PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On the Refractive Indices of Gaseous Potassium, Zinc, Cadmium, Mercury, Arsenic, Selenium and Tellurium

C. Cuthbertson and E. Parr Metcalfe

Phil. Trans. R. Soc. Lond. A 1908 **207**, 135-148
doi: 10.1098/rsta.1908.0003

III. *On the Refractive Indices of Gaseous Potassium, Zinc, Cadmium, Mercury, Arsenic, Selenium and Tellurium.*

By C. CUTHBERTSON *and* E. PARR METCALFE, *B.Sc.*

Communicated by Professor F. T. TROUTON, *F.R.S*

Received October 23,—Read November 18, 1906.

WE have continued, with more perfect apparatus, the enquiry recorded in a previous paper* on the refractive indices of the vapours of elements which are not gaseous at ordinary temperatures. The instrument employed was the refractometer of JAMIN, and the arrangement of the apparatus has been fully described in the paper just cited, so that it requires only a brief recapitulation here.

Two similar exhausted tubes are placed in the paths of the rays of monochromatic light between the mirrors, and a known weight of the element is vaporised in one of them, of which the volume is known. The tubes are heated by means of a simple form of electric furnace, consisting of two coils of nickel wire embedded in asbestos.

The number of interference bands which pass a fiducial mark in the field of the observing telescope during the evaporation, or return during the condensation, combined with the other data, give the index for the wave-length employed.

The calculation is as follows :—

If N be the number of bands observed to pass the fiducial mark, λ the wave-length X the length of the tube, m the refractive index observed, and μ the refractive index at the standard density selected, we have

$$N\lambda = (m-1)X$$

and

$$\frac{\mu-1}{m-1} = \frac{\text{standard density}}{\text{observed density}}$$

$$= \frac{\cdot 00009 \times \text{atomic weight of element}}{\text{atomic weight of hydrogen}} \times \frac{\text{volume of tube}}{\text{weight of element volatilised}}.$$

Hence

$$(\mu-1) = \frac{N\lambda}{X} \times \frac{\cdot 00009 \times \text{atomic weight of element} \times \text{volume of tube}}{\text{atomic weight of hydrogen} \times \text{weight volatilised}}.$$

---

* 'Phil. Trans.,' A, vol. 204, p. 323, 1905.

27.2.07

The *standard density* selected is that in which the number of atoms of the element per unit volume is equal to the number of atoms contained in unit volume of hydrogen at 0° C. and 760 millims.

In the present work the original procedure underwent several important improvements. Repeated failure had shown that the glass tubes formerly used, with plate-glass ends ground in and luted with shellac, were useless above 280° C., when the shellac charred and the tubes cracked.

Recourse was had, therefore, to tubes of fused silica, which were made with admirable skill by the firm of HERAEUS, of Hanau. The ends of the tubes, through which the interfering rays passed, were plates of the same material ground optically flat, fused into the tubes and again polished, so that the whole formed an air-tight, homogeneous enclosure, which could be heated to the highest temperature employed (about 850° C.) without fear of softening, and could be heated and cooled locally with great rapidity without cracking.

This property of the silica permitted the introduction of a second improvement in the procedure. In the earlier work the two sections of the furnace were joined up in the centre, and the whole length of the tubes was heated in one operation, so that the observer had sometimes to remain with his eye at the telescope for several hours while the furnace heated and cooled. This tedious method was now abolished. The two sections of the furnace were separated by a gap of about an inch, and their inner ends covered with thin asbestos boards. In these boards holes were punched, through which the silica tubes passed. In this way the greater part of the tubes could be raised to a high temperature while the gap in the middle remained comparatively cool. With the object of obtaining a reasonable equality in the temperature of the two halves of the furnace, the sections were made in all respects as nearly similar as possible, and the heating coils were connected in parallel to the lighting circuit.

