with bullocks' blood diluted with one-third its volume of water. The resulting briquettes set somewhat more quickly, and were very hard and firm. Their average tensile strength was :

After exposure to water during thirty-seven days, 68.3 pounds.
"   "   " air   "   "   "   " 69.8   "

Thus showing a gain over the water-tempering of ten per cent. for the briquettes set in air.

RENSSELAER POLYTECHNIC INSTITUTE,
June, 1894.

SOME ALLOYS OF IRON WITH MOLYBDENUM, TUNG-STEN AND CHROMIUM AS SOLUTIONS.

BY JAMES S. DE BENNEVILLE.

THE results obtained by the action of silver nitrate on a ferro-tungsten of markedly heterogeneous character appeared to make a study of the reactions of the alloys of iron with the sixth family of interest. In the former paper[1] it was indicated, that a connection existed between the combining ratio of the two constituents and the chemical action of the compound toward reagents. The probable high valency of the iron atom in these metallic compounds, indicated by the fact that all that element appeared to be in combination with the tungsten ; the chemical stability of the alloy and the very marked influence of the constituent tungsten on the compounds were noted, as also the nature of the alloy regarded as a solution. The work involved in the present paper is an attempt to broaden the scale of this previous investigation of one compound of a very interesting series. Alloys of the ferro compounds with the tungsten group were examined. The physical properties of these compounds as influencing their chemical properties were noted and the compounds analyzed and their quantitative composition established. The action of the weak solvent, silver nitrate, has been determined as also the reactions of the alloys with liquid and fused solvents. The discussion of the results obtained and their application to these alloys as solutions involved a short summary of the opinions expressed by others on valency and the nature of solution and the intimate connection between that state of matter and alloys.

[1] This JOURNAL, May, 1894.

The alloys were prepared by melting down cast iron with the metals at a white heat in a small Fletcher furnace working with a blast. One hour after reaching a white heat, the cast iron took up the quantity of the second metal indicated in the analyses. The melts were completely liquid and when cold were obtained in the form of buttons weighing twenty-five to thirty grams. The alloys investigated were ferro-molybdenum, ferro-tungsten and ferro-chromium.

FERRO-MOLYBDENUM.

Unalloyed molybdenum is practically infusible in furnaces working with blast. The metal probably could be obtained as a melt in the electric furnace as used by Moissan[1] in his investigations on the reduction by carbon of refractory oxides. As with many other metals of high melting-point, however, its alloys with the more fusible metals can be obtained at a much lower temperature. So with these iron compounds.

The information on these alloys is mainly due to Berthier and Thompson. Berthier states that molybdenum iron alloys are analogous to those with tungsten, a two per cent. molybdenum iron being fusible, very hard, brittle, but tenacious. Billings found that with one per cent. molybdenum, iron became red-short and worthless.[2] Thompson found that iron alloyed with molybdenum more readily than with any other metal. With equal parts of iron and molybdenum the alloy was fusible with the blowpipe. With thirty-three per cent. iron and sixty-seven per cent. molybdenum an alloy of a clear gray-white color was obtained. Twenty per cent. molybdenum iron was whiter than iron, very hard, brittle, tenacious, with granular fracture.[3]

The method of experiment followed was the use of the weak solvent silver nitrate to separate unstable alloys or the metals themselves from the more stable compounds. With the exception of chromium the elements under discussion all react with solution of the silver salt. Dr. Edgar F. Smith has shown[4] that the reaction between metallic molybdenum and the silver

---

[1] Since this paper was written Mr. Moissan has reduced molybdenum in his electric furnace obtaining the metal as a melt, *i. e.*, fused mass. See *Bull. Soc. Chim.*, [3], II, 857—5 Sept., *1894.*

[2] Howe, Metallurgy of Steel, p. 86.

[3] Hiorns, Mixed Metals, p. 359.

[4] *Ztschr. anorg. Chem.*, I, 360.

salt is very exact, silver being reduced to metal and molybdic acid formed. The ratio being Mo : 6Ag. With these iron alloys, the reaction is very complex owing to secondary reactions. The molybdenum is converted into the lower oxide of a blue color. On digesting with the neutral silver salt, no white precipitate of molybdic acid separates.

Separate portions of the alloys were crushed in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then digested with excess of solution of silver nitrate. After twenty-four hours these solutions were decanted and the residue washed by decantation with water. The residue from treatment with neutral silver salt was digested with ammonia. This solution was filtered and added to the first and iron and molybdenum determined. The final residue was treated with nitric acid and, after removal of the silver, molybdenum and iron determined. By this method were obtained: 1. Iron replacing silver. 2. Molybdenum replacing silver. 3. Iron and molybdenum in stable combination.

The quantity of iron extracted by hydrochloric acid was determined. The alloys were not completely decomposed by the acid. A considerable portion of the iron was attacked but the molybdenum would be acted on only to a small extent and would appear in any ratio calculated between total iron and total molybdenum found in the residue. This did not afford a method of separating alloys soluble in the acid solvent.

The experimental results tabulated gave:

Alloy A. Nos. 1–4, close grained crystalline mass showing under the glass segregations marked by a slight yellowish tinge. This sample was fused to a clear button. Brittle, hardness 7, scratching quartz but not topaz. Fracture granular, of a silver-white color, gradually assuming, on exposure to air, a yellowish and in places a brownish tint. Strongly magnetic, not malleable, sp. gr. 8.182.

Alloy B. Nos. 5–12, appearance as with alloy A. strongly magnetic, somewhat malleable,[1] brittle, hardness seven, not so readily oxidized on exposure of fresh fracture to the atmosphere, sp. gr. 7.830

[1] Used relatively. Flattened slightly before crushing.

These alloys slo⸱ ly decompose water on boiling.   The terms "free" iron and "free" molybdenum are used to indicate the iron and molybdenum replacing silver in the silver nitrate. "Free" is used in the same sense throughout the remaining experiments.

