

Summary.

1. It has been shown thermodynamically that only such liquids as have identical values of $(\partial P/\partial T)_V$ are capable of yielding solutions obeying Raoult's law under all conditions, *i. e.*, at all temperatures, pressures and compositions.

2. It is proposed to define internal pressure as $T(\partial P/\partial T)_V$, one of the terms of the thermodynamic equation of state.

3. Illustrative values are given for the internal pressures of certain liquids calculated in this way.

4. Since the internal pressure of a solution of non-polar liquids is probably a linear function of the composition expressed in terms of mol-fraction, it is probable that the difference between the internal pressures of the 2 pure liquids would determine, at least to a considerable extent, the deviation of the solution from Raoult's law. This is essentially the theory of solubility heretofore outlined and supported by abundant experimental data.

5. The criteria previously used for estimating relative values of internal pressure are shown to be in substantial accord with the thermodynamic definition of internal pressure here used, although it is theoretically preferable to use surface energy in place of surface tension.

BERKELEY, CAL.

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

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. I. THE REDUCTION OF NICKELOUS OXIDE.

BY GREGORY PAUL BAXTER AND LEON WOODMAN PARSONS.

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Because of recent suggestions as to the constitution of the atoms, especially as to the existence of isotopes, comparisons of material from different sources have become especially important. Nickel in particular is interesting from this point of view. The following investigation upon the atomic weight of meteoric nickel was completed several years ago and a brief preliminary report has already been published.¹ A similar comparison had previously been made between terrestrial and meteoric iron,² and the 2 varieties of material were found to be identical within the limit of experimental error. As nickel is the metallic element second in abundance in iron meteorites, it was a natural choice for further

¹ *Carnegie Inst., Yearbook* 14, 350 (1915).

² Baxter and Thorvaldson, *THIS JOURNAL*, 33, 337 (1911); *Z. anorg. Chem.*, 70, 348 (1911); Baxter and Hoover, *Orig. Comm. Eighth Inter. Congr. Applied Chem.*, 2, 37 (1912); *THIS JOURNAL*, 34, 1657 (1912); *Z. anorg. Chem.*, 80, 201 (1913).

investigation. Furthermore the atomic weight of terrestrial nickel has been established with a high degree of accuracy by Richards and Cushman,¹ and thus furnishes a safe starting point for comparison.

However the comparison was to be made, it was obviously desirable to apply the same method to both terrestrial and meteoric material. Since Richards and Cushman made a complete analysis of nickelous bromide, in order to avoid repeating their work and at the same time to furnish a confirmation of the atomic weight found by them, 58.678 ($A_g = 107.880$) we chose reduction of the oxide for the analytical procedure. The latter method possesses the obvious advantage of yielding a direct ratio between metal and oxygen, although the relatively small percentage of oxygen makes the method undesirably sensitive to experimental error. The experience gained by Baxter and Hoover² in the analysis of ferric oxide by reduction in hydrogen was invaluable in the present instance, as it was found possible to carry out the analytical operation in an essentially identical fashion. The chief difference in method was caused by the fact that, while ferric oxide made by ignition of ferric nitrate is practically free from occluded gases, nickelous oxide made in the same way may contain as much as 0.1% of occluded oxygen and nitrogen. Fortunately it is possible to determine the proportion of these gases and to apply a suitable correction.

The double outcome of the work has been, first to confirm Richards and Cushman's earlier value, and second to indicate the identity of terrestrial and meteoric nickel.

The problems involved in the research were as follows: (1) the purification of terrestrial and meteoric nickel; (2) the preparation of nickelous oxide in a definite condition; (3) the reduction of the oxide; (4) the determination of occluded gases. These subjects will be discussed in order.

Purification of Materials.

Water, reagents and gases were purified as previously described in many papers from this laboratory.³

In the purification of the terrestrial nickel material, dependence was placed chiefly on crystallization of nickel ammonia nitrate.⁴ "Cobalt free" nickelous nitrate was first recrystallized from slightly acid solution. The product was next dissolved and the nickel ammonia nitrate was caused to crystallize by passing into the solution ammonia gas which was generated by boiling a concentrated solution in a still constructed entirely of glass. After centrifugal drainage the salt was recrystallized once

¹ Richards and Cushman, *Proc. Am. Acad.*, **33**, 97 (1897); **34**, 327 (1898).

