Thermal Ionisation and the Saha Equation!

The stars contain matter in the form of the familiar chemical elements, but sometimes at extreme conditions of temperature and pressure which are not accessible in the laboratory. The physics of stars – the first chapter of the book of astrophysics – therefore needs theoretical insights into the behaviour of matter under these extreme conditions. In 1920, Meghnad Saha was able to contribute a crucial missing piece in the jigsaw puzzle of stellar spectra. Signs of hydrogen had been seen in the atmospheres of hot stars, but weakened as one came to cooler stars, being replaced by those of other chemical elements like sodium, or calcium in the ionised form (one electron removed, hence Ca^+). This pattern had attracted speculation but no physical explanation. Saha addressed the simple looking question: As a box of atoms of different elements in the gaseous state is heated, what determines the fraction which remain neutral, and the fraction which have one/two ... or more electrons removed?

The qualitative answer was of course already known. The first elements to get ionised would be those, like calcium, which required very little energy to remove an outer electron. In fact, Boltzmann's principle, the basis of the kinetic theory of gases (and much besides !) states that the populations in two states 1 and 2 whose energies differ by ($E_2 - E_1$) are in the ratio $N_2 / N_1 = \exp(-(E_2 - E_1)/k_B T)$. The denominator of the exponent has Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ Joules/K, which is just a conversion factor from temperature T to energy $k_B T$. For example, the energy required to remove an electron from a hydrogen atom is approximately 2×10^{-18}J, corresponding to 160,000°K. But the stars tell us that it does not take this high a temperature to ionise hydrogen! Boltzmann's principle carries some fine print – it refers to *single* quantum states. What we call a hydrogen atom in its lowest state still leaves four possibilities for the spins of electron and proton and hence counts as four states. More importantly, what we call an ionised atom has a freely moving electron which really has a very large number of possibilities. This tilts the balance favouring the ionised condition. This effect is stronger at lower densities. In fact, Boltzmann recognised that the logarithm of this number of states is just what physicists and chemists had long described as entropy.

Saha knew German and cited the great physical chemists Nernst and Van't Hoff, in the original! Treating $H \leftrightarrow H^+ + e^-$ etc as chemical reactions, and putting in the correct entropy for electrons, depending on the space available to them (i.e. density), he arrived at his famous formula. At one stroke it brought order to the chaotic appearance and disappearance of chemical elements in stellar spectra.

We exhibit the Saha thermal ionisation equation for the simplest case $H \leftrightarrow H^+ + e^-$

$$\frac{n_{H^+}}{n_H} = \frac{1}{n_e}\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{-\Delta E / k_B T}.$$

The quantity before the Boltzmann exponential is the (large) ratio of the volume per electron to the cube of the de Broglie wavelength at temperature T and thus counts the number of states of a free electron.

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