JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 69 APRIL 23, 1947 NUMBER 4

Thirteenth Report of the Committee on Atomic Weights of the International Union of Chemistry[1]

BY G. P. BAXTER (*Chairman*), M. GUICHARD AND R. WHYTLAW-GRAY

In the very regrettable death of Professor Otto Hönigschmid the International Committee on Atomic Weights has suffered a great loss. Professor Hönigschmid not only very actively promoted the work of the Committee but was himself responsible for a large portion of recent experimental work in this field.

Owing largely to difficulties of communication no report of the International Committee on Atomic Weights has been published for some time. The Twelfth Report was published in Germany and France, but essentially the same material appeared as the Report of the Committee on Atomic Weights of the American Chemical Society[2] at about the same time as the German and French Reports.[3] Since no changes in the Table of atomic weights have been made since the Eleventh Report of the International Committee was published in 1941 until this year, this situation can have caused no serious difficulty. In the Table of Atomic Weights at the end of this Report changes have been made in the cases of sulfur and copper. Attention is called to the fact that the atomic weight of common lead as determined from isotopic composition varies with the source over a range of 0.03–0.04 unit. At the present time it seems unwise to try to include values for the new elements nos. 93–96, neptunium, plutonium, curium and americium.

Beryllium.—Johannsen[4] synthesized beryllium chloride from beryllium oxide and carbon in a stream of chlorine and purified the product by sublimation without melting, first in chlorine, then in nitrogen, and finally in vacuum. The product was collected in sealed glass bulbs and was analyzed in the usual way both by comparison with silver and by weighing the silver chloride, with the same resulting atomic weight 9.013 for beryllium. This result is somewhat lower than that found earlier by Hönigschmid and Birkenbach by analysis of the chloride, 9.018, and agrees closely with the mass spectroscopic value 9.0126.

Carbon and Nitrogen.—Casado[5] has redetermined experimentally the densities of oxygen, nitrous oxide and methyl oxide at pressures of one atmosphere and below, as well as the deviations from Boyle's law at low pressures. Corrections of weights to the vacuum standard, for the contraction of the globes at pressures below one atmosphere and for gravity were made. The average values from a large number of determinations are given in the following table.

	Oxygen	Nitrous oxide	Methyl oxide
$1 + \lambda$	1.00089	1.00710	1.02574
d_1	1.428905	1.97747	2.16809
$d_{\frac{2}{3}}$	1.42844	1.97308	2.08987
$d_{\frac{1}{2}}$			2.08194
$d_{\frac{1}{3}}$	1.42799	1.96848	2.07330

If the densities plotted against the pressures are assumed to follow a straight line calculated by the method of least squares, the limiting densities and molecular weights are found to be as follows:

	Limiting densities	Mol. wt.
Oxygen	1.42760	32.000
Nitrous oxide	1.96380	44.019
Methyl oxide	2.0561	46.088

From the molecular weights of nitrous oxide and methyl oxide the atomic weights of nitrogen and carbon may be calculated to be 14.009 and 12.020. If the values of $1 + \lambda$ are used, together

---

[1] Authors of papers bearing on the subject are requested to send copies to each of the three members of the Committee at the earliest possible moment: Prof. G. P. Baxter, Coolidge Laboratory, Harvard University, Cambridge, Mass., U. S. A.; Prof. M. Guichard, Faculté des Sciences, Sorbonne, Paris, France; Prof. R. Whytlaw-Gray, University of Leeds, Leeds, England.

[2] THIS JOURNAL, **65**, 1443 (1943).

[3] *Ber.*, **76**, 35 (1943); *Bull. Soc. Chim.*, [5] **11**, 214 (1944).

[4] Johannsen, *Naturwissenschaften*, **31**, 592 (1943).