I. MOLYBDENUM ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

| | A. | B. | C. | D. | E. | F. | G | |
No.	Total Fe.	Total Mo.	"Free" Fe.	"Free" Mo.	Residual Fe.	Residual Mo.	Ratios A : B	E : F
1 ...	0.6710	0.3290	0.3638	0.0666	0.3072	0.2624	3.50 : 1	2 : 1
2 ...	0.7106	0.2894	0.2608	0.1250	0.4498	0.1644	4.22 : 1	4.70 : 1
3 ...	0.6694	0.3306	0.2162	0.0487	0.4532	0.2819	3.47 : 1	2.75 : 1
4 ...	0.7084	0.2916	0.4932	0.1728	0.2152	0.1188	4.16 : 1	3.15 : 1
5 ...	0.8703	0.1297	0.7185	0.0666	0.1529	0.0620	11.50 : 1	4.23 : 1
6 ...	0.8893	0.1107	0.7154	0.0682	0.1529	0.0635	13.80 : 1	4.13 : 1
7 ...	0.8584	0.1416	0.5706	0.0775	0.2879	0.0640	10.40 : 1	7.73 : 1
8 ...	0.8104	0.1896	0.5328	0.1344	0.2776	0.0552	7.30 : 1	8.63 : 1
9 ...	0.7882	0.2118	0.4634	0.1260	0.3248	0.0858	6.40 : 1	6.40 : 1
10...	0.6670	0.3330	0.4939	0.1612	0.1731	0.1718	3.43 : 1	1.73 : 1
11...	0.8414	0.1586	0.4832	0.0777	0.3582	0.0809	9.10 : 1	7.62 : 1
12...	0.8883	0.1117	0.5406	0.0574	0.3478	0.0542	13.70 : 1	11.10 : 1

Taken for analysis 0.20–0.25 gram.

II. MOLYBDENUM ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	A — 13.	B — 14.
Iron	0.5982	0.6933
Per cent. of total iron	86.74	83.86

Taken for analysis, two grams.

III. MOLYBDENUM ALLOYS, CARBON, SILICON, PHOSPHORUS.

		Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
No.	Sample.					
15	Pig iron[1]	2.99	0.37	2.62	2.92	0.33
16	Alloy A	2.90	0.17	2.73	0.74	0.31
17	Alloy B	2.97	0.20	2.77	0.66	0.30

A third sample was obtained by melting cast iron in the presence of twice its weight of molybdenum.   At the heat obtained this was fused down to an irregular mass but a clean button was not obtained.   It was very crystalline in structure, the luster in places being of the nature of "parrot" copper ore. The portion unattacked by the weak solvent is of interest, the remainder evidently containing unalloyed molybdenum.   The "residual" iron and molybdenum obtained, gave :

[1] Sp. gr., 6.980.

IV. MOLYBDENUM ALLOYS, C.

No.	Residual Fe.	Residual Mo.	Ratio.
18	0.7394	0.2606	4.85 : 1
19	0.4267	0.5733	1.40 : 1
20	0.1320	0.8680	1 : 5
21	0.0770	0.9230	1 : 7

By HCl 42.63 per cent. of total iron dissolved.

In table I the analyses appear to show that the silver nitrate acts not only on unstable alloys but on iron as such or on molybdenum as such. The attacked and unattacked portion varies considerably through the mass. Table IV indicates the influence of mass action. The quantity taken for experiment (0.20–0.25 gram) was small and any marked differentiation would appear. If iron be regarded as limited in its lower compounds by divalency the formula Fe_3Mo (molybdenum being regarded as hexavalent) would represent the saturation-point corresponding to 63.64 per cent. iron and 36.36 per cent. molybdenum. If now the alloy contain less molybdenum than thirty-six per cent., either: 1. The iron in excess must be regarded as present as such in the same sense that water in excess is present in an unsaturated solution, or 2, the alloy is analogous to a cryohydrate, there being present a definite compound or compounds and the excess of the solvent, forming one homogeneous system in its liquid and melted condition, but in the solid (*i. e.* frozen) form making up a system in which the parts bear a definite relation to each other as in cryohydrates, or in which the excess of the solvent is present in a form analogous to ice in such mixtures. 3. That while there may be definite compounds formed in the alloy yet the main bulk of the system is in chemical union, all the iron being united to all the molybdenum no matter how large the quantity of either constituent. 4. That in solution the iron and the molybdenum may be in combination up to the full power of their respective valencies, but that this valency is not exercised (or its power decreases) on cooling, on which the more stable forms of combination appear. Iron or molybdenum in excess may then be present in the solidified alloy and it is not unlikely that owing to the very high melting-point of molybdenum that, as the fusing-point of the mixture rises, a part of the molybdenum exists as a mechan-

ical mixture either never having been in combination with the iron or separating out from the alloy on cooling and the exercise of the more stable valency.[1] The action of a weak solvent, as of any solvent, is mainly dependent on the affinity between the constituents of the compound. That iron and molybdenum form a stable alloy is evidenced by the fact that the action of strong hydrochloric acid fails to decompose these compounds but leaves a residue more or less rich in iron. The silver nitrate can then be regarded as a solvent of a definite compound or compounds in the solidified alloy acting on these and on the metal in excess but failing to attack the more stable compound. Both iron and molybdenum react with the silver salt and the failure of this reaction to take place with considerable percentage of the alloys also points to a strong affinity between the two elements. As with tungsten this is to be expected from the nature of molybdenum as semi-metal. Increased percentage of molybdenum accompanied increased brittleness and decrease in fusibility. The alloys were decomposed by nitric acid which converted the molybdenum to molybdic acid; by potassium bisulphate with evolution of sulphurous anhydride; by fusion with mixture of sodium carbonate and saltpeter; hydrochloric acid left a residue rich in molybdenum.