When the furnace had reached the temperature which was found by experiment to be more than sufficiently high to evaporate the whole of the charge employed, cold water was dropped on the exposed part of the tube until it was certain that the temperature there must be below 100° C., and, consequently, that there could be practically none of the element in a state of vapour. The observer then noted the position of the bands in the telescope, in relation to a pointer fixed on the further mirror, and his colleague quickly heated the central portion of the tube with a Bunsen flame. The bands now moved rapidly and attained their maximum in a few minutes. The heating was continued for about a minute after the stopping of the bands indicated the complete vaporisation of the charge; the flame being then removed, a second reading was obtained as the element condensed. When nearly all the bands had passed, water was again dropped on the tube till it was certain that the zero had been reached. Meanwhile the temperature of the rest of the furnace was kept approximately constant, and thus many minor sources of error due to inequality of the length of the tubes, or of the thickness of the ends, or to unequal heating of the air, which had given trouble previously, were avoided.

In the case of zinc, the temperature necessary was so high that the glass diaphragms used to close the outer ends of the furnace began to soften and buckle. This difficulty was overcome by substituting worked plates of fused silica.

In the course of the work it was found that the dispersion would be considerable. Arrangements were therefore made for determining the index for more than one wave-length. A mercury vapour lamp of Bastian's pattern was found to give an excellent green ($\lambda = 4460$), and red light ($\lambda = 6562$) was obtained from a hydrogen vacuum tube. But these methods proved unsatisfactory, and eventually it was found possible to work with approximately monochromatic light sifted out with a slit from the spectrum of the white light of a Nernst filament dispersed through four glass prisms. The light thus obtained was sufficiently monochromatic to give twenty or thirty sharp black interference bands, and it was used in all the later experiments.

Potassium.

Of the elements whose indices still remain to be measured in the gaseous state, the most important group is that of the alkalis. It was, therefore, decided to begin with potassium, which seemed likely to prove the easiest.

So far as we are aware, only one attempt has hitherto been made to measure the index of a member of this group. In the course of his brilliant research on the optical properties of sodium vapour, Professor R. W. Wood* measured the retardation of light in passing through a column of dense vapour, and compared its value at different points of the spectrum with that produced at the wave-length of the yellow helium line. By the application of the Sellmeier dispersion formula to his results he deduces an index of 1·0000275 for infinitely long waves for sodium vapour saturated at 644° C. Unfortunately the density of the vapour corresponding to this temperature is yet unknown, so that it is impossible from the data available to calculate the absolute atomic refractivity of sodium.

The relative values for different wave-lengths are, of course, independent of the density, and in themselves constitute a most interesting exemplification of the variation of the index in the neighbourhood of an absorption band. Thus, the index increases from the infra-red to the line D_1, where it becomes very large. On the blue side of D_2 the index increases rapidly from very small values, but remains less than unity even as far as $\lambda = 2260$.

In view of these facts the investigation of the index of potassium seemed likely to yield results of similar interest. But, unfortunately, the chemical difficulties proved so great that, in spite of numerous attempts, it was found impossible to obtain absolute values with the apparatus employed. At the temperature at which

---

* 'Phil. Mag.' September, 1904.

potassium evaporates, it attacks both glass and silica, so that it is not possible to obtain, in vessels of these materials, a density of the vapour sufficient for a quantitative determination of the absolute index. Eventually, however, by adopting the device of heating all but a small portion of the refractometer tube to a sufficient temperature, and then rapidly heating the cool part, a sufficient density of vapour was attained to permit of some qualitative observations.

Since reliable numerical results could not be looked for, no attempt was made to purify the potassium beyond distilling it *in vacuo* after prolonged heating to expel occluded hydrogen. The distillate was run into capillary tubes, which were sealed off in short sections, and, by a device which need not be described, the operations of breaking the capillary and introducing it into the refractometer tube were performed entirely *in vacuo*.

Experiments were, at first, made with sodium light, but it was found that at a temperature of about 220° C. the interference bands disappeared, though the light was not wholly absorbed by the vapour. This effect might be accounted for by supposing that the potassium contained a small quantity of sodium, or that sodium was set free by the action of the potassium on the glass tube, for Wood has shown that the great dispersion of the vapour of sodium in the neighbourhood of the D lines has the effect of destroying interference bands formed by light of those wave-lengths, when even small quantities of vapour are present.

