



XI. Researches on spectrum analysis

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units of temperature ; therefore the absolute unit of temperature is equivalent to

$$\frac{273}{2.5} \times 10^{16} \text{ Centigrade degrees,} \\ = \text{about } 10^{18} \text{ Centigrade degrees.}$$

These figures are only intended to convey a very rough notion of the relation. They cannot of course be considered as even approximately correct, owing to the great uncertainty as to the mass of molecules.

Having seen that *temperature* is a quantity of the same dimensions as *energy*, and knowing that the same is also true of *heat*, it follows that *entropy*, whose dimensions are *heat* \div *temperature*, is a purely numerical quantity ; and the unit of entropy is therefore independent of all other physical units. In fact, *the entropy of a perfect gas increases by unity, when (without altering in temperature) it receives by conduction a quantity of heat equal to the mean energy of one of its molecules.* This is seen by putting

$$\frac{\Delta H}{\Theta} = 1 ; \therefore \Delta H = \Theta = E,$$

where Θ is the absolute (C.G.S.) temperature.

XI. *Researches on Spectrum Analysis.* By Prof. A. F. SUNDELL*.

CERTAIN natural phenomena, such as the aurora borealis, zodiacal light, and solar corona, have occasioned numerous attempts to obtain the spectra of gases in a highly rarefied condition and at a low temperature. Under these conditions spectra generally become very feeble, and therefore difficult to observe. The following experiments show that tolerably bright spectra may be obtained by an advantageous employment of means already known.

Since the brightness of the spectrum depends, in the first place, upon the thickness of the radiating layer, "end-on" tubes† are employed by preference. I have employed tubes as long as possible (up to $1\frac{1}{2}$ metre long). The end towards the spectroscope was simply melted together, and rounded as well as might be in the process. The other end was drawn out and melted on to the tubes leading to the mercury-pump.

* Translated from a separate impression from the *Acta Societatis Scientiarum Fennicæ*, vol. xv., communicated by the Author.

† Such tubes have been employed by Prof. P. Smyth for observations on gaseous spectra *in vacuo* (*Beibl.* vii. 1883, p. 286).

I have not employed electrodes fused into the tubes themselves. As a rule, the tubes have been rendered luminous by means of tinfoil coatings near the ends of the tubes, as employed by Salet, Hasselberg, and others. By the adoption of this method the process of discharge no doubt becomes most nearly like that of Nature, and the temperature is kept as low as possible. The source of electricity was a Holtz machine without Leyden jars, the terminals of which were connected by means of wires with the coating of the tube. The coating thus corresponded to the external coatings of the jars of the machine, the strata of air against the inner wall of the tube serving as the inner coating.

I have usually employed a spectroscope constructed by Wrede in Stockholm, belonging to the Central Meteorological Institute of Helsingfors, which was used by Prof. Lemström* in his observations on the aurora in the years 1871-73. The spectroscope consists of one dispersing-prism and one reflecting-prism. The dispersion is somewhat small, not being sufficient to divide the sodium-lines. Ten divisions on the head of the micrometer-screw correspond to intervals of 0.000006 and 0.000006 millim. in the extreme red and extreme violet respectively. The scale was constructed as follows:—A thin glass plate (a microscopic cover-glass) was covered on one side with indian-ink and five fine parallel lines ruled through the black coating. The other surface was coated with Balmann's luminous paint. This plate was then fixed in the eyepiece of the spectroscope, so that the fine lines were parallel to the lines of the spectrum and in focus at the same time and occupied about half of the field of view†. It was rendered luminous by burning a match before the eyepiece. If a bright line in the spectrum was to be measured, this was done just before the experiment; but for fainter lines the measurement was made after the phosphorescence had become feebler; and with very faint lines it is necessary that the index-lines should only be very slightly luminous, so that they may not overpower the lines of the spectrum. In such cases the adjustment was much easier, because there were five index-

* This spectroscope is fully described in the *Öfversigt af Finska Vetenskaps-Societets förhandlingar*, xv. pp. 21-23, 1873. Dr. Fuchs has described a reflecting direct-vision prism as new in the *Zeitschrift für Instrumentenkunde*, 1881, p. 352; this prism is the most remarkable feature of the Wrede spectroscope, and was described to the Royal Swedish Academy of Sciences so long ago as 1870.