[5] Casado, Thesis, University of Santiago, 1943.

with the densities at one atmosphere, the following results are obtained.

	d_1	$1 + \lambda$	d_0	M
Oxygen	1.428905	1.00089	1.42763	32.000
Nitrous oxide	1.97747	1.00710	1.96352	44.012
Methyl oxide	2.10809	1.02574	2.05518	46.066

from which the atomic weights N = 14.006 and C = 12.009 result.

Fluorine and Calcium.—In a series of papers, following the first by C. A. Hutchison and Johnston,[6] the method of calculating the atomic weights of fluorine and calcium from density and X-ray data has been continued by Johnston and D. A. Hutchison,[7] C. A. Hutchison,[8] and D. A. Hutchison.[9,10] The atomic weights and densities used in the calculations of the last paper are as follows:

Atomic weights		Densities (20°)	
C	12.0104	C	3.51540
Li	6.9390	LiF	2.64030
Na	22.9970	NaCl	2.16360
Cl	35.4570	KCl	1.98826
K	39.0960	$CaCO_3$	2.64030

The most reliable results as given in the last of the papers cited are as follows:

CALCIUM

Reference substances	Assumed atomic weights	Atomic wt., Ca
Calcite, NaCl	Na, Cl, C	40.0851
Calcite, KCl	K, Cl, C	40.0851
Calcite, C (diamond)	C	40.0844
Calcite, LiF	K, Cl, Li, C, Na	40.0850
		Av. 40.0849

FLUORINE

Reference substances	Assumed atomic weights	Atomic wt., F
LiF, KCl	K, Cl, Li	18.9967
LiF, NaCl	Na, Cl, Li	18.9967
LiF, C (diamond)	Li, C	18.9967
LiF, $CaCO_3$	Na, Cl, C, Li, K	18.9967
		Av. 18.9967

The extraordinary concordance of the above results is of course dependent upon the values assumed in the calculation. If, for instance, the atomic weight of sodium is 22.994, the most recent value determined by Johnson, all molecular weights depending on that of sodium chloride will be lowered by 0.005%, and if the atomic weight of potassium is 39.098 instead of the one used, values depending on potassium chloride will be raised by 0.003%. The effect of this upon the atomic weight of calcium in the first two instances in the above table would be −0.005 and +0.002 unit. Because of the small molecular weight of lithium fluoride these uncertainties would affect the atomic weight of fluorine by only 0.001 unit. At the present time these results are to be considered as confirmatory rather than definitive.

Potassium, Aluminum, Magnesium, Sodium.—Batuecas, Casado and Alonso,[11] using the method of Hutchison and Johnston,[6] have calculated the atomic weights of potassium, magnesium, aluminum and sodium. Calcium and carbon are assumed to have the atomic weights 40.080 and 12.010. They find

K = 39.091　　Mg = 24.317
Al = 26.963　　Na = 22.961
　　　　　　　　　22.989

Silicon.—Ney and McQueen[12] and Williams and Yuster[13] have obtained the following results for the isotopic proportions of silicon.

Isotope	28	29	30
Ney and McQueen	92.24	4.69	3.07
Williams and Yuster	92.27	4.68	3.05

If the packing fractions -4.86×10^{-4}, -4.54×10^{-4} and -5.79×10^{-4} are used the calculated atomic weight is 28.087. This value lies midway between that found by Baxter, Weatherill and Scripture, 28.063, by comparing the halides with silver and those obtained by Hönigschmid and Steinheil, 28.105, by the same method, and Weatherill, 28.103, from the ratio of the tetrachloride to the dioxide.

Sulfur.—Hönigschmid[14] has redetermined the ratio between silver and sulfur from the synthesis of silver sulfide, by essentially the method used by Hönigschmid and Sachtleben,[15] and with essentially the same result. Weighed quantities of fused buttons of pure silver were heated in a current of nitrogen and the vapor of purified sulfur, then in pure nitrogen at 250–300°. Below 300° the variations in the weight of sulfide were slight. Above 300° both the weight and appearance of the sulfide were attended with variations. Vacuum corrections were applied.

