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THEN & NOW

James Dewar and the vanishing electrical resistance at absolute zero temperature

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History of science is full of surprises and there is no end to instances where experimental observations or theoretical predictions come to overthrow intuitive expectations. But it is one thing to be faced with what for the specific period is considered counterintuitive, and it is another to deal with results whose mere description cannot be realized within the descriptive framework that contemporary theories allow. Of these events we do not have too many. There is, however, one area – low temperature physics – that has offered a plenitude of such events. From the observation of zero electrical resistance of mercury at helium temperatures to the phenomena of superfluid helium, low temperature physics has generously provided us with "counterintuitive" instances: the "unreasonable" effectiveness of the Gorter-Casimir thermodynamic calculations, the "unexpected" results of the Meissner-Ochenfeld experiment, the "unique" macroscopic wave function proposed by Fritz London, the "mysterious" case of the measurement of viscosity of liquid helium below 2 °K with two different yet perfectly equivalent ways and the difference of 100 000 in the measured values, the "phantasmagoric" fountain effect as well as the creeping film of liquid helium, these and more, became the trademark of low temperature physics.

The "birth date" of all these phenomena, was the discovery of superconductivity by H. Kamerlingh Onnes, who, between 1911 and 1913 at the Physical Laboratory of the University of Leiden, showed convincingly that mercury and a number of other metals lose all their electrical resistance at temperatures below 4 °K. Nevertheless, zero electrical resistance at absolute zero was a phenomenon which was not so much outside the range of expectations of a number of experimentalists during the 19th century.

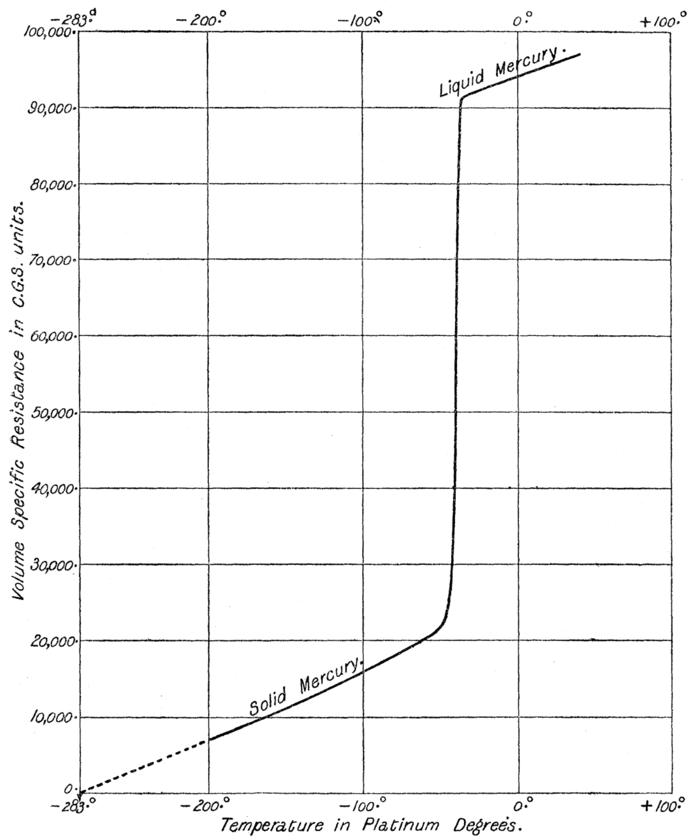

Figure 1 Variation of electrical resistance of mercury at liquid oxygen temperatures. The dotted part represents the extrapolated expected values (from [7]).

James Dewar was among these experimentalists, and his measurements led him, first, to claim that there would indeed be such a phenomenon, but subsequent measurements at lower temperatures convinced him of the impossibility of such a state of affairs.

