tion pressure of sound and the amount of energy necessary to convert a gram of substance from infinite radius to a small finite radius are both easy to estimate, but no specific mechanism can be formulated for the emulsification process and without this the two cannot be usefully equated. Since, moreover, the standing waves in liquids are shifting constantly both in intensity and in position, it seems certain that, even if it occurred, emulsification would under these conditions lead to no useful conclusions.

Summary

It has been demonstrated that emulsions produced by sound waves are due largely to action at the walls of the vessel. A method has been devised whereby the process of emulsification may be used as a fairly reliable measure of relative intensities of sound. An argument is advanced which makes it appear unlikely that absolute radiation pressures can be calculated from any similar process. It has been demonstrated that the walls of a glass vessel are slightly emulsified and that small uniform glass particles in liquids are not fractured by intense sound waves.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. III. THE ANALYSIS OF NICKELOUS BROMIDE

BY GREGORY PAUL BAXTER AND SABURO ISHIMARU

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In two recent investigations comparisons of terrestrial and meteoric nickel have been made by the quantitative determination of nickel in nickelous oxide[1] and of chlorine in nickelous chloride.[2] In both series of experiments the meteoric nickel was obtained from the same source, the Cumpas meteorite found in 1903, near Cumpas, Sonora, Mexico. In neither case could any difference be detected between the atomic weights of terrestrial and meteoric nickel larger than the error of the experiments. Since the origin of any meteorite must necessarily be largely a matter of conjecture, the possibility of a difference in the isotopic composition of nickel from different meteorites, although remote, is not negligible. Therefore, the availability of a considerable quantity of meteoric nickel from another source has led us to a new comparison of this material with that of terrestrial origin. In order to vary the method somewhat from those outlined above and in order to take advantage of the very great suitability of silver bromide for precision work, in this case nickelous

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[1] Baxter and Parsons, THIS JOURNAL, **43**, 507 (1921).

[2] Baxter and Hilton, *ibid.*, **45**, 694 (1923).

bromide was selected for analysis. As before, we have been unable to establish any difference between terrestrial and extra terrestrial material.

Purification of Materials

The preparation of reagents followed lines already proved to be adequate in numerous earlier investigations. Water, nitric acid, hydrochloric acid, formic acid, ammonium carbonate and ammonia were purified by distillation. Silver was especially important as being the standard of comparison. The processes employed were double precipitation of the chloride followed in each case by reduction with sugar solution made alkaline with electrolytically purified sodium hydroxide, fusion of the metal on a lime boat in a blast flame, solution in nitric acid and repeated crystallization of silver nitrate, precipitation of the metal with ammonium formate, fusion on pure lime in an electrically heated muffle, electrolytic transport through a concentrated silver nitrate solution made from the same silver, fusion on pure lime in an atmosphere of pure dry electrolytic hydrogen, etching with nitric acid and drying in a vacuum at 500°.[3]

Pure lime was made from calcium nitrate which had been recrystallized until free from iron and then precipitated as carbonate. To prepare receptacles for the fusion of silver, the carbonate was ignited and a mixture of the product with a small proportion of nitrate was used to line either porcelain crucibles or porcelain boats.

Bromine was first distilled from aqueous potassium bromide to remove the bulk of the chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate and the remaining three-fourths of the bromine was distilled from solution in the potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate and the potassium bromide was fused in a platinum dish with enough recrystallized potassium permanganate to oxidize all organic matter. In order to obtain bromine, the purified potassium bromide was dissolved in a solution of pure sulfuric acid and the potassium sulfate which separated was removed. The excess of permanganate in the bromide caused a small quantity of bromine, to be liberated. This bromine was removed by distillation, since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. After separation from the aqueous layer, the pure bromine was redistilled. In all the above operations cork and rubber were rigidly excluded from the apparatus.

