James Ballantyne Hannay

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RESUMEN. James Ballantyne Hannay (1855-1890), un autodidacta y hábil experimentador, descubrió que los fluidos supercríticos son capaces de disolver sólidos; estudió los efectos de la presión y la temperatura en el fenómeno y así, fijó las bases para el desarrollo de la extracción supercrítica, una poderosa herramienta de análisis y separación de fases. Demostró que el estado crítico no es la disolución de una fase en la otra, sino que las fases gas y líquido se unifican en una sola que posee propiedades homogéneas. Inventó la llamada técnica de tiempo, que permite determinar la existencia y naturaleza de hidratos en sales simples y complejas. Fue el primero en preparar diamantes artificiales y estudiar a fondo el proceso de tostación de la pirita para producir plomo, sus óxidos y sales, en un estado de elevada pureza.

ABSTRACT. James Ballantyne Hannay (1855-1890), a self-made scientist and skilful experimenter, discovered that supercritical fluids dissolve solids, studied the influence of pressure and temperature, and thus set the stage for the development of the powerful analytical and separation technique of supercritical gas extraction. He proved that the critical state is not the solution of one phase in the other, but the gas and liquid phases become one, having uniform properties throughout. He invented the time method technique that allows determining the existence and nature of hydrates in simple and complex salts. He was the first to prepare artificial diamonds and studied the toasting of pyrite and how to manufacture lead, its oxides and salts in a state of high purity.

LIFE AND CAREER
There is very little information regarding the life, family, and career of James Ballantyne Hannay. The following has been condensed from two papers related to the subject. James Ballantyne Hannay was born on January 1, 1855, at Glasgow, and passed away in 1890. He is buried in Barbour Cemetery, Cove, Helensburgh. His father was the proprietor of the Grand Theatre in Glasgow. He was educated at the Larchfield Academy but he did not like school, and left in 1869 at the age of fourteen to help his father in the theatre. A friend of the family lent him books on chemistry, and he set up a laboratory in his home. The tradition in his family is that he was mainly self-taught. In the year 1872 he joined the Chemical Society and a year later he published in the journal of the Society a series of papers on improved analytical methods. In 1873 he joined the firm of J.J. White, manufacturers of potassium bichromate at Shawfield Chemical Works, Rutherglen, Glasgow, where after some time he became works manager. In 1876 he left the firm, apparently on account of ill health. In that year he was elected Fellow of the Royal Society of Edinburgh, having become qualified for admission on attaining the age of 21 years. He then entered the Anderson’s College. In the year 1877 he was on the staff of the college, probably as private assistant to one of the professors. In January 1878, he was appointed Assistant Lecturer on the staff of the chemistry department of the Owens College, Manchester, where Henry Enfield Roscoe (1833-1915) and Carl Schorlernmer (1834-1892) held the chairs. He succeeded Mathew Moncrieff Pattison Muir (1848-1896), who took up an appointment in Cambridge, and had, as colleagues, W. C. Williams and Thomas Carnelley (1854-1890). Hannay did not take up his appointment until February 1878, and after Easter 1878 he was absent owing to illness. He was reappointed for the session 1878-79 but resigned in the month of September and was replaced by Peter Phillips Bedson (1848-1943).

According to Flint² Hannay was one of the earliest technical chemists to set up a private laboratory, the Annfield Chemical Works, and make a living by consulting and development of industrial processes. Hannay’s industrial activities were extremely varied and led to a large number of patents in England, Germany, Canada, and the United States. One of his earliest ones is on the use of sacrificial zinc anodes for protection of boilers against corrosion. Other patents relate to processes and apparatus for the manufacture and transportation of liquid chlorine; extraction of gold and other precious metals from ores; improved methods of recovering lead and its compounds from galena; an industrial lighting device which he named the Lucigen; white lead pigments and paints; anti-fouling paints for ships bottoms; and many others.
SCIENTIFIC CONTRIBUTION

Hannay published about 60 papers on subjects related to analytical and inorganic chemistry, as well as mineralogy and thermodynamics. Here we review the most significant contributions.

Analytical chemistry

As a consultant, Hannay was involved in the analysis of mercury ores and found that most of the processes then in use were either very tedious or not so accurate. For this reason he set about devising two new methods, one volumetric and the other voltaic (electrolytic), which were faster and at the same time accurate enough. The volumetric method was based on potassium cyanide. Addition of potassium cyanide to a mercury solution resulted in the complete transformation of the mercury salt into mercuric cyanide but at this point the solution became cloudy, probably due to the presence of potassium carbonate. Hannay found that adding a few drops of diluted ammonia could solve the problem. A white precipitate was produced that reddissolved totally when the conversion to cyanide was complete. The point of saturation could be determined with great accuracy with the help of a beam of light passed through the liquid, as both the mercuric and cyanide solutions were colorless.

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In a second paper on the subject Hannay indicated that the methods in use for the volumetric estimation of cyanide with a solution of a silver salt and iodide were appropriate only in the absence of ammonia and alkalis. In addition, it was often desirable to estimate the cyanide in an alkaline solution already containing silver cyanide. He then proceeded to describe the method he had developed for this purpose, which was based on the anomalous behavior of mercury cyanide with alkalis: if a mercuric salt is added to an alkaline solution containing cyanogen, no precipitation takes place until all the cyanogen has combined with mercury. The cyanide is dissolved in water, then rendered alkaline preferably with ammonia, and a standard solution of mercuric chloride is added until a bluish-white opalescence is produced, signaling the end of the reaction.