It is unfortunate that owing to decomposition above 300° the silver sulfide could not be fused in order to make certain of complete conversion, but the fact that repeated heating of the silver sulfide in sulfur vapor at the lower temperature failed to effect appreciable alteration tends to favor the view that the above difficulty was not serious.

In the following table the weights of sulfide are the averages of the concordant observations when the sulfide was heated at various temperatures between 250 and 300°.

(6) C. A. Hutchison and Johnston, This Journal, **63**, 1580 (1941).

(7) Johnston and D. A. Hutchison, *Phys. Rev.*, **62**, 32 (1943).

(8) C. A. Hutchison, *J. Chem. Phys.*, **10**, 489 (1942).

(9) D. A. Hutchison, *Phys. Rev.*, **66**, 144 (1944).

(10) D. A. Hutchison, *J. Chem. Phys.*, **13**, 383 (1945).

(11) Batuecas, Casado and Alonso, *Rev. Real Acad. Cienc. Madrid*, **38**, 349 (1944).

(12) Ney and McQueen, *Phys. Rev.*, **69**, 41 (1946).

(13) Williams and Yuster, *ibid.*, **69**, 556 (1946).

(14) O. Hönigschmid, *Ber.*, **75B**, 1814 (1942).

(15) O. Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **195**, 207 (1931).

Wt. of Ag in vacuum, g.	No. of heatings with S	Av. wt. of Ag_2S in vacuum, g.	$Ag_2S:Ag$	At. wt. S
22.63155	2	25.99501	1.148618	32.0658
23.35829	4	26.82982	1.148621	32.0665
22.54273	1	25.89313	1.148624	32.0671
21.83830	2	25.08394	1.148621	32.0665
21.47088	2	24.66194	1.148623	32.0669
20.98104	4	24.09928	1.148622	32.0663
17.35371	6	19.93282	1.148620	32.0663
16.84347	16	19.34675	1.148620	32.0663
		Average	1.148620	32.0665

Richards and Jones[16] from the ratio of silver sulfate to silver chloride found 33.069, while Scheuer[17] from the ratio $2Ag:SO_2:Ag_2SO_4:2AgCl$ obtained the value 32.067. On the basis of the above two investigations by Hönigschmid, especially in view of the extraordinary concordance of the one reported here, there seems little doubt that the atomic weight of sulfur is very close to 32.066 if silver is taken as 107.880, and this value has been adopted for the table in place of the less precise one, 32.06.

Potassium.—Paul and Pahl[18] have determined the relative abundance of K^{39} and K^{41} in common potassium to be 13.96 ± 0.1. With the packing fraction -6.1×10^{-4} and the conversion factor 1.000275 the atomic weight of potassium is found to be 39.099. This agrees closely with the average of the most recent determinations of this constant, 39.097.* In the same way a sample of potassium partially separated by ideal distillation by Hevesy and Lögstrup was found to have the atomic weight 39.011. Hönigschmid and Goubeau, and Baxter and Alter both obtained this same value for this sample.

* 39.096	Baxter and Alter, THIS JOURNAL, **55**, 3270 (1933).
30.096	Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933).
39.100	Johnston, *J. Phys. Chem.*, **39**, 781 (1935).
39.098	Baxter and Harrington, THIS JOURNAL, **62**, 1836 (1940).
39.096	McAlpine and Bird, *ibid.*, **63**, 2960 (1941).

Copper.—Hönigschmid and Johanssen[19] have analyzed cuprous chloride. Cupric sulfate was crystallized three times in the case of one sample, five times in the case of another. After electrodeposition on a platinum dish at 2 volts, the metal was dissolved in nitric acid and the nitrate crystallized and centrifugally drained. Decomposition to oxide in platinum followed. Spectroscopic examination by Dr. Schöntag revealed no impurities.

