PALLADAMMONIUM CHLORIDE, $Pd(NH_3Cl)_2$.—SALT A.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.89187	0.44885	106.40
2	0.77931	0.39218	106.38
3	0.66980	0.33711	106.41
4	1.08373	0.54541	106.40
5	0.96048	0.48338	106.40

Mean, 106.399

PALLADAMMONIUM CHLORIDE, $Pd(NH_3Cl)_2$.—SALT B.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.95615	0.48129	106.43
2	0.94037	0.47356	106.42
3	0.90106	0.45353	106.42
4	1.16994	0.58908	106.50

Mean, 106.442

PALLADAMMONIUM CYANIDE, $Pd(NH_3CN)_2$.—SALT C.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.85860	0.47463	106.41
2	1.19378	0.66002	106.45
3	1.41818	0.78408	106.45
4	1.05254	0.58206	106.51
5	1.39510	0.77153	106.51
6	1.66196	0.91881	106.42

Mean, 106.458
The mean of the 15 determinations, 106.434

When this study was begun, it was hoped to determine the electrochemical equivalent of palladium as compared with silver. Numerous experiments were tried, using the Richards type of coulometer, but the results were never concordant. About this time, L. Wöhler and F. Martin[1] stated that palladium used as the anode in nitric acid solution was oxidized to Pd_2O_3 and PdO_2. This explained the variable results and seems to prove the method useless for atomic weight purposes.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE SEPARATION OF THE ALKALI METALS IN THE ELECTROLYTIC WAY.

BY JACOB S. GOLDBAUM AND EDGAR F. SMITH.

By reference to earlier work,[2] done in this laboratory, it will be noticed how readily and completely halide salts of a number of metals, particu-

[1] *Chem.-Ztg*, 1908.
[2] THIS JOURNAL, **29,** 447; *Ibid.*, **29,** 1445; *Ibid.*, **29,** 1455.

larly the alkali and alkaline earth metals, were analyzed quantitatively
with the help of a mercury cathode and rotating silver anode.

The purpose of the present communication is to submit additional
results obtained with halide salts of other metals and also to outline
separations of the alkali metals which have, at last, been realized. An
inspection of the conditions and actual results will convince any one
that what, at first suggestion, might seem perplexing, is really not diffi-
cult and that these separations are, indeed, made with as much ease
as those of the other and more metallic metals, e. g., copper from cad-
mium. Before, however, entering upon these in more detail it is de-
sired to offer the experiences had in the electrolysis of several ammonium
salts. To this end, pure, resublimed ammonium chloride was electro-
lyzed with the conditions used in the electrolysis of sodium chloride
(Smith's Electro-analysis, 4th ed., pp. 308, et seq.). The results for
both the anion and cation were low and not concordant. It was found,
upon search, that there were very considerable amounts of ammonia
in both the inner and outer compartments of the decomposition cell,
so that evidently the amalgam, if formed in the electrolysis, had sus-
tained decomposition in the inner cup with the consequence that the
resulting ammonium hydroxide attacked the anode and dissolved a
portion of the silver chloride, forming $(NH_3)_3.(AgCl)_2$. At least, when
a few drops of dilute nitric acid were added to the clear liquid of the
inner cup, silver chloride was precipitated.

It soon became clear that, to avoid decomposition of the amalgam
in the inner cup, it would have to be removed as rapidly as it was formed.
This was accomplished by bringing the electrodes nearer together (1
cm. apart) and increasing the speed of rotation of the anode to 750 revo-
lutions per minute. It also proved advantageous to employ an initial
pressure of 3 volts, slowly increasing it to 8 volts and as the end of the
electrolysis was approached, gradually returning the pressure to 3 volts.
The cathode surface equaled 20 sq. cm.

To prevent loss of ammonia from the outer cup, because of its vola-
tility, a slight excess of standard acid was introduced and the level of
the liquid was raised to insure its complete absorption and retention.
The alkaline hydroxide produced in this way was estimated, as in the
analysis of sodium chloride, by titration with standard acid, the increase
in weight of the silver anode represented the amount of the anion found.