James Dewar (1842–1923) was an impulsive experimentalist if there ever was one, an experimenter of amazing versatility who worked in problems related to physical chemistry, spectroscopy and molecular physics. His researches led to a large number of particularly significant discoveries and improvements in instrumentation as well as experimental techniques (Dewar flask, improvements in spectrometers, thermometry and cryogenic apparatus, achieving high vacua). Apart from hydrogen, he was also the first to liquefy fluoride, develop smokeless cordite, propose the initial idea related to the benzene ring and study the chemical and physical properties of a large number of phenomena such as the constants of hydrogenium, the chemical reactions at the temperatures of the electric arc, the conditions affecting the excitation of spectra, and the absorptive power of charcoal. He was born in Scotland, was educated in Edinburgh and worked briefly there; he spent some time with Kekulé at Ghent; in 1875 he was elected as the Jacksonian Professor of Experimental Philosophy at the University of Cambridge and two years later he became the Fullerian Professor of Chemistry at the Royal Institution. He held both posts until his death and from 1896 to 1923 he was the Director of the Davy-Faraday Research Laboratory of the Royal Institution.[1]

In 1892, Dewar, together with J.A. Fleming (1849–1945), started their extensive measurements of the variation of electrical resistance with temperature in a large number of metals and alloys. Fleming was an electrical engineer and physicist, the inventor of an early version of the vacuum tube, and, at the time, holder of the Chair of Electrical Technology at University College, London. The initial measurements were performed at liquid oxygen temperatures. They measured resistances down to −200 °C with the large quantities of liquid oxygen that they could prepare. They found that "all the lines of resistance are more or less curved lines that tend downwards in such a way as to show that if prolonged beyond −200 °C they would probably pass through or near the origin of absolute zero" [2]. It was observed that the rate of decrease of the resistance was higher the more pure the metal was and they surmised that for perfectly pure metals "it seems probable that as the temperature is lowered towards absolute zero the specific electrical resistance decreases so that it either vanishes at the absolute zero or reaches a very small residual value" [3]. Another conclusion was about the effects of the smallest impurities in preventing the rapid decrease of the resistance. The variation of resistance with respect to temperature was different in a given metal with different degrees of impurity, and, thus, resistivity at low temperatures could be used as an indication of the chemical purity of a metal.

The next paper published about a year later [4][2] had a more dramatic title, stating that they would be measuring resistances at temperatures approaching absolute zero. Dewar and Fleming planned to obtain very low temperatures by evaporating liquid oxygen boiling under reduced pressure. It was, then, mentioned that the temperatures down to which measurements were taken were ''temperatures approaching absolute zero". They presented various details concerning the preparation of the experiments, discussing the two kinds of resistance, the volume specific resistance – which is what they measured – and the mass specific resistance, and gave their exact definitions. They, also, discussed analytically some further observations, such as that pure copper appeared to be the best conductor at low temperatures. This exhaustive set of measurements gave them more confidence and led them to assert that

> "The conclusion reached in our former paper is confirmed by these more careful experiments, viz., that the electrical specific resistance of all *pure* metals will probably vanish at the absolute zero of temperatures" [5].

Alloys, of course, showed a slower rate of decrease of their resistance than the pure metals. Bismuth was found to have an anomalous behavior in that its resistance showed a minimum (or a maximum depending on how it was prepared) in temperatures of solid air of approximately −80 °C. Uncharacteristically, they mentioned a theoretical paper by C.V. Burton who referring to their experiments had proved a theorem stating that at absolute zero every substance will either have an infinite specific resistance or infinite conductivity, and they were wondering whether the

[1] For a biography of Dewar, see [1].

[2] see [4]. Dewar and Fleming used the platinum thermometer constructed by H. L. Callendar in 1887 (since platinum had shown to have a very stable electrical resistance at each temperature) and the scale introduced by Callendar in H. L. Callendar, "On the practical measurement of temperature" *Philosophical Transactions* 1887, CLXXIII A, 161-230.

behavior of bismuth may be an indication of such behavior, since it also displayed non-metallic characteristics. Nevertheless, further measurements showed that bismuth prepared electrolytically was no exception to "the ordinary law, that resistivity of metals vanishes at (zero) absolute temperature" [6].

