even when a powerful coil was used, no spark would pass between platinum wires sealed into the tube one-fourth of an inch apart. The method remained underdeveloped until 1904 when Dewar made experiments with finely divided platinum and palladium, which were known to occlude gases, in particular hydrogen and oxygen, even at ordinary temperatures and to take up larger quantities when heated. Finding that their absorptive power was little affected by cooling, he remembered his results about charcoal and proceeded to compare its behaviour with that of the two metals mentioned. A surprising finding was the extraordinary absorption power that charcoal presented when cooled by liquid air. Further experimentation showed that the absorption power of charcoal depended on the way in which it was prepared and that the power was enhanced by carbonising the coconut shell slowly while gradually increasing the temperature; “whereas the specimens at first used absorbed only about 150 cm³ of air per gram, at −185°C those prepared subsequently with these precautions absorbed from 350 to 400 cm³ per gram.” Porous materials other than charcoal, such as alumina, meerschaum (sepiolite), and silica, also absorbed an increased proportion of gases at low temperatures but their retention power was much inferior to that of charcoal.

It was also found that pressure has but relatively little influence in increasing the amount of gas absorbed.

One of the most interesting series of observations made was related to the equilibria established when saturating charcoal at low temperatures with a mixture of gases. Charcoal that has been heated, exhausted, and then allowed to absorb atmospheric air at −185°C, presumably contained within its pores a mixture having about 80 percent nitrogen and 20 percent oxygen. If, at the same low temperatures, a stream of air was passed slowly and continuously over the charcoal, initially almost pure nitrogen escaped, showing that the system had preference for oxygen: after several hours, however, the occluded gas had a new and apparently definite composition. Displacement of the whole of the gas absorbed, produced a mixture containing on the average about 60 percent of oxygen. If charcoal saturated with such a mixture was subjected in a similar manner to the action of a slow current of hydrogen, then about one out of every five molecules of oxygen and nitrogen were displaced by hydrogen, giving rise to a composition of about two nitrogen molecules and two oxygen molecules per molecule of hydrogen. Other experiments led to the conclusion that the more volatile or less condensable the gas was, the less it was absorbed and retained in the charcoal.
Dewar concluded that charcoal could be used for separating the constituents of a mixture of gases of different degrees of volatility.

One great advantage attached to the use of charcoal was that it allowed the maintenance of a very high vacuum during any required period of time. In the pre-charcoal period, this was impossible due to the leakage of gas into the exhausted vessel either as a consequence of the mechanical imperfections of the glass vessel or because of the existence of air imprisoned in bubbles or tubes within the glass. Such leakage may now be counteracted by means of charcoal. Metallic vacuum vessels could not be made formerly for a similar reason, the gas occluded within the metal escaping gradually and spoiling the vacuum in the vessel. By enclosing a quantity of charcoal in a globular space so that it is cooled by the liquid air in the inner vessel, this difficulty is entirely obviated. Such metallic vessels are now made of nickel, brass, or copper. These vessels are as effective as chemically silvered glass vacuum vessels.

The Dewar flask

During his experiments on the liquefaction of gases Louis Paul Cailletet (1832-1913) found that observations were hampered by the frost, which formed on the outside of the glass tube of his apparatus. To eliminate this problem he surrounded this tube by a second one, fitted on to the inner tube with stoppers and filled at the bottom with calcium chloride, as a drying agent. This arrangement kept the internal tube surrounded by a dry atmosphere so that no condensation could take place. Further improvements were achieved by researchers trying to liquefy oxygen using liquid ethylene as the cooling medium: Cold ethylene vapor was drawn over the outer wall of the glass vessel containing the liquid ethylene, which in turn shielded the liquid oxygen from inflowing heat. This was the system adopted at the same time by Karol Olszewski (1846-1915) in Poland and Dewar in England. The specially designed container in which the liquefied gas was kept for observation became known as a cryostat and the art of producing cold was called cryogenics.

The heart of Dewar’s apparatus was a double-wall calorimeter made from an inner brass chamber surrounded by an external brass chamber. To improve the thermal insulation of the instrument Dewar evacuated the volume between the two chambers. Scientists had known the insulating properties of vacuum in preventing the influx of heat, by the virtual elimination of convection currents and minimizing conduction, for several years. However, Dewar was the first person to apply vacuum insulation for studying the properties of liquid gases.