All the determinations given in the following tables were made in
aqueous solutions of the various salts. The volume of liquid did not
exceed fifty cubic centimeters.

The behavior of these ammonium salts under electrolysis, which is
perfectly analogous to that of salts of sodium, potassium, barium, etc.,
seems to prove the existence of an ammonium amalgam and it should

SEPARATION OF ALKALI METALS.

contribute materially to our ideas regarding the metallic character of the NH_4 group.

AMMONIUM CHLORIDE.—RESULTS.

NH_4Cl present in gram.	NH_4 present in gram.	NH_4 found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N. D.$_{20}$.	Time, minutes.
0.1002	0.0338	0.0331	0.0664	0.0658	5	0.28–0.02	32
0.1000	0.0337	0.0328	0.0663	0.0658	5	0.25–0.02	35
0.1000	0.0337	0.0332	0.0663	0.0659	3–8–3	0.15–0.02	30
0.1057	0.0356	0.0350	0.0701	0.0695	3–8–3	0.15–0–02	35

AMMONIUM BROMIDE.

NH_4Br present in gram.	NH_4 present in gram.	NH_4 found in gram.	Br present in gram.	Br found in gram.	V.	A. N. D.$_{20}$.	Time, minutes.
0.2018	0.0371	0.0363	0.1647	0.1641	8	0.7 –0.02	20
0.2000	0.0367	0.0363	0.1633	0.1623	8–5	0.65–0.025	18
0.2015	0.0370	0.0368	0.1645	0.1641	5–7–5	0.35–0.02	20

AMMONIUM SULPHOCYANATE.

NH_4CNS present in gram.	NH_4 present in gram.	NH_4 found in gram.	CNS present in gram.	CNS found in gram.	V.	A. N. D.$_{20}$.	Time. minutes.
0.0964	0.0228	0.0223	0.0736	0.0731	6	0.27–0.01	25
0.1008	0.0239	0.0235	0.0769	0.0766	6	0.25–0.015	30

As the chlorides of cesium, rubidium and lithium had never been analyzed in the manner in which the corresponding salts of sodium, potassium and ammonium had been, it seemed desirable to devote some attention to them; accordingly, pure cesium chloride was prepared by the method of H. L. Wells,[1] and electrolyzed under the conditions that proved most favorable in the analysis of sodium chloride. The slightest impurity in the cesium salt will cause the amalgam to decompose not only in the outer cell but also in the inner compartment with the consequent formation of brown silver oxide on the anode.

CESIUM CHLORIDE.—RESULTS.

CsCl present in gram.	Cs present in gram.	Cs found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N. D.$_{20}$.	Time, minutes.
0.1154	0.0911	0.0916	0.0243	0.0240	3	0.051–0.02	35
0.1002	0.0791	0.0792	0.0211	0.0212	3	0.043–0.02	35
0.1085	0.0856	0.0853	0.0229	0.0225	3	0.043–0.025	38

Rubidium Chloride.—This salt was also purified by the method of Wells.[2] Impurities cause its amalgam to decompose in the inner cup after the manner of the cesium amalgam.

RUBIDIUM CHLORIDE.—RESULTS.

RbCl present in gram.	Rb present in gram.	Rb found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N. D.$_{20}$.	Time, minutes.
0.0841	0.0602	0.0597	0.0239	0.0247	3	0.043–0.025	40
0.0918	0.0649	0.0650	0.0269	0.0271	3	0.040–0.015	35
0.0916	0.0647	0.0644	0.0269	0.0269	3	0.040–0.02	35

[1] *Amer. J. Sci.*, **43**, 17 (1892).

[2] *Ibid.*, **46**, 189 (1893).

Lithium Chloride.—This salt was freed from sodium and potassium, then subjected to electrolysis under conditions indicated in the attached table. The results are most satisfactory. They demonstrate that the analysis of this particular lithium derivative is, indeed, better effected in the electrolytic way than by any other gravimetric procedure.

