

out the task of collecting and editing; and it only remains for those who are taking part in the preparation of the Catalogue, to do their best to secure that the Catalogue shall fulfil the hopes which have been raised.

"It gives me great pleasure to make this announcement in the presence of several of our foreign brethren, whose co-operation has tended so much to the success of the enterprise."

The following Papers were read:—

- I. "On the Spectrum of the more Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen.—Preliminary Notice." By Professor S. D. LIVEING, F.R.S., and Professor JAMES DEWAR, F.R.S.
- II. "Additional Notes on Boulders and other Rock Specimens from the Newlands Diamond Mines, Griqualand West." By Professor T. G. BONNEY, F.R.S.
- III. "The Distribution of Vertebrate Animals in India, Ceylon, and Burma." By W. T. BLANFORD, LL.D., F.R.S.
- IV. "Elastic Solids at Rest or in Motion in a Liquid." By C. CHREE, F.R.S.

The Society adjourned over the Christmas Recess to Thursday, January 17, 1901.

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"On the Spectrum of the more Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen.—Preliminary Notice." By S. D. LIVEING, M.A., D.Sc., F.R.S., Professor of Chemistry, University of Cambridge, and JAMES DEWAR, M.A., LL.D., F.R.S., Fullerian Professor of Chemistry, Royal Institution, London. Received November 15,—Read December 13, 1900.

In August last some tubes were filled at low pressure by an improved process with the more volatile gases of the atmosphere.\* The air was liquefied directly from that above the roof of the Royal Institution by contact at atmospheric pressure with the walls of a vessel cooled below  $-200^{\circ}\text{C}$ . When about 200 c.c. of liquid had

\* In this paper we describe researches in continuation of those previously communicated to the Society by one of us, in a paper entitled "Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination," 'Roy. Soc. Proc.,' vol. 64, p. 231.

condensed, communication with the outer air was closed by a stop-cock. Subsequently, communication was opened, through another stop-cock, with a second vessel cooled by immersion in liquid hydrogen, and a part of the liquid from the first vessel, maintained at  $-210^{\circ}$ , was allowed to distil into the second still colder vessel. When about 10 c.c. had condensed in the solid form in the second vessel, communication with the first vessel was cut off, and a manometer showed a pressure of gas of about 10 to 15 mm. of mercury.

This mixture of gases was passed into tubes previously exhausted by a mercury pump, but before reaching the tubes it had to pass through a U-tube immersed in liquid hydrogen so as to condense less volatile gases, such as argon, nitrogen, oxygen, or carbonic oxide, which might be carried along by those more volatile. Previous trials with tubes filled in the same way, except that the U-tube in liquid hydrogen was omitted, showed that these tubes contained traces of nitrogen, argon, and compounds of carbon. The tubes filled with gas which had passed through the U-tube showed on sparking no spectrum of any of these last-mentioned gases, but showed the spectra of hydrogen, helium, and neon brilliantly, as well as a great many less brilliant rays of unknown origin. In addition, they showed at first the brightest rays of mercury, derived, no doubt, from the mercury pump by which they had been exhausted before the admission of the gases from the liquefied air. After some sparking the mercury rays disappeared, probably in consequence of absorption of the mercury by the electrodes, which were of aluminium.

In one experiment the mixture of gases in the second vessel, into which a fraction of the liquefied air was distilled as above described, was pumped out without being passed through the U-tube in liquid hydrogen and examined. This mixture was found to contain 43 per cent. of hydrogen, 6 per cent. of oxygen, and 51 per cent. of other gases—nitrogen, argon, neon, helium, &c.—and it was explosive when mixed with more oxygen. This shows conclusively that hydrogen in sensible proportion exists in the earth's atmosphere, and if the earth cannot retain hydrogen or originate it, then there must be a continued accession of hydrogen to the atmosphere (from interplanetary space), and we can hardly resist the conclusion that a similar transfer of other gases also must take place. The tubes containing the residue of atmospheric gases uncondensed at the temperature of liquid hydrogen we have examined spectroscopically.

On passing electric discharges through them, without any condenser in the circuit, they glow with a bright orange light, not only in the capillary part, but also at the poles, and at the negative pole in particular. The spectroscope shows that this light consists in the visible part of the spectrum chiefly of a succession of strong rays in the red, orange, and yellow, attributed to hydrogen, helium, and neon.

Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. They are obscured in the spectrum of the capillary part of the tube by the greater strength of the second spectrum of hydrogen, but are easily seen in the spectrum of the negative pole, which does not include the second spectrum of hydrogen, or only faint traces of it. Putting a Leyden jar in the circuit, while it more or less completely obliterates the second spectrum of hydrogen, also has a similar effect on the greater part of these other rays of, as yet, unknown origin. The violet and ultra-violet part of the spectrum seems to rival in strength that of the red and yellow rays, if we may judge of it by the intensity of its impressions on photographic plates. We were surprised to find how vivid these impressions are up to a wave-length 314, notwithstanding the opacity of glass for rays in that part of the spectrum. The photographs were taken with a quartz calcite train, but the rays had to pass through the glass of the tube containing the gases.

