Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

Büchner, E.H., The radiactivity of rubidium and potassium compounds, in:
KNAW, Proceedings, 15 I, 1912, 1912, pp. 22-27

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Chemistry. — "*The radioactivity of rubidium and potassium compounds.*" II. By Dr. E. H. BÜCHNER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 26, 1912).

Some time ago I described a series of experiments undertaken with the object of demonstrating the radioactivity of rubidium and eventually of other alkali metals by the photographic method [1]). I then only noticed an action on the sensitive plate with rubidium sulphate; the salts of other alkalis produced no effect. I have repeated these experiments and, as announced previously, I have inquired more in particular, whether the phenomenon might be attributable to a previous exposure of the salt to the light; in that case there can be no question of a real radioactivity, but we should have here an analogism of the wellknown experiments with calcium sulphide. According to NIEWENGLOWSKI, this substance acts on a photographic plate by means of rays which penetrate through aluminium, but only when it has been previously exposed to the light. In the present meaning of the word we cannot call calcium sulphide radioactive, because an external influence is at work; if the same happened with rubidium and potassium, these substances could neither be included among the radioactive ones. And because they differ in various respects from the other active substances, there is still some doubt left about this matter. It was, therefore, desirable to carry out some experiments in this direction.

For this purpose I have exposed, simultaneously, in one box, some photographic plates to the action of RbCl, $RbNO_3$ and Rb_2SO_4 in the manner described previously, but of each salt two specimens were taken; one of these had been kept in complete darkness from 4 to 5 months, the other had been exposed to broad daylight for some days previous to the experiment. When developing after 90 days, no difference was found between the action of the two specimens, both having affected the plates in the same manner. Hence, it again becomes more probable that we are dealing here indeed with true radioactivity.

For the rest I have been able to confirm my previous results. Again, I have not succeeded in getting an action on the sensitive plate either with salts of potassium or with salts of caesium, sodium, and lithium, but on the other hand rubidium did affect the plate. With RbCl and $RbNO_3$, also with Rb_2SO_4 I found that the plate had

[1]) These Proc. 1909, p. 154.

darkened distinctly on those spots, where little holes or figures had been cut in the screen of copper foil which had been placed between the salt and the plate. The action is strongest with the chloride and weakest with the sulphate. I attribute this to the greater absorption which the rays undergo in the sulphate itself, for this salt has a higher density than the chloride and, therefore may be expected to show a greater absorption. This explanation can also serve for a few deviating results. In two experiments, it appeared that Rb_2SO_4 had produced no effect; now in these cases the salt had accidentally been used in the form of fairly large crystals and not in powder, as usual. The surface of the powder is, of course, larger and consequently more rays will reach the plate than in the case where crystals are employed. Perhaps, this reasoning may explain also the results of STRONG [1]) who, in the exposure of different potassium salts to photographic plates, observed effects of very varying intensity; for instance strong action with potassiumcyanide and practically none with the urate.

The rubidium salts investigated by me were obtained from different dealers (MERCK, KAHLBAUM, DE HAEN, SCHUCHARDT); the fact that they show no difference in action goes to prove that the phenomenon must be attributed really to rubidium and not to some impurity.

2. Other investigators have already shown that the radiation of potassium and rubidium consists mainly, probably even exclusively, of β-rays. Now, α-rays may, however, elude observation sometimes, as they act but faintly on sensitive plates and consequently practically not at all with slightly active substances. Moreover when we are dealing with α-particles of very small velocity and corresponding small penetrating power, only an exceedingly small portion of the α-particles will arrive in the surrounding gas and the ionisation current, generated by them, which is measured with the electroscope, will be very weak; it may even be of little importance in regard to the current caused by the β-rays. If now we may apply the results obtained with strongly active substances to feebly active compounds, the α-rays, if present here, may be expected to possess a slight velocity, since we may assume as a rule: the larger the activity of a substance, the greater the velocity of the α-particles. A possible occurrence of α-rays demands an investigation all the more, because the absorption of the radiation in different substances, like tin foil

[1]) Amer. Chem. Journ. 42, 127.

for instance, cannot be represented by a simple exponential formula; on the contrary, it seems as if the radiation is composed of a part decidedly penetrating and of another one less so; the latter is then only of slight importance.