Analytical Methods.—The direct analysis of these molybdenum alloys (for iron and molybdenum) can be readily made by two methods. 1. The powdered alloy can be fused with oxidizing mixture with addition of caustic soda, cooled and lixivated in water and the soluble sodium molybdate separated by filtration from the residual ferric hydroxide. The molybdenum can then be determined by neutralizing with nitric acid the whole, or an aliquot portion of the solution of alkali molybdate, using methyl-orange as an indicator, and precipitating in the neutral solution as lead molybdate according to Chatard's method.[2] 2. A convenient method of analysis was found by solution in nitric acid. Excess of acid is removed by evaporation and excess of ammonia and ammonium sulphide is then added, digesting in a warm place for at least an hour and acidifying with hydrochloric acid and boil-

1 Lothar Meyer, Modern Theories of Chemistry, pp. 307, 308.

2 Fresenius, Quantitative Analysis, p. 353.

ing. Hydrogen sulphide is then passed through the hot solution until saturation. In the indirect analysis (with silver nitrate), after removing silver by hydrochloric acid, it was found necessary to oxidize the boiling solution by nitric acid otherwise the molybdenum remains partly in the form of the lower oxide which does not appear to be readily converted to sulphosalt and on dissolving the iron sulphide in hydrochloric acid the blue color indicates the molybdenum in solution. The precipitated molybdenum trisulphide is oxidized by nitric acid, filtered from any residual sulphur and the cold acid solution precipitated by barium nitrate avoiding an excess. The barium sulphate is filtered off, the filtrate neutralized by ammonia, leaving it barely but distinctly acid, and the molybdenum precipitated as lead molybdate. Throughout these analyses iron is determined volumetrically in sulphuric acid solution by titration with permanganate. A very pure zinc was used for reduction.

Table III explains itself. There appears a decided decrease in the percentage of silicon and a slight increase in the graphitic carbon over the combined. The phosphorus shows no change. The two analyses are only suggestive not indicative of these differences as due to the molybdenum. In determining both phosphorus and silicon the formation of phospho- and silicomolybdate,[1] at least partly soluble, must be taken into account. The graphitic carbon is that determined after treating the iron with hydrochloric acid. In ordinary steels the combined carbon is readily decomposed by the acid and the residue in these irons is probably free from combined carbon. Combustion of the powdered alloy only gave partial results. These alloys slowly decompose water on boiling. Their heterogeneity was apparent on so treating fragments of the alloys, brownish and yellowish spots due to oxidation being scattered over the exposed surface. These were distinct from the iron rust which was also formed. Metallic molybdenum decomposes water on boiling. The richer the alloy in molybdenum the more readily it decomposes water.

FERRO-TUNGSTEN.

The experiments in a former paper[2] on ferro-tungsten were

[1] See under ferro-tungsten.

[2] This JOURNAL, May, 1894.

made on an alloy containing, on averaging twelve analyses, 53 per cent. iron and 46.3 per cent. tungsten and of 10.14 sp. gr.[1] A second alloy of eighteen per cent. tungsten was made. The method of preparation and experimentation followed was the same as with the molybdenum compounds. The action of tungsten on silver nitrate has been found by Smith[2] to be analogous to that of molybdenum. Tungstic acid is formed and silver reduced to metal, the ratio being $W : 6Ag$.

In the alloy previously described (Nos. 22–26) it was found that the iron and tungsten were present in a very stable form, only a small percentage of tungsten and iron being attacked by the silver solution. In view of the more extended experiments this soluble portion can be regarded as a part of the alloy more readily attacked than the residue. Schneider separated from a high tungsten iron what appeared to be two alloys, one magnetic and the other non-magnetic corresponding to the formulas Fe_3W and Fe_8W. He used hydrochloric acid as a means of separation from the soluble iron.[3] It must be taken into consideration, however, that tungsten is but little attacked by hydrochloric acid and in the case of an alloy of which the iron was readily attacked by acid it would be left in the residue and vitiate any ratio calculated from analysis of that residue. With silver nitrate, however, there is a definite reaction between the silver and the constituents of the alloy. They both act on it, although (and the varying ratios point to the latter alternative) the doubt exists as to whether the silver salt attacks a definite compound or varying quantities of alloys of different composition. The chemical inertness of these alloys is much more conspicuous than with the molybdenum compounds. Whatever compounds are formed in these alloys, are probably compounds made up of atomic linking and not the union of like molecules. These compounds are formed from a solution, and Heycock and Neville on determining the molecular weights of metals dissolved in sodium found for copper, silver, lead, antimony, zinc, cadmium and mercury, one atom in the molecule. Ramsay obtained like results by

[1] I am indebted to Dr. Wm. H. Wahl through Mr. F. Lynwood Garrison for this alloy.
[2] I am indebted to Dr. Smith in a private communication for reactions of molybdenum and tungsten bearing on these alloys. See *Ztschr. anorg. Chem.*, 1, 360.
[3] Howe, Metallurgy of Steel, p. 81.

determination of the variation of vapor tension of mercury.[1]

Analytical Methods.—The best method for direct analysis of these compounds was found to be fusion with the oxidizing mixture with addition of caustic soda and lixiviation in water. The soluble sodium tungstate was filtered from the residual ferric hydroxide and the tungsten precipitated in neutral solution by mercurous nitrate according to the method of Wolcott Gibbs.[2] In the indirect analysis, to the solution obtained on filtering from the unattacked residue, ammonia in excess was added and then ammonium sulphide. After digesting in a warm place for an hour this solution was acidified by hydrochloric acid and boiled. Hydrogen sulphide was then passed through it to saturation and the precipitate of silver sulphide and tungsten trisulphide filtered off and tungsten separated from silver by solution in ammonium sulphide. After removal of ammonium salts and oxidation, tungsten was determined as tungstic oxide, WO_3. The unattacked residue, after removal of silver,[3] was fused with oxidizing mixture and the sodium tungstate separated from the residual ferric hydroxide by lixiviation in water and filtration.

The experimental results gave:

Alloy D, Nos. 22–26.[4] Crystalline with marked differentiation throughout the mass showing a number of cleavage planes of a pyritous appearance, also lining the cavities. The body or cementing portion of the alloy being finely crystalline but without the luster of the molybdenum compounds. Hard, brittle and tough. Sp. gr. 10.14. Alloy E, Nos. 26–29. Fine-grained crystalline mass without visible differentiation. Color, dark gray, the original pig iron being lighter in color. Brittle. Hardness barely 7. Sp. gr. 7.935. This alloy scratched glass readily; quartz only with difficulty. On boiling in water and subsequent oxidation this alloy showed patches of brown, yellow and bluish spots distinct from the iron "rust" formed.

