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The Chemistry of the Stars

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The view that stars were solely objects of mathematical analysis that would forever lie beyond the realm of physics was dispelled by Gustav Robert Kirchhoff in 1860. Kirchhoff's science of spectroscopy revealed that distant stars are composed of the chemical elements found in earthly bodies. His revelations transformed the astronomer into something of a chemist, and the chemist into something of an astronomer.

Nearly two hundred years after Sir Isaac Newton demonstrated that the sun's light could be broken down into the colors of the spectrum, a Bavarian optician, Joseph von Fraunhofer (1787–1826) devised a superior method for viewing the spectrum. Instead of using Newton's method of looking through the prism with the naked eye (Fig. 1), Fraunhofer employed a telescope, placing the prism and the telescope at a distance of 24 ft from the slit. The placement of the prism was such that the incident and refracted rays formed nearly equal angles with its faces. Fraunhofer's procedure greatly enhanced the virtual image, since in this position, minimum deviation of the rays allowed them to form sharp, clear images of the slit.

With the aid of this apparatus, Fraunhofer noticed dark lines in the spectrum. Earlier, in 1802, William Hyde Wollaston (1766-1828), a scientist with interests ranging from astronomy to physiology, had described these lines in a paper that appeared in the *Philosophical Transactions of the Royal Society*. But where Wollaston had observed seven dark lines (which he took to be natural boundaries of the colors) traversing the spectrum, Fraunhofer found many more: he noted some 574 transverse streaks, some wider, some narrower, dividing portions of the spectrum. Fraunhofer knew that each color of the spectrum correlated with a unique wavelength of light. Shorter wavelengths fell at the violet end of the spectrum, while longer ones fell at the red end. Using a theodolite to measure the distances between them, Fraunhofer mapped out his observations. He carefully laid down the position of some 354 of the lines, working out their relative intensities, labeling the more conspicuous ones **A** through **K** (labels which are still used today), determining their wavelength, and observing that their positions in the spectrum always remained the same.

The strange black lines struck Fraunhofer as a kind of cipher. He found that they were always produced by sunlight, whether direct, diffused, or reflected from the moon and planets. But Fraunhofer also found that light from the fixed stars formed spectra having quite different lines from those in the sun, though he did recognize some of the same lines he found in the solar spectrum. The difference demonstrated to him that the cause of the dark lines must be related to the light of these self-luminous bodies, not to the atmosphere. Fraunhofer died of tuberculosis in

Figure 1. (*Facing page*) Isaac Newton's prism experiment, which revealed that light could be broken down into the colors of the spectrum.

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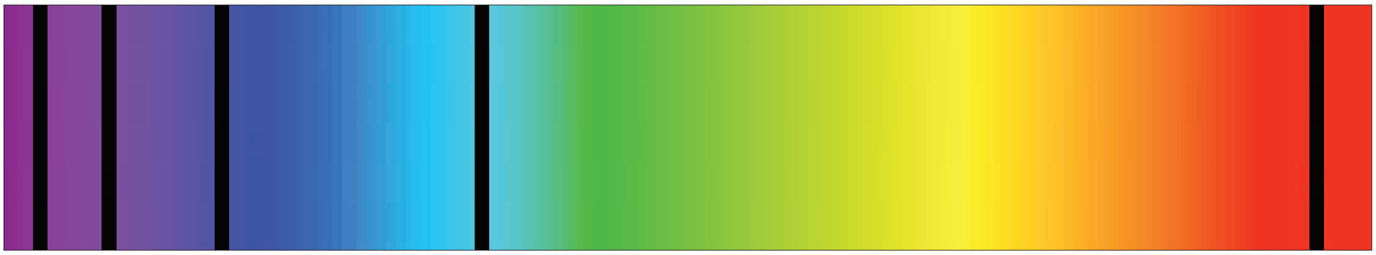

Figure 2. Hydrogen spectrum.