LITHIUM CHLORIDE.—RESULTS.

Li Cl present in gm.	Li present in gm.	Li found in gm.	Cl present in gm.	Cl found in gm.	V.	A. N.D.₂₀.	Time, minutes.
0.0970	0.0160	0.0159	0.0810	0.0809	4	0.24–0.015	30
0.0970	0.0160	0.0160	0.0810	0.0813	4	0.26–0.01	35
0.0970	0.0160	0.0162	0.0810	0.0811	4.5	0.29–0.02	30
0.1021	0.0169	0.0165	0.0852	0.0855	4	0.31–0.015	30
0.1021	0.0169	0.0852	0.0852	0.0850	4	0.31–0.01	30

Separations.

Having thus determined all the metals of the alkali group, steps were next directed towards their separation, using the rotating silver anode and mercury cathode. Kiliani, in 1883, showed that, by attention to differences in decomposition pressure, metals could be separated in the electrolytic way. In 1891, Le Blanc[1] measured the electromotive force required in order that a continuous constant current may be passed through an electrolyte so as to effect a continuous decomposition. He found that for a given substance under given conditions, this had a definite value which he termed the "decomposition value." Freudenberg,[2] in his development of this subject, showed that reliable separations of metals may be obtained by arranging the pressure so that it exceeds the polarization value of the one metal and continues below that of the other.

This procedure was followed in the present work. The actual decomposition values furnished by Le Blanc were of no avail because of the peculiar conditions employed in the Hildebrand cell. The use of the rotating silver anode and mercury cathode necessitated the re-determination of the decomposition values. This was done by the method described by Ostwald.[3] The electrolyte will not conduct continuously below the decomposition point of a salt in aqueous solution; that is, the pressure can be gradually increased without a corresponding increase in amperage. When, however, the decomposition point is reached, any increase in pressure meets with a proportionate increase in current density. If, then, a curve be plotted with current density as the abscissas and pressure as ordinates the sharp break in the curve, the "knick-punkt," will represent the decomposition value of the salt under investigation.

[1] *Z. phys. Chem.,* **8,** 299 (1891).

[2] *Ber.,* **25,** 2492 (1892); *Z. phys. Chem.,* **12,** 97 (1893).

[3] *Ostwald-Luther Physik-Chem. Messungen* (1902), p. 391.

It must be understood that these decomposition values are not absolute. They are relative only and must be re-determined by each experimenter because they vary with the distance between the electrodes, with the speed of rotation of the anode, with concentration of the electrolyte and with the area of the cathode surface. The determination of the "break-point," however, is merely the work of a few minutes.

Guided by these basic principles, the separation of the alkali metals was undertaken. The Hildebrand cell was used, as in the determination of the alkali metals. The current was derived from storage cells. A Weston milliammeter, a Weston voltmeter (graduated to 1/30 V.) and a very efficient rheostat, delicate to 0.01 volt, were placed in circuit.

The same apparatus and conditions prevailed in the separation of the metals as in the determination of the decomposition points of their halides. The silver-plated anode made 350 revolutions per minute. The total dilution was 60 cc. The cathode surface had an area of about 20 sq. cm. and the poles were 15 mm. distant from each other.

A mixture of sodium chloride and potassium chloride, for instance, was placed in the inner compartment of the decomposition cell. The anode was rotated and the circuit closed. It had been found that the decomposition point for potassium chloride was 4/30 volt higher than that of sodium chloride; hence the pressure was raised to 2/30 volt higher than the "break-point" of the mixture. This pressure was carefully maintained throughout the electrolysis. Sodium chloride alone was decomposed, the chlorine forming silver chloride at the anode while the sodium passed into the mercury and formed sodium hydroxide with the water in the outer cup. The liquid in the latter was tested spectroscopically after the manner suggested by Gooch[1] and found to be entirely free from potassium.

The disappearance of the "break" of sodium chloride and the substitution for it of the higher decomposition value of potassium chloride were evidences of the completion of the electrolysis.