† I have described an index of this sort in the *Astr. Nachrichten*, No. 2430 (1882). I have since learned that Prof. Vogel had employed phosphorescent marks in 1881 for the measurement of spectra of feeble luminosity (*Zeitschrift für Instrumentenkunde*, 1881, p. 20).

lines instead of only one. Generally the spectrum-lines were brought into coincidence with the central index-line by turning the micrometer-screw; only for three lines in the extreme violet the outer index-line was used, because the screw-thread ceased here. The wave-lengths were determined by means of a table which I had constructed from a curve of wave-lengths belonging to the spectroscop, from the difference between the position of a line and that of the sodium-line. By way of control, the lithium-line 5706 and the strontium-lines 4606 and 4205 were read in each series of measurements, the corrections for the spectrum-lines measured being determined by simple interpolation.

The larger spectroscop, belonging to the Physical Laboratory of the University, which I have employed for some measurements, is also constructed according to Wrede's principle. It has two prisms of heavy flint glass, and reflecting crown-glass prisms. The index was constructed by H. Biese, who had published the idea of a self-luminous index at about the same time as myself*. The index consists of a fine slit in a thin brass plate; the side of the slit turned towards the prisms is filled with a phosphorescent substance. The dispersion is considerable; ten divisions of the micrometer correspond to a change of 0.0000013 in the extreme red and 0.0000002 millim. in the extreme violet; the sodium-lines D_1 and D_2 are divided. The tables for the wave-lengths were calculated from a curve drawn by H. Biese.

Most of the observations were made in a dark room in the Physical Laboratory of the Polytechnic Institute of Helsingfors. I take the opportunity of expressing my thanks both to the Director of the Institute, H. Qvist, and to the Professor of Physics, Dr. Slotte, both for the use of the room so specially suited for these experiments, and also for the use of various apparatus necessary for my experiments from the collection of instruments belonging to the Laboratory. The electrical machine was stationed in a neighbouring room, where it was kept in action by means of a water-motor. For the rarefaction of the gas in the spectral tube, I employed the mercury-pump which I had constructed for the Polytechnic Institute†. The movable tube had neither tap nor stopper, and the globe with phosphoric anhydride was melted on. The spectral tube employed was 155 centim. long, and at one end had an internal diameter of 10.8 millim. and glass 2.1 millim. thick; at the other end the tube was 12.9 millim.

* *Öfversigt af Finska Vetenskaps-Societetens förhandlingar*, xxiv. p. 30.

† *Acta Societatis Scientiarum Fennicæ*, vol. xv. p. 169.

wide, and the glass 1·6 millim. thick. The tube rested in a horizontal position on glass supports, depending from wooden consoles attached to the wall of the room. The connexion with the air-pump was made by means of a Kundt's glass spiral. At the same time a spectral tube was put up in the same way in the Physical Laboratory of the University, by the kind permission of Prof. Lemström.

In the tube in the Polytechnic Institute the following gases were successively examined:—air, hydrogen, oxygen, air, nitrogen, hydrogen, air, oxygen. The apparatus was unaltered all the time; the new gas was introduced, in the manner peculiar to my pump*, after the former gas had been removed as completely as possible. I give here only the results for air, regarding the results obtained with the other gases merely as preliminary, since I was not able to work with pure gases. I therefore reserve the complete examination of these gases for a future occasion, and give here the results already obtained with them only briefly.

I wish to express my thanks to Herr G. Melander for the help he gave me during the whole investigation.