Inorganic chemistry

Halogen derivatives

According to Hannay, little information was available about the chlorides of iodine, and part of it was conflicting. Some alleged that the monochloride was a liquid, and others a solid; some said that it dissolved in water without decomposition while others claimed that it was instantly decomposed by water. The product could be prepared in two ways, by passing a stream of chlorine gas over iodine until it was liquefied and then rectifying the product between 100 and 102 °C; or by heating a mixture of iodine and potassium chloride, the monochloride distilling over almost pure. The liquid thus obtained could remain liquid for five or six days, but generally crystallized before. Hannay studied the properties of the monochloride, measured the change in density with temperature, and indicated that its most curious property was that when freshly distilled it remained liquid even when cooled down to –6 °C, although its melting point was 24.7 °C. When iodine chloride is decomposed by water, iodine precipitates and a deep red liquid is formed, which fumed slightly and had a density of 2.629. On heating it began to boil a little above the boiling point of bromine and the temperature steadily increased until only sulfur remained, suggesting that no compound was present. Another proof that there was no chemical combination was the fact that when the solution was in contact with humid air, sulfur separated as crystals, which were easily soluble in carbon disulfide.

If a chemical compound had been present, sulfur would play an electronegative part and the element deposited would be insoluble in carbon disulfide. Sulfur bromide was found to dissolve phosphorus with evolution of heat. Addition of arsenic resulted in the formation of a red solution, with strong heat release. When sufficient arsenic was added to the liquid, arsenic bromide was formed, and even arsenic sulfide. If the quantity added was small and the liquid consequently cooled to –18 °C, beautiful dark red crystals of the new compound could be separated. These melted at –17 °C forming a liquid containing arsenic, sulfur, and bromine, having density 2.789 and being decomposed by water into arsenic acid, hydrogen bromide, and sulfur. Analysis corresponded to the formula AsBr₃. Hannay thought that the latter was probably a compound of arsenic sulfobromide and sulfur dibromide, after the formula AsSBrBr₂.

Another memoir described the action of bromine on sulfur. Mixtures of both components remained liquid below the freezing temperature of bromine. The mixture could be cooled down to –30 °C without solidification but becoming more viscous. Hannay concluded that all the experimental evidence indicated that the action of bromine upon sulfur increased in a regular form up to the composition SBr₂, totally ignoring the point SBr, and followed by the possible formation of SBr and SBr₂. There was no evidence of the formation of SBr₂.

Today the author knows that of the possible pure sulfur-bromine compounds only disulfur dibromide and the bromosulfoanes (SnBr₃) are recognized. Disulfur dibromide is a garnet red liquid that can be obtained from its constituting elements or by treating gaseous hydrogen bromide with sulfur dichloride, S₂Cl₂, at room
temperature. Bromosulfanes are formed from chlorosulfuric acid and hydrogen bromide at room temperature. They are oily liquids whose color ranges from dark red, S₂Br₂, to raspberry red, S₈Br₂, and whose stability decreases as the sulfur chain is increased.

The time method

Hannay believed that an examination of the rate at which the volatile constituent of a compound is driven off might afford valuable information as to its constitution and bring out the relation between its varying vapor pressure and its chemical constituents. In order to test this possibility Hannay intended to extend this method to all kinds of compounds containing a volatile constituent, such as hydrates. William Ramsay (1852-1916; 1904 Nobel Prize for Chemistry) suggested to him that the composition of many of the amorphous hydrates, such as those of aluminum and iron having somewhat indefinite compositions, might be accurately determined by this method, as the vapor pressure of the hygroscopic and combined water would be sufficiently different to distinguish between them. The basic idea was to plot the loss in water against time and notice any singular changes in the slope of the curve (Hannay’s time method, the basis of today’s thermogravimetric analysis, TGA).

The first part of this work was devoted to crystalline hydrates, in particular, sodium sulfate hepta- and decahydrates and the heptahydrates of magnesium, zinc and ferrous sulfates. The first salt studied was sodium sulfate decahydrate in order to see if its vapor pressure would afford information about the formation of the heptahydrate. Hannay found that on heating the moisture was eliminated from this compound at a constant rate without the slightest change in rate at the point where the residue composition was equivalent to the heptahydrate, showing either that the compound was not directly formed from the decahydrate, or it had the same vapor pressure. Since the solubility of sodium sulfate decreases above 33 °C, and solubility of the anhydrous salt is less than that of the hydrate, Hannay supposed that at 33 °C the hydrate begins to dehydrate in solution. Considering 33 °C as a kind of critical point of the salt, he proceeded to examine it at this temperature. Isothermal dehydration showed a sudden falling of the rate when the loss of water was about 51 %, a composition equivalent to sodium sulfate monohydrate, that is, at 33 °C the decahydrate did not split into water and anhydrous salt but into water and the monohydrate. Repetition of the experiment at 10 °C indicated the appearance of the dihydrate when the loss of water had reached 44 %.

Similar experiments with magnesium sulfate heptahydrate indicated the presence of a hexa-, a tri-, a di-, and a monohydrate. For ferrous sulfate heptahydrate the curve indicated the existence of the di- and monohydrate, the latter already known. Zinc sulfate heptahydrate proved the existence of the hexa-, penta-, tri-, di-, and monohydrates. Of these, only the zinc sulfate trihydrate was unknown before.

In a following publication Hannay reported the results of applying the time method to β-double salts such as MgZn(SO₄)₂ · 14H₂O, Fe₂Mg(SO₄)₂ · 14H₂O, Cu₂Mg(SO₄)₂ · 14H₂O, and Cu · 3Zn(SO₄)₂ · 28H₂O. The time method showed that two hydrated salts forming a double salt containing the normal amount of water (in this case seven molecules), spent one half of the affinity of the anhydrous salt for its water of crystallization in combining with each other, showing that the formation of double salts is comparable with other forms of chemical action. For example, where dehydration of a physical mixture of the two heptahydrates of magnesium and zinc left the compound MgZn(SO₄)₂ · 4H₂O when 33.75 % of moisture had been eliminated, the two salts when combined, left a residue of MgZn(SO₄)₂ · 2H₂O when 40.50 % of the moisture had been eliminated. In other words, the individuals of the compound held only one-half of the moisture they would retain when free.

