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GUEST EDITORIAL

The Saha equation turns hundred

Four years after joining the University College of Science in Calcutta as a lecturer in 1916, Meghnad Saha submitted a paper entitled 'Ionization in the solar chromosphere' to the *Philosophical Magazine*. This was quickly followed by three more, the last of which, 'A physical theory of stellar spectra' appeared in 1921 in the *Proceedings of the Royal Society of London*, forwarded by A. Fowler, Saha's host at Imperial College, London. Fowler suggested many improvements on Saha's original draft made in Calcutta. These papers were based on the concept of thermal ionization. At the high temperatures found in stars, some electrons can be removed from atoms. The precise ratio between the numbers of neutral atoms and the various ions is given by an equation which, ever since, has borne Saha's name. This centenary provides an excuse to revisit the scientific background to this work, its immediate impact, and the aftermath.

Let us start with the questions which he answered which were wide open at that time. Fraunhofer, Bunsen and Kirchoff founded the science of spectroscopy in the mid 19th century and showed that the same chemical elements which we see on earth are present in the Sun. The spectrum of the Sun shows prominent absorption lines, signatures of sodium, calcium, magnesium, iron and other elements. These are interpreted as a cooler outer layer, filtering out very specific wavelengths from a continuous spectrum coming from a hotter inner layer. Atoms which can absorb can also emit. Solar eclipses offer a rare opportunity to view the emission from the outermost layers of the Sun, looking side on, without been glared by the main disc. Helium was first discovered as a yellow line in spectra taken in Guntur during the total eclipse of 1868. It was puzzling that helium was hardly seen in the absorption spectrum, and that different elements were seen at different heights in this outer layer, known as the 'chromosphere'.

The second puzzle concerned the spectra of stars, which came in a rich variety. The Harvard College observatory accumulated photographic plates with half a million stellar spectra by the early twentieth century – big data indeed! These were examined and classified, purely empirically, by a team of 'computers' – this being the designation in those days for women analysing astronomical data and carrying out tedious calculations. This effort was led for decades by a remarkable woman scientist, Annie Cannon. The categories ABFGKM into which she grouped the spectra formed a sequence of decreasing temperature, with our Sun standing at G. The appearance of different species in this series was bizarre – titanium oxide at M and hydrogen and helium at A!

Saha's answers to these questions drew on his grasp of contemporary atomic physics. The allowed energy states of different elements were just being revealed by spectroscopy, and by the Franck–Hertz experiments on excitation and ionization of various atoms by collisions with electrons in an electrical discharge. Surprisingly to us today, he also used his knowledge of the thermodynamics of chemical reactions, pioneered by van t'Hoff and perfected by Nernst who was awarded the Nobel Prize for Chemistry in 1920. The key idea is that measuring the heat released or absorbed in various processes allows one to compare the entropy of different states of matter – for example, hydrogen plus oxygen as compared to water. This made it possible to predict chemical equilibrium – the ratios of different reacting species – as a function of temperature and pressure. Eggert, a student of Nernst, used the equations of equilibrium for ionization, considered as a reaction between electrons and ions giving neutral atoms. His rough estimate was enough to verify that the unobserved insides of stars are close to fully ionized. Saha's instant insight was that this process of thermal ionization was the key to understanding the systematic but hitherto strange appearances and disappearances of different chemical elements in the spectra observed from the outer layers of the sun and other stars. His theory went beyond the obvious observation that higher temperatures push matter into states of higher energy. The number of these states, which is a measure of entropy, is just as important as temperature. At the low densities in the outer layers of the Sun and other stars, the spatial volume available to the electrons is larger, giving them many states to occupy. This biases the equilibrium towards the ionized state, as explicitly recognized in Saha's formula by the appearance of the pressure.

Recognition was swift and enthusiastic. In science, citation and follow up are the sincerest form of flattery. Eminent astrophysicists took up Saha's ideas. Henry Norris Russell, already famous for putting stars on a diagram of colour versus luminosity, extended Saha's theory to multiple elements sharing a common pool of electrons.

Near the Sun's surface, hydrogen is largely neutral at 5600 Kelvin, but elements like calcium have given up their electrons. This 'doping' pushes the equilibrium to include negative ions of hydrogen, which one would not normally expect since they are very weakly bound – just three quarters of an electron volt..