The next step was replacement of the metallic chambers by others made of glass. Dewar performed a large number of experiments searching for an improved vessel and by 1893 he had improved the time storage of liquid nitrogen by a factor of 5. Other experiments demonstrated that heat losses could be significantly cut by introducing into the vacuum space powders such as charcoal, lamp black, silica, alumina, and bismuth oxide. Addition of a small amount of charcoal in the vacuum space served to improve the vacuum by cryoabsorption. These experiments were followed by the finding that coating the glass with a thin layer of silver or mercury reduced radiation losses by a factor of 13. Dewar also found that using three turns of aluminium sheet was not as good as using silvered surfaces. As stated by Scurlock, had Dewar gone on to apply further turns of aluminium, he would have discovered the principle of multi-layer insulation, which is superior to silvering. His final version, which is virtually the same as the thermos bottle of today, was first demonstrated in a lecture at the Royal Institution early in 1893.

Dewar had substantial difficulty in finding competent glass blowers to undertake the construction of his double-walled vessels and was forced to make them in Germany; by 1898, a ready supply became available. However, it was said that the discovery by a German glassblower, Muller of Coburn, that a silvered vacuum flask could also be used for keeping milk hot overnight for feeding his baby, lead to a major commercial development, namely the Thermos Flask for keeping liquid hot. The flask was not manufactured for commercial or domestic use until 1904, however, when two German glass blowers formed Thermos GmbH. They held a contest to rename the vacuum flask and a resident of Munich submitted “Thermos”, which came from the Greek word “Thermē” meaning “hot.” In 1907, Thermos GmbH sold the Thermos trademark rights to three independent companies: The American Thermos Bottle Company of Brooklyn, NY; Thermos Limited of Tottenham, England; and Canadian Thermos Bottle Co. Ltd. of Montreal, Canada. (Thermos is a proprietary name or trademark applied to a type of Dewar flask protected by a metal casing.

Following Dewar’s invention in 1892, the design of Dewar vessels for containing cryogenic liquids did
not change for over 60 years, until the growing availability of liquid helium in the 1950s gave rise to its use in open cryostats without liquid hydrogen shielding. From the 1960's on there have been significant improvements in the economy of storage of cryogenic fluids. In 1955 a charge would last for about 6 hours and the evaporation rate per day was dramatic improvements were achieved by modified shielding. From the significant improvements in the economy of storage aluminised plastic film, etc. Scurlock has described them in detail.

Low temperature physics

Between 1892 and 1895 Dewar and John Ambrose Fleming (1849-1945, the inventor of the thermoionic valve) of University College, London, collaborated in the study of the behaviour of materials at low temperature. Their work covered a wide variety of subjects, such as heat conduction, thermoelectricity, the temperature dependence of the electrical resistance of several materials and elements, the thermopower of some 24 metals and alloys, the dielectric constant of metals, alloys, and inorganic materials, and the magnetic behaviour of steel, liquid oxygen, and liquid air at low temperatures.

The study of electrical resistance was the most interesting because resolution of a theoretical controversy was at stake. It was well known by this time that the electrical resistance in a metal decreased with temperature. Exactly what would happen to resistance at temperatures approaching absolute zero, however, was hotly debated. Lord Kelvin believed that the flow of electrons, which seemingly improved with decreasing temperatures as the lower resistance indicated, might actually stop altogether, the electrons becoming frozen in place. The resistance at absolute zero would then be infinitely high. Others, including Kamerlingh Onnes and Dewar, assumed that the decrease in resistance with falling temperature would continue in an orderly fashion, ultimately reaching zero at the zero temperature point.

