

Although a variance is quite noticeable when examining solutions of *ordinary* strength, it may not be considered of sufficient practical importance to seriously interfere with the use of this method. It would, however, be necessary to take particular care that a very slight excess only of silver nitrate is present.

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THE SIGNIFICANCE OF THE PERIODIC LAW.

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The physical significance of the periodic law has been the subject of much speculation and of many important investigations. The conclusion seems inevitable that the chemical elements have been built up step by step, from some simpler substance or substances, but thus far all attempts at identifying the original substance have failed. Meanwhile, the discovery of radioactivity and the successive disintegrations of the uranium and thorium atoms seem to have shown us how these atoms were originally put together. In this process we see one elementary atom changing into another of lower atomic weight by releasing one or more alpha particles or one or more negative electrons, or in some cases, perhaps, by giving off both an alpha particle and an electron in a single change. Since the electron has but little, if any, influence upon the atomic weight, we find these successive atoms differing in atomic weight by four or eight, or in the case where only an electron is set free we may have two successive atoms with the same atomic weight but with different chemical properties.

Since the disintegration products of uranium seem to fall into their proper positions in the periodic series and to have properties analogous to the other members of their periodic groups, radium, for example, showing the characteristic properties of the barium group and emanation forming an inert gas of the argon group, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight.

A difficulty in constructing the elementary series in this way arises from the fact that the atomic weights of successive elements do not increase by four or by multiples of four. This difficulty is largely overcome for a considerable part of the series, by assuming two parallel lines of development, one line starting from helium and one from lithium. In the following table the elements have been arranged in two series from that point of view, the attempt being made to select the elements which would most nearly meet the atomic weight requirements:

		He	Be	C	O	Li	B	N	F
		4	9	12	16	7	11	14	19
		Ne	Mg	Si	S	Na	Al	P	Cl
		20	24	28	32	23	27	31	35 ^{1/2}
		A	Ca	Ti	Cr	K	Sc	V	Mn
		40	40	48	52	39	44	51	55
Fe	Ni	Co	Zn	Ge	Se	Cu	Ga	As	Br
56	59	59	65	72	79	63	70	75	80
		Kr	Sr	Zr	Mo	Rb	Yt	Nb	(Cb)?
		82	88	90 ^{1/2}	96	85 ^{1/2}	89	94	93 ^{1/2}
Ru	Rh	Pd	Cd	Sn	Te	Ag	In	Sb	I
102	103	106	112	119	127	108	114	120	127
		Xe	Ba	Ce	Pr	Cs	La	Nd	Sa
		128	137	140	140 ^{1/2}	133	142	144 ^{1/2}	150
		Eu	Gd	Tb	Dy
		152	156	159	162
		W	Er	Yb	Lu	...
					184	167 ^{1/2}	172	174	...
Os	Ir	Pt	Hg	Pb	Po	Au	Tl	Bi	...
191	193	195	200	207	(210)?	197	204	208	...
	
		Em	Ra	...	U	...	Th
		222	226	...	238	...	232

Starting with helium, it will be seen that the series is regular up to and including iron, Be being the only element whose atomic weight does not conform to our requirements, its atomic weight being 9 instead of 8. With the occurrence of the triplets Fe, Ni, Co, the orderly arrangement is broken up, though the preponderating influence of the quantity four may still be observed. Thus the increase in atomic weight from cobalt to rhodium is 44 and from rhodium to osmium 88. If the lowest atomic weight in a column be subtracted from the highest above the first series of missing elements, we have Xe — He = 124, Ba — Be = 128, Ce — C = 128, and Pr — O = 124^{1/2}.

In the disintegration of uranium three alpha particles seem to be given off between uranium and radium, allowing an element of atomic weight 234 or 230 to fall in the carbon group, and one alpha particle is given off between radium and emanation, bringing the latter in its appropriate group of the argon gases. The proper positions of the other disintegration products are unknown to me.

The table also indicates that another radioactive series starts from tungsten with Pr as probably its last element.