Capillary flow

In 1843 Jean Louis Poiseuille (1799-1869) developed a very accurate relation describing the laminar flow of an incompressible viscous flow through a capillary tube, indicating that the phenomenon was affected by the length and diameter of the tube, the pressure acting on the liquid, and the temperature. He also made experiments with saline solutions, but was unable to find a connection between the concentration (expressed in percentage weight) and the results. Others, such as Thomas Graham (1805-1869), had studied the phenomenon using organic liquids but had performed all the experiments at the same temperature. Thus water flowed five times as quickly at 1 00 °C as at 0 °C, and in a series of alcohols, the difference between their boiling points was so great that it was not possible to correlate the pertinent vapor pressure with the mobility (today, viscosity).

Hannay believed that the study of the phenomenon should be widened to include the effect of temperature and the effect of concentration expressed in terms of equivalents of the solute (today, molar fraction). In order to do so he modified the apparatus originally used by Poiseuille; his apparatus consisted of a capillary tube at the bottom of which are attached two bulbs, one for the purpose of measurement and the other as a receiver. A thermometer is located mid-way between the tubes to register the average temperature of the experiment. Two tubes pass up from the bulbs and end in Y-pieces. One of the Y-tubes from each tube is connected to an inverted Y-tube and also provided with a stopcock. One (of each) of the inverted Y-pieces is connected with the pressure chamber, while the other left open to the air. By this arrangement pressure may be applied on either side, and moreover, the apparatus may be filled with any gas other than air. The form of the apparatus allowed conducting with a given liquid as many experiments as desired, while varying the pressure, temperature, and the gas atmosphere.

Graham had suggested that the passage of gases through capillary tubes be named transpiration, Hannay thought that the name microrhoeis (from the Greek μικροζ, meaning small, and ροζο, meaning to flow) was more appropriate, and to name the instrument microrheometer. The microrhoeis of a liquid was then the time required for the passage of a certain volume of liquid through a tube of such dimensions that the rate of flow varied as the pressure, the standard comparison being water.

Hannay measured the microrhoeis of water between 0° and 25 °C and found that the retardation of the flow increased very rapidly as the temperature approached the freezing point, but it was known that as the temperature of the water falls, the contraction of water ceases at 4 °C and below that becomes negative. Thus it appeared probable that two forces were at work, which acted in the same direction in retarding the rate of flow in the microrheometer, but which acted in opposite directions in the case of the thermal expansion of water. One force was due to the vibrations caused by temperature and the other was due to the gradual arrangement of the water molecules to form ice crystals.
Hannay went on to measure the microrheosi of many saline solutions, among them, the nitrates, chlorides, bromides, iodides, and sulfates of sodium, potassium, ammonia, barium, strontium, calcium, and copper (II), as well as nitric hydrochloric, and sulfuric acids. His results indicated that the rate of flow did not depend on the crystalline form of the salt or on its molecular volume and solubility, but on the mass or energy of the salt in solution. By mass of the salt he meant the atomic mass or the equivalent mass; by energy of the salt he meant the amount of work which could be obtained from the salt by successive combinations until it was degraded to such a state that no more work could be obtained from it (exhausted). He then asked the question: Does each metal change its value when uniting with an acid, or does each metal and each acid radical have a value of its own which is a constant? He found that each element had a value of its own, which persisted in all its compounds. Thus all the salts of potassium and sodium formed by the same acids had a constant difference. Similarly, each halogen and acid radical had a value, which persisted in all its combinations. Then, the greater the combining value of an element the quicker was its microrheosis; thus potassium has a higher rate than sodium, barium than strontium, etc. According to Hannay microrheosi also varied with the amount of energy in the compound, nitrates standing highest as they contain most energy, followed by chlorides, and ending in the sulfates, which are exhausted compounds.

**Thermodynamics**

**Solubility of solids in gases**

Hannay's skilful experiments and careful results on the issue represent the first solid evidence of the phenomenon of supercritical extraction, which today has become an important scientific research subject and industrial technique.

In their study about the solubility of solids in gases, Hannay and Hogarth stated that it was instigated "with the view of throwing some further light" on what Thomas Andrews (1813-1885) had called the critical state of matter. In his famous Bakerian lecture in 1869, announcing the concepts of critical temperature and critical pressure and the continuity of the liquid and gaseous states, Andrews had said: "Carbonic acid at 35.5 °C and under a pressure of 108 atmospheres, stands nearly midway between a gas and a liquid, and we have no valid grounds for assigning it to the one form any more than to the other." Andrews had reached this conclusion after optical tests had failed to show any difference between the gas and the liquid. Hannay and Hogarth decided to study the critical state further in the hope that by an examination of the conditions of liquid matter up to the critical point, sufficient knowledge might be gained to enable them to determine under what particular conditions liquids were dynamically comparable, in order that the microrheometrical method might be applied to determine their molecular mass and energy relations. Hannay and Hogarth believed that the question related to the state of matter immediately beyond the critical point could be answered by dissolving in the liquid a solid substance having a fusion point high above the critical point of the liquid and noticing whether on passing its critical point and assuming the gaseous conditions, the solid was precipitated or remained in solution. Hannay and Hogarth found that the solid was not deposited but remained in solution, or rather in diffusion, in the atmosphere of vapor, even when the temperature was raised 13 °C above the critical point and the gas was considerably expanded. They observed that when a red-hot iron was brought near the tube containing a "strong" gaseous solution of a solid (the use of the word strong by Hannay and Hogarth is misleading because super-critical solutions are always highly diluted), the side of the tube next to the heat source became coated with a crystalline deposit, which slowly re-dissolved when the hot iron was removed. Rarefaction seemed to be the cause of the solid deposition because the phenomenon did not take place when the temperature was increased in a constant volume process. The experiments were done using solvents such as ethanol, methanol, ether, carbon disulfide, carbon tetrachloride, paraffins and olefins, and such solids as sulfur, metal chlorides, iodides, and bromides, chlorophyll and aniline dyes. Some of these solutions showed a curious behavior at the critical point, for example ethanol or ether deposited ferric chloride just below the critical point but re-dissolved in the gas when it had been raised by 1 °C above that temperature.