Accordingly, in 1896 Dewar and Fleming studied the resistance of mercury and confirmed that there was a large decrease in the resistance at roughly 230 K as the liquid froze, and noted further that the resistance continued to drop as the temperature decreased. They found that all metals behaved similarly to mercury below its freezing point. The resistivity of all pure metals decreased with increase of cold, but many abnormalities and peculiarities were brought to light. The various metals did not, in all cases, maintain the same relative places on the scale. At -200°C copper was a better conductor than silver, iron than zinc, aluminium than gold. The extraordinary reduction in resistance of some of the metals at the boiling point of hydrogen was very remarkable. Thus copper has only 1/105, gold 1/30, platinum 1/35 to 1/17, silver 1/24 the resistance at melting ice, whereas iron was only reduced to 1/8 of the same initial resistance.

It was left to Kamerlingh Onnes to perform very delicate experiments on the electrically conductivity at very low temperatures of highly purified mercury and prove definitely the phenomenon of superconductivity. Kamerlingh Onnes found that at all measured temperatures the expected regular decrease in resistance. At liquid-helium temperatures still measurably higher than absolute zero, however, the resistance already appeared to have completely vanished. Kamerlingh Onnes published his findings in November 1911 in a paper entitled “On the Sudden Change in the Rate at Which the Resistance of Mercury Disappears”. Subsequent tests of tin and lead showed that superconductivity was a property of many metals, if they were cooled sufficiently.

Dewar and Fleming were unable to offer an explanation for many of their experimental findings. For example, cooling substances such as glass, paraffin, gutta-percha, and ebonite that were good insulators at room temperature turned them into better insulators after being immersed in liquid air. Most magnets gained strength when subjected to intense cold, some did not; moreover, when pure iron was immersed in liquid oxygen, it afterwards required a much greater magnetic field to magnetize it than was needed under normal conditions. Even mercury at very low temperature became a good magnet, whereas at room temperature if exhibited virtually no magnetic power. Mechanical strength was also changed significantly: Iron, copper, and zinc exhibited enhanced rigidity and greater strength: a coil that at room temperature could support only a pound or so of weight could support three times as much after immersion in liquid oxygen. When balls of various metals taken from the bath were dropped on an anvil, they bounced higher than they normally did.

These results led Dewar and Fleming to test the flow of a metal into wire about the temperature of liquid air. The only metal that could be examined in
this way was lead. At the ordinary temperature in the apparatus used, lead flowed into wire under a pressure of 7.5 tons, but at -170°C, it was necessary to apply the pressure of 67.5 tons, or nine times the pressure, to cause flow. In the same manner solder flowed into wire at the ordinary temperature when 35 tons pressure was applied, but at the temperature of -170°C the application of 125 tons pressure caused no motion of the alloy through the aperture. This was the greatest pressure that any of the dies used in the experiments would stand without rupture.

Perhaps the most striking case of alteration in properties resulting from extreme cold was afforded by natural rubber, which is one of the most elastic of substances at ordinary temperature. When cooled in liquid air, however, it became so rigid and brittle that it was easily pulverized. One of the most interesting illustrations of the increased strength and elasticity of a body at the lowest temperatures was to take a very thin transparent film of natural rubber, to stretch one end its ends over a test tube and the insert and seal the other one in a long narrow tube. The test tube end was immersed in liquid air while the other end was placed in a vessel containing mercury to observe the diminution in pressure, which was between 9 to 10 inches of mercury. The film thus treated was shown to be impermeable to gaseous oxygen by molecular diffusion. Repeating the experiment with liquid hydrogen instead of liquid oxygen produced a pressure drop of almost 29 inches of mercury, the film being known impermeable to hydrogen diffusion. In the cooled state such films struck with a cork hammer gave out a clear metallic ring; repeating the striking while the film heats back to room temperature, produced a gamut of notes by the varying elasticity.

A most curious and unexpected result was related to the optical properties of materials. Under the extreme cold, substances such as mercuric oxide, normally bright scarlet, faded to light orange, while white-coloured substances intensified their whiteness, and blue coloured substances did not change their colour at all. Dewar and Fleming thought that changes in colour corresponded to changes in the substances' specific absorption of light, but they could not be certain.

Chemical affinity was almost completely abolished by cold and chemical combinations that at room temperature would always generate electricity failed to do so at the temperature of liquid oxygen. For example, phosphorus, sodium, and potassium remained inert in liquid oxygen and failed to react; voltaic combinations brought down to its temperature ceased to give electric currents. Photographic film, however, retain about one-fifth of their ordinary sensitiveness to light, nor does it wholly disappear even through the agency of liquid hydrogen. Dewar and Fleming speculated that possibly the decomposing force which came into play under these circumstances was not chemical but mechanical.