In the lithium series the agreement with theory is about equally good throughout with that of the helium series. The irregularity begins at about the same atomic weight and is about equally great, though there seem to be more recurrences of six as a difference between two successive atomic weights. In both series these irregularities begin where each

group of the series seems to split into two groups, as the group of the alkali metals and the copper, silver and gold group. These irregularities offer a serious difficulty to the acceptance of the theory of atomic development outlined here.

In the lithium series the radioactive group, which is assumed to start from tungsten in the helium series, is represented by a succession of very rare elements whose rarity suggests that they are also unstable, and the radioactive group starting from uranium is represented by a similar group starting from thorium. I have not attempted to represent the position of any of the products of thorium disintegration, as I am not sufficiently familiar with their properties, and it is altogether probable that other elements are placed in wrong groups.

It is well known that certain fundamental differences seem to exist between the two groups of elements which are here characterized as the helium series and the lithium series. The two series have, in fact, long been separated on the basis of their chemical valency, the elements of the helium series having zero valency or even valencies, while the elements of the lithium series have odd valencies. They have likewise been separated on the basis of their spectra, the elements of the helium series having their spectral series made up of single lines or groups of three, while the elements of the lithium series have their spectral lines arranged in pairs. From the researches of Sir Norman Lockyer and others on the spectra of the stars, it would seem that in the hottest stars only elements of the helium series are found, several of these elements apparently appearing before any of the lithium elements appear. Thus calcium and iron are said to appear before sodium.¹

This hypothesis as to the structure of the elementary atoms suggests a possible cause of radioactivity and the possibility of artificially changing one element into another. The alpha particle is known to be very strongly electropositive, and the elements of at least some of the groups become increasingly electropositive as their atomic weights increase. I have attempted elsewhere to show that many of the elements carry positive charges which are proportional to the square roots of their atomic weights.² As their electropositive charges increase their hold upon the alpha particles must decrease, and the heavier elements must accordingly become more and more unstable. This hypothesis seems to gain probability from the fact that in the radioactive disintegration of uranium eight alpha particles and only four electrons seem to be set free in changing a uranium atom to one of lead. If this be the correct explanation of their instability it does not seem impossible that by submitting an atom of an electropositive metal to a powerful electropositive stress it may

¹ Messrs. Jessup, *Phil. Mag.*, 15, 21, Jan., 1908.

² On Positive Atomic Charges, *Phys. Rev.*, 32, 512, May, 1911.

be made to throw off an alpha particle and become an atom of some element of lower atomic weight. Thus the sodium atom by giving off an alpha particle might become a fluorine atom, or a potassium atom might in the same way become a chlorine atom. In fact, there seems to be some evidence that alpha particles have been given off from metals in this way, and that many of the phenomena of the *Kanalstrahlen* can best be explained by the assumption that some of them are alpha particles sent off from the anode.

Thus in an article on "Rays of Positive Electricity,"¹ Sir J. J. Thomson calls attention to the fact that while the particles which constitute the *Kanalstrahlen* have different velocities after passing through the cathode their maximum velocity (presumably for anodes of the same metal) is always the same, regardless of the fall of potential along the tube. This velocity was previously found to be 2×10^8 cm./sec. whether the fall of potential in the tube was 3,000 volts or 40,000 volts. It was also shown that their velocity was much greater than could be given to them by the electric field of the tube. Similar positively charged particles were also sent off from the cathode with the same speed as from the anode, though they had to travel against the electric field of the tube throughout the whole of their path.

The ratio of charge to mass was determined for the particles which constituted the *Kanalstrahlen* by passing them through an electrostatic and a magnetic field after they had passed through the cathode. The particles were sorted into seven quite distinct groups by this method, each group producing its own fluorescent patch on the screen at the end of the tube. These groups are indicated on p. 759 of the article referred to by the letters *a*, *b*, *c*, *d*, *e*, *f*, while the central fluorescent spot which was made by undeflected particles is not indicated by a letter. The values of e/m determined for these groups of particles seem to the present writer to indicate that three of them were due to alpha particles. Thus the value of e/m for the group marked *d* was determined as 5.8×10^3 . The ratio e/m for the alpha particle as determined by Rutherford, and Geiger² varied from 4.8×10^3 to 5.7×10^3 . This would seem to make it almost certain that patch *d* was caused by alpha particles.