---

[1] Mendelejeff, Principles of Chemistry, 1, 123. Ramsay obtained with barium, calcium, and potassium abnormal results, the number representing the first two metals being one-half the atomic weights. With potassium a number considerably less than its atomic weight was obtained.—*J. Chem. Soc. Trans.*, *1889*, 521.

[2] Blair, Chemical Analysis of Iron, p. 123. Modified as described in Classen (trans. of Smith) p. 174.

[3] This residue was not attacked by dilute nitric acid.

[4] As described by Dr. Wahl.

These oxidation-points were distributed all through the mass with considerable uniformity.

V. TUNGSTEN ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A. Total Fe.	B. Total W.	C. "Free" Fe.	D. "Free" W.	E. Residual Fe.	F. Residual W.	G. Ratios A : B.	E : F.
22..	0.5166	0.4834	0.0122	0.0403	0.5044	0.4431	3.51 : 1	3.74 : 1
23..	0.4109	0.5891	0.0283	0.0526	0.3826	0.5365	2.30 : 1	2.34 : 1
24..	0.5276	0.4724	0.0566	0.0370	0.4709	0.4355	3.66 : 1	3.54 : 1
25..	0.5270	0.4730	0.3156	0.0632	0.2093	0.5881	3.66 : 1	1.17 : 1
26..	0.5265	0.4735	0.0152	0.0541	0.5096	0.4211	3.66 : 1	4 : 1
27..	0.8053	0.1947	0.7104	0.0652	0.0949	0.1295	13.6 : 1	4.17 : 1
28..	0.8119	0.1881	0.7111	0.0760	0.1008	0.1121	14.1 : 1	3.4 : 1
29..	0.8124	0.1876	0.6980	0.0721	0.1144	0.1155	14.2 : 1	3.15 : 1
30..	0.8584	0.1416	0.7393	0.0331	0.1221	0.1055	20 : 1	2.6 : 1

Taken for analysis, 0.20–0.25 gram.

VI. TUNGSTEN ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	D-31.	E-32.
Iron.....................	0.3728	0.6223
Per cent. of total iron.......	70.34	75.70

Taken for analysis, two grams.

VII. TUNGSTEN ALLOYS, CARBON, SILICON, PHOSPHORUS.

No.	Sample.	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
33..........	Alloy D[1]	2.40	1.84	0.56	2.07	0.25
34.........	Pig iron[2]	3.06	0.77	2.29	3.30	0.32

These alloys also are marked by heterogeneity, containing more and less stable compounds. Their crystalline character is more prominent than with the molybdenum compounds, cavities in the alloys being lined with imperfect crystals by no means microscopic and showing cleavage planes of a pyritous appearance. Poleck and Grützner[3] have examined one of these forms in a ferro-tungsten. Their description of the alloy is of a crystalline mass, dense and hard, of a steelish gray color, metallic luster, with cavities lined with small crystals, found by Hintze to be of the hexagonal system or possibly rhombohedral if hemihedral in form. They were nearly as hard as corundum and were completely attacked by sodium potassium carbonate, giving the formula FeW_2 analogous to FeS_2. The cementing material

[1] Made from tungsten and pig iron, No. 34.
[2] Sp. gr., 7.146.
[3] Abstracted *Bull. Soc. Chim.*, No. 8, *1893*.

gave the formula $Fe_2W_2C_2$ and was nearly as hard as the crystals. Density 12.92–13.14. F. N. Riddle[1] smelted Lake Superior hematite with tungstic oxide and carbon. In the crystalline mass were obtained steel-gray crystals insoluble in hydrochloric acid and found to contain 98–99.5 per cent. tungsten. Density 15–16. With nickel he states the separation of this crystalline tungsten was still more marked. The variation of results among different observers shows the influence the conditions of preparation have on alloys of iron and tungsten.

The chemical reactions of these' tungsten alloys strongly indicated the influence of the tungsten. Acid solvents were practically useless as a means of analysis. Both nitric acid and aqua regia decompose them but very slowly and only by removing the protecting coating, the yellow hydroxide $Wo(OH)_2$ and adding fresh acid. Potassium bisulphate (sulphuric acid at a red heat) decomposes them with evolution of sulphurous anhydride. An oxidizing mixture of sodium carbonate and saltpeter was a complete and ready means of decomposition, as also was caustic soda. Hydrochloric acid acts only partially on the iron. These reactions are those of metallic tungsten and indicate a combination of iron and tungsten equally inert.

The formation of phosphotungstate and silicotungstate, partly, at least, insoluble and remaining with the tungstic acid, necessitated some modification in the determination of these elements. The separation was made by fusing the powdered alloy with oxidizing mixture and caustic soda dissolving the melt and filtering from the residue. This residue was treated in the usual manner for silicon. To the solution containing alkali tungstate, silicate (in part), and phosphate, enough ferric chloride is added to precipitate silicic and phosphoric acid. The solution is now acidified, the ferric carbonate formed dissolving. Carbon dioxid is expelled by boiling, and ammonia in excess added to re-solutio.. of precipitated tungstic acid. Silicic and phosphoric acids are now determined as usual. In determining arsenic and phosphorus in pig copper this method was found to be accurate, these elements going with iron in preference to lead, antimony, tin, or bismuth.[2]

[1] *Am. J. Sci.*, *1889*, [3], **38**, 160.
[2] Modification of a method described in Crookes' Select Chemical Methods, p. 430.

FERRO-CHROMIUM.