In two ways, I have attacked the problem of the presence of α-rays; firstly by observing whether zinc sulphide became luminous under the influence of the salts. This method has the advantage that we can bring together the salt and the zinc sulphide as closely as we like, and reduce as far as possible the absorption which the α-particles undergo in the air; consequently we may, perhaps, find in this manner α-rays of very slight penetrating power which would not be detected by other means.

We know that light emitted under the influence of α-particles possesses a peculiar character and that, when examined under the microscope, it breaks up into numerous points which are formed at the spots, where the α-particles meet the zinc sulphide; each scintillation, therefore, indicates an α-particle. In order to show the α-particles eventually present, an object-slide with a little KCl was put under the microscope; above it at a distance of about 2 m.m. was placed another slide which was coated at its lower surface, by means of Canada balsam, with a layer of zinc sulphide. The whole arrangement is placed in the dark; it is, however, advisable, in imitation of REGENER, to faintly illuminate a portion of the field of vision (for which purpose a "VERKADE waxine" light is very serviceable) in order to facilitate the adjustment. In this manner, we can readily show the α-particles of pitchblende, uranium oxide, and thorium oxide; we shall be able to observe also all α-particles which can traverse a distance of at least 2 m.m. in the air. Neither with KCl, nor with RbCl, however, any scintillation was noticed in different experiments, though the observation lasted each time ten minutes. I then made the experiment in another way: to render the distance between the salt and the zinc sulphide as small as possible, I mixed the two compounds. But even then I did not succeed in observing a single flash of light. These experiments thus confirm the results communicated by HENRIOT [1]) in a paper which appeared after my experiments were closed, namely that rubidium and potassium do not emit α-rays.

3. There is yet another way to demonstrate the emission of α-particles. It is well known that the heat generated by radium and other radioactive substances originates in the kinetic energy of the α-particles, which are stopped in the surrounding matter. A large

[1]) Comptes Rendus, 152, 1384 (1911).

portion of the α-rays gets already absorbed in the emitting substance, because they penetrate into solid matter but a few hundredths of a m.m.; consequently the active substance is heated above the temperature of the surrounding air and, of course, remains warmer, because the radiation process proceeds continuously. α-Particles which do not possess a sufficient velocity to ionise gases, or to render the zinc sulphide luminous, may still have a considerable kinetic energy; and when they are absorbed, their energy being converted into heat, they might raise the salt from which they originate to a higher temperature. This argument has also been applied by GREINACHER [1]) during an investigation on the radioactivity of several ordinary substances; he, however, did not study the salts which are now of particular interest to us.

I have investigated this question by placing in a large galvanised iron basin, on pieces of cork, two silvered vacuum flasks of about $1^1/_2$ litre capacity. The basin was placed in another and the space between was filled with ice; the whole was placed in a wooden box isolated by means of slag-wool. A third bath serves as a cover, which was also filled with ice and covered with blankets. In this manner, the flasks are entirely surrounded by ice, and it may be assumed that the surrounding air possesses a constant temperature. Every two days, the accumulated water is drawn off and fresh ice is added. The flasks are filled with about 2 kilogrammes of potassium or sodium chloride respectively, and closed with a solid plug of cotton-wool, upon which is poured a layer of paraffin. Through this seal penetrates a very thin-walled glass tube which reaches to the centre of the bulb and contains one of the junctions of a thermo-couple copper-constantan. The constantan wire connects directly the junctions, the copper wires are carried away through an opening in the box and connected to the galvanometer which is suspended according to JULIUS and read off by means of a mirror and a telescope.

If now potassium chloride emits α-rays, it may be expected to reach a higher temperature than sodium chloride and, owing to a thermoelectric force the galvanometer will deviate; by gauging with a definite difference in temperature it may be found with how many degrees corresponds a deviation of, say, 1 mm.; this proved to be 0.003°. As soon as the circuit is closed a deviation of the galvanometer is observed, but without further discussion we may not conclude to a difference in temperature between the two salts. There are, necessarily, always some places of contact between different

[1]) Ann. der Phys. [4] 24, 79 (1907).

