CONTROVERSIAL HISTORY OF DIAMOND MAKING

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Most of us were taught that diamond could be made from carbon under high heat and tremendous pressure. The story was indeed one to capture the imagination. It involved famous chemists, a thoroughly fascinating subject, and very striking experimental techniques.

Today informed scientists soberly agree there is no certain example of diamond production in the laboratory. Attesting to the extraordinary fascination of the subject and the extreme difficulty of the experimental techniques is more than a century of claims and counter-claims for the synthesis of diamond. Henri Moissan dissolved sugar charcoal in molten iron and quenched the solution in cold water in order to crystallize the carbon under the great internal pressure supposedly generated by contraction as the mass cooled from the outside. When the metal was dissolved from the solidified melt, there remained traces of transparent material having optical properties similar to those of diamond and giving some carbon dioxide upon combustion. Moissan therefore believed he had made diamond. In 1920 Sir Charles Parsons, summarizing some thirty years of experiments on diamond making, confirmed and extended Moissan's work.

At this time the matter of man-made diamonds seemed well authenticated. It was so treated in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," which appeared in 1924 giving a detailed history

of diamond making from the first claim in 1828. Nevertheless, the story was not universally accepted. Le Chatelier, for example, was skeptical of the way in which the identification of the supposed diamond had been made. Parsons himself began to entertain doubts about his own earlier identifications and undertook a scrupulous re-investigation.

Parsons submitted his new evidence to the editor of Nature at whose request Desch in 1928 summarized the situation as follows. Parsons' new work clearly and unequivocally demonstrated how he had been misled into regarding as diamond various transparent, singly refracting minerals (spinels) which were very resistant to chemical reagents and would not burn. Parsons repeated Moissan's work many times and obtained many particles which resembled diamond but would not burn. Unfortunately, none of Moissan's own products could be found for re-examination. Parsons also repeated the work of previous investigators who had claimed to have made diamonds, but with negative results. It was Parsons' final conviction that neither he nor anyone else had ever succeeded in making diamond in the laboratory.

Now let us turn to the other major thread of the diamond-making story. J. B. Hannay reported in 1880 that he had made diamonds by heating a mixture of hydrocarbons, bone oil, and lithium at red heat in sealed wrought iron tubes. The project was said to be fraught with great difficulty because of exploding tubes; only three out of eighty held. Hannay's identification of his diamonds seemed very conclusive since it even included a density of 3.5 and a carbon analysis of 97.85%.

The evidence was impressive, but there must have been some undercurrents of bad faith, for in 1902 we find Hannay taking the Encyclopedia Britannica to task for calling his diamonds silicon carbide. In 1920 a direct contradiction of Hannay's work came from Parsons, who said he could not repeat it.

Later, gems reputed to be Hannay's synthetic diamonds were obtained from the British Museum by Bannister and Lonsdale and shown by x-ray analysis to be true diamonds of a rare type.

Lord Rayleigh in Nature in 1943 says that his father had told him that a later paper submitted by Hannay to the Royal Society in about 1894 was rejected by the publication committee because there was distrust of his good faith. An offer of a demonstration was refused on the ground that no demonstration by Hannay himself would satisfy the skeptics. Rayleigh's communication also pointed out two instances in which Hannay's work in other fields was branded by his contemporaries as being in bad faith. Rayleigh himself felt that one of these instances clearly showed that Hannay's critics had something more than prejudice to go on.

On the other hand, Travers dismissed this same incident as an honest youthful mistake, and a little later French, whose father had been Hannay's partner, reported that Hannay was not the type to fake a result. Whatever may have been the actual facts in Hannay's case, the uncertainty and undertones of bad faith that have for so long shrouded the affair are certainly not such as to inspire confidence.

Professor N. V. Sidgwick, Oxford, in his Chemical Elements and Their Compounds, published in 1950, again discusses the evidence. He points out that Rayleigh in 1943 attacked the credibility of Hannay and that later defense by Travers and French do not seriously weaken Rayleigh's charges. He concludes that the artificial production of diamonds has never been shown to have been a success and that thermodynamic calculations of Simon make it very improbable that any of the efforts so far made to produce diamonds have succeeded.

Eyring in 1952 adds further weight to the thermodynamic argument by discussing the situation that must prevail if diamonds are to be formed metastably and concludes that while this method of formation cannot be ruled out, we cannot believe that a catalyst capable of this action is possible.

The statements of the very eminent authorities cited are quite confusing, but the modern consensus is that successful synthesis of diamonds has not yet been reported in the literature.

RESUME: SCIENTIFIC LITERATURE OF DIAMOND MAKING

Note: References centering about the claims of Hannay and of Moissan, which are the major ones, are dealt with chronologically. Earlier references extending back to 1828 are considered in J. W. Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume V, Longmans Green and Co., 1924.

1. J. B. Hannay, Proc. Roy. Soc., 30, 188 (1880) or Chem. News, 41, 106 (1880). Preliminary announcement of diamond synthesis by heating a mixture of hydrocarbons, bone oil, and lithium at red heat in a sealed wrought iron tube. A product identification including a density of 3.5 and a 97.85% carbon content is given.

2. N. Story-Maskelyne, The Times, February 20, 1880 or Chem. News, 41, 97 (1880). The British Museum on the basis of its own analysis labels as genuine diamonds received from Hannay and lauds him for his successful synthesis.

3. J. B. Hannay, Proc. Roy. Soc., 30, 450 (1880) or Nature, 22, 255 (1880). A detailed account of the work announced in (1).