We have made approximate measurements of the wave-lengths of all the rays which are sufficiently strong to be seen easily or photographed with an exposure of thirty minutes, and give a list of them below. These wave-lengths are computed to Rowland's scale, and were deduced from the deviations produced by two prisms of white flint glass for the visible, and of calcite for the invisible, rays. The wave-lengths assigned to the helium lines are those given by Runge and Paschen, and some of these lines were used as lines of reference. In general, the iron spark spectrum was the standard of reference.

The tubes when first examined showed the lines of the first spectrum of hydrogen vividly, and the earlier photographs of the spectrum of the negative pole contained not only the violet lines of hydrogen, but also the ultra-violet series as far up as  $\lambda$  377. In order to get impressions of the fainter rays, exposures of half an hour or more were required, and a succession of photographs had to be taken so as to get different sections of the spectrum into the middle of the field, where measurement of the deviations would not be impeded by the double refraction of the calc spar. As the light of the negative pole only was required, the electric discharge was made continuously in one direction only, with the result that the hydrogen lines grew fainter in each successive photograph, and soon disappeared altogether. Along with the ultra-violet rays, the less refrangible rays of hydrogen also disappeared, so that no trace of the C or F line could be seen, nor yet of the second spectrum, so long as the current passed in the same direction as before. Reversal of the current soon made the F line show again, so that it seems that the whole of the hydrogen was driven by the current to the positive pole. The conditions under which this ultra-violet series shows itself are a matter of interest. It appears here in the midst of a brilliant spectrum due to gases other than

hydrogen, and yet it is very difficult to obtain a photograph of it when no gas but hydrogen is known to be present, or, at least, to become luminous in the electric discharge.

We have had an opportunity of comparing the spectrum of the volatile residue of air with that of the more volatile part of gas from the Bath spring. The tube did not admit of the separate examination of the light from the negative pole, but was examined end-on, so that the radiation probably included rays emitted from the neighbourhood of the negative pole. The whole of the hydrogen had been removed from the Bath gas, but not all the argon. In the spectrum of this gas the rays of helium are dominant, decidedly stronger than those of neon, although the latter are very bright. In the spectrum of the residue of atmospheric air, the proportion of helium to neon seems reversed, for in this the yellow neon line is as much more brilliant than the yellow helium line as the latter is the more brilliant in the spectrum of Bath gas. All the prominent lines in the spectrum of the volatile residue of Bath gas were also in that of the residue of atmospheric air, except the argon lines. There were, on the other hand, many lines in the latter not traceable in the former, some of them rather conspicuous, such as the ray at about  $\lambda$  4664. It is, of course, probable that such rays are the outcome of some material not contained in the Bath gas. A very conspicuous pair of lines appears in photographs of the spectrum of the air residue, at about  $\lambda$  3587, which is not traceable in the spectrum of Bath gas. The helium line,  $\lambda$  3587.4, is seen in the latter spectrum, but is quite obscured in the former spectrum by the great intensity of the new pair. This helium ray is really a close double, with the less refrangible component much the weaker of the two, but the new pair are wider apart, and of nearly equal intensities; this character also distinguishes them from the strong argon line at  $\lambda$  3588.6. They are, however, very much more intense at the negative pole than in the capillary, and it will require a good deal more study to determine whether these rays, and many others which we have not tabulated, are due to the peculiarity of the stimulus at the negative pole, or to the presence of a previously unrecognised material.

As our mixture of gases probably includes some of all such gases as pervade interplanetary and interstellar space, we early looked in their spectra for the prominent nebular, coronal, and auroral rays. Searching the spectrum about  $\lambda$  5007 no indication of any ray of about that wave-length was visible in the spectrum of any one of the three tubes which had been filled as above described. Turning to the other green nebular line at about  $\lambda$  4959, we found a weak rather diffuse line to which our first measure assigned a wave-length 4958. The correctness of this wave-length was subsequently verified by measuring with a micrometer eye-piece the distances of the line from the helium lines  $\lambda$  4922.1 and  $\lambda$  5015.7 which were in the field of view at the same

time. The position of the line was almost identical with that of the iron spark line  $\lambda$  4957·8, and the conclusion arrived at was that the wave-length was a little less than 4958, and that it could not be the nebular line. There remained the ultra-violet line  $\lambda$  3727. Our photographs showed a rather strong line very close to the iron spark line  $\lambda$  3727·8, but slightly more refrangible. As the line is a tolerably strong one, it could be photographed with a grating spectrograph along with the iron lines. This was done, and the wave-length deduced from measuring the photograph was 3727·4. This is too large by an amount which considerably exceeds the probable errors of observation, and we are forced to conclude that the nebular material is either absent from our tubes, or does not show itself under the treatment to which it has been subjected.

