dioxide in the more polar solvents, but distinctly more soluble in the non-polar solvents, both by reason of its smaller polarity and the larger value for the ideal solubility.[26]

Summary

1. Solubilities of chlorine have been measured in heptane, carbon tetrachloride, silicon tetrachloride and ethylene dibromide.
2. These data, together with other data upon freezing-point depressions in liquid chlorine, are discussed in the light of the theory of solubility previously outlined, and shown to be in accord with earlier predictions.
3. Solubility data for hydrogen, nitrogen, carbon monoxide, oxygen, methane, carbon dioxide, nitrous oxide, chlorine, phosgene, niton and actinium emanation are summarized and their theoretical relations discussed.

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

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. II. THE ANALYSIS OF NICKELOUS CHLORIDE

BY GREGORY PAUL BAXTER AND FRANK ARTHUR HILTON, JR.

Received December 12, 1922

In a recent investigation, Baxter and Parsons[1] compared nickel extracted from a meteorite with that contained in commercial nickel salt, by quantitative reduction of nickelous oxide. In this way the atomic weight of terrestrial nickel was found to be 58.70, and that of meteoric nickel 58.68. While the concordance of the results obtained with terrestrial material was satisfactory, the three results with the meteoric sample varied from 58.66 to 58.72. This variation was unquestionably due to the fact that the magnitude of a correction for occluded gases in the oxide was less certain in the latter case. Although there seemed to be no real indication of a difference in the two sorts of material, the subject was taken up anew with material from the same meteorite but by the less troublesome and more satisfactory method of analyzing the anhydrous chloride.

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[26] Kunerth has used his own data and those of Just as a basis for a denial of any connection between solubility and internal pressure for gases. He has, however, neglected to make the distinction previously insisted upon by the present author between liquids of low and high polarity. The reader can see that if the more polar liquids are omitted from Table VI the solvent powers of the non-polar liquids for carbon dioxide fall in the same order, within the limits to be expected, as was found for the other gases.

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

Purification of Materials

Water, reagents and gases were purified as previously described in many papers from this Laboratory.[2]

Terrestrial Nickel Salt.—The terrestrial nickel salt consisted in part of fairly pure nickelous chloride remaining from the research of Baxter and Parsons, and in part of a specimen of an imported "cobalt-free" nickelous nitrate. The nickelous chloride solution, which had already been freed from cobalt, was first poured into a large excess of ammonia and filtered. Next, after evaporation, it was saturated with ammonia gas at 0° so that nickel ammonia chloride crystallized. Centrifugal drainage of the crystals was employed and the crystals were dissolved and crystallized again. From an ammoniacal solution of the crystals metallic nickel was deposited electrolytically upon a platinum dish, and the deposit, after being washed, was dissolved in redistilled nitric acid. Owing to the limited solubility of the ammonia chloride, the electrolysis was carried out in several operations, each deposit being dissolved in the acid solution of nickel nitrate already obtained. In order to make sure of the absence of copper, the nitrate solution was evaporated to dryness to remove excess of acid and a small sulfide fraction was precipitated by passing carefully scrubbed hydrogen sulfide into an aqueous solution of the nitrate. This sulfide consisted entirely of nickel, so far as could be determined. A second electrolytic deposition and solution in nitric acid followed, and the resulting nickelous nitrate was later combined with the purified imported material.

The imported nitrate was dissolved in water and 4 successive fractions of sulfide were removed. Although the first 3 of these contained copper in decreasing amounts, the fourth did not contain a detectable amount of copper. Cobalt could not be discovered by the Vogel thiocyanate test. After three crystallizations as the ammonia nitrate; purification was continued by two successive electrolytic depositions from ammoniacal solution, followed by prolonged electrolysis of the acid nitrate to remove any platinum which might have accompanied the nickel during solution of the deposits. After filtration through a platinum sponge crucible the combined nickel nitrate solutions were evaporated in platinum vessels and subjected to fractional crystallization, with centrifugal drainage. In order to convert the crystals into oxide they were heated in a platinum dish, first on an electric stove, finally in a large platinum boat in a porcelain muffle at redness. Next, the oxide was dissolved, in a quartz dish, in redistilled constant-boiling hydrochloric acid. Because the oxide certainly contained some undecomposed or partially decomposed nitrate, and consequently the chloride solution contained chlorine, the chloride solution was thrice evaporated nearly to dryness in a quartz dish to eliminate chlorine. The chloride was finally separated from the concentrated solution by saturating the solution with hydrogen chloride, at 0°, and the product was once recrystallized in the same way. Subsequently, the mother liquors, which had been preserved in quartz vessels, were worked up for a small quantity of additional material. The extreme mother liquor gave negative tests for iron, sulfate and platinum. The purified chloride was preserved in a quartz dish in a desiccator containing fused sodium hydroxide.