In order to save time it might, theoretically, have been possible to still effect a separation by maintaining a higher voltage at first and then reducing it towards the end to nearly the decomposition value of the sodium chloride. The number of sodium ions at the beginning would be present in sufficient amount to carry the entire charge and it would only be necessary, near the end of the separation, to keep the pressure close to the decomposition value of the sodium chloride. This point, however, was not thoroughly investigated.

This separation may prove to be most helpful in the estimation of small quantities of the alkali metals which occur in silicates.

[1] *Am. J. Sci.*, **42**, 448 (1891).

SEPARATION OF SODIUM FROM POTASSIUM.

NaCl present in gram.	KCl present in gram.	Na present in gram.	Na found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0.1169	0.1490	0.0461	0.0451	0.0708	0.0696	2.23	0.022	2 h. 40 m.
0.1169	0.1490	0 0461	0.0448	0.0708	0.0696	2.23	0.022	2 h. 40 m.
0.1169	0.1500	0.0461	0.0456	0.0708	0.0713	2.23	0 022	2 h. 45 m.
0.1169	0 1500	0.0461	0.0463	0.0708	0.0713	2.23	0.030	3 h. 15 m.
0.1070	0.1500	0.0421	0.0431	0.0649	0.0656	2.23	0.030	3 h.
0.1169	0.1500	0.0461	0.0463	0.0708	0.0711	2.23	0.031	3 h. 15 m.
0.1169	0.1500	0.0461	0.0467	0.0708	0.0706	2.23	0.031	3 h. 15 m.
0.0571	0.1500	0.0225	0.0221	0.0346	0.0345	2.23	0.024	1 h. 45 m.
0.0599	0.1500	0.1236	0.0229	0.0363	0.0364	2.23	0.026	1 h. 35 m.
0.0600	0.1500	0.0236	0 0233	0.0364	0.0366	2.23	0.028	1 h. 35 m.
0.0315	0.1500	0.0124	0.0128	0.0191	0.0194	2.23	0.026	55 m.
0.0311	0.1500	0.0122	0.0126	0.0189	0.0192	2.23	0.027	60 m.

The following separations were carried out in a manner similar to the separation of sodium from potassium. The same principles were observed.

SEPARATION OF SODIUM FROM AMMONIUM.

NaCl present in gram.	NH$_4$Cl present in gram.	Na present in gram.	Na found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0 1169	0.1102	0.0461	0.0474	0.0708	0.0720	2.30	0.030	3 h. 30 m.
0.0502	0.1102	0.0197	0.0201	0.0305	0.0313	2.30	0.026	1 h. 50 m.
0 0507	0.1102	0.0199	0.0210	0.0308	0.0319	2.27	0.026	2 h.
0.0533	0.1102	0.0210	0.0212	0.0323	0.0327	2.23	0.028	1 h. 50 m.
0.0502	0.1102	0.0197	0.0196	0.0305	0.0309	2.23	0.025	2 h.

SEPARATION OF SODIUM FROM CESIUM.

NaCl present in gram.	CsCl present in gram.	Na present in gram.	Na found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0.0589	0.0650	0.0232	0.0230	0.0357	0.0357	2.33	0.030	1½ hr.
0.0510	0.0700	0.0201	0.0198	0.0309	0.0306	2.30	0.028	1½ hr.

SEPARATION OF SODIUM FROM RUBIDIUM.

NaCl present in gram.	RbCl present in gram.	Na present in gram.	Na found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$	Time.
0.0600	0.0810	0.0236	0.0239	0.0364	0.0368	2.30	0.025	1 h. 25 m.
0.0645	0.0720	0 0254	0.0257	0.0391	0.0390	2.30	0.027	1 h. 30 m.

SEPARATION OF SODIUM FROM LITHIUM.