The sodium flame was therefore replaced by a Bastian mercury lamp which gave good bands with the wave-length 5460. Several experiments were made with this light with refractometer tubes both of glass and of silica; and it was found that the evaporation of the potassium was attended by a movement of the bands in the direction corresponding to a refractive index less than unity. On one occasion no less than four bands were observed to pass during the heating and to return during the cooling.

These experiments at first suggested that the quantity of sodium present was greater than had been suspected, and that its influence on the index dominated that of the potassium. If this were so we should find that an experiment with light of greater wave-length than that of the D lines would give a very high refractive index. In order to test this surmise, experiments were made with the red light supplied by a hydrogen vacuum tube whose H_α line was so strong as to give good interference bands. But in this case also the bands moved in the same direction as those formed by the light of the mercury lamp. We are, therefore, driven to the conclusion that the index of potassium is less than unity both for $\lambda = 5460$ and for $\lambda = 6562$.

These results showed that no experiments on the indices of the alkali elements were likely to repay the labour involved until the chemical difficulties had been overcome and arrangements could be made for obtaining the index for very long waves. It was, therefore, determined to abandon the attempt for the present, and to turn to some other series.

Cadmium. (*Atomic Weight* 112.)

For experiments with this element the purest metal to be obtained from Kahlbaum was used. The arrangement described above acted very well. At a temperature between 600° C. and 700° C. enough cadmium evaporated to give a shift of 20 or 30 bands. There was no marked absorption. The principal difficulty in obtaining concordant results lay in the reading of the bands, which were unsteady owing to the mirage caused by currents of unequally heated air, and in many cases were badly illuminated. It was never possible to read to less than a quarter of a band; and if the conditions were bad, it was exceedingly easy to miss a whole band, or even two, or to count one twice. It was for this reason that the number of readings recorded is so large.

Table I. exhibits the results obtained. Those readings which appear obviously incorrect are enclosed in brackets. Four different charges of cadmium were used and numerous readings were made with each. The results obtained with the second charge may be neglected. In this case the bands were observed by the old method, while the whole furnace was heated in a single operation, and the correction for "end effects" was found to be of the order of 25 per cent. of the reading, and was not trustworthy. The other three charges gave fairly consistent results, as will be seen from the summary.

Zinc. (*Atomic Weight* 65.)

The next element dealt with was zinc, in the hope that the completion of the series zinc, cadmium, mercury might afford useful information. Again, in this case, the pure metal supplied by Kahlbaum was used. Only two charges of zinc were used, and much trouble was experienced in overcoming the effects of air convection currents. No absorption band was observed. It is to be regretted that the number of bands read was so small; but the furnace was not adapted for reaching a higher temperature than about 850° C., and it was not possible to evaporate a larger quantity at this temperature.

Table II. exhibits the results.

Arsenic. (*Atomic Weight* 75.)

Arsenic, free from iron, was obtained from two sources, and a series of determinations was made with each specimen.

This element proved the easiest of all those attempted, and concordant results were quickly obtained (see Table III.).

Selenium. (*Atomic Weight* 79.)

Experiments were made with two charges of this element. In the first series the readings were somewhat uncertain, and the result may be neglected. The second