In the same year, 1896, they also completed an exhaustive study of the resistance of mercury which could be prepared in a very pure state at liquid air temperatures and their results indicated again that the resistance of mercury would vanish at zero degrees Kelvin: "these measurements afford a further confirmation of the law which we have enunciated as a deduction from experimental observations, that the electrical resistivity of a pure metal vanishes at the absolute zero of temperature" [7]. For the first time they talked about a law deduced from experiment – an overall approach very dear to the heart of Dewar the chemist who was, also, strongly attached to the tradition of systematic empirical observations annunciated by Francis Bacon nearly three centuries earlier.

Even though electrolytic bismuth did show a similar pattern as that displayed by other metals, it was found that its resistance increased when subjected to a transverse external magnetic field [8]. This was rather remarkable and their assessment was that at very low temperatures electrolytic bismuth turned into a non-conductor through the application of strong magnetization: "this result will have to be taken into consideration in framing any theory of electrical conduction" [9]. Considering the difficulties in formulating even a phenomenological theory of superconductivity few decades later, since most of the theoreticians insisted on solving a problem of electricity rather than magnetism, little did Dewar and Fleming realize how prophetic they were!

However, trouble and disappointment lurked ahead. In 1899 Dewar had managed to liquefy hydrogen and, in fact, for a short while he thought that he had also liquefied helium, only to realize that what appeared as liquid helium was the impurities in the gas. Nevertheless, liquefying hydrogen was a feat in itself, and he was the first to do it, a priority he much valued. But his achievement was marred by complications in the thermometry, since the only reliable thermometer would have been a gas thermometer filled with very pure helium gas. In fact when tests were made with fifteen electric-resistance thermometers, he found widely differing results (in some instances, as large as 15%) for the boiling point of hydrogen. And though it was found that at liquid hydrogen temperatures electrical resistances of the various metals continued to diminish, he could not rely on any of the thermometers and, hence, "the real law correlating electric resistance and temperature . . . (remained) unknown" [10].

Further measurements at liquid hydrogen temperatures appeared to be giving rather disappointing results. The resistance of unalloyed metals was diminishing, and all samples appeared to be reaching asymptotically a value which remained stable independent of whether temperature was lowered. And by studying carefully the various curves of temperature vs. electrical resistance of a large number of alloys and unalloyed metals, it became clear that not all of these metals displayed a behavior which could be represented by a parabola-like curve such as the one in Fig. 1. Dewar started to think that electrical resistance may not be disappearing at absolute zero, and that there may not be any law which could express the observed diminishing of the resistances of metals all the way down to absolute zero.

Lord Kelvin had in 1902 suggested a theory whereby at absolute zero the "gas of electrions" in a metal would, in a way, condense on the atoms and, thus, the metal would become a perfect electrical insulator. Dewar mentioned this in his presidential address to the British Association for the Advancement of Science in 1902. And Lord Kelvin, making use of Dewar's results, proceeded by 1904 into making his theory even more quantitative "predicting" the temperature at which the resistance of the metals will show an upward turn, having reached its minimum value.

Dewar did not feel much disappointed, since there was a lesson to be learnt:

> Supposing all difficulties to be overcome and the experimenter to be able to reach within a few degrees of the zero, it is by no means certain that he would find the near approach of the death of matter sometimes pictured. Any forecast of the phenomena that would be seen must be based on the assumption that there is a continuity between the processes studied at attainable temperatures and those which take place at still lower ones. Is such an assumption justified [11]?

Dewar's own experiences with the measurement of the variation of electrical resistance with temperature led him to answer negatively to this question. The predictions at low temperatures for what would happen at lower temperatures turned out to be untrustworthy, and he started to realize that, notwithstanding the difficulties in thermometry, even a few degrees difference may undermine expectations.

But all this was a prelude to what was in store in the years to come: that liquid helium, in the words of Sir William Bragg, would bring about a situation much like the strange and disorderly world of *Alice in Wonderland*.

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