4. H. Moissan, Comptes rendus, 118, 320 (1894) and 123, 206, 210 (1896). Work summarized in "Fours Electrique," published in 1904; English translation, "The Electric Furnace" (Easton, Pa., 1920). Diamond is made by dissolving carbon in molten iron and quenching the solution to crystallize the carbon. The products have the optical properties of diamond and give some carbon dioxide on combustion.

5. J. B. Hannay, Chem. News, 86, 173 (1902). Takes the Encyclopedia Britannica to task for calling his diamonds carborundum.

6. W. Crookes, "Diamonds" (London 1909). Confirms Moissan's work.

7. O. Ruff, Z. anorg. allgem. Chem., 99, 73 (1917). Confirms Moissan's work.

8. C. A. Parsons, Proc. Roy. Soc., 79, 532 (1907); J. Inst. Metals, 20, 5 (1918); Phil. Trans., A, 220, 67 (1920). Confirms and extends Moissan's work, differing only on details and underlying causes. Reports failure with Hannay's method.

9. H. Le Chatelier, "Lecons sur le carbone" (Paris, 1926), page 24. Expresses skepticism of the way in which the identification of supposed synthetic diamonds has been made.

10. C. H. Desch, Nature, 121, 799 (1928). Summarizes new evidence submitted by Parsons to the Editor of "Nature." Parsons' new work clearly and unequivocally demonstrates how he has been misled into regarding as diamond various transparent, singly refracting minerals (spinels) which are very resistant to chemical reagents and will not burn. Parsons repeats Moissan's work many times and obtains many particles which resemble diamond but will not burn. Unfortunately, none of Moissan's own products can be found for re-examination. Parsons also repeats the work of other investigators who have claimed to have made diamonds, but with negative results. It is Parsons' final conviction that neither he nor anyone else has ever succeeded in making diamond in the laboratory.

11. J. W. Hershey, Trans. Kansas Acad. Sci., 31, 52 (1929) and 40, 109 (1937); "The Book of Diamonds," Hearthside Press, 1940. Duplicates Moissan's work with production of even bigger diamonds. (No more has been heard from anyone concerning this claim.)

12. F. A. Bannister and K. Lonsdale, Nature, 151, 334 (1943); Mineral Mag., 26, 309 (1943). The diamonds Hannay sent to the British Museum are shown by x-ray analysis to be true diamonds of a rare type. There is a great improbability that natural diamonds of such a rare type unrecognized at the time should be selected for fraudulent introduction either by dispirited workmen or by Hannay himself. These workers feel that Hannay has in fact succeeded in making diamonds.

13. C. H. Desch, Nature, 152, 148 (1943). Reviews his previous article (10) and then summarizes Hannay's experiments. In view of the findings in reference (12) he feels that the whole question of man-made diamonds is re-opened and that perhaps diamond can be made under the conditions used by Hannay, Moissan, and Parsons.

14. Rayleigh, Nature, 152, 597 (1943). Reports that his father has told him that a later paper submitted by Hannay to the Royal Society in about 1894 was rejected by a publication committee because there was distrust of his good faith. An offer of a demonstration was refused on the ground that no demonstration by Hannay himself would satisfy the skeptics. Rayleigh also points out two instances in which Hannay's work in other fields was branded by his contemporaries as being in bad faith. Rayleigh himself feels that one of these instances clearly shows that Hannay's critics had something more than prejudice to go on.

15. M. W. Travers, Nature, 152, 726 (1943). Dismisses the foregoing incident as an honest youthful mistake and repeats the praise and trust he accorded Hannay in an earlier memoir — Chemistry and Industry, 17, 507 (1939).

16. J. W. French, Nature, 153, 112 (1944). Reports that Hannay was not the type to fake a result but that he had indeed become concerned lest some practical joker had interfered with his experiments. French's father had been Hannay's partner.

17. K. Lonsdale, Nature, 153, 669 (1944). Her work proves that the crystals in the British Museum were diamonds but not that Hannay made them. She feels that Hannay has a strong case and that his claim should be given the benefit of the doubt.

18. D. P. Mellor, J. Chem. Phys., 15, 525 (1947); Research, 2, 314 (1949). Feels that Hannay has a very strong case but that its validity can finally be established only by a successful repetition of the work.

19. P. W. Bridgman, J. Chem. Phys., 15, 92 (1947). Contributes data valuable in thermodynamic consideration of the equilibrium between graphite and diamond.

20. F. D. Rossini, "Chemical Thermodynamics," page 453, Wiley, 1950. Discusses the thermodynamics of the transition of graphite to diamond.

21. N. V. Sidgwick, "Chemical Elements and Their Compounds," Volume I, pages 491-3, Oxford Clarendon Press, 1950. Feels that the artificial production of diamonds has never yet been shown to be a success.

22. T. Moeller, "Inorganic Chemistry," page 669, Wiley, 1952. Says the synthetic production of diamond has been singularly unsuccessful.

23. H. Eyring and F. W. Cagle, Jr., Z. Elektrochem., 56, 480 (1952). State that the literature contains no certain example of the artificial production of diamond. Also conclude on thermodynamic grounds that it is exceedingly unlikely that synthetic diamonds have been produced.

24. A. Neuhaus, Angew. Chem., 66, 525 (1954). Reviews scientific literature on diamond making and concludes that it is at least dubious that diamonds have ever been made in the laboratory.