The positive charge of an alpha particle is almost exactly twice as great as the negative charge of an electron, so that when two electrons unite with an alpha particle to form a helium atom they give the most completely electrically neutral particle known. This is shown chemically by the fact that the helium atom has less affinity or cohesion than any other known atom. Accordingly, when an alpha particle has taken up one electron its ratio e/m must be exactly half what it was before, and

¹ *Phil. Mag.*, 19, 424.

² *Proc. Roy. Soc., London (A)*, 81, 162.

an alpha particle which captured an electron before it reached the cathode would have a value $e/m = 2.9 \times 10^8$. This value was actually determined for the particles which produced patch *c*.

There still remains the probability that a considerable number of alpha particles would combine with two electrons and form neutral helium atoms before reaching the cathode, and these would be undeflected in the space back of the cathode and would form the central bright patch. On the whole, then, it seems established within the limits of error of the experiment that alpha particles were given off from the anode and formed an important part of the *Kanalstrahlen*.

This explanation will also account for the sometimes unaccountable appearance of helium in vacuum tubes through which an electric charge has been passed. A striking example of this is given by Soddy in *Proc. Roy. Soc., London (A)*, **80**, 94, and while the explanation which he there offers may be the correct one it seems not impossible that the one here suggested may be the true one, instead.

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THE OXIDATION OF HYDRAZINE. V. REACTION BETWEEN POTASSIUM IODATE AND HYDRAZINE SULFATE.¹

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The most characteristic of the chemical properties of hydrazine is its vigorous reducing action. This behavior has led to the suggestion of several oxidimetric methods for use in the determination of hydrazine in its inorganic compounds. Among the oxidizing agents that have been employed are ammonium metavanadate,² potassium permanganate in acid³ or in alkaline⁴ solution, ammonium and potassium persulfates,⁵ Fehling's solution,⁶ ammoniacal cupric sulfate,⁷ mercuric chloride,⁸

¹ For the earlier articles of this series see Browne and Shetterly, *THIS JOURNAL*, **29**, 1305-12 (1907); **30**, 53-63 (1908); **31**, 221-37 (1909); **31**, 783-99 (1909).

² Hofmann and Küspert, *Ber.*, **31**, 64-7 (1897). See *THIS JOURNAL*, **29**, 1305 (1907).

³ Petersen, *Z. anorg. Chem.*, **5**, 1 (1893); Roberto and Roncali, *l'Industria chimica*, **6**, 178 (1904); *Chem. Zentralbl.*, **1904**, II, 616; Medri, *Gazz. chim. ital.*, **36**, I, 373-8; *Chem. Zentralbl.*, **1906**, II, 459. See also *THIS JOURNAL*, **31**, 226 (1909).

⁴ Sabanejeff, *Z. anorg. Chem.*, **17**, 480 (1898); **20**, 21 (1899). See also *THIS JOURNAL*, **31**, 230 (1909).

⁵ Pannain, *Gazz. chim. ital.*, **34**, I, 500-4 (1904); Rimini, *Atti accad. Lincei*, [5] **15**, II, 320-25; *Chem. Zentralbl.*, **1906**, II, 1663. See also *THIS JOURNAL*, **31**, 222 (1909).

⁶ Petersen, *Loc. cit.* See also *THIS JOURNAL*, **31**, 787 (1909).

⁷ Ebler, *Z. anorg. Chem.*, **47**, 371-6 (1905).

⁸ Rimini, *Atti accad. Lincei*, [5] **12**, II, 376-81 (1903); **15**, II, 320-5 (1906); *Chem. Zentralbl.*, **1904**, I, 213; **1906**, II, 1662. Ebler, *Z. anorg. Chem.*, **47**, 377-85 (1905). See also *THIS JOURNAL*, **31**, 790 (1909).