NaCl present in gram.	LiCl present in gram.	Na present in gram	Na found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time, minutes.
0.0630	0.1021	0.0248	0.0252	0.0382	0.0384	2.27	0.022	95
0.0631	0.1021	0.0248	0.0250	0.0383	0.0383	2.27	0.019	90
0.0635	0.1021	0.0250	0.0252	0.0385	0.0387	2.30	0.024	90

SEPARATION OF POTASSIUM FROM RUBIDIUM.

KCl present in gram	RbCl present in gram.	K present in gram.	K found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0 0851	0.0800	0.0446	0.0446	0.0405	0.0408	2.30	0.020	1 hr. 30 m.
0.0750	0.0800	0.0394	0.0390	0.0356	0.0356	2.33	0.023	1 hr. 30 m.
0.0508	0.0850	0.0266	0.0266	0.0242	0.0246	2.30	0.021	1 hr. 15 m.

SEPARATION OF POTASSIUM FROM CESIUM.

KCl present in gram.	CsCl present in gram.	K present in gram.	K found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time. minutes.
0.0830	0.0850	0.0435	0.0437	0.0395	0.0399	2.33	0.019	1 hr. 50 m.
0.0852	0.0900	0.0447	0.0445	0.0405	0.0406	2.33	0.021	1 hr. 45 m.

SEPARATION OF POTASSIUM FROM LITHIUM.

KCl present in gram.	LiCl present in gram.	K present in gram.	K found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time, minutes.
0.0715	0.1021	0.0375	0.0371	0.0340	0.0332	2.30	0.019	85
0.0622	0.1021	0.0326	0.0325	0.0296	0.0299	2.27	0.017	90
0.0636	0.1021	0.0333	0.0331	0.0302	0.0302	2.30	0.020	85

SEPARATION OF CESIUM FROM RUBIDIUM.

RbCl present in gram.	CsCl present in gram.	Rb present in gram.	Rb found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time.
0.0509	0.0690	0.0360	0.0367	0.0149	0.0160	1.20	0.008	2 hr. 10 m.
0.0493	0.0690	0.0347	0.0350	0.0146	0.0143	1.23	0.010	2 hr. 10 m.
0.0473	0.0690	0.0334	0.0326	0.0139	0.0131	1.20	0.008	2 hr. 30 m.
0.0508	0.0690	0.0359	0.0358	0.0149	0.0150	1.23	0.010	2 hr. 30 m.
0.1009	0.1235	0.0713	0.0711	0.0296	0.0306	1.20	0.010	5 hr.

SEPARATION OF LITHIUM FROM RUBIDIUM.

LiCl present in gram.	RbCl present in gram.	Li present in gram.	Li found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time, minutes.
0.0237	0.0560	0.0039	0.0037	0.0198	0.0190	2.47	0.012	70
0.0237	0.0560	0.0039	0.0039	0.0198	0.0199	2.45	0.015	75

SEPARATION OF LITHIUM FROM CESIUM.

LiCl present in gram.	CsCl present in gram.	Li present in gram.	Li found in gram.	Cl present in gram.	Cl found in gram.	V.	A. N.D.$_{20}$.	Time. minutes.
0.0451	0.0520	0.0074	0.0033	0.0377	0.0361	2.30	0.012	60
0.0328	0.0520	0.0054	0.0052	0.0274	0.0270	2.30	0.013	120
0.0328	0.0520	0.0054	0.0054	0.0274	0.0273	2.30	0.015	125

The decomposition values of potassium and ammonium salts lie so close together that no success was had in the attempts to separate them.

It may be of interest to add in conclusion that Wolcott Gibbs[1] in 1880 predicted that possibly sodium and potassium might be separated in the electrolytic way with the use of a mercury cathode.

UNIVERSITY OF PENNSYLVANIA.

ON THE PREPARATION AND THE COMPOSITION OF THE ACID CARBONATES OF CALCIUM AND BARIUM.

By Edward H. Keiser and Sherman Leavitt.

The acid carbonates of calcium, strontium and barium have never been isolated or separated from solution as far as we have been able to find by searching the chemical literature at our command. We first

[1] *Chem. News*, **42**, 291.