² *Loc. cit.*

³ See for example, Baxter and Grover, *THIS JOURNAL*, **37**, 1027 (1915).

⁴ Richards and Cushman, *Proc. Am. Acad.*, **33**, 106 (1897).

from solution in water containing ammonia. Even the original material, when tested for cobalt by adding ammonium thiocyanate and shaking with ether, according to Vogel, gave negative results.

Next, metallic nickel was deposited electrolytically upon a platinum dish from a solution of purified nickel ammonia nitrate in strong ammonia. After thorough washing of the deposit, which usually was partially coated with a slight precipitate of hydroxide, it was dissolved in the platinum dish in nitric acid which had been distilled through a quartz condenser. The solution of the nickel was very materially assisted by making the dish strongly anodic.¹ Owing to the limited solubility of nickel ammonia nitrate in ammonia, the electrolysis was distributed over many separate operations, each succeeding deposit being dissolved in the acid solution of nickel nitrate already obtained.

Although the solution of the nickel nitrate seemed to be clear, it was now filtered through a platinum sponge Gooch crucible, held in a platinum funnel, into a quartz flask, and then was evaporated in a platinum dish to the point of crystallization of the nitrate. The product was twice recrystallized from dil. nitric acid solution in platinum vessels. In all the crystallizations of the nickel ammonia nitrate and of the nickelous nitrate the crystals were centrifugally drained and rinsed in platinum Gooch crucibles, the mother liquors also being carefully received in platinum vessels.²

The meteoric material was all obtained from the Cumpas meteorite found in 1903 near Cumpas, Sonora, Mexico. This meteorite contains about 88% of iron, the remainder being chiefly nickel and cobalt. A portion of the meteorite (about 100 g.) had previously been given for the work upon meteoric iron, by Professor John Eliot Wolff, Curator of the Mineralogical Museum of Harvard University. In preparing pure iron from this material the nickel salt had been carefully preserved. Professor Wolff very generously gave us a new portion of 210 g., which also was treated for its nickel content. Nickel was extracted from the residues of the first portion by precipitating the mixed sulfides of iron, nickel and cobalt, and extracting the iron with very dilute hydrochloric acid. The bulk of the iron was removed from the second portion by dissolving the metal in nitric acid, and, after removing a small amount of insoluble matter by filtration, evaporating the solution and allowing the ferric nitrate to crystallize. The mother liquors were evaporated and a second crop of ferric nitrate was removed. All the ferric nitrate was then recrystallized from conc. nitric acid in order to preserve any included nickel salt. The remainder of the iron was removed from the combined mother liquors by adding a large excess of ammonia and filtering out the ferric

¹ *Proc. Am. Acad.*, p. 105.

² Baxter, *THIS JOURNAL*, 30, 286 (1908).

hydroxide, the precipitate being dissolved and reprecipitated, so as to avoid unnecessary loss of nickel. Because of the presence of large amounts of ammonium salts, a part of the nickel was next precipitated as sulfide, which, after washing, was dissolved in nitric acid; the remainder was deposited electrolytically and dissolved in nitric acid. Further purification was accomplished essentially as with the terrestrial material, except that the nickel ammonia nitrate was 4 times recrystallized from ammonia solution.

Although the original material contained a fairly large amount of cobalt, the mother liquors of the second recrystallization were found by Vogel's test to contain only a trace, and the last 2 mother liquors gave negative results when tested in the same way. Owing to the fact that with both kinds of material the original quantity was inadequate for all the experiments, the supply was replenished by working over the products resulting from the analytical operations. The chloride solutions obtained in the gas determinations (see page 516) were evaporated repeatedly with conc. nitric acid in quartz dishes, until all chloride had been expelled. Nickel was then deposited electrolytically and the nitric acid solution of the deposit was combined with the nitric acid solution of the metal resulting from the reduction of the oxide, and the salt was recrystallized.