Since the publication in 1820 by Berthier[1] of his experiments on alloys of chromium with iron, these compounds have been carefully studied both from a chemical and physical standpoint with regard to their metallurgical application. Physically, chromium increases the hardness and tensile strength of iron, but makes it brittle. As noted in the discussion of ferro-molybdenum the properties of hardness and density appear to be connected with condensation, and in the case of both these properties they increase with the content of chromium. Brustlein[2] notes that the carbon increases with the chromium, giving a series from twelve per cent. chromium, two per cent. carbon to eighty per cent. chromium with eleven per cent. carbon. Howe[3] also notes this increase of the carbon content and also that, as in the case of manganese, the chromium prevents the separation of graphitic carbon. According to the same authority chromium combines with iron "in all proportions or at least up to eighty per cent." the alloys being markedly heterogeneous in nature, samples from the same piece giving very different results when subjected to physical tests. He etched a plate of chrome steel with sulphuric acid and noted in it the presence of portions not attacked by the acid and which he considered probably to be alloys rich in chromium. The analyses made for this paper give the same results in regard to heterogeneity in these chromium alloys and in the other alloys examined and show the necessity of taking from half to one gram of an average for analysis. The experimental method pursued was the same as with the molybdenum and tungsten alloys. Nitric acid, dilute or concentrated, does not attack metallic chromium. The silver nitrate would not, therefore, attack the chromium constituent of these alloys. The action of the reagent, however, is of interest as showing the amount of iron in stable combination and the figures so obtained are given. The chromium alloys of iron show the influence of the chromium in almost as positive a manner as with tungsten compounds. Acid solvents act very slowly on high chrome alloys. Potassium bisulphate and the oxidizing mixture decompose them

1 *Annales des Mines.* [1] 6, 573.
2 Hiorns, Mixed Metals, p. 359.
3 Howe, Metallurgy of Steel, p. 75.

readily, and the latter energetically, the oxidation of the fine powder giving rise to a considerable evolution of heat which rapidly raises the crucible to bright redness; only one alloy was made.

Alloy F. Brilliantly crystalline; acicular, with a cleavage appearance like antimony. Brittle. Scratches glass with difficulty. Does not scratch quartz. Specific gravity, 7.464. Hydrochloric acid decomposed this alloy.

VIII. CHROMIUM ALLOY WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A Total Fe.	B Total Cr.	C "Free" Fe.	D Residual Fe.	E Residual per cent. total Fe.	Ratio A:B.
35......	0.8706	0.0794	0.4832	0.3874	44.49	10:1
36......	0.8684	0.0804	0.4497	0.4187	48.21	10:1
37......	0.8481	0.0999	0.4770	0.3711	43.75	8:1
38......	0.9154	0.0360	0.5092	0.4062	44.37	24:1

Taken for analysis 0.20–0.25 gram.

IX. CHROMIUM ALLOY, CARBON, SILICON, PHOSPHORUS.

No.	Sample	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
40	Alloy F.....	2.46	1.64	0.82	3.37	0.29
41	Pig iron	3.06	0.77	2.29	3.30	0.32

No. 40 was made by melting No. 41 with ninety per cent. ferrochrome.

Analytical Method.—In direct analysis for determination of chromium and iron the fusion with oxidizing mixture was adopted and separation of the chromate from ferric hydroxide effected by filtration. In determining iron and chromium digested with silver salt, the insoluble residue was dissolved in aqua regia, the silver chloride filtered off and the solution made alkaline by sodium hydroxide, boiled and bromine added. The residue of ferric hydroxide was filtered from the chromate. In the acid filtrate the chromic acid was reduced by hydrogen sulphide and the boiling solution precipitated by ammonia. Adhering alkali, forming chromate on ignition, was tested for by mercurous nitrate.[1]

GENERAL CONSIDERATIONS.

In connecting solutions and alloys the part that the metal in excess plays is that of water in aqueous solutions of salts. That

[1] A Method used for chromite analysis by Dr. F. A. Genth.

this is not a purely mechanical part but that a distinct force is acting between the components of a solution is evident from the modification both of solvent and of the dissolved substance.   The physical state of the latter changes, probably assuming the liquid form,[1] and the specific gravity, refractive power, tension of vapor, boiling and freezing-points,[2] are affected often considerably.   The thermic effect resulting in evolution or absorption of heat, and alteration in volume[3] shown by contraction or expansion, further indicate chemical action.   The combination is an indefinite one in so far as addition of the solvent is concerned ; but the amount of dissolved substance is strictly limited by temperature and pressure (in the case of gases).   Van 't Hoff[4] has intimately connected gases and solutions comparing diffusion to evaporation and solution to vaporization.   His experiments on osmotic pressure, showing that solutions obeyed the laws of gases and that Avogadro's law could be applied to them.

The formation of definite compounds in solution is well established, the halogen acids and nitric acid affording examples of solutions of constant boiling-point ; and until that concentration is reached the products of evaporation are mainly water or, as the case may be, acid.[5]   The cryohydrates are also examples of this definite combination, and such substances as $H_2SO_4H_2O$ and salts with water of crystallization.   Although these very definite compounds are formed with water, solution itself is a homogeneous system[6] and the existence of these compounds as such in the fluid cannot be asserted.   Sterry Hunt, who considers solution as the type of chemical action in its "identification of the different," regards the state as one in which all definiteness is lost and in which we cannot assert the existence of any one compound, or even element, more than another.[7]   We can only possibly predict what, under altered conditions, we can obtain from it.[8]   He sums up the theory of solution as "the formation of

[1] Mendelejeff, Principles of Chemistry, 1, 70.

[2] Ibid, 1, 86, 87.

[3] Lothar Meyer, Modern Theories of Chemistry, 466, 481.

[4] *Trans. Swedish Acad. Sciences*, Part 21, No. 17, *1886;* quoted by Mendelejeff, 1, 64, 65. See translation by Ramsay, *Phil. Mag.*, 26, 81, *1888*, from *Ztschr. phys. Chem.*

[5] Ostwald, Solutions. p. 9, trans. by Muir.

[6] Ibid, p. 148.