Meteoric Nickel Salt.—The source of material was the Cumpas meteorite found in 1903 near Cumpas, Sonora, Mexico. Portions of this meteorite have already been used in the comparison of terrestrial and meteoric iron,[3] as well as nickel.[1] In the investigation by Baxter and Parsons, the nickel from a little over 300 g. of meteorite was used. The owner of the meteorite, Professor John E. Wolff, Curator of the Mineralogical

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[2] See, for example, Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

[3] Baxter and Thorvaldson, *ibid.*, **33**, 337 (1911). Baxter and Hoover, *ibid.*, **34**, 1657 (1912).

Museum of Harvard University, generously provided us with about 250 g. additional. The nickel extracted from this was added to that already used in the earlier investigation, so that all the material came from the same source.

The new portion of meteorite was dissolved in nitric acid, the solution was evaporated and the ferric nitrate allowed to crystallize. The mother liquor was several times evaporated and crystallized, until nearly saturated with nickel nitrate. The crystals were all recrystallized from conc. nitric acid once or twice, and the mother liquors concentrated. In order to remove the remainder of the iron the diluted mother liquors were poured into a large excess of ammonium hydroxide and, after the precipitated ferric hydroxide had been removed by filtration and leaching with boiling water, the filtrate was evaporated to small bulk. From this solution nickel ammonia nitrate was separated by saturating the solution with ammonia. The meteoric nickel chloride used by Baxter and Parsons, after conversion to nitrate, was added at this point.

Since recrystallization of the nickel ammonia nitrate in this instance failed to give rapid separation of the cobalt, the cobalt was precipitated by the addition of a large excess of potassium nitrite and acetic acid. After removal of the potassium cobaltinitrite by filtration, the filtrate was evaporated until saturated with potassium salt and the salt was allowed to crystallize. The mother liquor was then further evaporated and crystallized several times until the solution was nearly saturated with nickel salt. Ammonia in excess was now added and after filtration the nickel ammonia nitrate was again formed by evaporation and saturation with ammonia gas. Since the mother liquor of this precipitation gave a faint test for cobalt, the crystallization of the nickel ammonia nitrate was twice repeated. No cobalt could be detected in the mother liquor of the second crystallization.

Electrolytic deposition and solution in nitric acid followed. Two small sulfide fractions were then removed, and the nickel was again deposited electrolytically. This nickel nitrate was then recrystallized twice and converted to oxide as previously described.

The meteoric oxide was changed to chloride by solution in hydrochloric acid, evaporation nearly to dryness several times with hydrochloric acid in a quartz dish, and three crystallizations. From the mother liquors a second sample of material crystallized four times was recovered.

Method of Analysis

Since we hoped that the nickelous chloride was free from all impurities except water, we expected to be able to prepare material suitable for analysis by careful dehydration of the hydrated salt. Preliminary experiments showed, however, in spite of the fact that after the second electrolytic deposition of the nickel the material was always contained in either platinum or quartz vessels, that the chloride was contaminated with a few hundredths of a per cent. of silica. We found, furthermore, that the simplest way to eliminate this silica was to sublime the nickelous chloride in a quartz tube in a current of dry hydrogen chloride. One sublimation, however, was not sufficient, owing apparently to mechanical blowing along of the relatively voluminous silica residue. All the material analyzed was sublimed three or more times except in the case of Analysis 1 in which only a single sublimation was carried out.

Preparatory to drying and sublimation, the nickelous chloride crystals were kept in exhausted desiccators containing fused sodium hydroxide, and thus were deprived of a large part of their crystal water. They were then placed in a platinum or quartz boat, in a transparent quartz tube and were heated by means of an aluminum block oven in a stream of dry hydrogen chloride to gradually increasing temperatures up to 400°, in such a way that no melting of the hydrated material occurred. Then the aluminum oven was replaced by an electrically heated sleeve, and the salt was sublimed from the boat to the tube. The residual silica was plainly visible in the boat. In the first experiments, the boat and salt were removed separately from the tube and after the tube had been cleaned the sublimation was repeated in the same way. In later experiments, without opening the tube the salt was several times sublimed along the quartz tube, leaving the silica in small deposits at different points. The silica was swept out of the tubes by means of a brush made of acid-extracted cotton cloth, and then the salt was removed and sublimed anew from the boat until siliceous residue could no longer be observed. In all but the first three experiments where a platinum boat was used, a boat of transparent fused silica was employed.