Hydrogen bromide was prepared from the bromine by catalytic synthesis

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[3] See especially Richards and Wells, *Pub. Car. Inst.*, No. 28, p. 16 (1905); Baxter, THIS JOURNAL, **44**, 591 (1922).

with hydrogen. Electrolytic hydrogen dried by fused potassium hydroxide was charged with bromine at about 44° and the mixture passed over hot platinized asbestos in a hard glass tube. To prepare an aqueous solution the product was collected in water and the solution distilled through a quartz condenser with rejection of the extreme portions. To obtain the pure, dry gas a slight excess of bromine was used and the product freed from bromine by being passed through an aqueous solution containing pure ferrous bromide. The comparatively small amount of water which evaporated from the saturated hydrogen bromide solution was removed by fused calcium bromide since phosphorus pentoxide reacts with the gas. Calcium bromide leaves 0.2 mg. of water per liter of gas. There was no evidence, however, that this small quantity of moisture reacted with nickelous bromide in the presence of a high concentration of hydrogen bromide.

Nitrogen was prepared from air with an excess of ammonia by the Wanklyn catalytic process and the hydrogen produced catalytically was oxidized by hot copper oxide. After drying the gas thoroughly, oxygen liberated from the cupric oxide was removed by hot nickel.

Air was passed over aqueous silver nitrate and potassium hydroxide, concentrated sulfuric acid and phosphorus pentoxide and through a sintered glass filter.

All the apparatus for purifying gases was constructed of glass with fused or well ground joints. No lubricant whatever was used on the ground joints since past experience has shown that organic greases evaporate sufficiently to introduce carbonaceous residues into substances otherwise free from organic material, while inorganic lubricants are likely to carry moisture to the interior.

Purified terrestrial nickel chloride and metal remaining from earlier work were converted to nitrate by treatment with nitric acid, and nickel ammonia nitrate was produced by saturating the solution with distilled ammonia. This salt was recrystallized four times by solution in hot water kept saturated with ammonia, followed by cooling. Centrifugal separation of crystals from mother liquor was carried out in platinum Gooch crucibles. From the nickel ammonia nitrate the hydroxide was prepared by hydrolysis. The salt was treated with a considerable amount of water in platinum dishes and kept at boiling temperature until ammonia ceased to be evolved. The precipitate was washed, dried and ignited. The product was then dissolved in nitric acid and the nitrate crystallized three times from concentrated nitric acid. Decomposition of the nitrate at a high temperature in a platinum boat yielded the oxide a second time. This was dissolved in pure aqueous hydrogen bromide, in a quartz vessel to avoid the action of bromine liberated by the higher oxides of nickel. The bromide was then crystallized four times in platinum vessels with centrifugal drainage.

The meteoric nickel was obtained in the course of the extraction of cobalt for the earlier investigation. The source was a meteorite probably found in the western part of the United States, and possibly was a portion of the Cañon Diablo meteorite. Professor Emeritus J. E. Wolff, of Harvard University, very generously donated this material. Originally about 7 kilograms of the meteorite was dissolved in nitric acid and the iron largely separated by crystallization as ferric nitrate. Nearly all the remaining iron was removed by precipitating the sulfides and extracting with dilute hydrochloric acid. The cobalt was then separated by treatment with a large excess of potassium nitrite in the presence of acetate. The remaining salts were converted to chlorides by evaporation with hydrochloric acid and those metals forming less soluble sulfides were removed by fractionation with hydrogen sulfide in slightly acid solution. Conversion of the salts to nitrates by evaporation with an excess of nitric acid was followed by precipitation of the iron with a large excess of ammonia in dilute solution. After evaporation of the solution, nickel ammonia nitrate was prepared as with the terrestrial material. The subsequent steps in the preparation of nickelous bromide were identical with those outlined above.

To prepare anhydrous nickelous bromide for analysis the hydrated salt was first partially dehydrated over fused potassium hydroxide at room temperature. The residual water was then removed by heating the salt, contained in a quartz boat, in a quartz tube through which a mixture of nitrogen and hydrogen bromide was passed at about 360°. Sublimation of the anhydrous material from the boat to the tube in the same atmosphere then followed and the product was twice resublimed to adjacent portions of the tube. As in the case of nickelous and cobaltous chlorides which had been similarly prepared, a slight siliceous residue remained, diminishing with each sublimation. In a second triple sublimation no evidence of silica could be detected. The final product was preserved over fused potassium hydroxide for analysis.