Hannay and Hogarth found that reduction of the pressure resulted in the solid being deposited in a crystalline state; the precipitation occurred as a snow in the gas or on the glass as a frost, but the solid always easily re-dissolved in the gas on increasing the pressure. The phenomenon was of a solid having no measurable vapor pressure, dissolving in a gas and not being affected by the passage of the carrier through the critical point to the liquid state, in other words, it was a true case of a gaseous solution of a solid.

In their second paper, Hannay and Hogarth described in detail their experiments and equipment. To test their ideas about the influence of a non-volatile solute on the passage of a solvent through its critical state, they heated a concentrated alcoholic solution of potassium iodide in a sealed glass tube and observed that no precipitation of the solute took place even at 300 °C, a temperature more than 100 °C above the critical temperature of ethanol. After some experimental work Hannay and Hogarth devised a modified Andrews apparatus, which allowed changing the experimental tube in a few minutes, and so arranged that only mercury, and not mercury and water as in the original apparatus, needed be used in it. With this apparatus they showed that in the case, for instance, of alcohol and potassium iodide, there was no distinction between the solvent action of the liquid and of the vapor near to the critical point. Alcoholic solutions of potassium bromide, calcium chloride, cobalt chloride, and ferric chloride, of sulfur and selenium in carbon disulfide, etc., showed the same behaviour. Water was not tested as a solvent because of his high critical point and corrosion of the glass tubes.

Hannay and Hogarth used a saturated alcoholic solution of potassium iodide to test the possibility that the presence of a solid in a solution affected the critical pressure and temperature of the solvent. They found the critical parameters to be 237.1 °C and 71.1 atm, compared to 258.7 °C and 77.8 atm for pure ethanol. Hannay and Hogarth concluded that the results of their experiments were further proof of the perfect continuity of the liquid and gaseous states and also a complete proof of the solubility of solids in gases.

In a following paper, he repeated his experiments on the alteration of the critical point of alcohol as a consequence of adding potassium iodide, this time taking extreme care that the alcohol did not absorb humidity from the air. Twenty repetitions of the measurements gave as mean values 233.1 °C and 65.8 atm, compared
to 234.3 °C and 64.5 atm for absolute ethanol. He now summarized his findings as follows: (a) the gas must have a certain density before it will act as a solvent, and when its volume is increased more than twice its liquid volume, its solvent action is almost destroyed, (b) at constant volume, the higher the temperature the greater the solvent power, that is, the two conditions that represent molecular closeness and kinetic energy. He proved this point by contacting potassium, sodium, or lithium with hydrogen compressed to 1 000 atm; in all cases the metals dissolved when the mixture was heated to 100 °C.

Hannay’s results were questioned by William Ramsay (1852-1916) who claimed “what had been observed was merely the ordinary phenomenon of the solubility of a solid in a hot liquid... Hannay and Hogarth found that the absorption spectrum of colored salts remains unaltered, even when the liquid in which they are dissolved loses its meniscus. Surely no clearer proof is needed to show that the solids are not present as gases, but are simply solutions in a liquid medium.” Hannay used physical arguments to rebuke Ramsay’s criticism and also saying “we do not want proof that they (the solids) are present in the gaseous state, which is very different from being dissolved in the gas.”

**States of matter**

On discussing the state of fluids at their critical temperature, Andrews wrote that there are two states of fluids, first the gaseous, in which the kinetic energy of the molecules has overcome cohesion, or their mutual attraction, and they are prevented from grouping, and second, the liquid where the attractive power is greater than the kinetic energy and the molecules are enabled to group themselves, but still are in sufficient motion to prevent the grouping from becoming permanent, hence we have cohesion but not rigidity. With proper precautions the loss of cohesion or capillarity at the critical temperature can be observed very accurately, and the level of a liquid in a fine capillary tube seen to coincide with the plane surface of the liquid just before the final disappearance of the line of demarcation. Hannay described an experiment, using the same apparatus as the one used for determining the solubility of solids in gases, in which he proved that the surface tension of liquids, and hence their cohesion, diminished as the temperature increased towards the critical point. It was seen that as the temperature rose, the height of the liquid diminished, and disappeared at the critical temperature, the phenomenon being only slightly affected by the presence of free nitrogen. Hence, pressure had little or no effect on the cohesion of the liquid, and that it was reduced to zero at about the same temperature, not withstanding the pressure. He performed this experiment with several liquid and liquefied gases, including carbon dioxide, ammonia, carbon disulfide, chlorine, ether, methanol, and methyl alcohol, and found the same results. He concluded that the liquid state ceases at the critical temperature and that pressure will not materially alter the temperature at which the cohesion limit occurs. Hence, the critical points of liquids were truly the absolute boiling points and were closely comparable to the melting points of solids, which depend almost solely upon temperature, and requiring very large pressures to alter them.