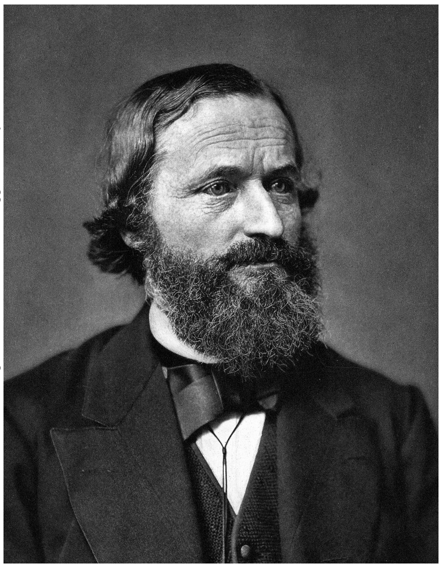

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Figure 3. Gustav Robert Kirchhoff, 1824-87.

1826, at the age of 39, without ever having discovered the origins of the famous lines in the spectrum which bear his name.

It is tempting to see Fraunhofer as a pioneer in the science of spectroscopy, but this label would not be entirely accurate. An intriguing figure in the history of science, Fraunhofer was a self-educated artisan who worked with achromatic lenses for astronomical instruments, like telescopes and heliometers, and ordnance surveying instruments, like theodolites. His work afforded him little time for ruminating on the theoretical issues raised by the “fixed lines” (as they were originally called) of the solar spectrum. Other scientists of the time, however, did not share such practical constraints; hypotheses as to the origin of the fixed lines were plentiful. One popular opinion was that sunlight was stripped of its missing beams by the atmosphere of the earth. Although a few of the dark lines, which were invisible when the sun reached its apex in the heavens, became increasingly conspicuous as the sun began to set, this opinion was undermined by the discovery that the vast majority of the dark lines were impervious to the thickness of the atmosphere.

The first compelling scientific account of the nature of the solar lines was advanced in the autumn of 1859 by a team of researchers at the University of Heidelberg. Led by the physicist Gustav Robert Kirchhoff (1824-1877) and the chemist Robert Wilhelm Bunsen (1811-1899), the team developed an improved version of Fraunhofer’s instrument that passed light through a narrow slit before passing it through a prism. The slit controlled the source of the light and, as a result, when viewed against a scale, the display of the different wavelengths became much easier to differentiate and interpret. With this instrument, which they called a spectroscope, Kirchhoff and Bunsen were able to exploit the observation (c. 1832) of the physicist David Brewster (1781-1868) that certain colored gases have the power of absorbing some of the sun’s rays. When the rays are made to pass through the gas before falling on the prism, the spectrum is crossed by a series of dark lines. This process produced additional lines not previously observed by Fraunhofer, though the 574 lines he described were still present. Using a special burner devised by Bunsen, which gave off very little light in and of itself, the researchers heated various chemicals to incandescence, the heat at which they gave off light, noting that each chemical gave off its own distinctive pattern of colored lines (Fig. 2). Sodium vapor, for example, when brought to a glowing heat, produced a double yellow line. This double yellow line was its thumbprint.

In his presentation to the Berlin Academy in October 1859, Kirchhoff ascribed the origins of the Fraunhofer lines to absorption of the corresponding spectral wavelengths in the atmosphere of the sun. He then proceeded to advance his celebrated principle that the lines of a given element can be seen in emission or in absorption, depending on the temperature of the light source emitting the continuous spectrum that is intercepted by the element. The interpretation of this principle later became the focus of all blackbody radiation physics. The implication was that through a comparison of the lines in the spectrum of the sun (or some other heavenly body) with those obtained in the laboratory for known elements, it would be possible to discover the chemical composition of heavenly bodies.

The spectroscope presented scientists with a powerful tool for investigating matter with the aid of the light it emits. Kirchhoff stressed the fact that chemical elements were clearly and indisputably distinguished by their characteristic spectrum. Within a year, Bunsen and Kirchhoff had discovered the metal cesium in a series of alkaline earths. A year later, they detected the metal rubidium. William Crookes (1832-1919), remembered for his research on cathode rays, discovered thallium in 1861 as a result of his observation of a striking green line in the spectrum of selenium. At approximately the same time, the British astronomer Norman Lockyer (1836-1920) identified a new element, which he called helium, in the sun.