An elaborate course of experiments on thermal transparency, carried out in 1897-1898, completely negated Raoul Pictet’s (1846-1929) conclusion that at a given degree of cold, non-conducting substances lose their faculty of insulation. Pictet after an elaborate investigation had concluded that below a certain temperature all substances had practically the same thermal transparency and that a non-conducting body became ineffective at low temperatures in shielding a vessel from the influx of heat. Dewar and Fleming proved that the substances tested by Pictet remained unimpaired at the boiling point of liquid air, the abnormal transferences of heat observed by Pictet were not so much due to the materials themselves, but to the air contained in their interstices.

The comparative absorption of X-rays by various frigid bodies was used to determine that the atomic weight of argon is double its density relative to hydrogen, obtained confirmation from the approximately equal opacities found for that substance in the liquid state, for liquid chlorine and for potassium. This was the first use of X-rays for determining atomic weight.

**Phosphorescence and photographic action**

Phosphorescence may be regarded as a kind of fluorescence which lasts a long time after the excitation has ceased, and may be briefly defined as the phenomena observed when certain substances give out light through the transformation of absorbed vibrations of shorter period. Temperature was known to play an important part in the phenomena of phosphorescence and Pictet had shown that at very low temperatures it might inhibit the phenomena totally. He had first exposed a powder of a phosphorescent substance such as calcium sulphide, barium sulphide, and strontium sulphide to sunlight and then suddenly, inserted it in a double wall glass cylinder full of nitrogen monoxide at -140°C. The tube was cooled to about -100°C and then transferred to a dark environment. Pictet observed that under these conditions the material did not emit light but as
the tube started to warm up the material regained its normal brilliance, without the help of external light and without having received any significant influence of diffuse light. In other words, the material kept a latent store of light energy that was again evolved on allowing the sulfide to rise to ordinary temperature. These results were common to all the substances studied. He also determined that the temperature limit for the extinction of visible gleam was between −60° to −70°C. Pictet concluded that the production of luminous phosphorescence required a certain movement of the particles that constituted the bodies. Cooling to a sufficiently low temperature cancelled the oscillating caloric movements, prevented the generation of light waves, and phosphorescence disappeared.

Dewar extended Pictet’s results to materials that showed little or no phosphorescence. He found, in general, that the great majority of substances exhibiting weak phosphorescence at ordinary temperature would become markedly more active at very low temperatures. Thus gelatin, celluloid, paraffin, ivory, horn, and natural rubber all of which are not phosphorescent, become distinctly luminous, with bluish or greenish phosphorescence, after cooling to −180°C with liquid air and being stimulated by the electric light. All alkaloids forming fluorescent solutions invariably became phosphorescent at low temperatures. Glycerine, sulphuric acid, hydrogen chloride, and strong ammonia, were also very bright, as well as most substances containing a ketone group. Milk was highly phosphorescent; water when pure was only feebly phosphorescent, but remarkably so when impure. Colored salts generally showed little activity, but a large number of colorless salts were very luminous. Remarkable results were obtained with an eggshell and a feather, respectively. The egg shone brilliantly as a globe of blue light and the feather was equally brilliant, its outline showing clearly in the darkened room. The white of egg was more phosphorescent than the yolk, white substances generally being superior in this respect to the colored ones. Other organic substances giving good results were cotton wool paper, leather, linen, tortoise shell, milk, and sponge. Complexity of structure was inferred to be one of the main conditions upon which the possession of this quality depended.

An unexpected result was that only oxygen among the simple gases showed this ability. A current of oxygen flowing into an exhausted tube, after exposure to an electric spark, emitted hazy white light accompanied by ozone formation, indicating the simultaneous progress of molecular change. The effect was completely stopped by the presence of hydrogen, or by the least trace of organic matter. At the temperature of liquid hydrogen, phosphorescent action was further intensified.