In a letter to the editor Hannay discussed the limit of the liquid state in these terms: “The conditions under which an investigation is carried out often predetermine the conclusions to be drawn from the observations made. That this has been the case with the observations made upon the upper confines of the liquid state there is now ample evidence to show. When Cagniard de Latour, on heating liquids in seated tubes, noticed the disappearance of the liquid surface, he came to the conclusion that the liquid state had ceased to be possible and that the substance had passed into the gaseous state. But Latour had no means of varying the volume of his liquid to observe whether or not increase of pressure might again induce liquefaction. Andrews removed this defect by constructing the well-known apparatus for varying the volume by means of a screw. And it is to the work performed with this apparatus that the above remark is applied. By two modes of observation Andrews arrived at the conclusion that the liquid and gaseous states of matter were continuous. The experiments being conducted in transparent glass tubes, the appearance of the contained fluid constituted one mode and the registration of the pressure constituted the other. Neither of these methods could be by the necessities of the case give any aid in determining the state of matter. Andrews’s method of demonstrating the continuity, by passing from a lower to a higher temperature under a pressure which prevented the formation of vapor, ensured the homogeneity of the fluid under examination, and precluded the existence of a visible liquid surface and as liquid and gas are equally transparent, no tidings of the state of the fluid under examination could come to him by observations of its appearance.

“How did Andrews tell when his tubes contained liquid? By lowering the pressure until a meniscus was seen. Then the formation of a meniscus is the only test of the liquid state. Andrews then obliterated the only ocular test of the fluid’s condition by increasing the pressure and raised the temperature until on again reducing the pressure no meniscus was formed, showing the fluid to be gaseous and he then declared that no sudden change of state had occurred, that is to say, that it was impossible to say that the fluid was either liquid or gaseous, but that it had probably passed through an intermediate state. Of course a choice of state had taken place, and if we only reflect that the thermal velocity of the molecules, and causes the change from cohesion to repulsion not by the number of them in a space, the change should depend upon temperature and not upon pressure.

“The characteristic property of the liquid state is then the possession of cohesion sufficient to form a surface, or simply surface tension; and could this property be retained in a visible form at all pressures, the existence of the continuity enunciated by Andrews could be put to a crucial test. By compressing hydrogen over various liquids in which it is insoluble, I was enabled to carry the above proposition into effect, and after several hundreds of experiments, detailed in a paper read before the Royal Society, the conclusion was arrived at that the two states are not more continuous than are the solid and liquid states, but are separated by an isothermal passage through the critical point. In fact by Latour’s or Andrews’s method, where the liquid was in contact with its own vapor, the critical point is the only place where the direct passage from liquid to gas is visible, but the employment of hydrogen for retaining a free surface enables us to observe the passage at any pressure, and it takes place as suddenly at 200 atmospheres pressure as at the critical pressure. Thus the critical point is the termination of an isothermal line, which is the limit of the liquid state.

As to the other mode employed by Andrews, namely, pressure, continuity of pressure does not prove continuity
of state. If it did the continuity of the solid and liquid states could easily be proven. In fact, the irregularities observed by Andrews in the vicinity of the critical point rather lend support to the views that a change of state takes place there.

‘We may state the change thus: The cohesion of the liquid state is weakened as the thermal motion increases, till the repulsion is in excess of the attraction, and the gaseous state ensues. The evidence I have collected from capillary phenomenon in the paper above referred to proves this to be the case, and shows that pressure has no effect in altering the occurrence of the phenomenon. Thus we are led to the conclusion, that so far from the liquid and gaseous states of matter being continuous and indistinguishable, the liquid limit or «absolute boiling point» is the only fixed point among the properties of matter. The freezing point can be altered by pressure, and besides, many bodies like ethyl alcohol may have no freezing point, probably becoming more and more viscous till absolute zero is reached. But all substances may be made to pass into the gaseous state, and even delicate compounds may be rendered gaseous without decomposition when under sufficient pressure. We see then that this important change of state, for which I propose the name Cohesion Limit, and which till lately was supposed to have no existence, is in reality the only fixed point in the relations of the states of matter; being determined by temperature alone.26

Artificial diamonds

Yarnelle has published a short description of the history of the production of artificial diamonds and of the state of the art.27 Before the 1955 report that the General Electric Company38 had produced diamond artificially there were three scientists who had claimed achievement of the goal. The first was Hannay, followed by Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry)39 who was unable to repeat Hannay’s procedure but claimed success by his own method, which was later shown to be without validity. The third was Charles Algernon Parsons (1854-1931), inventor of the steam turbine.2

In 1880, Hannay published a short working report that he had achieved the synthesis of artificial diamonds.40 He wrote that while pursuing researches into the solubility of solids in gases he had noticed that many substances, such as silica, alumina and zinc oxide, which are insoluble in water at ordinary temperatures, dissolved to a very considerable extent when treated with water vapor at a very high pressure. Lowering the pressure deposited the solid in crystalline form. It occurred to Hannay that a solvent might be found for carbon and from which it might be deposited in the crystalline state. After performing a large number of experiments, he found that ordinary carbon, such as charcoal, lampblack, or graphite, were not affected by the most probable solvents he could think of; the actual process was chemical action instead of solution. Nevertheless, Hannay noticed that when a gas containing carbon and hydrogen was heated at near red-heat under pressure in presence of certain metals, the metal attracted its hydrogen and left its carbon free. This result was consistent with the findings of George Downing Liveing (1827-1924) and James Dewar (1842-1923), that hydrogen at very high temperatures formed extremely stable compounds with certain metals, notably magnesium.41 An additional crucial finding was when the process was carried out in the presence of a stable compound containing nitrogen the carbon set free was so acted upon by the nitrogen compound that it was obtained in the clear, transparent form of the diamond. These experiments were extremely difficult to conduct because they needed the inclosing vessel strong enough to withstand the required high pressure and high temperature. To obviate these problems Hannay used strong hydraulic tubes constructed on the gun barrel principle (with a wrought iron coil), of only ½-inch bore and four inches external diameter, which burst in nine cases out of ten. According to Hannay, the carbon obtained in the successful experiments was as hard as natural diamond, scratching all other crystals and it not affecting polarized light; some of the crystals had curved faces belonging to the octahedral form, and diamond was the only substance crystallizing in this manner. The crystals burnt easily on thin platinum foil over a blowpipe, leaving no residue; after two days immersion in hydrofluoric acid they showed no sign of dissolving, even when boiled. A splinter heated on the electric arc, turned black, a very characteristic reaction of diamond.40