TABLE I.—Refractivities of gaseous Cadmium.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Mean (approx.).	Refractivity. $(\mu - 1) 10^6$.	Remarks.
	centims.	cub. centims.		grammes.				
January 16 . . .	34·8	48·17	5893	0·00823	$26\frac{1}{4}$, 26	$26\frac{1}{8}$	2605	
" 23 . . .	34·8	48·17	5460	0·00823	$28\frac{3}{4}$, 29 to $29\frac{1}{2}$, $28\frac{3}{4}$ to $29\frac{1}{2}$	29·04	2675	
" 27 . . .	34·8	48·17	5893	0·01141	35·8	35·8	2575	A bad experiment. A large correction for "end effects" was involved.
" 27 . . .	34·8	48·17	5460	0·01141	$38\frac{1}{4}$ or $39\frac{1}{4}$, $39\frac{1}{4}$, 38, $37\frac{1}{2}$, $38\frac{1}{2}$, 38	$38\frac{1}{3}$	2550	
February 3 . . .	34·8	48·17	5893	0·00621	20, 20, $19\frac{1}{2}$, $19\frac{3}{4}$,	19·8	2620	
" 3 . . .	34·8	48·17	5460	0·00621	22, $(20\frac{3}{4})$, 22, $22\frac{1}{4}$	22·1	2725	
June 8	34·8	48·17	6562	0·00777	22, (24), $22\frac{3}{4}$, 23, 23, 23, 23, $22\frac{1}{2}$, 23	$22\frac{3}{4}$	2675	
" 8	34·8	48·17	5893	0·00777	$25\frac{1}{4}$, $25\frac{1}{4}$, $25\frac{1}{4}$, $25\frac{1}{4}$	$25\frac{1}{4}$	2675	
" 8	34·8	48·17	5183	0·00777	(31)*, (29)*, $(30\frac{3}{4})$,* $(30\frac{1}{4})$, $30\frac{1}{2}$*, $30\frac{1}{2}$*, $30\frac{1}{4}$, $29\frac{3}{4}$, $29\frac{7}{8}$, 30, $29\frac{3}{4}$, $29\frac{3}{4}$	$29\frac{7}{8}$	2780	* Bad readings, owing to poor light and mirage.

	λ.	$(\mu - 1) 10^6$.		
Refractivities observed for	6562	2675		
	5893	2605,	(2575),	2620, 2675
	5460	2675,	(2550),	2725
	5183	—	—	2780
Probable best values	6562	2675		
	5893	2675		
	5460	2725		
	5183	2780		

TABLE II.—Refractivities of gaseous Zinc.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Mean (approx.).	Refractivity. $(\mu - 1) 10^6$.	Remarks.
	centims.	cub. centims.		grammes.				
February 8 and 14	34·8	48·2	5460	0·00379	$17\frac{3}{4}$, $17\frac{1}{4}$ or $18\frac{1}{4}$, $17\frac{1}{2}$, (19 or $18\frac{1}{2}$), 17 or 18, 17, 18·3, $17\frac{3}{4}$, $18\frac{1}{2}$, $18\frac{3}{4}$	18·3	2150	
" 8 " 14	34·8	48·2	5893	0·00379	$16\frac{1}{4}$, $16\frac{1}{4}$, $16\frac{1}{2}$, $15\frac{3}{4}$, $16\frac{1}{2}$, 16	16·2	2050	
June 12	34·8	48·2	6562	0·00544	$20\frac{3}{4}$, 21, $19\frac{3}{4}$ or $20\frac{3}{4}$, 19, 20, 20	20	1960	Bad readings; much mirage.
" 15	34·8	48·2	6562	0·00544	$19\frac{1}{2}$, $20\frac{1}{2}$, (18), 20 or 21, $19\frac{1}{2}$, 20 or 21, 21, $20\frac{1}{2}$, $19\frac{1}{2}$			
" 20	34·8	48·2	6562	0·00544	20, 20, (19), ($18\frac{3}{4}$), $19\frac{1}{2}$, 20, 20, 20, ($18\frac{1}{2}$), 20, $19\frac{3}{4}$, 20			
" 11	34·8	48·2	5893	0·00544	$23\frac{1}{2}$, $23\frac{1}{2}$, ($23\frac{1}{2}$ or 24), $23\frac{1}{4}$, $23\frac{1}{2}$, $23\frac{1}{2}$, $23\frac{1}{2}$	$23\frac{1}{2}$	2065	
" 15	34·8	48·2	5630	0·00544	$24\frac{1}{4}$, $23\frac{3}{4}$, $23\frac{3}{4}$ or $24\frac{3}{4}$, 24, 24, 24, 24, 24	24	2020	
" 15	34·8	48·2	5183	0·00544	$26\frac{1}{2}$, $26\frac{3}{4}$, $26\frac{3}{4}$, $26\frac{3}{4}$	$26\frac{3}{4}$	2070	

	λ.	$(\mu - 1) 10^6$.
Refractivities observed	6562	1960
	5893	2050, 2065
	5630	2020
	5460	2150
	5183	2070