The electric stimulation of crystals by cooling brought about actual discharges between the molecules. In some platinocyanides and nitrate of uranium, the temperature of liquid air suffices to develop marked electrical and luminous phenomena, which are intensified and expanded through the agency of liquid hydrogen. Some crystals when placed in liquid hydrogen became for a time self-luminous, on account of the high electric stimulation brought about by the cooling causing actual electric discharges between the crystal molecules. This was very marked with some platinocyanides and nitrate of uranium. Even cooling such crystals to the temperature of liquid air is sufficient to develop marked electrical and luminous effects.

Considering that both liquid hydrogen and air are highly insulating liquids, the fact that electric discharges took place under such conditions proved that the electric potential generated by cooling must be very high. When the cooled crystal were taken out of the either liquid and allowed to heat, luminosity and electric discharge took place again during the return to the normal temperature. A crystal of nitrate of uranium got so highly charged that, although its density is 2.8 and that of liquid air about 1, it refused to sink, sticking to the side of the vacuum vessel and requiring a marked pull on a silk thread, to which it was attached, to displace it. Such a crystal rapidly removed cloudiness from liquid air by removing all the suspended particles onto its surface.

Along with these experiments on phosphorescence, a number of photographs were taken at −180°C, using various sensitive plates and films, and compared with similar photographs taken at the same time under similar conditions at room temperature. It was found that the photographic action was reduced by 80% at the temperature of −180°C.

**Hydrogenium**

Thomas Graham (1805-1869) studied diffusion of several gases in metals and found that palladium adsorbed large amounts of hydrogen gas upon heating and cooling. Graham believed that hydrogen was the vapour of a very volatile metal, hydrogenium, which had alloyed with the palladium. Others held to an
alternative hypothesis, which was simply that the hydrogen had been absorbed without chemical reaction. Graham measured the specific gravity of the occluded hydrogen by observing the increase in length of palladium wire after being fully charged with hydrogen and estimated the density of the absorbed hydrogen to be 0.733. Dewar measured the specific gravity, specific heat of hydrogen and the coefficient of expansion of hydrogen in palladium, as well as its absorption in the metal at red heat\(^\text{27-29}\). On the basis of Regnault’s findings that the specific heat of an alloy was equal to the sum of its constituents\(^\text{30}\) he calculated the specific heat of absorbed hydrogen as 3.1 cal per atom weight, nearly identical to that of gaseous hydrogen. He then measured the specific gravity of the absorbed hydrogen in palladium during the saturation process and obtained a constant value of 0.620, which meant that the atomic volume of hydrogen was 1.6. The coefficient of expansion of hydrogen was found to be 0.000246, a value about one and a half larger than that of liquid mercury.

All these results led Dewar to conclude that hydrogen was present as an absorbed gas and not forming an alloy, as claimed by Graham.

**Cordite**

Dewar was appointed to the Government Committee on Explosives (1888-1891) and with Sir Frederick Augustus Abel (1827-1902), a chemist and military explosives specialist, invented cordite (1889), a type of smokeless gunpowder. Before the invention of cordite, battles could not be fought without the obscuring smoke clouds of gunpowder weapons. Cordite was mixed from purified ingredients of nitroglycerine, nitrocellulose and petroleum jelly then extruded as cords. When dried, this explosive could be measured more precisely and handled more safely than gunpowder. Cordite was later adopted as the standard explosive of the British army, and proved vital in WWI.

**References**

12. Moissan H & Dewar J, Compt Rendu, 125 (1897) 505.
15. Dewar J, Proc Roy Inst, 16 (1899) 1, 212.
27. Dewar J, Phil Mag, 44 (1872) 400.
29. Dewar J, Phil Mag, 47 (1874) 334.

**Notes**

1. The Dewar flask or vacuum flask/bottle is a container for storing hot or cold substances, i.e. liquid air. It consists of two flasks, one inside the other, separated by vacuum. The vacuum greatly reduces the transfer of heat, preventing a temperature change. The walls are usually made of glass because it is a poor conductor of heat; its surfaces are usually lined with a reflective metal to reduce the transfer of heat by radiation. The whole fragile flask rests on a shock-absorbing spring within metal or plastic container, and the air between the flask and the container provides further insulation. The common thermos bottle is an adaptation of the Dewar flask.