Afterwards, Hannay built a small apparatus for carrying on the combustion of the crystals and determining their composition: the diamonds were laid on a thin piece of platinum foil and then ignited by an electric current while submerged in pure oxygen. The result indicated that the assumed diamond contained 97.85 percent carbon, a very close approximation considering the small quantity at his disposal. The specific gravity of the diamond was as high as 3.5, which was determined by flotation using a mixture of arsenic bromide and fluoride.40

In a following memoir41 he gave a very detailed account of his methods and results for obtaining artificial diamond. He was searching for a solvent for the alkali metals and had tried many liquids and gases and invariably found that above the critical point a chemical action took place. This was the case even with hydrocarbons; the metal combined with the hydrogen and carbon was set free. In the first experiments he had used paraffin spirit boiling at 75 °C and containing a considerable amount of olefins. The latter seemed to split up in the same way as saturated hydrocarbons. The experiments were conducted in thick tubes made of hard glass, having 1 to 1.5 mm internal diameter and 10 to 15 mm external diameter. In some cases when the carbon was set free, a considerable proportion of the hydrogen seemed to have combined with the higher olefins and paraffins, rendering them gaseous; most of the gas, however, was formed by the reaction discovered by Thomas Edward Thorpe (1845-1923) and J. Young,44 where high paraffins split into lower olefins and paraffins.

Hannay’s second largest problem was to prevent the escape of gaseous material through the walls of the iron containers. Out of 34 trials described in his two papers only four contained any liquid material or highly compressed gas after the furnacing operation, although a test by hydraulic pressure showed that no leakage had taken place. Hannay realized that at dull red-heat the iron coil-tube became porous to gases and although he tried various ways of lining his tubes (electroplating with copper; silver; gold or siliceous linings of fusible enamels and glass) he only succeeded in retaining any liquid or condensed gaseous matter in the tubes in one out of 34 subsequent experiments.44

The alkali metal, which decomposed the hydrocarbon, retained a quantity of pure hydrogen. The carbon deposited on the tube was of a hard scaly nature, and when the sodium was slowly oxidized and dissolved in water; some very hard scales of carbon were often obtained. This was the reaction that Hannay decided
to explore further. Since potassium is a metal of strong reactivity, Hannay thought that it would lead to better results, but this was not the case. Lithium was then tried and yielded more promising results: A rapid reaction set on as the temperature rose and carbon was deposited more plentifully. Hannay reasoned that higher tempera-
tures might lead to solution of the nascent carbon in the metal and produce diamond, but after many trials he did not succeed. The next alternative was to look for a gaseous solvent for carbon and so he first tried water vapor at higher pressures and temperatures. Following these failures he concluded that the distillate from bone oil containing the nitrogenous bases would be most likely to yield such a solvent (Hannay had experimented with this oil with a view to finding some commercial applications for it). Bone oil, the nitrogenous distillate obtained in the manufacture of bone char, was distilled and the portion boiling between 115 and 150 °C separated. To insure the freedom of the bone oil from moisture, oxygen, and sulfur, it was triple-distilled; first to obtain the fraction boiling between 115 °C (the boiling point of pyridine) and 150 °C, then over caustic potash, and finally over metallic sodium. The other liquid ingredient was paraﬃn spirit boiling at 75 °C. After various trials, a mixture of 10 % bone oil and 90 % of hydrocarbon was selected as most suitable.  

The iron cylinders were drilled out axially to give the desired cavity volume, and then ﬁlled to two-thirds its depth with a mixture of 10 % paraﬃn and 90 % bone oil and the desired amount of lithium; while the lower part of the cylinder was cooled, the upper part was heated and welded. The tube was placed in a reverberatory furnace in an inclined position, heated to a bright red head for 14 h, and then cooled slowly.  

After release of the gas through the borehole and pouring off the liquid, a hard, smooth, black mass remained which was removed with a chisel. The resulting material was found to be a mixture of carbon and lithium compounds with some cyanides. Some of the carbon was very hard, but could be crushed by agate, and would not scratch it. The results obtained by the use of two liquids were so promising that further experiments were conducted with the components mixed in diﬀerent proportions. For a mixture of 90 % bone oil, 10 % paraﬃn oil, and 4 g of lithium, the product was quite black, with part of it being mostly transparent pieces embedded in a hard matrix. In Hannay’s words: “On opening the tube a great volume of gas was given oﬀ, and only a little liquid remained. In the end of the tube which had been the upper end in the furnace [our italics], the tube lying obliquely, there was a hard smooth mass adhering to the sides of the tube, and entirely covering the bottom. As I had never obtained all the solids in one piece before, I wished to examine it, and so had the other end of the tube cut oﬀ exposing the hard mass. It was quite black, and was removed with a chisel, and as it appeared to be composed principally of iron and lithium it was laid aside for analysis. I was pulverizing it in a mortar, when I felt that some parts of the material were extremely hard, not resisting a blow, but hard otherwise. On looking closer, I saw that these were mostly transparent pieces imbedded in the hard matrix, and on triturating them I obtained some free of the black matter. They turned out to be crystalline carbon exactly like diamond... The carbon obtained in the successful experiment is as hard as natural diamond, scratching all other materials, and it does not aﬀect polarized light. I have obtained crystals with curved faces belonging to the octahedral form... The crystals burn easily of platinum foil over a good blowpipe and leave no residue, and after three days immersion in hydrofluoric acid they show no sign of dissolving, even when boiled. On heating a splinter in the electric arc, it turned black, a very characteristic reaction of diamond”.  