Although the residual gases of the atmosphere uncondensed at the temperature of liquid hydrogen do not show the nebular lines, we found that another tube gave a ray very close indeed to the principal green nebular ray. This tube had been filled with gas prepared in the same way as the others, with the exception that, in passing from the vessel into which the first fraction of liquid air was distilled, it was not passed through a U-tube immersed in liquid hydrogen on its way to the exhausted tube. In consequence it contained traces of nitrogen and argon, and when sparked showed the spectra of these elements as well as those of hydrogen, helium, &c. The nitrogen spectrum disappeared after some sparking, but the tube still shows rays of argon as well as those of the gases in the other tubes. On examining the spectrum of the negative pole in the neighbourhood of the principal nebular green ray, a weak ray was seen in addition to those given by the other tubes. It was found by comparison with the nitrogen rays  $\lambda$  5002·7 and  $\lambda$  5005·7 to be a little less refrangible than the latter of these rays, and by measuring its distance from the nitrogen rays and from the two helium rays  $\lambda$  4922·1 and  $\lambda$  5015·7 with a micrometer eye-piece, the wave-length  $\lambda$  5007·7 for the new ray was deduced. This looks as if we might find the substance which is luminous in nebulae to be really present in the earth's atmosphere, and we hope shortly to be able to verify the observation of it.

Turning to the coronal rays, our tubes emit a weak ray at about  $\lambda$  5304. This is not far from the wave-length  $\lambda$  5303·7 assigned by Sir N. Lockyer to the green coronal ray. It is, however, greater than that assigned by Campbell, namely, 5303·26.\* Other lines observed by us near the places of coronal lines are at wave-lengths about 4687, 4570, 4358, 4323, 4232, 4220, 3985, 3800. These are all weak lines except that at  $\lambda$  4232, which is of tolerable strength, and that at  $\lambda$  4220, which is rather a strong line. The wave-lengths 4323, 4232, 4220, and 3800 come very close to those assigned to coronal rays, but

\* 'Astroph. J.,' vol. 10, p. 190.

the others hardly come within the limits of probable error. The ray 4220 seems too strong in proportion to the others, but the strength of that at 4232 seems to accord with the strength of the corresponding ray in the corona. It will be seen that the rays we enumerate above correspond approximately to the stronger rays in Sir N. Lockyer's list.\* Further measures of the wave-lengths of the faint lines are needed before we can say definitely whether or no we have in our tubes a substance producing the coronal rays, or some of them.

As to the auroral rays, we have not seen any ray in the spectrum of our tubes near  $\lambda$  5571.5, the green auroral ray. We have observed two weak rays at  $\lambda$  4206 and  $\lambda$  4198 which may possibly, one or both, represent the auroral ray  $\lambda$  420. The very strong ray of argon,  $\lambda$  4200.8, would make it probable that argon was the origin of this auroral ray, if the other, equally strong, argon rays in the same region of the spectrum were not absent from the aurora. Nor have we found in the spectrum of our tubes any line with the wave-length 3915, which is that of another strong auroral line. On the other hand it seems probable that the strong auroral line  $\lambda$  358 may be due to the material which gives us the very remarkable pair of lines at about the place of N of the solar spectrum,  $\lambda$  3587, which are very strong in the spectrum of the negative pole, but only faint in that of the capillary part of our tubes. It may well be that the auroral discharge is analogous to that about the negative pole. We have also a fairly strong ray at  $\lambda$  3700, which may be compared to the remaining strong ray observed in the aurora  $\lambda$  3700. This, however, is a ray which is emitted from the capillary part of our tubes as well as from the negative pole, and is, moreover, emitted by Bath gas, and may very likely be a neon ray.

We hope to pursue the investigation of this interesting spectrum, and if possible to sort out the rays which may be ascribed to substances such as neon and those which are due to one or more other substances. The gas from Bath, even if primarily derived from the atmosphere—which is by no means sure—seems to have undergone some sifting which has affected the relative proportions of helium and neon, and a more thorough comparison of its spectrum with that of the residual atmospheric gases may probably lead to some disentanglement of the rays which originate from different materials. The arrangement of the rays in series, if that could be done, would be a step in the same direction.

We are indebted to Mr. Robert Lennox, F.C.S., for the great help he gave us in the complicated manipulation with liquid hydrogen required to fill the spectral tubes, and to Mr. J. W. Heath, F.C.S., for kind assistance.

\* 'Roy. Soc. Proc.,' vol. 66, p. 191.