Nickelous oxide was prepared from the crystallized nitrate by heating the salt to gradually increasing temperatures, at first in a platinum dish over an electric stove, then in a large platinum boat in an electrically heated porcelain tube. The temperature eventually reached bright redness and was maintained for several hours.

The Preparation of Nickelous Oxide in a Definite State.

One of the most important considerations in the research was that of finding conditions under which nickelous oxide could be obtained pure and dry. Two dangers which were to be feared were, first, dissociation of the oxide into nickel or a lower oxide during ignition, and second, combination with an excess of oxygen during cooling either to form a higher oxide or by adsorption. Evidence as to the dissociation of nickelous oxide has already been obtained by Foote and Smith¹ who obtained the following dissociation pressures of oxygen.

Temp. ° C.	Mm.
800	0.0
{ 900	0.0
1000	2.0
1100	5.5
1200	13.0
1245	18.0

¹ Foote and Smith, *THIS JOURNAL*, 30, 1348 (1908).

We also tested this point by heating nickelous oxide contained in a platinum boat in an exhausted quartz tube and measuring the pressure with a McLeod gage. At the highest temperature reached, which, although not accurately measured, we estimate to be about 1000° , the pressure was only 0.01 mm. In another experiment a platinum boat containing about 8 g. of nickelous oxide which had been ignited in air until the weight was constant, was ignited at about 1000° at a pressure of 8 cm. of air and allowed to cool in air at this pressure. When the boat and its contents were reweighed no loss in weight was found, in fact the system gained 0.02 mg., a difference, however, within the error of weighing the system. In the light of this evidence there seems to be no danger of loss of oxygen by nickelous oxide when it is ignited in air below 1100° , a temperature which was not exceeded in our experiments.

In order to find out whether nickelous oxide takes up oxygen at higher oxygen pressures than that of the air, a specimen of oxide which had been heated to constant weight in air was ignited and cooled in a current of pure dry oxygen at atmospheric pressure. A gain in weight of 0.27 mg. was found. So small a gain as this certainly does not indicate the formation of a higher oxide of nickel.

In this connection it is interesting to note that Baxter and Hoover¹ found ferric oxide to exhibit a similar gain when ignited and cooled in oxygen after ignition to constant weight in air. At the time, since the evidence seemed ample that ferric oxide does not dissociate in air at temperatures below 1200° , the difference in weight when ferric oxide is ignited in oxygen and in air was laid to occlusion of either oxygen or a higher oxide.

More recently another explanation has been proposed by Hostetter and Sosman² who have shown that ferric oxide and the magnetic oxide form a series of solid solutions,³ the oxygen pressure from which rises rapidly as the proportion of magnetic oxide approaches zero. Between 1100° and 1300° this dissociation can be measured by the change in weight when ferric oxide is heated and rapidly cooled in oxygen and air. With 12 g. of oxide at 1100° this difference was hardly measurable, at 1150° about 0.5 mg. and at 1200° about 1.0 mg. They also find that "at a temperature of 1200° or higher, the platinum reacts with the ferric oxide, absorbing iron and giving off oxygen; the net result is a loss in total weight, but a gain in the weight of the boat as determined after removing the oxide and cleaning the boat in hydrochloric acid. Below 1200° there is still a continuous loss in total weight, though less than at higher temperatures; but the weight of the boat alone shows an equivalent loss.

¹ Baxter and Hoover, *THIS JOURNAL*, **34**, 1663 (1912).

² Hostetter and Sosman, *THIS JOURNAL*, **38**, 1188 (1916).

³ *Ibid.*, **38**, 807 (1916).

In other words, the ferric oxide, while remaining constant in weight, seems to have acted as a catalyzer for the oxidation of the platinum by gaseous oxygen."