Probable values range from 1960 in red (λ = 6562)
to 2100 in green (λ = 5183)

TABLE III.—Refractivities of gaseous Arsenic.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Mean (approx.).	Refractivity. $(\mu-1)\,10^6$.	Remarks.
	centims.	cub. centims.		grammes.				
February 19 and 22	34·8	48·07	5460	0·01784	$55\frac{1}{4}$, $55\frac{1}{4}$ $(55\frac{3}{4}\pm 1)$, $55\frac{1}{2}$	55·5	1580	
„ 23 . . .	34·8	48·07	5893	0·01784	$(50\frac{1}{2}\pm 1)$, $50\frac{1}{2}$ to $\frac{3}{4}$	50·6	1550	
„ 23 . . .	34·8	48·07	5460	0·01760	(53 ± 1), (53), 54, $54\frac{3}{4}$*	54·5	1577	* Good reading.
March 8	34·8	48·07	5893	0·01760	$49\frac{1}{2}$, 50, $49\frac{3}{4}$	49·7	1554	

	λ.	$(\mu-1)\,10^6$.
Refractivities observed	5893	1550, 1554, mean 1552
	5460	1580, 1577, „ 1579

TABLE IV.—Refractivities of gaseous Selenium.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Mean (approx.).	Refractivity. $(\mu-1)\,10^6$.	Remarks.
	centims.	cub. centims.		grammes.				
March 23 . . .	34·8	48·2	5893	0·01347	35, $36\frac{1}{2}$ (37 or 38), 38, 36	37	1592	
May 14	34·8	48·2	5893	0·00836	23, 22 (21 or 22), $21\frac{3}{4}$, $(22\frac{3}{4})$, $21\frac{3}{4}$, $21\frac{3}{4}$, $21\frac{3}{4}$	$21\frac{3}{4}$	1505	
„ 14	34·8	48·2	5460	0·00836	$24\frac{1}{4}$, $24\frac{1}{2}$, $24\frac{3}{4}$, $24\frac{1}{2}$	$24\frac{1}{2}$	1570	
„ 28	34·8	48·2	6540	0·00836	20, $19\frac{3}{4}$, 20, 20, 20 (bare), 20, $19\frac{1}{2}$ to $19\frac{3}{4}$	$19\frac{7}{8}$	1530	
June 6	34·8	48·2	6562	0·00836	$19\frac{7}{8}$	$19\frac{7}{8}$	1535	
„ 6	34·8	48·2	5893	0·00836	$22\frac{3}{4}$, $22\frac{3}{4}$, $22\frac{1}{2}$ (full), $22\frac{1}{2}$, $22\frac{1}{2}$, $22\frac{1}{4}$, $22\frac{3}{4}$	22·6	1565	
„ 6	34·8	48·2	5540	0·00836	$23\frac{1}{2}$, 24, 24, 24	23·9	1560	

	λ.	$(\mu-1)\,10^6$.
Refractivities observed	6562	1535
	6540	1530
	5893	(1592), (1505), 1565
	5540	1560
	5460	1570

series gave values consistent with each other. The vapour exhibits a strong absorption band extending from the violet so far towards the red that no readings could be made at the wave-length 5183, as, when five or six bands had passed, the light was completely absorbed (see Table IV.).

Tellurium. (*Atomic Weight* 128.)

The specimen used was obtained from KAHLBAUM and, for the first experiment, was redistilled. In this case also there is a strong absorption band in the violet, which prevented readings being made beyond $\lambda = 5460$. Tellurium was found to evaporate with difficulty at a temperature hardly lower than that required for zinc, and it was necessary to use very small quantities, so that the number of bands observed was small, and the values obtained possibly less accurate. Two charges were used. In the first day's work with the second charge the temperature was not taken sufficiently high, with the result that the band readings are about 6 per cent. too low; but they are nevertheless recorded, as they show relative numbers for the dispersion effect which are useful in corroborating the other results (see Table V.).

Mercury. (*Atomic Weight* 200.)