The crystalline and mostly transparent particles had the appropriate speciﬁc gravity of 3.5 (determined by flotation in a mixture of bromide and ﬂuoride of arsenic). A sample was analyzed and found to contain 97.85 % of carbon and a minor percentage of nitrogen. Hannay drew the tentative conclusion that diamond had been formed by decomposition of the nitrogen-containing material (pyridine), and not of the hydrocarbon, but admitted that the evidence was too scanty for any ﬁrm statement to be made.  

Hannay immediately sent specimens of his product to Nevil Story-Maskelyne (1823-1911), Professor of Mineralogy, Oxford University, Keeper of Minerals, British Museum, and the leading British authority on diamond of the period. Story-Maskelyne lost no time in reporting the results of his examination of Hannay’s specimens in a letter to the London Times, published February 20, 1880, and entitled Artificial Production of the Diamond:  

“Sir: A few weeks since I had to proclaim the failure of one attempt to produce the diamond in a chemical laboratory. Today I... announce the entire success of such an attempt by... J. Ballantyne Hannay... who has today sent me some small crystallized particles presenting exactly the appearance of fragments of a broken diamond. In luster, in certain lamellar structure on the surfaces of cleavage in refractive power, they accorded so closely with that mineral that it seemed hardly rash to proclaim them even at ﬁrst sight to be diamond... Like the diamond, they are nearly inert in polarized light, and their hardness is such that they easily scored deep grooves in a polished surface of sapphire, which the diamond alone can do. I was able to measure the angle between the cleavage faces of one of them... the mean of the angles so measured on the goniometer was 70° 29’, the correct angle on a crystal of the diamond being 70° 31.7. Finally, one of the particles, ignited on a foil of platinum, glowed and gradually disappeared exactly as mineral diamond would do. There is no doubt whatever that Mr. Hannay has succeeded in solving this problem...”  

Hannay’s work remained practically forgotten until 1943 when it was found that the British Museum still had some of his samples in its possession. These consisted of twelve tiny specimens mounted on a glass slide, labeled as diamonds made by Hannay and presented to the Museum in 1880. F.A. Bannister, Deputy Keeper of Minerals, British Museum, and Kathleen Lonsdale (1903-1971) of the Royal Institution reported the discovery and identiﬁcation of the specimens.  

They aﬃrmed their belief that these were the samples submitted by Hannay because of agreement in certain physical characteristics with those described by Story-Maskelyne. X-ray diﬀraction photographs proved that eleven of the twelve specimens were unquestionably diamond; the twelfth was a fragment of ceramic material. Furthermore, one of the specimens examined in more detail was thought to be of the Type II variety and of comparatively rare natural occurrence (about one per cent of natural diamonds). Bannister and Lonsdale concluded that Hannay had been successful in his attempts at prepared artiﬁcial diamonds.  

The following attempt at producing artiﬁcial diamonds was done by Moissan in 1893. Initially, Moissan thought that since ﬂuorine was a mineralizing agent it should facilitate the transformation of amorphous car-
bon into crystalline carbon. He studied many combinations of fluorine with carbon but was unable to transform the amorphous carbon into another form. He believed that it was very probable that in natural deposits diamonds were also present in microscopic sizes. He proceeded to study the diamond sands of Brazil and the blue earth of the Cape (South Africa) and discovered the presence of very small natural diamonds that he believed should be similar to the ones that he expected to manufacture. At the same time he found that the diamond earths contained graphite, a carbon variety that formed at relatively high temperatures. From these findings he got the first hint for preparing diamonds at high temperatures.

He then proceeded to burn with oxygen a large number of diamonds of different origin and varieties. Analysis of the ashes showed the presence of a constant impurity of iron. Hence he initiated his research on the solubility of carbon in iron with very encouraging results: the variety of carbon obtained was also graphite. He now believed that other carbon solvents could be used equally well for the same purpose. In the blue earth of the Cape he found that diamond was accompanied by many mineral species. Although this did not prove that these different minerals came from the same medium where diamond had originated, it did not disprove that some of them have the same origin. Among the many impurities he detected the presence of titanium. This element was present in the blue earth in the form of many oxides. Unfortunately, the metals in which he was particularly interested were the least known ones. Some of them had been described only as infusible powders, while others had been prepared in minute quantities and in a very impure form.

Meanwhile, Georges Friedel (1865-1933) and others had observed a curious fact in a meteorite found at Cannon Diablo, Arizona. This celestial body, of ferro-nickel nature, contained a variety of diamonds, from transparent to black ones, and accompanied by carbon of medium density and graphite. Moissan obtained a small sample of the meteorite and was fortunate to study in situ a very small diamond of the boorit variety that resisted the action of the milling wheel used to cut the meteorite. The diamond formed a needle enclosed in the metal and surrounded by a sheath of carbon in which it was possible to identify graphite. To Moissan this composition indicated the medium in which the diamonds had been synthesized: Carbon was originally dissolved in a bed of molten iron, the surface of the iron had suddenly cooled subjecting the core to very high pressures because solid iron containing carbon in solution expanded during solidification.

Moissan concluded that it should be possible to realize the synthesis of diamond in a liquid metallic medium under the influence of large pressures. He reasoned that one way of solving the problem was to plunge the molten melt in cold water; solidification would create the required external envelope. On doing so he found that the metallic ferrules thus formed were cracked, but had a smooth surface that had seemingly tried to resist the pressure. Treating the ferrules with the appropriate reagents allowed dissolution of the metallic mass and destruction of the graphite. Moissan obtained a small amount of residue formed of small transparent crystals that he identified as having the same physical and chemical properties as natural diamonds.