Before being weighed the dehydrated bromide was again heated to the sublimation point in a current of dry nitrogen and hydrogen bromide. The salt, contained in a weighed platinum boat, was placed in a transparent quartz tube which formed part of a Richards and Parker[4] bottling apparatus. After the air had been displaced the tube was electrically heated at gradually increasing temperatures until finally the bromide began to sublime. After the tube had been allowed to cool, the hydrogen bromide was displaced by dry nitrogen and this in turn by dry air before the boat was transferred to the weighing bottle in which it had been originally weighed. A second weighing of the bottle and boat followed.

The boat and contents were next covered with about 1000 ml. of pure water in a precipitating flask, and allowed to stand for several days until

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[4] Richards and Parker, *Proc. Am. Acad.*, **32**, 59 (1896).

solution was complete. There was never the slightest evidence of insoluble matter. The boat was then carefully removed and at the same time was thoroughly rinsed. Pure silver nearly equivalent to the bromide was weighed out, dissolved in nitric acid and diluted to approximately 0.1 N concentration. The silver solution was then added to the bromide solution in small portions with frequent shaking and the flask was allowed to stand at room temperature for some days with occasional agitation. The clear supernatant solution was next tested in a nephelometer for excess of bromide or silver, and the estimated deficiency of either was added in the form of 0.01 N solution. The solution was then shaken, allowed to clarify and tested as before and the process was repeated until exactly equivalent quantities of silver and bromide had been used. A period of six to eight weeks in every case elapsed between the precipitation and the final adjustment of equilibrium, since long experience has shown that this is necessary for the leaching out of material initially occluded by the precipitate.

In all but two analyses, after the end-point of the comparison had been reached, an excess of silver nitrate (from 0.002 to 0.02 g.) was added and the analyses were allowed to stand for some time longer. Then after the silver bromide had been washed many times with pure water it was collected on a weighed platinum sponge Gooch crucible and dried in an electrically heated porcelain air-bath at a temperature not far from 400° before being weighed. In Analyses 10, 11 and 13, the main bulk of the precipitate was transferred to a porcelain crucible and the loss on fusion, presumably due to retained moisture, was determined.

In Analysis 9 the silver bromide was accidentally fused in the Gooch crucible during the initial drying. Since no apparent deterioration of the bromide resulted, in Analysis 12 the bromide was first dried at 370° and weighed and then was fused for a short time in the Gooch crucible. A loss in weight of 0.12 mg. resulted. Three repetitions of the fusion for periods of two, two and four hours resulted in changes in weight of -0.05, $+0.03$, and -0.11 mg. In Analysis 14, also, the silver bromide was once fused in the Gooch crucible after having been dried at 360° and weighed. These experiments so far as they go indicate that a short period of fusion in the platinum sponge crucible introduces little danger from decomposition of the silver bromide, although prolonged fusion is doubtless objectionable. This method has the great advantage of avoiding the transfer of the dried precipitate to a porcelain crucible for the fusion. Further experiments in this direction are obviously desirable. The small proportion of moisture found in these precipitates, 0.0005%, is in accordance with the observation by Hönigschmid and Birckenbach[5] that silver chloride dried at 300° is nearly if not quite anhydrous.

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[5] Hönigschmid and Birckenbach, *Z. anorg. allgem. Chem.*, **163**, 332 (1927).

Slight corrections were applied to the weight of silver bromide for solubility in the mother liquors and wash waters,[6] for silver bromide found in an ammoniacal solution with which the precipitating flask was finally rinsed, and for bromide introduced during the nephelometric comparison of the nickelous bromide with silver.

All objects were weighed by substitution for similar counterpoises. Weights were standardized to hundredths of a milligram by the Richards substitution method.[7] Vacuum corrections were applied on the basis of the air density observed at the time of weighing, and the following densities: weights, 8.3; $NiBr_2$, 4.64; AgBr, 6.47; Ag, 10.49.