This was the first element dealt with by C. CUTHBERTSON three years ago. As a check on the older method of working, another measurement of the refractivity of mercury vapour was made by E. P. METCALFE, the silica refractometer tubes and the divided furnace being now used. One charge only was employed, and observations were taken with light of four different wave-lengths. The value of the refractivity now obtained for D light (1866) is in good agreement with the previous determination (1857). The accuracy of the band readings seems to be, for the D line, to within about $\frac{1}{2}$ per cent., for the other wave-lengths to within about 1 per cent. (see Table VI.).*

REMARKS.

Dispersion.

The present research was designed to obtain a single value for each element, and it was only with the object of satisfying ourselves that the refractivity measured was not affected to an abnormal degree by the existence of an absorption band for a wave-length near to that by which the observations were made that readings were taken with different wave-lengths. Each band reading being completely independent of the rest, and the degree of accuracy being, apparently, not much greater than to

---

[* Subsequent work by Mr. METCALFE renders it probable that the true value for $\lambda = 6562$ is $1\frac{1}{2}$ to 2 per cent. higher than that given in Table VI.—*January* 24, 1907.]

TABLE V.—Refractivities of gaseous Tellurium.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Mean (approx.).	Refractivity. $(\mu - 1)\ 10^6$.	Remarks.
	centims.	cub. centims.		grammes.				
June 21	34·8	48·00	6562	0·00402	9, (9 or 10), 9, 9, $9\frac{3}{8}$, $9\frac{3}{8}$, $9\frac{3}{8}$, $9\frac{3}{8}$, $9\frac{1}{4}$, $9\frac{1}{4}$	$9\frac{1}{4}$	2405	
„ 21	34·8	48·00	5893	0·00402	11, $10\frac{3}{4}$, 11, $10\frac{3}{4}$	$10\frac{7}{8}$	2543	
„ 21	34·8	48·00	5460	0·00402	$12\frac{1}{4}$, 12, 12, 12, 12	12·0	2600	
„ 26	34·8	48·00	6562	0·00464	10 or 11, 10, 10, 10, 10, 10, 10 (bare), 10 (bare), 10,	10·0	2250	Temperature not high enough. Inserted for comparison of dispersion effect.
„ 26	34·8	48·00	5893	0·00464	$11\frac{1}{2}$, $11\frac{1}{3}$ or $11\frac{1}{4}$, $11\frac{1}{2}$, $11\frac{1}{2}$, $11\frac{1}{2}$	$11\frac{1}{2}$	2330	
„ 26	34·8	48·00	5460	0·00464	$13\frac{1}{8}$, 13 or 14, $13\frac{1}{4}$, 13, $13\frac{1}{4}$, 13, $13\frac{1}{8}$	$13\frac{1}{4}$	2480	
„ 28	34·8	48·00	6562	0·00464	$10\frac{1}{4}$ to $10\frac{1}{2}$, $10\frac{3}{8}$, $10\frac{3}{8}$	$10\frac{3}{8}$	2335	
„ 28	34·8	48·00	5893	0·00464	$11\frac{1}{2}$, $11\frac{1}{8}$, $11\frac{3}{4}$, 12, 12 (full), 12 (full)	$11\frac{7}{8}$	2410	
„ 28	34·8	48·00	5460	0·00464	14, 14, 14, 14, $14\frac{1}{4}$, $14\frac{1}{4}$, $14\frac{1}{4}$, $14\frac{1}{8}$	$14\frac{1}{8}$	2640	

	λ.	$(\mu - 1)\ 10^6$.
Refractivities observed	6562	2405, 2335, mean 2370
	5893	2543, 2410, „ 2495
	5460	2600, 2640, „ 2620

TABLE VI.—Refractivities of gaseous Mercury.