If this explanation of the gain in weight of the ferric oxide when ignited in oxygen is the correct one, the weights of ferric oxide given in the paper by Baxter and Hoover are on an average about 0.004% too small. On applying a correction of this magnitude, the atomic weight of iron as determined by reduction of the oxide is lowered by 0.007, becoming 55.840. This value agrees much more closely with that obtained from ferrous bromide¹ by comparison with silver, 55.838, if $Ag = 107.880$; 55.833 if $Ag = 107.870$. The original small difference between the results of the analyses of bromide and oxide is not disturbing, however, because of the difficulty in securing complete reduction of ferric oxide, so that the better agreement after applying the above correction can not be taken as evidence that the correction is justifiable. In any case the uncertainty is a small one.

An analogous explanation of the higher weight of nickelous oxide after ignition in oxygen, would seem to go beyond the facts now known. For the present at any rate we have preferred to retain the weight after ignition in air as representing nickelous oxide free from higher or lower oxides.

Method of Analysis.

During both the preparatory treatment and the reduction the nickelous oxide was contained in a platinum boat completely lined with thin platinum foil. The lining was renewed in each experiment owing to incipient alloying of the nickel with the platinum. In this way alloying with the boat itself was completely prevented.

Since Baxter and Hoover,² who used a similar expedient, found that both the boat and its lining weighed slightly more after ignition in an atmosphere containing oxygen than after ignition in hydrogen, we also tested this point, with similar results.³ The boat was ordinarily prepared for an analysis by scouring with sand, boiling with hydrochloric acid, igniting in air and boiling with nitric acid. The foil was shaped and separately treated in the same way except that the scouring with sand was omitted, and then, after the foil had been fitted to the boat, the two were again boiled with nitric acid. Ignition in air was carried out by placing the lined boat in a quartz tube, which was part of a Richards and Parker bottling apparatus, and igniting to bright redness in a current of pure air.⁴

¹ Baxter, Thorvaldson and Cobb, *THIS JOURNAL*, 33, 319 (1911); *Z. anorg. Chem.*, 70, 325 (1911).

² Baxter and Hoover, *THIS JOURNAL*, 34, 1663 (1912).

³ Baxter and Hoover suggested the obvious explanation that the difference in weight is due to the presence of iron or a similar metal in the material of boat and lining.

⁴ Air was purified in the same way and with the same apparatus as by Baxter and Hoover.

The boat was then transferred to the weighing bottle and was weighed by comparison with a counterpoise similar in shape, volume and material. Ignition in a current of the purest electrolytic hydrogen¹ followed. The loss in weight during the ignition in hydrogen varied from 0.08 mg. to 0.52 mg. In only 2 experiments did it exceed 0.28 mg. and usually was not more than 0.2 mg. Varying the ignition period in air or hydrogen produced no perceptible effect. Furthermore ignition in air after ignition in hydrogen always caused the weight of the boat to return to very nearly its original value after the first ignition in air, showing that the loss was not due to volatilization of material from the boat. This second ignition in air was always carried out in order to afford a check upon the earlier weights.

Since in the course of an analysis the boat with nickelous oxide was first ignited in air and then the system was heated in hydrogen, it was obviously necessary to know the change in the weight of the boat itself during this treatment. In each experiment allowance was made for the observed loss during ignition in hydrogen.

Richards and Rogers² first pointed out the fact that oxides prepared from nitrates even after intense ignition still contain important proportions of occluded gases. While Richards and Baxter³ found ferric oxide to be an exception in not retaining perceptible amounts of gas, Richards and Rogers⁴ found nickelous oxide, on the other hand, to show this tendency to a marked degree, their experiments yielding between 0.3 and 0.4 cc. of gas per g. of oxide. In preliminary experiments with oxide ignited to a temperature certainly no higher than in Richards and Rogers' experiments, we found somewhat less than 1 cc. of gas per g. of oxide. The latter proportion is large enough to make the preliminary ignition of the oxide in such a fashion as to secure a constant proportion of gas, a very important matter. Fortunately we found in practice that fairly large variations in the treatment produced only small variations in the percentage of occluded gas.

This was shown as well by the constancy in weight of the oxide during continued ignition in air after it had been ignited for a few hours. One specimen when heated for 4 periods of 4 hours each, weighed 6.14216, 6.14034, 6.14001, and 6.13999 g. Here the earlier losses are caused by the gradual escape of occluded gases, while the ultimate constancy in weight both shows that this escape of gases has practically ceased and is further evidence that under these conditions nickelous oxide does not lose appreciable amounts of oxygen either by dissociation or by reduction owing to contact with metallic platinum.