[7] New Basis of Chemistry, p. 22.   [8] Ibid, p. 10.

definite compounds with water accompanied with all the phenomena of chemical union," further addition of water giving rise either to decomposition and formation of new compounds or to admixture of "one definite solution or liquid species with another less dense solution, or with water." These compounds "being separable in a solid state by change of temperature or in a liquid state (theoretically) by gravity;" liquidity is but an accident of solution, depending on temperature and pressure.[1] Arrhenius from his investigations of the depression of the freezing-points and lowering of the vapor pressure of solutions of electrolytes came to the conclusion that the system was one of dissociation.[2] Mendelejeff bringing all such compounds as solutions, cryohydrates, colloids, and amorphous silicates, under the law of definite and multiple proportions regards solutions as fluid unstable definite chemical compounds in a state of dissociation.[3]

Alloys, with the exception of some of the amalgams, are solids at the ordinary temperature and require a more or less elevated degree of heat for fusion, their melting-point depending on that of their constituents and on the nature of the alloy. As solutions, therefore, they only exist at high temperatures and it is at those temperatures that the laws of solutions must be applied to them. As is the case with liquids, they may be saturated or unsaturated compounds, in the latter case one of the constituents being present in excess and acting as the solvent, *i. e.*, corresponding to the part excess of water plays in the solution of a salt. If the solution be regarded as a state of dissociation, then while the mass of the alloy is in the liquid state (fused) we have a homogeneous system, and two elements may be in unstable combination which on cooling, *i. e.*, solidifying or freezing, separate in definite compounds limited by the valency of the constituents, any excess of one of the elements being indicated by the presence of that element in an uncombined state. When, therefore, there is no excess indicated in an alloy of one constituent over another it can be justly assumed that all is in combination, and the presence of an excess of one of the metals

[1] Systematic Mineralogy, pp. 77, 78, 82.

[2] Ostwald, Solutions, pp. 189, 214. Trans. of Muir.

[3] Mendelejeff, Principles of Chemistry, 1, 105.

would correspond to the ice present when an aqueous solution of a salt is cooled below its freezing-point, or to those compounds of salts with much water known as cryohydrates. The freezing-points of metals and their alloys, with a few exceptions, are much higher than the normal temperature, $15°$ C. In his study of the solution of liquids in liquids W. T. Alexeef found that two liquids mutually soluble, intermix in all proportions at certain temperatures. At lower temperatures the solubility is limited, finally reaching a minimum.[1] This may be and probably is the case with melted metals, but the condition in which we can observe and examine them corresponds, as said before, to the frozen state.[2] Hardness and indifference to chemical reagents have long been associated with condensation, increased density being generally associated with these properties and indicating complexity of structure advancing from the gaseous to the solid form.[3] In liquids, although friction appears as a factor, yet there is free communication within the bounds of the liquid ; a considerable condensation, however, takes place. In the conversion of steam, gaseous H_2O, to water and ice, Sterry Hunt found this condensation to be for water, 1192 H_2O, and for ice, 1094 H_2O,[4] and in mineral species increased density was found to be associated with hardness and chemical indifference.[5] Ramsay in determining the molecular formulas of liquids by means of their molecular surface energy, found that condensation increased with fall in temperature and obtained for sulphuric acid of 1.82 sp. gr. the very complex formula not lower than $(H_2SO_4)_{32}$ at ordinary temperatures.[6]

Regarding alloys as solutions, many of their physical properties can be explained. The alloy changes its nature both physical and chemical, differing from its constituents in volume (i. e. density) and melting-point, and forming often definite molecular compounds. This modification of its properties is greater or

[1] Mendelejeff, Principles of Chemistry, 1, 74, and Ostwald, Solutions, p. 40, trans. of Muir.

[2] Ibid, 1, 105.

[3] Sterry Hunt, Systematic Mineralogy, p. 86, seq.

[4] New Basis of Chemistry, p. 109.

[5] Researches of J. B. Mackintosh, *J. Anal. Chem.*, 1, 10. Sterry Hunt, Systematic Mineralogy, p. 93.

[6] *J. Chem. Soc.*, **63**, 1089, Sept. *1893*. **65**, 167; March, *1894*.

less according as the constituents are separated in their nature. Mendelejeff cites the series formed by sodium with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, changing its properties from the distinctly saline sodium chloride to the sodium zincide and with this change in properties as the union is with the element more and more like in nature to sodium increasing in valency; but they are distinct and definite compounds and not to be distinguished on the ground of chemical nature. He notes the same properties in the union of metallic oxides, instancing the large number of complex aluminum silicates in which the two constituents are very like in nature acting as feeble base or feeble acid, and united in such a substance as lava glass in varied proportions giving on crystallization definite compounds, the silicates.[1] The analogy between these vitreous substances, with their microcrystalline structure, and alloys is a striking one.

The question of variable valency of the elements arises in these compounds of like elements. Are they to be regarded in the same light as with those of rigidly defined proportions with unlike elements? This is evidently the case. Definite crystallized compounds of alloys are known, with well-defined properties unlike those of either of the constituents. The alloys $SnCu_3$ and $SnCu_4$, as also $PbSn_3$, are examples. Polymerism has also its analogue in allotropism.[2] But in the union between unlike elements this variability appears. Sodium forms several oxides, as likewise gold, silver, copper, etc. The elements under consideration, chromium, molybdenum, and tungsten, unite with oxygen in several ratios. These latter are especially interesting in their relation to the silicates. The complexity of their silico-compounds and phospho-compounds, was long ago established by Wolcott Gibbs[3] and if this complexity is related to the union of like properties in these oxides the same complexity is to be expected in the union of elements of like nature—as these metals. These alloys in the melted state are solutions, as the melted lava glass is a solution. There is a homogeneous system

[1] Mendelejeff, Principles of Chemistry, I, 111,112. See Matthiessens Conclusions, *Brit. Ass. Reports, 1863*, p. 97, cited in Fownes' Chemistry, p. 290.

[2] Ernest Meyer, History of Chemistry, pp. 377, 454.