Date, 1906.	Internal length of tube.	Volume of tube.	Wave-length of light employed, A.U.	Weight of element.	Bands observed.	Probable best number of bands.	Refractivity. $(\mu - 1) \times 10^6$.
	centims.	cub. centims.		grammes.			
July 13	34 8	48·46	6562	0·01235	13·3, 13·5, 13·5, 13·5	13·5	1799
„ 12	34·8	48·46	5893	0·01235	15·6, 15·5, 15·6, 15·6	15·6	1866
„ 12 and 13 . .	34·8	48·46	5459	0·01235	16·9, 16·8, 17·0, 17·0	17·0	1882
„ 13	34·8	48·46	5183	0·01235	18·0, 17·8, 17·9, 17·9	17·9	1885

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

within about 2 per cent., an accurate record of the dispersion was hardly to be expected. We have not overlooked the importance of determining the dispersion in every case through a wide range of wave-lengths; but the difficulty of obtaining values sufficiently accurate to yield useful information when introduced into a dispersion formula was found to be insurmountable with the present apparatus in the time at our disposal. We hope, however, in the future, to make a further attempt to obtain the dispersion with improved apparatus.

The results appear interesting. In every case, except that of potassium, the dispersion observed is normal in direction.* But its magnitude is very great. Thus, in the case of tellurium, the refractivity varies from about 2370 for $\lambda = 6562$ to 2620 for $\lambda = 5460$, or nearly 10 per cent. For zinc the variation is about 7 per cent. for the same range.

Refraction and Refraction Equivalents.

It is probable that the refractive indices for infinitely long waves would be considerably smaller than those here observed. But even after making the most liberal deduction, it is certain that the indices of zinc, cadmium, and tellurium are higher than the highest (viz., that of iodine) of which we had previous knowledge. It is interesting to compare them with the refraction equivalents of GLADSTONE and others. This is done in Table VII.

TABLE VII.

	Refraction equivalents.						Refractivities now found (gaseous).			
	GLADSTONE.		HAAGEN.§		KANNONIKOFF.||		$(\mu-1)\,10^6$.			
	Early.†	Later.‡	R_α.	R_A.	R_α.	R_A.	λ 6562.	λ 5893.	λ 5460.	λ 5183.
As	15·4	15·4	20·22	18·84	—	—	—	1550	1580	—
Zn	10·2	9·8	19·89	18·64	9·8	9·4	1960	2060	2150	2070
Cd	13·6	13·1	—	—	13·03	12·66	2675	2675	2725	2780
Se	—	30·5	—	—	—	—	1530	1565	1570	—
H	1·3	—	—	—	—	—	—	139	—	—

---

* The apparent exceptions to this statement are attributable to errors of observation.

† 'Journal Chem. Soc.,' 1870, p. 101; 'Phil. Trans.,' 1870, p. 9.

‡ 'American Journal of Science,' 3, 29, 1885, p. 57.

§ 'Pogg. Ann.,' 131, 1867, p. 125.

|| 'Journal für Praktische Chemie,' 31, 1885, p. 339.

The results are very curious. GLADSTONE'S refraction equivalent for arsenic* is about twelve times that for hydrogen, while the gaseous refractivity is eleven times that of hydrogen. But the values of GLADSTONE for zinc and cadmium are just half those now obtained for the gaseous state. HAAGEN, however, has a value for zinc which corresponds fairly well with the refractivity. Finally, GLADSTONE'S value of selenium is about double that shown by the refractivity.

Relative Refractivities of the Elements.

Previous work in this field had brought to light certain relations between the refractivities of the elements which seemed too regular to be due to chance, and the present work was undertaken mainly with the object of ascertaining whether similar relations existed in the case of other elements.

The results have been partly successful and partly unsuccessful. It was at once manifest that, in view of the great dispersion and in the absence of trustworthy values for infinitely long wave-lengths, the search for simple integral ratios between the refractivities must be postponed. But in one group of elements traces of a tendency to conform to such a rule may, we think, be fairly claimed.

Table VIII. shows the elements arranged in the order of their atomic weights, with the refractivities appended in those cases in which they have been measured in the gaseous state for the D line. The form of the table is suggested by the ratios existing between the refractivities of some of the elements, and is, so far as we know, somewhat different from previous forms of the periodic table.

Thus, since the refractivities of nitrogen, oxygen, fluorine and neon are respectively one fourth of those of phosphorus, sulphur, chlorine and argon, it would seem that each of these groups should form a horizontal row, and since the refraction equivalents of potassium, rubidium and cæsium are in the same ratio as those of argon, krypton,

---

* In this connection it is interesting to compare the values now found with those suggested by the indices of some compounds of the elements.