The sublimed material absorbed water only slowly; nevertheless, before being weighed, it was always again heated to the sublimation point in a current of dry hydrogen chloride. The salt, contained in a weighed platinum or quartz 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 by dry hydrogen chloride, the tube was heated by means of the aluminum block oven and subsequently the electrically heated sleeve at gradually increasing temperatures until finally the chloride began to sublime. After the tube had been allowed to cool, the hydrogen chloride 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 500 cc. of pure water in a flask, and the water was kept at a temperature not far below the boiling point until solution was complete. This usually required 18 to 24 hours. After being cooled the solution was quantitatively transferred to a glass-stoppered precipitating flask. Pure metallic silver equivalent to the chloride within a few tenths of a milligram was weighed out, dissolved in nitric acid and diluted to approximately 0.1 *N* concentration. The silver solution was then added to the chloride 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 chloride or silver, by adding equivalent amounts of 0.01 *N* silver nitrate and potassium chloride solutions to separate portions. The estimated deficiency

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

of either was added in the form of 0.01 *N* solution, the solution was again shaken, allowed to clarify and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used. A period of several weeks always elapsed between the precipitation and the final adjustment of equilibrium, so that occluded material had abundant opportunity to be leached out.

In a few analyses, after the end-point of the comparison had been reached, an excess of 0.05 g. of silver nitrate was added for each liter of solution and the analyses were allowed to stand for some time longer. Then the silver chloride was washed several times with silver nitrate solution containing 0.05 g. per liter and many times with cold water, before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically heated air-bath at 290° for at least 18 hours and weighed. Residual moisture was determined by the loss in weight when the main bulk of the precipitate was fused in a porcelain crucible. The weight of silver chloride dissolved in 1 liter of the filtrate and silver nitrate washings was assumed to be 0.00005 g. per liter.[5] Chloride dissolved in the aqueous washings, together with that obtained from the precipitating flask by rinsing with ammonia, was estimated by nephelometric comparison with standards. Since the portions of the original solution removed for nephelometric comparisons were returned, a correction was applied for the silver chloride thus introduced.[6]

	Sp. gr.	Vacuum corr. per g.
Weights	8.3	......
$NiCl_2$	3.54[a]	+0.000196
AgCl	5.56	+0.000071
Ag	10.49	−0.000031

[a] See following paper.

THE ATOMIC WEIGHT OF NICKEL

SERIES I

$NiCl_2 : 2Ag$

Ag = 107.880 Cl = 35.458

Number of analysis	Sample of $NiCl_2$	Wt. of $NiCl_2$ in vacuum G.	Wt. of Ag in vacuum G.	Wt. of Ag added or subtracted G.	Corr. wt. of Ag in vacuum G.	Ratio $NiCl_2$: 2Ag	At. wt. of nickel
1	Terrestrial	5.43432	9.04618	−0.00010	9.04608	0.600738	58.699
2		4.12207	6.86148	+0.00010	6.86158	0.600746	58.701
3		4.26173	7.09400	+0.00030	7.09430	0.600726	58.697
4		6.06602	10.09778	0.00000	10.09778	0.600728	58.697
5		3.69766	6.15449	+0.00080	6.15529	0.600729	58.697
6		4.01449	6.68065	+0.00220	6.68285	0.600715	58.694
					Av.	0.600730	58.698

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[5] Calculated from the solubility product of silver chloride at 20° as found by Kohlrausch, 1×10^{-10} [*Z. physik. Chem.*, **64,** 167 (1908)].

[6] The determinations of silver chloride were completed by Merrill J. Dorcas.