¹ Also purified as by Baxter and Hoover, *loc. cit.*

² Richards and Rogers, *Proc. Am. Acad.*, **28**, 200 (1893).

³ Richards and Baxter, *ibid.*, **35**, 257 (1900).

⁴ *Loc. cit.*, p. 208.

Since it was obviously impossible to determine the occluded gases in the specimen of oxide used for reduction, the expedient was used of preparing a sufficient quantity of oxide in as nearly as possible an identical fashion so that different portions of the same sample of oxide could be used for both reduction and gas determination experiments. After the pure nitrate of each sample had been ignited for several hours, in portions, in the porcelain muffle at 1000° , it was mixed as thoroughly as possible by gentle grinding in a large agate mortar. One or more portions were then heated for from 1 to 2 hours in the weighed boat at a definite temperature, about 800° , and were then weighed and analyzed by reduction. Other portions were heated in exactly the same way and were then analyzed for occluded gases as described on p. 516.

The Reduction of Nickelous Oxide.

In order to reduce the nickelous oxide, the boat with its weighed charge of oxide was placed in the quartz tube of the bottling apparatus, which could be connected with a supply of pure electrolytic hydrogen as well as of pure air. The heating of the oxide was effected by means of a removable coil of Nichrome ribbon and the temperature was maintained at a little above 600° until water ceased to be formed in quantity sufficient to condense in the tube. Then the temperature was raised to about 900° , as determined with a platinum-platinum rhodium thermocouple, and was maintained at that point continuously for about 50 hours in most cases. This period was always found ample to secure complete reduction, for a second ignition at 900° for 16 hours in no case produced a change in weight of as much as 0.1 mg., the extremes being -0.05 mg. and $+0.07$ mg. Furthermore evidence was obtained in the course of the work that a lower temperature was sufficient to produce complete reduction, for in one experiment metal which had been reduced at about 750° , when reheated in hydrogen at 900° remained essentially constant in weight.

Before transferring the boat to the weighing bottle, after the reduction was complete, it was allowed to cool in hydrogen and then the hydrogen was exhausted from the tube by means of a Töpler pump before admitting dry air. This step was shown to be necessary by Baxter and Hoover¹ in the case of reduced iron, who found that, if the hydrogen is merely displaced by a current of air, water is formed by the catalytic effect of the platinum or iron or both. After the air had been once admitted the tube was again exhausted and air admitted. Finally a current of air was passed through the bottling apparatus for 15 to 30 minutes before the boat was bottled and the weighing bottle removed to a desiccator preparatory to weighing. When the system had been weighed the first time, ignition in hydrogen for an additional period of about 16 hours was

¹ *Loc. cit.*, p. 1666.

carried out. As has already been stated no further loss in weight was ever detected.

Since nickel possesses the property of occluding hydrogen to a greater extent than most metals, this matter was especially investigated in one experiment by allowing the nickel, which had been brought to constant weight in the usual way after cooling in hydrogen, to cool in a vacuum. After admitting air the metal was found to have gained instead of lost, but by the unimportant amount of 0.00004 g.

So far as we could determine no difficulty existed from the volatilization of platinum. This was evident from the fact that the weight of the empty boat when ignited for long periods in either air or hydrogen remained constant within a few hundredths of a milligram. Less convincing evidence in the same direction lies in the constancy in weight of the boat containing nickelous oxide, and the reduced metal. Hostetter and Sosman¹ found only slight losses at higher temperatures than those we employed, but Burgess and Sale² obtained considerable losses at 1200°.

That metal actually volatilized from the boat was evident from a slight black sublimate which appeared in the quartz tube in certain experiments. The quantity of material was so small, however, that a qualitative examination failed to indicate its nature.

All weighings were made on a No. 10 Troemner balance sensitive to 0.02 mg., which was used only for the most exact work. The weighing bottle was always compared by substitution for a counterpoise of nearly the same weight, shape and volume. The weights were standardized to hundredths of a milligram by Richards' method.³ Ample time was always allowed the boat and counterpoise to come to equilibrium with the atmosphere of the balance case.