*List of Approximate Wave-lengths of the Rays, Visible and Ultra-violet, observed about the Negative Pole.*

The rays of hydrogen and helium, and those attributed to neon by other observers, are indicated by the chemical symbols of those substances :—

A “b” prefixed to the number expressing the wave-length indicates that the ray is emitted by gas from the Bath spring as well as by that obtained from the atmosphere.

A “c” similarly prefixed indicates that the ray has been observed to be emitted from the capillary part of the tube as well as from about the negative pole.

A “w” indicates a weak line; “s” a strong one; “d” a diffuse one; “vw” a very weak; and “vs” a very strong one.

bc He	7281·8	bc He	5875·9		5031
	7247	vsbc Ne	5852·7	b He	5015·7
	7174	sb	5820	wd	4958
bc He	7065·5	sb	5804	b He	4922·1
vw	7058	sbc	5763	vw	4884
bc Ne	7034	bc	5747	sc H	4861·5
bc Ne	6931	bc	5718	vw	4838
bc Ne	6716	bc	5689	vw	4819
bc He	6678·4	wbc	5662	vw	4811
bc Ne	6601	bc	5656	wd	4791
sc H	6563		5592	wd	4754
bc	6535	b	5561	b Ne	4715
bc Ne	6508		5532	b Ne	4710
vwbc	6446	vw	5503	b Ne	4704
bc Ne	6404	vw	5447	w	4687
bc Ne	6382	w	5432	w	4680
bc Ne	6334	vw	5417		4664
bc Ne	6304	vw	5409	w	4657
bc Ne	6266	b Ne	5400	w	4647
bc	6244		5372	w	4640
bc	6232		5360	w	4636
bc Ne	6217		5355	w	4628
b	6183	bc Ne	5341 a pair	w	4616
vwbc	6176	bc Ne	5330	w	4589
bc Ne	6163	w	5304	w	4583
bc Ne	6144	w	5298		4576
vw	6128		5234	w	4570
b Ne	6097	b	5222		4540
b Ne	6075		5209		4538
b Ne	6031	b Ne	5204	w	4526
b	6001	b	5192	w	4523
b	5991	b Ne	5188	w	4518
w	5987		5152	w	4508
bc Ne	5976	b Ne	5145	w	4500
w	5964		5122	w	4488
sdb Ne	5945	b Ne	5116	vs He	4471·6
w	5919	b Ne	5080	vw	4460
w	5914		5074		4457
w	5905	b He	5047·8	vw	4438
bc	5882	sbc	5038	w	4437·7

	4431	b ? He ?	3927	wbe	3510
	4429		3905	w	3504
	4424		3900	be	3500
	4422	vsbe He	3888 ·8	be He ?	3598
	4413	wbe He ?	3872		3482
	4409	be He	3867 ·6		3481
	4398	w	3866	sbe	3473
	4392	w	3862	be	3467
b He	4388 ·1	we ?	3860	be	3464
	4380	w	3856	be	3460
w	4370	w	3842	w	3456
vw	4365	w	3840	be	3454
w	4363	c H	3836	we	3451
w	4358	b	3830	sbe He	3447 ·7
vw	4347	sbe He	3819 ·75	w	3429
s H	4340 ·7	we He ?	3806	w	3424
w	4334	w	3800	sbe	3418
vw	4322	c H	3798	vw	3417
vw	4315		3777	w	3407
vw	4306	w H	3770	w	3404
w	4290		3766	b	3393
	4276		3754	b	3388
w	4270		3751	s	3378
w	4261	vw	3745	vw	3374
w	4258	w	3738	w	3372
	4251	? c	3735	be	3370
	4241	? c	3728		3367
	4234	w	3722	w	3363
	4232	w	3721 ·5	vw	3362
	4220	s	3713		3360
w	4218		3710		3358
w	4206	be He	3705 ·2	b He	3354 ·7
vw	4198	w	3703	s	3345
we	4176		3701	w	3344
wb He	4169 ·1	s c ?	3694	s	3335
w	4151	c	3686		3329
b He	4143 ·9	c	3683		3327
w	4134	sc	3664	s	3324
b	4131		3655	sb	3319
wb	4128		3651	w	3315
b He	4121	w	3650	w	3313
w	4112		3644 a pair	w	3311
sc H	4102	sc He ?	3634 a pair		3310
w	4099	vw	3628	b He ?	3297
vw	4086	be He	3613 ·8	vw	3254
w	4080	w	3609	wb	3250
w	4063	be He ?	3600	s	3244
	4047	sbe	3593		3233
vw	4043	vs	3587 ·5 a pair	? pair	3230
vw	4037		3575		3225
vsbe He	4026 ·3	w	3571	s	3218
b He ?	4009		3569		3214
w	3996	w	3561		3209
vw	3985	w	3558		3199
vw	3980	vw	3548	sb He	3187 ·8
sc H	3970		3543	w	3165
s He	3964 ·9	vsbe	3521	w	3142
vw	3933	be	3515		