Conversion of the cupric oxide to cuprous chloride was carried out in the following operations: drying of the oxide in nitrogen at 200°, reduction in electrolytic hydrogen at 800°, conversion of the metal to cuprous chloride in nitrogen and chlorine mixtures, and resublimation of the cuprous chloride in nitrogen into a weighing tube, all in a quartz bottling apparatus. In the last two steps it was important to avoid a temperature above 600°.

Analysis followed by solution in ammonia, oxidation to the cupric state with oxygen, acidification with nitric acid and comparison with silver in the conventional way.

Vacuum corrections were applied. In the following table two analyses believed by the authors to have been made with defective material.are omitted.

ATOMIC WEIGHT OF COPPER

Wt. of CuCl in vacuum	Wt. of Ag in vacuum	CuCl:Ag	At. wt. Cu	Wt. of AgCl in vacuum	CuCl: AgCl	At. wt. Cu
5.62293	6.12742	0.917682	63.542	8.14097	0.690695	63.545
5.27787	5.75129	.917685	63.543	7.64158	.690678	63.543
6.08707	6.63310	.917681	63.542	8.81308	.690686	63.544
4.84195	5.27638	.917665	63.541	7.01062	.690659	63.540
5.93141	6.46362	.917661	63.540	8.58810	.690655	63.539
5.74879	6.26460	.917663	63.541	8.32345	.690674	63.542
5.83204	6.35517	.917684	63.543	8.44382	.690687	63.544
6.54858	7.13604	.917677	63.542	9.48162	.690660	63.540
6.21862	6.77653	.917670	63.541	9.00373	.690672	63.542
6.03859	6.58024	.917685	63.543	8.74323	.690659	63.540
	Av.	.917675	63.542		.690673	63.542

The outcome of this work, 63.542, is appreciably lower than that of Richards and his collaborators, 63.57, on which the international value has depended for some time, but is in close agreement with that obtained by Ruer,[20] 63.54, by reduction of cupric oxide, and with a recent isotopic analysis of copper by Ewald[21] which gives the value 63.53.

Selenium.—Hönigschmid and Görnhardt[22] prepared pure selenium oxychloride by distillation in high vacuum in a glass still and collected the product in sealed glass bulbs. Analysis by comparison with silver chloride gave 78.961, while determination of the silver chloride produced 78.963 for the atomic weight of selenium. This investigation confirms the present International value which depends on the earlier synthesis of silver selenide by Hönigschmid and Kapfenberger. The value calculated from the proportions of isotopes is 78.95 (Flügge and Mattauch[23]).

Ruthenium.—Ewald[24] has determined the isotopic proportions of ruthenium to be as follows:

Isotopic weight	96	98	99	100	101	102	104
Per cent.	5.68	2.22	12.81	12.70	16.98	31.34	18.27

With the packing fraction -6.49×10^{-4} and the conversion factor 1.000275 the atomic weight

---

(16) Richards and Jones, THIS JOURNAL, **29**, 826 (1907).

(17) Scheuer, *Sitzber. Akad. Wiss. Wien, Math. naturw. Klasse*, Abt. IIa, **123**, 1004 (1914).

(18) Paul and Pahl, *Naturwissenschaften*, **32**, 228 (1944).

(19) Hönigschmid and Johanssen, *Z. anorg. allgem. Chem.*, **252**, 364 (1944); *Naturwissenschaften*, **31**, 548 (1943).

(20) Ruer, *Z. anorg. allgem. Chem.*, **137**, 101 (1924).

(21) Ewald, *Z. Physik*, **122**, 487 (1944).

(22) Hönigschmid snd Görnhardt, *Naturwissenschaften*, **32**, 68 (1944).

(23) Flügge and Mattauch, *Ber.*, **76A**, 1 (1943).

