

of work done in his laboratory was a study of colored glasses and mosaics, the results of which led to the establishment of a factory, still in successful operation, near St. Petersburg.

The achievements of Lomonosoff outside of chemistry were as remarkable as those within that science. He wrote a treatise on Metallurgy, made investigations in Meteorology and especially atmospheric electricity, in Geology, and in Mineralogy, and he superintended the equipment of expeditions for geographical exploration. He observed the transit of Venus of 1761, and drew from his observations the conclusion that the planet had an atmosphere "similar to, or perhaps greater than that of the earth," a discovery generally attributed to Schröter and Herschel (1791).

No undertaking that required courage and originality was outside the comprehensive sphere of his interests. He was the first to attempt to apply modern forms to the writing of poetry in the Russian language, and was the author of odes, poems, and even of tragedies to be performed in the Court Theater. He prepared a Russian grammar and a treatise on rhetoric. He devised a vocabulary for expressing scientific conceptions, and his terms are those now in use in Russia. As the most prominent Russian man of science of his time, public affairs claimed much of his strength. Taking him all in all, the rediscovery of Lomonosoff has added at once a chemist of the first magnitude and a personality of marvelous force and range to the limited gallery of the World's very greatest men.

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### THE POTENTIAL OF THE POTASSIUM ELECTRODE.

BY GILBERT N. LEWIS AND FREDERICK G. KEYES.

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The method employed by Lewis and Kraus<sup>1</sup> for the determination of the potential of the sodium electrode is applicable in a number of similar cases. We shall describe in this paper a similar determination of the potential of the potassium electrode, together with some preliminary experiments carried out for the purpose of seeing how far the same method is available in the case of lithium, rubidium, caesium and the metals of the alkaline earths.

We first determined the potential of a dilute potassium amalgam in an aqueous solution of potassium hydroxide, against a normal calomel electrode, and thus were able to calculate the potential of this potassium amalgam against a normal solution of potassium ion in water. It remained to determine the difference in potential between this amalgam of potassium and pure metallic potassium. This difference of potential

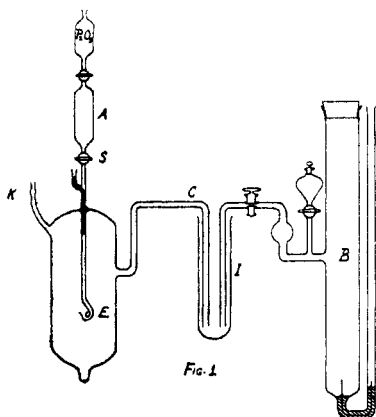
<sup>1</sup> THIS JOURNAL, 32, 1459 (1910).

is measured by the electromotive force of a cell with electrodes of pure potassium and this potassium amalgam, and with a suitable electrolyte. Any electrolyte will serve which contains potassium salt and remains unattacked by the electrodes. A solution of potassium iodide in liquid ethylamine fulfils these conditions.

The apparatus for preparing and storing the amalgam and the anhydrous ethylamine has been described in the preceding paper. The cell was made and filled substantially as before. The vessel in which the potential of the amalgam was measured against the normal electrode was somewhat modified, as described in the following section.

#### Electrode Potential of 0.2216 per cent. Potassium Amalgam.

The apparatus here used is shown in Fig. 1. The amalgam was admitted to the electrode E from the reservoir A through the stopcock S. The



electrode chamber was filled through K with a solution of potassium hydroxide of concentration 0.2026 N, which, moreover, completely filled the connecting tube C. The tube I contained the intermediate liquid 0.2 N KCl, and into this also dipped the end of a normal electrode, B, of the form commonly used in this laboratory.

The electromotive force of this combination at first was 2.1892 volts, but changed slowly on standing. A little more amalgam was admitted to E, effecting a removal of the electrode surface. Since

this forced a certain amount of the hydroxide into the intermediate solution, the latter was also renewed. The electromotive force then returned to the initial value. This process of renewal was repeated many times and frequently the potassium hydroxide in the electrode chamber was also renewed through K. On standing, the e. m. f. usually diminished at the rate of 2-3 millivolts per hour, owing to small changes in concentration occurring at the surface of the amalgam electrode. On renewing the surface the e. m. f. almost always returned to the value 2.1890 or 2.1891, although occasionally it deviated from this value by several tenths of a millivolt. As a final value we have chosen 2.1891.

This value includes the two liquid potentials 0.2 N KOH-0.2 N KCl, and 0.2 N KCl-N KCl. The latter potential we will neglect. We have taken for the former the value 0.0169 from the work of Lewis and Sargent.<sup>1</sup> This potential is in such a direction that the total e. m. f. exclusive of liquid potentials is  $2.1891 + 0.0169 = 2.2060$ . Assuming the degree

<sup>1</sup> THIS JOURNAL, 31, 367 (1909).

of dissociation to be 0.83, the concentration of potassium ion in the 0.2026 *N* potassium hydroxide would be 0.1681 *N*. By means then of the Nernst equation we find for the potential of the dilute potassium amalgam against normal potassium ion, 2.1603 volts at 25°, the potential of the normal electrode being taken as zero.