metals which, perhaps, have not exactly the same temperature and therefore also yield a thermo-current. This influence may be eliminated by placing between the galvanometer and the thermoelement a commutator; on commuting, only that part of the current which has to be measured, namely the current of the thermoelement itself, takes another direction; it may, therefore, be determined from the difference. Only care must be taken that no differences in temperature occur in the commutator itself. As such served two three-limbed glass tubes well wrapped up in cotton-wool and placed in a little box, which was suspended and moveable round a horizontal axis. In both tubes was poured a little mercury, while in each of the limbs were introduced wires which effected communication with the galvanometer and the thermoelement, respectively. By inclining the box to 45° in any direction, the current is closed, but this, in both cases, passes through the galvanometer in a different direction. There is still another source of error due to the thermoelement itself whose wires are often not quite homogeneous; and if there should be no equal temperature over their whole length, a thermo-current may be generated. Although these irregularities seem to occur but rarely with copper wires (and only these were here at different temperatures), care was taken all the same that they should not influence the final result, by changing the junctions in the two flasks after a series of measurements.

We then must take again the difference of the resulting figures of different series to obtain the thermo-electric force of the copper-constantan and to calculate thence the difference in temperature between the potassium and sodium chloride. I refrain from giving a detailed communication of the results of the measurements because, anyhow, my conclusion must be that the two salts do not show a difference in temperature, at least none exceeding 0,001°. As I look upon this figure as representing the accuracy attained, I do not attach any importance to the fact that the final result showed sodium chloride to be about 0.001° warmer than potassium chloride. Four experiments were carried out, the junctions of the thermoelement being changed after each; an experiment consisted of five to six measurements which were each composed of three to seven readings, carried out one after another with continuous commutation.

From these experiments also, I must conclude to the absence of α-rays in potassium compounds; this result did not afford reason to make also an experiment with rubidium chloride.

My best thanks are due to Dr. A. H. W. Aten, who placed his galvanometer at my disposal for these experiments.

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Mathematics. — *"On a differential equation of* SCHLÄFLI." By Prof. J. C. KLUYVER.

As a suitable example of the method of solution due to PFAFF SCHLÄFLI has determined the general integral of the equation

$$a_1 (x_2p_3 - x_3p_2)^2 + a_2 (x_3p_1 - x_1p_3)^2 + a_3 (x_1p_2 - x_2p_1)^2 = 1$$

(Annali di matematica pura ed applicata, serie 2, t. II, p. 89—96) and in his Theorie der partiellen Differentialgleichungen MANSION has repeated the calculation of SCHLÄFLI. As MANSION remarks this treatment of the equation does not allow to maintain the symmetry with respect to the variables; therefore we will show in the following lines that it is possible to obtain the complete integral of the equation with preservation of the symmetry by means of JACOBI's method.

By putting

$$\begin{aligned} x_2p_3 - x_3p_2 &= A_1, \\ x_3p_1 - x_1p_3 &= A_2, \\ x_1p_2 - x_2p_1 &= A_3 \end{aligned}$$

the given equation passes into

$$f = a_1A_1^2 + a_2A_2^2 + a_3A_3^2 - 1 = 0.$$

The system of simultaneous differential equations to be considered here becomes

$$\frac{dx_1}{a_2x_3A_2 - a_3x_2A_3} = \ldots = \frac{dp_1}{a_2p_3A_2 - a_3p_2A_3} = \ldots .$$

One derives from it immediately

$$\frac{dx_1}{a_2x_3A_3 - a_3x_2A_3} = \frac{dA_1}{(a_2 - a_3)\,A_2A_3} = \ldots = \frac{\Sigma A_1dA_1}{0} = \frac{\Sigma p_1dp_1}{0}.$$

This furnishes two integral equations

$$\begin{aligned} f_1 &\equiv p_1^2 + p_2^2 + p_3^2 - m^2 = 0, \\ f_2 &\equiv A_1^2 + A_2^2 + A_3^2 - k^2 = 0. \end{aligned}$$

The two functions f_1 and f_2 are in involution. For we have

$$[A_1^2, p_1^2] = 0, \quad [A_1^2, p_2^2] = 4\,A_1p_2p_3, \quad [A_1^2p_3^2] = -\,4\,A_1p_2p_3.$$

From this ensues

$$[A_1^2, \Sigma p_1^2] = 0$$

and furthermore also

$$[f_1, f_2] = 0.$$

So one has to solve the partial derivatives p_1, p_2, p_3 out of the three equations

$$f = 0, \quad f_1 = 0, \quad f_2 = 0$$

and to integrate afterwards the differential equation

$$dz = \Sigma p_1\,dx_1.$$

A direct solution of p_1, p_2, p_3 cannot be given. Therefore we