(24) Ewald, *Z. Physik*, **122**, 491 (1944)

INTERNATIONAL ATOMIC WEIGHTS

1947

	Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	92.91
Copper	Cu	29	63.54
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.76
Iodine	I	53	126.92
Iridium	Ir	77	193.1
Iron	Fe	26	55.85
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.98
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

is calculated to be 101.04. Although Gleu and Rehm[25] by analysis of the purpureo-chloride obtained the value 101.08, the uncertainties in their determination make it unwise to make any change in the Atomic Weight Table at the present time.

Silver, Bromine and Potassium.—McAlpine and Bird,[26] by quantitative decomposition of potassium bromate, have found the ratio of potassium bromide to oxygen and by comparison of the resulting potassium bromide with silver have found the ratio of these two substances. The results furnish a direct determination of the molecular weight of potassium bromide and an indirect determination of the atomic weight of silver.

Silver and bromine were purified by methods standard in atomic weight work. Potassium bromate was prepared from high-grade potassium hydroxide and an excess of bromine. After the solution had been boiled to remove excess of bromine and possibly iodine, the bromate was many times recrystallized until essentially free from bromide and sodium.

After prolonged drying in a vacuum the salt was further dried at 85–90° in the special weighed quartz decomposition flask, which was provided with a quartz filter disk to prevent loss of solid material, in a dry air stream, and was weighed.

---

(25) Gleu and Rehm, *Z. anorg. allgem. Chem.*, **235**, 352 (1937).

(26) McAlpine and Bird, THIS JOURNAL, **63**, 2960 (1941).

Very slow decomposition in a dry air stream followed, at gradually increasing temperatures up to 550°, until constant weight was obtained. During the decomposition the outgoing air stream was passed through a weighed phosphorus pentoxide tube to absorb residual water in the potassium bromate. In preliminary experiments it was found that decomposition of the bromate was complete and that the resulting bromide was neutral.

In the following table the weight of potassium bromate has been corrected for the water content as determined in each experiment. Vacuum corrections have been applied.

THE MOLECULAR WEIGHT OF POTASSIUM BROMATE

$KBrO_3$, g.	KBr, g.	Ratio, $KBr:O_3$	Mol. wt. KBr
10.67696	7.60833	2.47939	119.011
7.54279	5.37493	2.47937	119.010
7.44818	5.30753	2.47940	119.011
9.72572	6.93055	2.47947	119.015
9.62010	6.85524	2.47942	119.012
8.50007	6.05711	2.47941	119.012
10.69361	7.62021	2.47941	119.012
10.36524	7.38620	2.47939	119.011
9.76351	6.95738	2.47935	119.009
9.78441[a]	6.97233	2.47942	119.012
		Average 2.47940	119.011

[a] Corrected in private communication from the authors.

Further evidence that the potassium bromide resulting from the decomposition was normal and free from moisture was obtained by comparing this bromide with silver in the conventional way by the nephelometric method. Similar experiments were made with potassium bromide prepared from pure bromine and potassium oxalate, and fused in nitrogen. Weights are corrected for air buoyancy.

THE ATOMIC WEIGHT OF SILVER, KBr = 119.011

KBr, g.	Ag, g.	Ratio, KBr:Ag	At. wt. of Ag[a]
	KBr from $KBrO_3$		
5.37498	4.87217	1.103200	107.878
5.30758	4.81110	1.103195	107.878
6.93122	6.28281	1.103204	107.878
6.85536	6.21410	1.103194	107.879
6.05813	5.49155	1.103173	107.881
7.62092	6.90813	1.103181	107.880
7.38622	6.69531	1.103193	107.879
6.95738	6.30663	1.103185	107.879
6.97265	6.32040	1.103197	107.878
		Average 1.103191	107.879

[a] Recalculated from authors' data.