[3] Gibbs, *Am. J. Sci.*, [3], 14, 61.

the equilibrium of which is disturbed on cooling and at different temperatures different salts crystallize out. These salts may represent combinations of the atoms as truly as NaCl or they may be molecular compounds of a salt with the solvent metal, *i. e.*, present in definite proportion analogous to water of crystallization as in the salt $Na_2CO_3,10H_2O$. The number of such compounds separating out during the slow cooling of an alloy may be, and probably is, very great. In many alloys with slow cooling, a macrocrystalline structure often results, but with rapid cooling the result is the microcrystalline form. This is of such importance that the commercial use of many alloys requires their rapid cooling, from their tendency to coarsely crystalline structure and consequent loss of homogeneity. That the valency of an element is related to its electro-chemical behavior has been shown and the value of an element increases toward like elements and decreases or concentrates itself in union with unlike elements, *i. e.* " Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity but the higher valency when uniting with those for which they have but small affinity.[1] The possibility of self-saturation must be taken into account[2] and valency established on indirect determination is doubtful. In these compounds or alloys the question of valency becomes a very difficult óne. The quantitative composition of a well-developed individual, such as a crystal, is no guide in itself to the valency of the constituents as crystallization is essentially molecular. We know that the passage from gas to liquid and to solid involves a condensation and most frequently a very great condensation of volume, and experiment on the solutions of metals in mercury and in sodium show many of them to be monatomic ; therefore, while the molecule itself may contain but a comparatively small number of atoms, the union of these simple molecules to form larger ones brings about great complexity of structure indicated by the increased density, hardness, and chemical inertia. If this is the case the molecule of these ferro-compounds must be very complex and assuming the simplest formulas from the

[1] Lothar Meyer, Modern Theories of Chemistry, p. 349.

[2] Ibid on valency, p. 307 seq.

analyses—which, while representing the average of a number of alloys in the solid state, can be carried back to the liquid state when the system was homogeneous—very large integral weights or equivalents are obtained. The valency of iron to tungsten is at least equal to its valency to chlorine or to oxygen, and these are only minima. Ruthenium and osmium have been shown to be at least octovalent, and if the ammonia (NH_3) in the ammonium cobalt salts be considered as atomic and not molecular, cobalt, a metal closely allied to iron, must be accepted as dodeca-valent.[1] The ratios obtained in column G of the tables do not afford an indication of the value of the iron atom in these alloys. The ratio E : F of the residues give for the highest form-ulas $Fe_{11}Mo$ and Fe_4W, but unquestionably represent mixtures.[2] The presence of an allotropic form of iron, β iron, as taught by Prof. Osmond, is also to be taken into account. These elements of the sixth family, tungsten and chromium, come under the list of β forming elements. As far as the solution of steels in acids or in the copper alkali salt, this β or hard "adamantine" form of iron appears to act as other modifications. There is no reason to believe it would act differently with silver nitrate.[3] The influence of mass appears in the increased ratio of the pre-dominant metal in E : F. This is not so marked in the case of tungsten. A considerable uniformity runs through the analyses but several numbers (as 1, 8, 9, 10) evidently mark points of segregation.[4]

[1] Lothar Meyer, Modern Theories of Chemistry, pp. 347, 348.

[2] The silicides and phosphides of iron are very inert. A ferro-silicon containing fif-teen per cent. silicon was insoluble in nitric or hydrochloric acid, but soluble in aqua regia.

[3] Prof. Osmond in his paper (*J. Iron and Steel Inst.*, p. 38, *1890*) ascribes the power of retaining at the normal temperature iron in this β or hard form, to a number of ele-ments among them tungsten and chromium ; the hardness of such iron being due not only to the mechanical strains set up in the solid on cooling but to molecular strains, perhaps due to osmotic pressure exerted by elements of small atomic volume (discus-sion of Prof. J. O. Arnold's paper, May, *1893*). Prof. Arnold considers the hardening property as due to mechanical strains on cooling probably caused by the formation of definite compounds such as Fe_3C. These authorities do not appear to regard as worthy of notice the theory that all the carbon, phosphorus, silicon, etc., is uniformly distributed through the iron and in combination with it ; and in view of the small quantities of such elements present such a view appears chemically untenable. I am indebted to Mr. Garrison, who kindly brought these papers to my attention and placed them at my dis-posal for consultation.

[4] In the action of silver nitrate on these alloys there is a considerable evolution of heat. This is also the case with iron.

That the melting-point of alloys is not the mean of the melting-points of their constituents but is influenced by properties probably chemical, is well known. An example of this is afforded by platinum which is only fusible by the oxyhydrogen flame in a lime furnace, but which with iron forms a readily fusible alloy at the highest temperature of the blast-furnace and also with a number of other elements, alloys fusible at the heat of the Bunsen lamp. This lowering of temperature is found with other still more infusible elements of this group: *viz.*, palladium, iridium, ruthenium, and osmium.[1] Tungsten, molybdenum, and chromium, form a group of very infusible substances but these iron alloys are formed readily at the temperature of the blast-furnace. Hardness, chemical indifference, and density are associated with molecular complexity and the tungsten group in their metallic forms are probably represented by formulas expressing great condensation and affinity between the like atoms. The formation of these iron alloys, therefore, must be preceded by a breaking up of this union between like atoms and molecules and this is brought about by a state of solution. The affinity of iron and the sixth family is then greater than the affinity of the like atoms, for on cooling from the homogeneous system of solution stable alloys of iron and the second constituent separate out. Now, as before cited, Heycock and Neville found (confirmed by Ramsay) that on determining the molecular weights of the metals dissolved in sodium and in mercury the results gave one atom in the molecule for a large number of metals, indicating that in solution in metals, a state of dissociation exists analogous to that of the aqueous solution. If this holds good, therefore, for these iron compounds, that in the liquid or melted condition the complex molecule of iron and tungsten existing in the solid state is broken up into a simpler form, then the affinity between the constituents of these alloys can act. The investigators found that on dissolving the metals in atomic proportions in molten tin on applying Raoult's method[2] to the lowering of temperature of solidification a con stant was obtained, this being in accordance with Coppet's law

1 Howe, Metallurgy of Steel, p. 79. A. Joly., *Compt. rend., 1893,* 116,430, on melting-point of the platinum metals.

2 See *Am. Chem. J.,* 11, 67, 72.

that "solutions whose contents are in the ratio of the molecular weights of the dissolved salts freeze at nearly the same temperature."[1] That is, the freezing-point is a function of the molecular weight. Indium and aluminum gave abnormal results indicating a more complex molecule in solution.