The weights of nickelous oxide and nickel are corrected to vacuum by adding 0.000035 g. per gram of nickelous oxide and subtracting 0.000008 g. per gram of nickel, the densities of these substances and the weights being assumed to be 6.7, 8.8, and 8.3 respectively.

Determination of Occluded Gases.

The occluded gases in the nickelous oxide were found by dissolving the oxide in conc. hydrochloric acid and, after measurement, determining the oxygen content by absorption. The apparatus was similar to that already used by Richards and Rogers⁴ for the purpose.

A weighed quantity of oxide contained in the small flask was covered with pure boiled water and the flask was exhausted as far as possible with a water pump in order to free the oxide from entangled gases. The flask

¹ *Loc. cit.*, p. 1191.

² Burgess and Sale, *J. Ind. Eng. Chem.*, **7**, 561 (1915).

³ Richards, *THIS JOURNAL*, **22**, 144 (1900).

⁴ *Loc. cit.*

was frequently agitated during the exhaustion to facilitate the escape of gases. The system was then completely filled with cold freshly boiled 20% hydrochloric acid solution, which for a short period was without effect upon the oxide. In order to promote the solution of the oxide, the flask was then warmed and the gas evolved was collected in the side arm. As soon as solution was complete the gas was drawn into a buret of small bore and carefully measured. Next the gas was transferred to a small Hempel pipet containing potassium pyrogallate and the residue after absorption of the oxygen was remeasured. Because of the small difference in density between oxygen and nitrogen, the determination of the proportion of total gas was far more important than that of the proportion of oxygen. On this account pains were taken by working rapidly to avoid loss of gas through solution in the aqueous liquid. With most specimens of oxide 2 or more gas determinations were made. Unfortunately the quantity of meteoric material was so small that except with one specimen only one gas run could be carried out.

Results.

In the following tables are given the data for all experiments except one preliminary analysis for which no comparable gas determination was made.

TABLE I.
The Atomic Weight of Nickel.
O = 16.000.

Number of analysis.	Sample of NiO. ^a	Weight NiO in vacuum. G.	Weight of occluded gases. G.	Corrected weight of NiO in vacuum. G.	Weight of Ni in vacuum. G.	Ratio Ni : O.	Atomic Weight of nickel.
1	T ₁	6.11685	0.00723	6.10962	4.80103	3.66886	58.702
2	T ₁	6.42056	0.00760	6.41296	5.03963	3.66964	58.714
3	T ₁	6.91857	0.00820	6.91037	5.43008	3.66825	58.692
4	T ₁	4.60629	0.00546	4.60083	3.61530	3.66838	58.694
5	T ₂	5.57759	0.00654	5.57105	4.37793	3.66931	58.709
6	T ₃	5.59888	0.00664	5.59224	4.39444	3.66876	58.700
					Average	3.66887	58.702
7	M ₁	6.66401	0.00732	6.65669	5.23021	3.66650	58.664
8	M ₂	4.46324	0.00705	4.45619	3.50201	3.67018	58.723
9	M ₃	4.65291	0.00483	4.64808	3.65209	3.66680	58.669
					Average	3.66783	58.685
					Average of all 9 analyses	3.66852	58.696

^a T indicates terrestrial, M meteoric material.

In view of the rather large correction for occluded gases and its attendant uncertainty, the agreement between the results of the experiments with terrestrial material may be considered fairly satisfactory. The difference

TABLE II.
The Gas Content of Nickel Oxide.