The spectroscope would also play a critical role in the discussion surrounding the bold prediction of the existence of three new elements by the Russian chemist Dmitry Ivanovich Mendeléev (1834-1907). Mendeléev had gone so far as to project the elements’ physical and chemical properties, corresponding to gaps in his new periodic table of elements, arranged according to atomic weights. Discovery of the three elements would therefore certify both Mendeléev’s Periodic Law of the Chemical Elements and the effectiveness of the new method of chemical analysis offered by spectral analysis. And indeed, the new elements gallium (1875), germanium (1875), and scandium (1879) were each found to have characteristic spectral signatures.

Kirchhoff and Bunsen together can be credited with the establishment of the terrestrial science of spectrum analysis, but its application to the chemistry of the stars is attributed to Kirchhoff alone. The principle advanced by Kirchhoff in 1860 revealed the cipher of the chemistry of the stars. It provided a key to the code of the Fraunhofer lines: the same characters that are written bright in terrestrial spectra are written dark in the unrolled sheaf of sunrays.

Kirchhoff exploited this insight and so produced a complete map of the solar spectrum, drawn to scale with superb accuracy and printed in three shades of ink to convey the graduated obscurity of the lines. It was published in the *Transactions of the Berlin Academy* for 1861 and 1862. For Kirchhoff, preparation of this elaborate picture proved so trying that failing vision compelled him to surrender the second half of the task to a pupil. When completed, the map measured nearly eight feet in length. Kirchhoff's work was furthered by Father Angelo Secchi (1818-1878), the eminent Jesuit astronomer of the Collegio Romano (Rome), who pioneered the use of photography in astronomy. With a 10-in. reflector and a spectroscope, Secchi executed the first spectroscopic survey of the heavens. He reviewed approximately 400 stars in all, classifying them according to the varying qualities of their light. This enormous outburst of astrophysical research gave Secchi and Pietro Tacchini (1838-1905) the idea of founding a society to coordinate the research of observatories all over the world and publish their results. Harvard University astronomers began a spectroscopic survey in 1885, eventually producing the *Henry Draper Catalogue* with its classification of stars into seven spectral types. Efforts to photograph the solar spectrum soon followed. Astronomer William Draper (1811-1882) produced the first photograph of the spectrum of a star (Vega) in 1872. With the work of Kirchhoff and Secchi, astronomy had at last found a place among the physical sciences.

The great astronomer Johannes Kepler (1571-1630) had forecast in 1609 what he called a "physical astronomy," a science that would treat celestial bodies as having the same physical nature as earthly bodies. Kepler's prediction, which opposed the Aristotelian assertion that celestial bodies were subjects for mathematical analysis alone, was realized to some extent by Isaac Newton. Newton revealed that the symmetrical revolutions of the solar system are governed by a uniformly acting cause: gravity, which gives stability to all our terrestrial surroundings.

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Figure 4. Robert Wilhelm Bunsen, 1811-99.

Kepler's program for bridging the gap between the terrestrial sciences (physics and chemistry) and the mathematical science of astronomy was carried no further until the invention of spectral analysis. From antiquity to 1860, astronomy had been set apart from the other sciences and positioned as the application of mathematical techniques to astronomical phenomena in a context that would forever lie beyond the grasp of physical analysis. To this end, astronomers had been outfitted with the telescope, the calculus, and little else. Thanks to Kirchhoff, the astronomer became something of a chemist and the chemist something of an astronomer. The old Aristotelian conviction that astronomy was the science of the movements of unearthly bodies was finally put to rest.

Further Reading

1. W. McGucken, *Nineteenth Century Spectroscopy*. Baltimore: Johns Hopkins University Press, 1969.
2. J. B. Hearnshaw, The Analysis of Starlight. Cambridge: Cambridge University Press, 1986.

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