The conducting-globes had a diameter of 27·8 millim.; the sparks were generally 5 millim. long. It appeared that a great length of spark might be injurious to the tube. On one occasion a tube of thin glass broke whilst a discharge passed between the tinfoil coating and the layer of air clinging to the inner wall of the tube. I have further remarked that of the capillary canals, which always exist in the walls of the tube parallel to its length, those which lie nearest the inside easily burst and discharge the air which they contain into the tube, when the discharges are powerful. It therefore often happens that the pressure in the tube suddenly increases very much, and the luminosity becomes very vivid, if, after having produced a great exhaustion, the air has been driven from the inner wall of the tube by electric discharges. In one case I was able, after such an occurrence, to detect the small holes in the capillary channel which had burst, and the little splinters of glass.

I have made the following observations with regard to the mercury-lines which are to be expected when the mercurial pump is employed. In tubes containing *pure* air, nitrogen, or oxygen, the mercury-lines appear only at high exhaustions. Only the strongest line 546 appears in tubes containing air; but in nitrogen and oxygen tubes also the lines 579 (double), 492, and 436. In hydrogen tubes, and in tubes with impure air (containing carbon dioxide), these lines appear already at

* *Loc. cit.* p. 178.

considerable pressure, together with the hydrogen and air lines; in hydrogen tubes the lines 408, 405, and (at high exhaustion) 483* feebly, were also seen.

Under the circumstances named, the air began to be luminous at a pressure of 10–12 millim.†; the end with the positive coating became luminous somewhat sooner (at 14 millim.) than the whole tube. It was, however, possible to produce a feeble luminosity of the tube at a considerably higher pressure (about 50 millim.) by pushing a conductor along the tube in contact with the wall until a spark passed between the conductor and the one coating. An unexpected phenomenon was observed at a pressure of about 8 millim., inasmuch as the light appeared to be stratified in a peculiar manner. As I propose to examine this stratification more particularly, I describe it here only briefly. The first quarter from the positive coating was strongly luminous, the intensity diminishing slightly towards the end of this portion. The second quarter also began with a strong luminosity, which became somewhat weaker towards the middle of the tube. The third quarter was distinctly stratified; in one case there were only three or four luminous stratifications, which oscillated tolerably rapidly and appeared like luminous balls; in another experiment I observed a number of thinner layers. Only towards the beginning of the fourth quarter was there a thicker layer: all the stratifications oscillated rapidly‡. The last quarter next the negative coating was always strongly luminous without stratification§. The narrow spiral glass tube which made connexion with the pump was also generally strongly luminous, whether the coating at this end was negative or positive.

The spectroscope showed a large number of bands. With narrow bands the reading was taken for the middle; with broader bands for both edges. The following wave-lengths are the arithmetic means of various measurements within the limits of pressure (0.2 to 1.2 millim.) between which the

* E. Wiedemann has investigated the spectroscopic behaviour of mercury-vapour mixed with other gases at high temperatures, *Wied. Ann.* v. p. 547 (1878). Compare also H. W. Vogel, *Berlin. Monatsberichte*, 1879, p. 536.

† All measurements of pressure are given in columns of mercury at about 20° C.; for details of the method of measuring pressure, I refer to the paper already cited on the air-pump (*Acta Soc. Scient. Fennicæ*, xv. p. 169).

‡ Similar balls of light (*Glimmlichtkugeln*) have been observed under certain conditions by Reitlinger and v. Urbanitzky in short and wide tubes (*Wied. Ann.* xiii. p. 673).

§ I have observed a similar stratification in a hydrogen-tube.

spectrum was the brightest. The observations made with the large spectroscope are noted. The intensity, estimated for the spectrum as seen in the small spectroscope, is given on a scale from 1 to 5. The minus sign after a number indicates that the intensity falls short of that number, and the plus sign that it exceeds it; so that 1+ means an intensity between 1 and 2 but nearer 1 than 2, whilst 2- means intensity nearer 2 than 1.