Chemical action is also indicated by change in volume and in his researches on dilute solutions Ostwald determined the amount of chemical change — in this case representing the avidity of the acids—by the contraction or expansion of the liquid.[2] With alloys, the same phenomena is observed. As a rule with the formation of definite compounds, *i. e.*, on cooling, contraction ensues. Alloys of bismuth, however, expand being analogous in this respect to ice. These iron alloys show change in volume, indicating by their increased density that with them a contraction has taken place. In every case there is a marked increase in specific gravity. Comparing the specific gravities:

X. Table on Comparative Densities.

Nos.	Samples.	Sp. gr. of metal.	Sp. gr. of alloy.	Composition.	Sp. gr. of pig iron.	From composition, difference.	Equivalent weights.
1-4	A......	Mo=8.6	8.182	Fe_4Mo	6.980	+0.88	175052
5-12	B......	....	7.830	Fe_8Mo	6.980	+0.67	167562
22-26	D	W=19.2	10.140	Fe_7W_2	.....	......	216996
27-30	E......	....	7.935	$Fe_{16}W$	7.146	+0.08	169809
35-38	F......	Cr=6.8	7.446	$Fe_{20}Cr_3$	7.146	+0.27	159629

Fe here represents the complex compound containing phosphorus, silicon, and carbon—pig iron. The sign—minus is to be expected with chromium. If these alloys are to be considered as chemical compounds and as atoms bound together into molecules and these molecules into still more complex molecules then these composition formulas, can be taken as representing the simplest average composition of the definite compounds in the alloy in the solid state. There may be and certainly are compounds in these alloys represented by formulas more complex than these simple formulas, for the elements, carbon, silicon, etc., have not been taken into account. Assuming these latter, however, column VI gives the equivalent weights $H_2O = 21400$.

1 *J. Chem. Soc. Trans.*, *1889*, 666, *1890*, 376. Ramsay, Ibid, *1889*, 521. Quoted in Ostwald, Solutions, p. 231, by Muir.

2 Lothar Meyer, Modern Theories of Chemistry, p. 481 seq.

These high equivalents explain the physical properties, such as hardness and density, and the chemical inertia of these compounds.[1]

In this connection it should be noted that there is a difference in density in a metal as solid and when in the melted condition. Wrightson[2] in his experiments on the relative specific gravity of cast iron in the two states found that the maximum volume was obtained on passing from the liquid to the solid. The same result was obtained from experiments made on melting solid iron or on cooling molten iron to solid. In the latter case there was observed : first an expansion, followed by contraction and again by expansion. The observed differences were small. Henri Moissan in his experiments on carbon dissolved in iron made use of this change of volume of the iron to subject the carbon, on sudden cooling, to great pressure.[3]

From these results it can be concluded :

1. That these alloys by their resistance to chemical reagents, their hardness and increased specific gravity, indicate a chemical union between the constituents. That in these alloys there are present a number of compounds, some of which are more stable than others, the latter being readily attacked by weak solvents. That these compounds are distributed with considerable uniformity throughout the mass of the alloy, segregation being the exception, not the rule, and that their freezing-points must be approximately the same, preventing the segregation of alloys of great density in any one portion of the alloys; that the more stable of these alloys are definite chemical compounds; that the less stable may be definite compounds or of the nature of cryohydrates or with one of the constituents present in the mixture in a state analogous to that of ice in a frozen salt solution in which water is in excess.

2. That, therefore, in these alloys the existence of definite compounds differing in their action toward solvents; their contraction as indicated by their specific gravity, hardness, etc., the fact that chemical union exists involving the breaking up of the

[1] Sterry Hunt, New Basis of Chemistry, p. 51 seq. and 100. Systematic Mineralogy, p. 86.

[2] Howe, Metallurgy of Steel, p. 254.

[3] *Bull. Soc. Chim.*, 11, 8, January, 1893.

complex iron, molybdenum, tungsten, and chromium molecules and their union to form a new compound, *i. e.*, the passing of a heterogeneous system of molecules of like elements to a homogeneous system in the melted condition and again to a heterogeneous system in the resultant alloy; that these properties indicate a condition in these alloys analogous to an aqueous solution of a salt converted by cold to the solid state.

3. The high melting-point of the element in combination with the iron and its chemical affinity for iron is especially favorable to the separation of alloys from the cooling solution, and is the cause of the heterogeneity of these compounds. This separation of salts, *i. e.*, segregation, draws the analogy between these alloys and solutions closely.

XI. COMPOSITION OF ALLOYS.

Alloys.	A.	B.	C.	D.	E.
Molybdenum	0.2979	0.1665	......	......	......
Tungsten	......	......	0.4646	0.1696	......
Chromium	......	......	......	......	0.0702
Iron	0.6626	0.7942	0.5251	0.7832	0.8799
Phosphorus	0.0031	0.0030	0.0004	0.0025	0.0029
Silicon	0.0074	0.0066	0.0014	0.0207	0.0337
Combined carbon	0.0017	0.0020	} 0.0075 {	0.0184	0.0041
Graphitic carbon	0.0273	0.0277		0.0056	0.0082

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

Another trial was made by treating 400 grams of bean-meal, previously exhausted by benzine, with one per cent. sodium chloride solution, dialyzing the extract for twenty-four hours, and filtering off the precipitated phaseolin. The clear filtrate after standing over night, deposited a considerable quantity of proteid, but the solution with this deposit was returned to the dialyzer and left for two days longer, when it was filtered, the precipitate washed with water, alcohol, and ether, dried over sulphuric acid, and six grams of preparation 36 obtained.