As an instance we may take the case of arsenic trichloride, whose index (as found by HAAGEN) is approximately 1·6. Converting this number into the corresponding one for a gas by the formula of LORENZ, $\frac{\mu^2-1}{\mu^2+2}\frac{\text{P}}{\alpha}$ = constant, we arrive at the figure 1920; of this 1152 may be subtracted for the chlorine atoms, leaving a balance 768 for one atom of arsenic, or 1536 for two atoms of arsenic, a result which corresponds well with the number 1550 now found. But the additive rule, as is well known, is not of universal application. It fails conspicuously in the case of the fluorine compounds of the sulphur, selenium, tellurium group. The present writers were, through the courtesy of Dr. E. B. R. PRIDEAUX, afforded the opportunity of measuring the refractivities of these compounds. The results have been published already in Dr. PRIDEAUX' paper in 'Trans. Chem. Soc.,' 1906, vol. 89, p. 330. For the refractivities of the hexafluorides of sulphur, selenium, and tellurium we found the values 783, 895, and 991, the corresponding numbers deduced by the additive rule being 1116, 1356, and 1826 respectively.

TABLE VIII

						H 139											
						He 144 × ½	Li	Be	B	C							
			N 297	O 270	F 192	Ne 137	Na	Mg	Al	Si							
			P 1197 = 299 × 4	S 1101 = 275 × 4	Cl 768 = 192 × 4	Ar 568 = 142 × 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zn 2060 = 343 × 6	Ga	Ge	As 1550 = 258 × 6	Se 1565 = 261 × 6	Br 1125 = 187 × 6	Kr 850 = 142 × 6	Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag
Cd 2675 = 267 × 10	In	Sn	Sb	Te 2495 = 249 × 10	I 1920 = 192 × 10	X 1378 = 138 × 10	Cs	Ba	La	Ce	Di						
									Yb		Ta	W		Os	Ir	Pt	Au
Hg 1866	Tl	Pb	Bi							Th							
												U					

and xenon (*i.e.*, as 2 : 3 : 5) the table has been rearranged so as to bring these together in such a way that a single factor is characteristic of each row.*

From such a table we should expect the refractivities of selenium and tellurium to be to that of sulphur as 3 and 5 respectively to 2. The values found are in both cases rather low, but that for selenium is not notably so. In the other cases the regularity breaks down. The value for arsenic is much nearer $\frac{5}{4}$ that of phosphorus than $\frac{6}{4}$. The values for zinc do not bear to those for cadmium the ratio 3 : 5, while the refractivity of mercury is actually less than that of either, thus exhibiting the only case yet observed of a gaseous refractivity which is lower than that of another element of the same group and of lower atomic weight.

In short, it may be said that the rule of simple integral ratios between their refractivities is probably confined to the elements lying near the centre of the table which are shown enclosed within the heavy rectangular boundary. To these we may possibly add the group potassium, rubidium, cæsium, in which the refraction equivalents seem to indicate conformity to the rule. Within the heavily marked enclosure the regularity is very striking, except for the two, or possibly three, elements in the lower left-hand corner.

A general survey of the table, with the new additions, confirms the view already held that, in each group of elements, refractivity increases with atomic weight. But mercury, which stands in a lower horizontal row than the other elements examined, forms a striking exception to this rule, and it remains to be seen whether this is merely an isolated case, or whether it is characteristic of all the heaviest elements. The refraction equivalents of GLADSTONE lend some colour to the conjecture that there may be a falling off in refractive power when the atomic weight exceeds a certain limit, but, in view of the discrepancies exhibited in Table VII., it would be dangerous to place much reliance on their indications. It is also remarkable that in each horizontal row of Table VIII. refractive power increases as we move to the left, in spite of the decrease in atomic weight; there can be little doubt, therefore, that it is intimately connected with the valency.

We have to express our cordial thanks to Professor TROUTON and the staff of the Physical Laboratory at University College, London, for assistance and advice, and to the Royal Society for a grant in aid of the research.

---

* This arrangement was first suggested by Professor A. W. PORTER. It will be observed that it fits in very well with the sequence of the atomic volumes.