Soon after Saha's work, Fowler (R.H, not A.!) and Milne improved the theory. They included the excited states of the neutral atom, not just its ground state. They went beyond Saha's criterion of the first appearance of line, and were able to deduce the pressure in the atmosphere, rather than assuming it as Saha had done. Perhaps their greater contribution was to encourage a young woman student, Cecilia Payne, to study this field in depth for her doctoral thesis at Harvard (since Cambridge, UK, would not even give a woman a B A, just a certificate of equivalence!). With the improved thermal ionization theory and atomic data as her guide, Annie Cannon's cooperation in giving her access to the plates, and the blessings of the head, Harlow Shapley, she undertook a thorough study of the abundance of elements in the stars, essentially on her own. Astronomers, Russell in particular, had made rough estimates which were consistent with the abundances on earth. Very little hydrogen or helium is found on earth, and the lines in the solar spectrum are weak, so it was tacitly assumed that these were rare in the Sun. But Payne's application of basic physics dictated otherwise. The weak Balmer lines of hydrogen originating from the first excited state, $n = 2$, were just the tip of the iceberg, most of the atoms being in the ground state, ten electron volts below. Hydrogen and then helium were inferred to be overwhelmingly the most abundant species on the Sun. This was such a profound reversal of received wisdom that Payne inserted cautionary remarks, casting doubt on the results for hydrogen and helium, in her 1925 thesis. This was very likely under the influence of Russell. By 1929, the same Russell, applying a different method, realized and admitted, that her results were correct. Today the credit for discovering the dominant abundance of hydrogen and then helium in our universe rightly goes to Payne.

Saha moved to take up a professorship in Allahabad University in 1923. One of the noteworthy products of this period is a text book, written in 1931 with B. N. Srivastava, his research student and later his colleague. This is called *A Treatise on Heat* and was still popular thirty five years later when I was a physics undergraduate. Looking back on it today gives us a glimpse of Saha as a scientist and a teacher, much as the Feynman lectures or Purcell's text on electromagnetism tell us about the authors of these two books. One sees not just theory but detailed discussion of experiments and applications, even to meteorology, and meticulous citation of original sources.

Saha's other 'equation' – with C. V. Raman – has always excited interest. It is well known that after 1934, these two men had strong differences and were regarded as the north and south poles of Indian science, being prominent in two academies headquartered in Calcutta (later Delhi) and Bangalore. At the University Science College in 1917, Raman was the Palit professor, while Saha and S. N. Bose (of the statistics) were fresh lecturers. They must have regarded Raman's acoustics and optics as old fashioned, and it is interesting that Saha actually made his journey abroad in 1920, ahead of Raman in 1921! Saha did get the Khaira professorship on his return from UK and Germany, but this did not come with a laboratory or funding. His move to Allahabad in 1923 reminds one of Cesar's statement – 'I had rather be first in a village than second in Rome'. Indeed, Saha had to start from scratch, and built up a flourishing school, no doubt at the price of slowing down his own science at the peak of his powers.

Given this background, here are two passages which show a different side to the equation between these two scientists. When Saha and Srivastava brought out the first edition of their *A Treatise on Heat* in 1931, whom do they turn to for a foreword? C. V. Raman, who responded handsomely and surely sincerely too. Here is an extract, 'The familiarity with thermodynamics and its applications to physical and chemical theories which led Professor Saha to these classical researches has also made him a most successful expositor of the subject. His experience in the lecture-room and laboratory, first at Calcutta and later at Allahabad, has helped him to produce, with the assistance of the junior author, a book in which freshness and width of outlook are combined with clearness and accuracy in detailed exposition.'

Two years later, Raman leaves Calcutta for the Indian Institute of Science in Bangalore, and here is Saha writing on this major event: 'After twenty-five years' stay at Calcutta, Professor Raman is called away to his native South for shouldering the responsibility of the Indian Institute of Science at Bangalore. He leaves with the best wishes from the people of the land of his adoption, who sincerely hope that his new mission will be as much crowned with success as his labours at Calcutta had been. Though he is gradually passing into the afternoon of life, his store of dynamic energy shows no sign of deterioration, and it is hoped that they will be more fruitful in the new land of venture!' Neither Saha nor Raman were known for diplomacy, so we should take this textual evidence of respect for each other's scientific achievements at face value, co-existing no doubt with other feelings on both sides.

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