No.	Wave-length.	Intensity.	Remarks.
1.	0,0006778	1-	
2.	6680	1	Nos. 2-17 observed in the large spectroscope; Nos. 2-10 with a wider slit.
3.	6600	1+	
4.	6527	1	
5.	6445	1	
6.	6373	1	
7.	6294	1	
8.	6229	1-	
9.	6164	1-	
10.	6111	1-	Breadth 31×10^{-7} . " 38. " 36. " 33. " 33 (double?). " 30 (double?).
11.	6052	2-	
12.	5996	1+	
13.	5934	1	
14.	5881	1-	
15.	5833	1-	
16.	5784	1-	
17.	5734	1	
18.	5665	1--	Very weak.
19.	5621	1-	
20.	5382	{ Sharp edge of a band, beginning about 557° , very weak, and gradually becoming stronger.
21.	5304	1--	Very weak.
22.	5228	2-	In the large spectroscope four lines: 5224, 5195, 5179, 5145.
23.	5164	1+	
24.	{ 5067 } 4996	2	{ In the large spectroscope 5060, 5029, 4983.
25.	4910	2	In the large spectroscope 4832, 4812. " " 4715, 4707. " " 4663, 4647.
26.	4813	2	
27.	4700	3+	
28.	4659	2+	
29.	4574	3	In the large spectroscope 4500, 4488.
30.	4491	2+	
31.	4415	1	In the large spectroscope 4278, 4269.
32.	4341	3	
33.	{ 4293 } 4275	5	In the large spectroscope 4140. " " 4057. " " 3995.
34.	4209	1	
35.	4152	1	Broad band.
36.	4074	2+	
37.	4020	2-	
38.	3910	1-	

The spectrum underwent no change if the connexions of the coatings with the conductors were reversed. I have

observed the following changes with change of pressure. With a tolerably wide slit the spectrum could be measured at a pressure of 12 millim. Feeble continuous light began at 557. The bands 22 and 23 appeared as a continuous band of mean wave-length 5192. Further, 24, 25, 26, 27, and 28 appeared united into one band, which was also the case with 29, 30, 32, 33, 34, 36, 37. Nos. 11 and 31 appeared at a pressure of 5.5 millim.; and all the bands became visible at 2.3 millim. When the pressure sank below 0.2 millim. all the bands became decidedly weaker, the feebler bands disappearing first with increasing exhaustion. Thus, at a pressure of 0.02 millim. the bands 1 to 9, 21 to 26, 31, 34, 35, and 38 had disappeared, and the bands 11 to 17 had united to form a continuous glcw. At 0.01 millim. there were left only 10, 27, 28, 33; and at 0.0023 millim. only 27, 28, and 33; whilst at 0.0013 millim. the band 28 also vanished. If I pushed the exhaustion still further I could see no air-lines, although the tube was still faintly luminous, the mercury-line 546 being quite distinct. No luminosity was produced by single discharges; at a pressure of 0.0007 millim. the tube only became luminous very seldom, and if the pressure was less than 0.0003 millim. there was generally no light to be perceived. With the same velocity of the induction machine the sparks followed each other much more rapidly than at higher pressures. We may therefore conclude that with high values the tube no longer acts as a conductor, because the rarefied air is no longer present in sufficient quantity.

With a very high exhaustion the walls of the tube fluoresced strongly, especially near the positive coating; and at each discharge this coating emitted a sharp sound, like that of a spark. Some of Crookes's kathode-rays were seen at a pressure of 0.002 millim.

In one case, however, each discharge produced light in the tube, although fully exhausted. The tube had been heated in an air-bath to a temperature of about 250° C. for several hours daily during ten days, in order to disengage the air from the sides of the tube as much as possible. The pressure was reduced on each occasion to a few millionths of a millimetre by continuous pumping. In the intervals while the tube was not heated, the pressure rose from one day to another by about 0.00015 millim. After this preparation I examined the effect of discharges, and found that a tolerably strong luminosity was produced, which was finely stratified throughout the tube. In the spectroscope only the five previously mentioned mercury-lines 579, 546, 492, 483, 436 were seen. Since pure air generally shows only the mercury-line 546 in high vacua,

the air in this tube was probably a little contaminated with coal-gas, introduced when the apparatus was last fused together. After the discharge had gone on for some minutes, the pressure was measured and found to be 0.00053. Hence we see that, in spite of the persistent heating, gas still adhered to the wall of the tube and was disengaged by the electricity.