KBr, g.	Ag, g.	Ratio, KBr:Ag	At. wt. of Ag
	KBr from $K_2C_2O_4$		
5.08563	4.60984	1.103212	107.877
4.94988	4.48694	1.103175	107.880
5.64545	5.11714	1.103243[b]	107.874
5.38516	4.88142	1.103195	107.878
5.92139	5.36755	1.103183	107.880
4.62504	4.19245	1.103183	107.880
5.30793	4.81142	1.103194	107.879
4.50218	4.08093	1.103224	107.876
4.34549	3.93902	1.103191	107.879
5.25160	4.76034	1.103199	107.878
5.06778	4.59372	1.103197	107.878
		Average 1.103200	107.878

[b] 1.103200 in the authors' paper.

If the established ratio of bromine to silver, 0.740786, is assumed, the atomic weights of bromine and potassium referred to silver as 107.879 are 79.915 and 39.096, respectively. All three values are in excellent agreement with those in the Table.

Incidental to the investigation three syntheses of silver chloride from silver were made.

THE RATIO OF SILVER TO SILVER CHLORIDE

Ag, g.	AgCl, g.	Ag : AgCl
6.95254	9.23774	0.752623
7.03045	9.34116	.752631
6.63263	8.81249	.752640
	Average	.752631

The previously established value of this ratio is 0.752632.

Silver.—Paul[27] has determined the proportions of the two isotopes of silver electrometrically with a mass spectroscope. The mean ratio from twelve determinations was found to be $Ag^{107}/Ag^{109} = 1.080 \pm 0.006$. If the packing fraction -4.8×10^{-4} is used the atomic weight of silver is found to be 107.880.

Dysprosium.—Wahl[28] finds the following isotopic proportions for dysprosium.

Isotope	158	160	161	162	163	164
Per cent.	Trace	0.1	21.1	26.6	24.8	27.3

The mean mass number calculated from these percentages is 162.581 and with the packing fraction -1.3×10^{-4} and the conversion factor 1.000275 the atomic weight may be calculated to be 162.52. Owing apparently to the fact that the author's percentages total only 99.9, he calculates the incorrect value 162.42. Hönigschmid found, by analysis of the chloride, 162.46.

Hafnium.—Mattauch and Ewald[29] by photometric measurement of intensities in mass spectrographic plates have found the relative abundances of the hafnium isotopes to be as follows:

Isotope	174	176	177	178	179	180
Per cent.	0.18	5.30	18.47	27.10	13.84	35.11

The mean mass number calculated from these results is 178.54, and the atomic weight calculated with the packing fraction $+0.2 \times 10^{-4}$ and the conversion factor 1.000275 is 178.50 ± 0.01. This result is appreciably lower than the atomic weight found by Hönigschmid and Zintl[30] in the

---

(27) Paul, *Naturwissenschaften*, **31**, 419 (1943).

(28) Wahl, *Suomen Kemistiseuran Tiedonantoja*, **51**, 64 (1942); *C. A.*, **38**, 5142 (1944).

(29) Mattauch and Ewald, *Z. Physik*, **122**, 314 (1944).

(30) Hönigschmid and Zintl, *Ber.*, **58**, 453 (1925).

usual chemical way. With two samples containing 0.57 and 0.16% of zirconium Hönigschmid and Zintl's results after correction for the zirconium content were 178.64 and 178.57.

Lead.—Permyakov[31] has determined the atomic weight of lead from both Sadon galena and Khito-Ostrov uraninite by the conventional chloride–silver–silver chloride method. Weights are corrected to the vacuum standard.

Wt. of $PbCl_2$	Wt. of Ag	Ratio $PbCl_2$: 2Ag	At. wt. of Pb	Wt. of AgCl	Ratio $PbCl_2$: 2AgCl	At. wt. of of Pb
			Sadon Galena			
3.9615	3.0733	1.28900	207.20	4.0835	0.97010	207.19
2.2722	1.7628	1.28897	207.19	3.3423	.97008	207.19
3.1425	2.4378	1.28907	207.21	3.2394	.97009	207.19
		1.28901	207.20		.97009	207.19
			Khito-Ostrov Uraninite			
1.6599	1.2928	1.28396	206.11	1.7175	0.96646	206.14
2.3032	1.7939	1.28391	206.10	2.3834	.96635	206.12
2.2354	1.7411	1.28390	206.10	2.3132	.96637	206.12
		1.28392	206.10		.96639	206.13