7	Meteoric	3.96766	6.60431	+0.00030	6.60461	0.600741	58.700
8		4.06949	6.77381	+0.00050	6.77431	0.600724	58.696
9		3.52204	5.86252	+0.00055	5.86307	0.600716	58.695
10		4.22509	7.03293	+0.00040	7.03333	0.600724	58.696
					Av.	0.600726	58.697
					Av. of all	0.600729	58.697

SERIES II

$NiCl_2 : 2AgCl$

Number of analysis	Sample of $NiCl_2$	Wt. of $NiCl_2$ in vacuum G.	Wt. of AgCl in vacuum G.	Loss in wt. on fusion G.	Dissolved AgCl G.	Corr. wt. of AgCl G.	Ratio $NiCl_2 : 2AgCl$	At. wt. of nickel
11	Terrestrial	3.69766	8.17814	0.00036	0.00097	8.17875	0.452106	58.692
12		4.01449	8.87863	0.00026	0.00070	8.87907	0.452130	58.699
						Av.	0.452118	58.696
13	Meteoric	3.96766	8.77434	0.00037	0.00081	8.77478	0.452166	58.709
14		4.06949	8.99966	0.00035	0.00088	9.00019	0.452156	58.706
15		3.52204	7.79001	0.00023	0.00053	7.79031	0.452105	58.692
						Av.	0.452142	58.702
						Av. of all	0.452133	58.700

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were standardized to hundredths of a milligram by the Richards[7] substitution method. The preceding vacuum corrections were applied.

The foregoing evidence seems conclusive that there is no real difference between terrestrial nickel and that contained in this meteorite. Aston[9] has recently shown that ordinary nickel contains two isotopes, of masses 58 and 60, and estimates the relative proportions as 2 to 1, respectively. In the meteorite which we have examined these isotopes are apparently present in very nearly if not exactly the same proportions as in terrestrial nickel.

It is obvious that the source of this meteorite cannot be determined. If it originated in the solar system and if, in the evolution of the solar system, the elements were produced from hydrogen, so that presumably all parts of the system contained the isotopic elements in the same proportions, it is evident that no process to which this meteorite has been subjected has altered the proportion of the isotopes of nickel. If it originated in the same way in some other system the evidence would indicate that the proportions of isotopes are not the result of chance but are determined by conditions during their formation.

So far as the atomic weight of terrestrial nickel is concerned, the value found here agrees well with that found by Baxter and Parsons, and is slightly higher than the result obtained by Richards and Cushman by analysis of nickelous bromide, 58.68. The difference, however, is very small,

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

[9] Aston, *Nature,* **107,** 520 (1921).

in view of the fact that Richards and Cushman did not have the facilities for preparing salt of the highest purity, and were forced to correct the final result for contaminations. Probably the average of all four methods is the best value which can be selected at the present time.

Richards and Cushman	$NiBr_2:2\ Ag$	58.680	Baxter and Parsons	$NiO:Ni$	58.702
	$NiBr_2:2\ AgBr$	58.683	Baxter and Hilton	$NiCl_2:2\ Ag$	58.697
	$NiBr_2:Ni$	58.682		$NiCl_2:2\ AgCl$	58.700
				Av.	58.691

Summary

1. Nickel extracted from the Cumpas meteorite is found to possess an atomic weight identical with that of terrestrial nickel.

2. The value found for both specimens is 58.70 if Ag = 107.880 and Cl = 35.458.

3. The average of this value with those obtained by Richards and Cushman, and by Baxter and Parsons is 58.69.

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THE SPECIFIC GRAVITY OF ANHYDROUS NICKELOUS CHLORIDE. THE DETERMINATION OF SPECIFIC GRAVITY BY DISPLACEMENT OF AIR

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In order to correct to the vacuum standard the weights of nickelous chloride used in the research described in the preceding paper, a knowledge of the specific gravity of this substance was necessary. This is given as 2.56 by Schiff,[1] a value which we have found much too low.

Two experimental methods have been used in our work. In one the weight of air displaced was determined,[2] in the other the weight of toluene. In the former method 2 glass-stoppered tubes provided with stopcocks were so constructed as to be of nearly the same shape and internal as well as external volume. These were first compared by exhausting the tubes and finding the difference in weight by substituting one for the other on the balance. Pure dry air was then admitted to both and the difference in weight was again found. In three experiments the differences of the difference in weight exhausted and full of air were found to

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[1] Schiff, *Ann.*, **108**, 21 (1858).

[2] Baxter and Tilley, THIS JOURNAL, **31**, 214 (1909). Baxter and Jones, *ibid.*, **32**, 298 (1910). Richards and Baxter, *ibid.*, **32**, 507 (1910).