How obstinately air adheres to a glass surface is particularly shown by the tube put up in the Physical Laboratory of the University. This tube had been exhausted from time to time for four months, each time to a few millionths of a millimetre; yet, after some time, there was always a considerable pressure. Thus, on the 8th of January the pressure was 0.0013 millim., on the 14th 0.0011 millim., on the 21st 0.0005 millim., and on the 22nd of February 0.0028 millim.* This tube was provided with electrodes of a special kind. Before the tube was closed, thin aluminium-foil was introduced into the tube, corresponding to the external tinfoil coatings, from which narrow strips projected along the axis of the tube towards the middle, and served as electrodes. I was led to this arrangement, not being able to melt the electrodes into the tube; the action may be considered as nearly the same as that of the ordinary electrodes melted into the glass. This tube, in fact, ceased to be luminous at a pressure of about 0.004 millim. and a spark-length of 5 millim. When the pressure was still smaller (a few millionths of a millimetre), I could not perceive any luminosity, even with the greatest possible spark-length (15 millim.); but the luminosity commenced suddenly upon the bursting of one of the capillary canals mentioned above.

In the hydrogen-tube I obtained a very pure hydrogen spectrum; although the gas had been prepared in the usual way from zinc and sulphuric acid, both free from arsenic, the gas had a strong odour of hydrocarbons. The luminosity began at a pressure of 30 millim. (with gas containing air at 43 millim.). At a pressure of 0.35 millim. the spectrum showed the lines C (=656), F (=486), and 434 (united with the mercury-line 436 to a band?), as well as numerous faint lines (especially in the red and orange) of the second hydrogen spectrum investigated by Hasselberg. The tube was luminous at the highest vacuum attainable, at least at the positive coating; the light failed only in individual discharges. Crookes's rays were seen even at a pressure of 0.008 millim.

* I have not observed the phenomenon mentioned by Bessel-Hagen (*Wied. Ann.* xii. p. 440, 1881), that the air liberated from the walls of the tube by electric discharges condenses again, so that after some time the pressure decreases again.

Only in one case (with hydrogen containing air) have I observed fine stratifications in a high vacuum.

If the tube contained oxygen (prepared from potassium chlorate) the luminosity began at about 30 millim.; the spectrum was brightest at about 0.2 millim. The two bands 563-556 and 529-523 were specially conspicuous, and these two could be recognized with greater exhaustion when the tube was only faintly luminous. At high vacua the light failed oftener than with the hydrogen-tube.

With nitrogen I obtained in the small spectroscopie the same spectrum as with air.

Helsingfors, May 26, 1885.

XII. *On the Electrostatic Force required to produce Sparks in Air and other Gases.* By G. A. LIEBIG, Ph.D., Johns Hopkins University*.

[Plate II.]

THE following experiments were undertaken at the suggestion of Prof. Rowland, and the results submitted from time to time to his inspection.

Historical.

Determinations of the difference of potential required to produce sparks in air appear to be numerous. But the earlier measurements, such as those made by Volta †, Riess ‡, and Gauguin §, in which the difference of potential was determined in arbitrary units by means of electroscopes, unit jars, &c., have little more than a historic value. It was, however, noticed by these observers that the length of spark increased more rapidly than the charge; and Van Oettingen || deduced an empirical formula,

$$q = c \log (1 + \epsilon l),$$

in which c and ϵ are constants, l is the length of spark, and q the charge, to express this relation. The first experiments on the subject, giving results in absolute measure, were made by Sir William Thomson ¶. In his investigation the sparks were made to pass between two plates, one of which was flat, the other slightly convex; and the difference of potential

* Communicated by the Author.

† *Identita*, p. 53.

‡ Pogg. *Ann.* xl. p. 333 (1837).

§ *Ann. de Chim. et de Phys.* viii. p. 108 (1866).

|| Pogg. *Ann.* Jubelbd., p. 275 (1874).

¶ 'Electrostatics and Magnetism.'