Moissan communicated his synthesis of diamond to the Académie on the meeting that took place on February 6, 1893. Moissan’s claims of having synthesized diamonds were criticized and discarded by several people. Charles Parsons (1854-1931) tried unsuccessfully for many years to synthesize diamonds and to duplicate Moissan’s results. Parsons also tried other methods like producing instantaneous high pressures by means of explosives and by fitting high-velocity rifle bullets into cavities containing the materials to be compressed. He thought that it was easy to mistake spinels for diamonds; the spinels formed are octahedral and optically isotropic crystals looking very much like diamonds. When a residue containing spinels is placed in a platinum boat and heated in a stream of oxygen in a tube of transparent silica, flashes are often observed, but the crystals of spinel are found to be unchanged. The flashes are probably caused by carbon dust, which is often present in the air to such an extent that when an apparently clean boat is placed in the tube, many flashes are still seen. Parsons later works tended to show that pressure alone was not responsible for the separation of carbon in the form of diamond, but that the entrapped gases played an essential part. In all these experiments the crystals obtained were very small, and were chiefly identified by their hardness, high refractive index, density and single refraction.

Later on Sidgwick wrote that calculations based on the Nernst equation indicated that the two allotropes (graphite and diamond) could exist only under extreme conditions, such as 300 K and 15 GPa, and 1 500 K and 40 GPa. Bunbury et al. claimed that according to the phase diagram of carbon diamonds could be formed at the very extreme conditions of 3 to 10 GPa at temperatures in the range of 1 000 to 3 000 K, conditions well beyond those attained by Moissan.

Lead and its compounds

Hannay had been engaged during the seven years in the study of the treatment of lead ores, and it became apparent very early in his work that the accepted explanations of the chemistry of lead smelting were not in accord with the observed facts, so he decided to conduct a systematic study of the matter. In this extensive memoir he reported his findings on (a) the relations between lead and sulfur, (b) the specific gravity of lead sulfide (galena), (c) the methods of analysis, (d) furnace reactions of lead compounds, (e) lead smelting, and (f) a proposed new metallurgy of lead.

Since the smelting of lead sulfide is attained through the burning out of a portion of the sulfur, Hannay decided to examine first the supposed sub-sulfides that other had claimed were present in the ores. He found that when any compound of sulfur and lead with less sulfur than the monosulfide was fused, it was impossible to pour two samples of identical composition. Hannay inferred that no such sub-sulfides existed, but that all sulfur compounds containing less that the theoretical amount of sulfur required to form PbS were actually mixtures of the monosulfide and metallic lead. He found that any compounds of lead and sulfur may be separated into the two extremes (metallic lead and its monosulfide), by fractional crystallization of a compound containing sulfur and lead in the proportion to form a hemisulfide, Pb3S5.

In order to determine by measurements of the specific gravity, whether or not any combinations (however weak) existed between the PbS and the Pb in the lower sulfurized mixtures, he prepared a series of hypothetical compounds (PbS3, PbS5, Pb3S5, Pb5S7, and Pb7S9) by mel-
ting the necessary amounts of pure lead and galena. The samples were then reduced to powder and their specific gravities determined in benzene. The results showed again that the supposed sub-sulfides were simply mixtures of the monosulfide with metallic lead.

In order to find the amount of sulfur and lead present in a given sample, Hannay developed a new method of analysis based on the oxidation of the sulfide to sulfate, with the aid of concentrated nitric acid, mixed with a little of potassium chlorate, at 50 °C. The mixture was first evaporated to dryness and then sodium carbonate and some water were added. After boiling the mixture for a few minutes the lead was completely converted into carbonate. After cooling, sodium bicarbonate was added to precipitate all the lead as carbonate and convert the sulfide into sodium sulfate, which remained in solution. The lead carbonate was dissolved in dilute nitric acid and precipitated as barium sulfate.

Hannay developed all the chemistry and determined the many chemical reactions that took place during the smelting of lead and on the basis of his findings he proposed a new metallurgy of lead, roughly stated as follows: the galena is placed in a basic lined converter in the molten sate and air blown into its surface as well as forced through it to produce as much volatilization as possible. One half of the lead is volatilized and converted by excess of air into lead sulfate. If the ore is sufficiently rich in silver to render it advisable to obtain a concentrated silver lead, the greater part of the sulfate is returned to the metallic lead in the converter and air forced through the load to maintain a high temperature and induce the reaction

\[
PbSO_4 + Pb = 2PbO + SO_3,
\]

by which litharge is produced. Using less than the quantity of sulfate required and forcing an excess of air through the bed, then the above reaction becomes

\[
PbSO_4 + 2Pb = 4PbO + PbS,
\]

the sulfide formed is now entirely oxidized and a good litharge obtained. The small quantity of lead in excess of the reaction will now be found to contain all of the silver. Conversion of all the galena into the metal was easily achieved by adding lead sulfate to a fresh charge of galena, forcing the reaction

\[
12PbS + PbSO_4 = 2PbS_2O_2 + 2PbS + 9PbS
\]
to take place (The compound PbS_2O_2 corresponds to PbS · SO_3). The metallic lead dissolved in the sulfide and lowered the melting point. If the temperature was allowed to fall, the overall reaction that took place was equivalent to burning out of the sulfur by the oxygen of the sulfate. In other words, the final result of the action of an insufficient quantity of sulfate is to produce a low sulfide, which may then be finished off by air, and metallic lead produced. Summarizing, Hannay’s method allowed converting the galena into metal, or its oxide or sulfate in any proportion. In addition, the process generated a concentrated stream of sulfur dioxide, free from any association of lead, which could be utilized for other uses.

**BIBLIOGRAPHIC REFERENCES**

7. Hannay JB. Separation of Thallium and Rare Metals from Lead Ores, German Patent No. 264326, December 14, 1912.