TABLE I

THE ATOMIC WEIGHT OF NICKEL

Ag = 107.880 Br = 79.916

$NiBr_2$:2Ag, Series I

		Wt. of $NiBr_2$ in vac.	Wt. of Ag in vac.	Wt. of Ag added	Corr. wt. of Ag in vac.	Ratio $NiBr_2$: 2Ag	Atomic weight of Ni
1	T	4.97931	4.91632	−0.00011	4.91621	1.012835	58.697
2	T	5.33870	5.27128	− .00027	5.27101	1.012842	58.699
3	T	7.91596	7.81825	− .00245	7.81580	1.012815	58.693
4	T	4.63096	4.57239	+ .00003	4.57242	1.012803	58.690
5	T	5.35138	5.28445	+ .00097	5.28348	1.012851	58.701
					Average	1.012829	58.696
				Series II			
6	M	6.31054	6.22997	+0.00071	6.23068	1.012817	58.693
7	M	5.66561	5.59408	+ .00011	5.59419	1.012767	58.683
8	M	6.08659	6.00959	− .00011	6.00948	1.012831	58.696
					Average	1.012805	58.691
				Average of Series I and II			58.694

$NiBr_2$:2AgBr, Series III

		Wt. of $NiBr_2$ in vac.	Wt. of AgBr in vac.	Loss on fusion	Dissolved AgBr	Corr. wt. of AgBr	Ratio $NiBr_2$:- 2AgBr	Atomic weight of Ni
9	T	4.97931	8.55738		0.00049	8.55787	0.581840	58.702
10	T	7.91596	13.60528	0.00007	.00012	13.60533	.581828	58.698
11	T	4.63096	7.95987	.00000	.00008	7.95995	.581783	58.681
						Average	.581817	58.694
				Series IV				
12	M	6.31054	10.84634	0.00012	0.00006	10.84628	0.581816	58.693
13	M	5.66561	9.73791	.00002	.00008	9.73797	.581806	58.690
14	M	6.08659	10.46106	.00006	.00006	10.46106	.581833	58.700
						Average	.581818	58.694
					Average of Series III and IV			58.694
					Average of Series I and III			58.695
					Average of Series II and IV			58.693
					Average of all Series			58.694

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[6] Calculated on the basis of a solubility of silver bromide in water of 0.1 mg. per liter.

[7] Richards, THIS JOURNAL, **22**, 144 (1900).

Within the experimental error the terrestrial and meteoric samples are identical in isotopic composition. The combined average result, 58.694, would be raised only 0.002 unit by the omission of the two most discordant determinations, Analyses 7 and 11.

Modern determinations of the atomic weight of nickel are given in chronological order in the following table.

Richards and Cushman	$NiBr_2$:2Ag	58.680	Baxter and Parsons	NiO:Ni	58.702
	$NiBr_2$:2AgBr	58.683	Baxter and Hilton	$NiCl_2$:2Ag	58.699[8]
				$NiCl_2$:2AgCl	58.701[8]
	$NiBr_2$:Ni	58.682	Baxter and Ishimaru	$NiBr_2$:2Ag	58.695
				$NiBr_2$:2AgBr	58.693
	Average	58.682		Average	58.698

As has been pointed out before, the material analyzed by Richards and Cushman was not ideal for the purpose since it contained impurity extracted from the porcelain tube during sublimation. The average of the more modern values is almost 0.02 unit higher than the older one of Richards and Cushman and probably is nearer the truth.

During a temporary absence of the senior author, for a portion of the time, oversight of this work was undertaken by the late Professor T. W. Richards. We gratefully acknowledge our indebtedness for his kind advice.

Summary

1. Nickel extracted from a new meteorite has been found to have the same isotopic composition as terrestrial nickel.

2. The atomic weight of nickel has been found to be 58.694.

3. The average of the most recent determinations of this constant is 58.697.

CAMBRIDGE, MASSACHUSETTS

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[8] Calculated with the value 35.457 for chlorine.