#### **Difference in Electrode Potential between Potassium and the Potassium Amalgam.**

The first cell with electrodes of potassium and potassium amalgam, and with an electrolyte consisting of a solution of potassium iodide in liquid ethylamine, was set up during the course of the preceding investigation. The cell was found less satisfactory than the corresponding sodium cell. In the first place, owing to the much smaller solubility of potassium iodide, the potentiometer was much less sensitive. Moreover, the solid metal appeared to be attacked by the amine solution. This is extraordinary, as we have since sealed up potassium with ethylamine and heated to 70–80° without any observable reaction, and even after standing for some months the metal retained its bright untarnished luster, while the liquid above the metal showed no measurable electrical conductivity.

Nevertheless, in this first cell, a blue color, due doubtless to solution of the metal, appeared near the potassium electrode. In the course of several days loose particles of metal, which had obviously come from a kind of disintegration of the potassium electrode, were seen floating about in the solution. However, during the first day or two it was possible to obtain fairly satisfactory values of the e. m. f. when the contents of the cell were thoroughly stirred. These values varied between 1.0475 and 1.0485, the mean being 1.0480.

The solution which had remained for more than a year in contact with metal and amalgam in this cell we decanted into a new cell with fresh electrodes, suitable precautions being taken to avoid the entrance of air or moisture. The electromotive force of this cell varied over an extreme range of 0.0006 volt, the mean value of the e. m. f. being 1.0482. A third cell, containing fresh materials throughout, gave an e. m. f. varying through a range of 0.0008 volt, with a mean of 1.0481. This value, 1.0481 volts, may be taken as the mean of the three cells. In order now to obtain the electrode potential of solid potassium against a normal solution of potassium ion in water, it is only necessary to add this value to the electrode potential of the potassium amalgam, namely, 2.1603 + 1.0481 = 3.2084 volts.

#### **The Heat of Solution of Potassium in Mercury; Experiments on Other Metals.**

The temperature coefficient of the e. m. f. of the cell with potassium and potassium amalgam electrodes was measured between 25° and 0°

and found to be  $-0.000272$  volt per degree. We may therefore determine the heat of solution of potassium in  $0.2216\%$  potassium amalgam with the aid of the Gibbs-Helmholtz equation,

$$E - Q/F = T dE/dT,$$

where  $Q$  is the heat evolved in the solution of one equivalent of potassium in a large quantity of  $0.2216\%$  amalgam, and  $F$  is the Faraday equivalent. Using the same values of  $F$  and the mechanical equivalent of heat as in the preceding paper, we find  $Q$  equal to  $109060$  joules or  $26050$  cal.

Experiments are in progress to determine how far the method used for the electrode potential of sodium and potassium is applicable to other metals of the alkalis and alkaline earths. Lithium is soluble in ethylamine and it has therefore been necessary to prepare for this purpose dry propylamine in which lithium iodide proves to be readily soluble. In the case of rubidium and caesium a serious difficulty has been encountered, due to the fact that their iodides are practically insoluble in ethylamine. It will therefore be necessary in these cases to choose another type of solvent or of salt. The iodides of calcium, strontium and barium are soluble in ethylamine, the solubility diminishing in the order given.<sup>1</sup> Therefore the problem consists in obtaining the metals in a state of sufficient purity, and in devising a method of introducing them into the cell, for on account of their high melting point the method hitherto employed is impossible.

### Summary.

The potential of potassium in a normal solution of potassium ion at  $25^\circ$  is found to be  $3.2084$  volts against the normal calomel electrode taken as zero.

This is the sum of two values: (1)  $2.1603$  volts, the potential of  $0.2216\%$  potassium amalgam against normal potassium ion, and (2)  $1.0481$  volts, the difference in potential between potassium and  $0.2216\%$  potassium amalgam in a solution of potassium iodide in ethylamine.

The temperature coefficient of the latter electromotive force is  $-0.000272$  volt per degree; hence the heat of solution of potassium in mercury is  $26050$  cal.

We wish to express our indebtedness to the Bache fund of the National Academy for financial aid in prosecuting this investigation.

<sup>1</sup> An interesting phenomenon has been observed in the case of several of the iodides when treated with ethylamine. The dry salt dissolves until a definite concentration (as measured by conductivity) is reached. The solubility then remains constant for some hours until a new voluminous solid phase appears which undoubtedly contains ethylamine of crystallization. In the case of calcium iodide the swelling of the solid, due to the formation of this new phase, was so considerable as to burst the containing tube.