Radium.—Attention is again called to the fact that in the most recent and accurate determination of the atomic weight of radium by Hönigschmid and Sachtleben,[32] by conversion of radium bromide to radium chloride, no correction was made for the fact that weights of salt are too low since the temperature of the salts is always higher than that of the balance. The ratio involved is $RaBr_2$: $RaBr_2$–$RaCl_2$, in which the second term is far less affected than the first. In earlier work by Hönigschmid a positive correction of 0.01 unit was used. Although the mass spectrographic value is 226.05, identical with Hönigschmid and Sachtleben's uncorrected result, the application of the above rather uncertain correction produces a discrepancy of 0.01 unit.

---

[31] Permyakov, *Bull. acad. sci. U. R. R. S.*, 581 (1941).

[32] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **221**, 65 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Potassium Chloride in Dilute Aqueous Solution

BY HERBERT S. HARNED AND RALPH L. NUTTALL

The problem of the determination of diffusion coefficients of electrolytes, particularly in dilute solutions, has perplexed physical chemists for more than sixty years. Indeed, in the past, there has been no experimental evidence to prove the validity of Nernst's[1] fundamental law which predicts the diffusion coefficient at infinite dilution from the electrical properties of the electrolytes.

Recently, Harned and French[2] have described a conductance method and some preliminary experiments by which they obtained values of the diffusion coefficient of potassium chloride at concentrations between 0.002 and 0.005 *N*. They estimate the accuracy of their final results to be ±0.9% and, in the concluding sentence of their paper, they stated that "our experience indicates that considerable improvement in accuracy can be effected."

We shall now describe an improved apparatus and technique which we believe is an experimental solution to this problem. The results to be described are in the region of concentration 0.001 to 0.01 *N*, suitable for testing the theory. Their accuracy is of the order of 0.1% which is sufficient to assure their use as standards for the calibration of other methods, in particular the diaphragm cell method.

Theory of the Method[3]

The most important feature of this method is the attainment of maximum simplicity of mathematical treatment by the mechanical construction of the apparatus. In the first place, the solution is completely confined in the cell so that "restricted diffusion" occurs. Under this condition, the boundary conditions are such as to render the integral of the differential equation of diffusion both complete and in a form suitable for further simplification.

The simplest form of cell is an accurately machined rectangular parallelopiped with electrodes at top and bottom positions which may be suitably determined by theory. A schematic cross section of the cell with electrodes at distances ξ from the top and bottom is shown in Fig. 1. The electrolyte diffuses in the x direction and the height of the cell is α. Fick's first law of diffusion may be expressed by

$$\mathbf{J} = (c\mathbf{v}) = -\boldsymbol{D}\nabla c \qquad (1)$$

where **J** is the flow, c the concentration of diffusing component, **v** its velocity, $\boldsymbol{D}$ its diffusion coefficient and ∇c the gradient of the concentration. The equation of continuity is

$$\frac{\partial c}{\partial t} + \nabla\cdot(c\mathbf{v}) = 0 \qquad (2)$$

and therefore

$$\frac{\partial c}{\partial t} = -\nabla\cdot(c\mathbf{v}) = \nabla\cdot\boldsymbol{D}\nabla c \qquad (3)$$

For unidirectional flow in the x direction, we obtain

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\boldsymbol{D}\frac{\partial c}{\partial x} \qquad (4)$$

which is Fick's second law. We shall assume that

---

[1] Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

[2] Harned and French, *Ann. N. Y. Acad. Sci.*, **44**, 267 (1945).

[3] The idea of utilizing the difference of conductance at the top and bottom pairs of electrodes was suggested by Professor Lars Onsager some years ago at which time he developed the theory of the method.