Sample of NiO.	Weight of NiO. G.	Volume of gas. Cc.	Pressure. Mm.	Temperature ° C.	Volume per cent. of oxygen.	Volume per gram. NiO at 0° and 760 mm. Cc.	Per cent. of gas.
T ₁	2.325	2.36	755	20	11.9	0.918	0.1168
T ₁	4.418	4.42	759	20	10.9	0.912	0.1157
T ₁	4.389	4.62	767	22	13.0	0.958	0.1220
T ₁	3.249	3.34	767	22	9.9	0.935	0.1187
					Average	0.931	0.1183
T ₂	3.061	2.99	764	22	7.7	0.888	0.1123
T ₂	3.098	3.38	751	24	10.4	0.962	0.1221
					Average	0.925	0.1172
T ₃	2.585	2.64	757	22	4.2	0.917	0.1153
T ₃	2.012	2.16	757	22	9.3	0.965	0.1223
T ₃	2.739	2.88	753	24	7.3	0.930	0.1175
					Average	0.937	0.1184
M ₁	3.236	3.29	766	23	6.1	0.882	0.1113
M ₁	1.979	1.91	752	24	6.3	0.856	0.1080
					Average	0.869	0.1097
M ₂	1.177	1.67	757	26	8.4	1.248	0.1580
M ₃	3.150	2.94	756	26	7.8	0.820	0.1037

between the highest and the lowest value, 0.022, corresponds to a difference in the weight of nickel obtained from 5 g. of oxide of 0.32 mg., or to a difference of 0.4 mg. in the weight of the oxide itself. The extreme difference between the results with meteoric nickel is between 2 and 3 times as large, 0.059; while the difference between the average result with terrestrial and that with meteoric nickel is 0.017. Although the lowest 2 results were obtained with the meteoric sample, the highest result also was found with the same material. All things considered, the evidence seems to indicate identity of the 2 sorts of material. We feel, however, that while it seems unlikely that a real difference exists, the point should be tested further and plans have been made to do this by a different method.

The average atomic weight found with terrestrial material, 58.70, which is essentially identical with the average result of all 9 experiments, is 0.02 unit higher than the result found by Richards and Cushman by analysis of nickelous bromide, 58.68 (Ag = 107.880). Because of the comparative ease with which constant weight of the metal was secured, incomplete reduction is not a probable cause of the difference. If the weight of the oxide after ignition in air is too low owing to dissociation and the weight after ignition and cooling in oxygen is used instead (see p. 511), a value nearly 0.02 unit lower is obtained, and the above difference disappears.

As has been emphasized before, however, the large correction for occluded gases is a weak point in the evidence, and the fair agreement

between the results of widely different methods is to be considered reassuring rather than otherwise.

The outcome of the investigation may be summarized as follows.

1. Nickelous oxide prepared by ignition of the nitrate at about 1000° is found to contain 0.11% of occluded gases.

2. After a correction for the gas content is made, the oxide is found by reduction in hydrogen to contain 0.78582% of nickel, whence the atomic weight of nickel is 58.70.

3. The atomic weight of meteoric nickel is found by an exactly similar method to be 58.68, a difference within the experimental error.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 129.]

THE EQUILIBRIUM BETWEEN NITRIC OXIDE, NITROGEN PEROXIDE AND AQUEOUS SOLUTION OF NITRIC ACID.

BY CHARLES L. BURDICK AND E. STANLEY FREED.

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1. Introduction.

The absorption and conversion into nitric acid of the nitrous gases, such as are produced by the processes of ammonia oxidation or arc fixation of nitrogen, have been found to be attended with considerable difficulty, making necessary the installation of large and expensive systems of reaction chambers and absorption towers in order to accomplish the oxidation and absorption of these nitrous gases. The mechanism of this process and the conditions controlling it seem not to have been made the subject of any very precise or careful study, so in accordance with a suggestion of Prof. A. A. Noyes, at the time Consulting Chemist to the Ordnance Department, an investigation, part of the results of which are here presented, was carried out.

It was hoped that the careful study of the mechanism of the absorption process would yield information which would enable more favorable conditions for the carrying on of the reactions to be established. Early it was seen that the reactions of importance were limited to two, namely, (1) $2\text{NO} + \text{O}_2 = 2\text{NO}_2$; (2) $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$.

The first of these reactions under ordinary conditions, that is, with dilute gases, progresses very slowly and the second, although it goes on with great rapidity, comes to an equilibrium considerably short of completed reaction.

Reaction 2, namely, the absorption of nitrogen peroxide in water to form nitric acid with the simultaneous liberation of nitric oxide is the