lished too late for inclusion in the report for this year [*Z. anorg. allgem. Chem.*, **221,** 129 (1935)].

Lead.—Marble[15] has determined the atomic weight of radiogenic lead extracted from pitchblende found near Great Bear Lake, North West Territories, Canada. The lead was purified successively as sulfide, sulfate, sulfide, nitrate and chloride and the chloride was finally twice distilled in dry hydrogen chloride. Analysis by the conventional chloride method gave the following results. Weights are corrected to vacuum.

THE ATOMIC WEIGHT OF LEAD

Wt. of $PbCl_2$	Wt. of Ag	Ratio $PbCl_2$:2Ag	At. wt. Pb
2.27721	1.77393	1.283709	206.059
2.22354	1.73219	1.283658	206.048
2.22397	1.73249	1.283684	206.054
	Average	1.283684	206.054

The value found by Aston from the isotopic constitution of this same lead, when corrected to the chemical scale, is 206.08. The difference is no greater than present accuracy of the mass spectrograph but is greater than the apparent uncertainty of the chemical method.

Radium and Protactinium.—Two investigations on radioactive elements were published too late for detailed inclusion in this report. Hönigschmid and Sachtleben[16] using 2.2–3.5 g. of radium bromide, from the ratio $RaBr_2$:$RaCl_2$ find the atomic weight of radium to be 226.05, while v. Grosse,[17] from the ratio $2K_2PaF_7$ (0.07–0.09 g.): Pa_2O_5 finds Pa = 230.6.

Batuecas[18] takes exception to the conclusions of Cawood and Patterson concerning the densities of certain gases and their coefficients of deviation from Boyle's law. His own figures based on average values obtained by several experimenters are:

	Density	1 + λ	*M*	
C_2H_4	1.2605 (4)	1.0076 (6)	28.040	C = 12.004
CO_2	1.9766 (5)	1.0068 (4)	44.005	C = 12.005
$(CH_3)_2O$	2.1099	1.0270	46.050	C = 12.001 (5)
N_2O	1.9780	1.0073 (5)	44.013	N = 14.0065
SO_2	2.9263	1.0239	64.061	S = 32.061

---

[15] Marble, THIS JOURNAL, **56,** 854 (1934).

[16] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **221,** 65 (1935).

[17] A. V. Grosse, THIS JOURNAL, **56,** 2501 (1934).

[18] Batuecas, *J. chim. phys.*, **31,** 65 (1934).

RECEIVED FEBRUARY 20, 1935

[CONTRIBUTION FROM THE MACKAY CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA]

The Reaction Tungstic Oxide–Carbon–Chlorine[1]

BY GEO. W. SEARS AND FRED LOHSE

The use of chlorine as an extraction agent for certain of the rarer metals from their ores has received the attention of investigators at various times and several processes utilizing the reaction have been patented.[2] Except for the recovery of tungsten from certain tin ores in England, little commercial use of the reaction has apparently been made.[3] Of the different methods described, as applicable for tungsten ores, that involving the reaction of chlorine on the ore mixed with carbon or other reducing agent appeared to be the most promising. Little information, however, could be obtained as to the nature of the reaction. While it seems to have been generally assumed that the oxychlorides, $WOCl_4$ and WO_2Cl_2, are formed and that the carbon acts as a reducing agent,[4] but little experimental evidence supporting it could be found. It was decided, therefore, to make a more careful study of the nature of the reaction and especially of the role of carbon in it with the hope that information might be obtained that would lead to its more general use.

The yellow C. P. tungstic oxide of commerce was used as a source of tungsten. Except in the preliminary experiments, the chlorine was from a cylinder of the commercial liquid. The carbon was in the form of pulverized wood charcoal or lampblack. The reaction was carried out in an electric tube furnace arranged in such a way that the progress of the reaction could be observed. The mixture of tungstic oxide and carbon was placed in a porcelain boat within the tube and dry chlorine passed over it. The solid reaction products were collected in a series of bulbs which had previously been sealed directly to the furnace tube. The mixed red and yellow colors of the distillation products pointed quite definitely to the formation of both WO_2Cl_2 and $WOCl_4$ with possibly some WCl_6. The mixture, however, was subjected to a process of fractional

---

[1] Presented before the Pacific Intersectional Division of the American Chemical Society at Salt Lake City, June, 1933.

[2] British Patents 176,428 and 134,891.

[3] Colin J. Smithells, "Tungsten," D. Van Nostrand Co., New York, p. 14.

[4] British Patent 134,891.

sublimation by means of which the red and yellow compounds were separated from each other as completely as possible. Analyses confirmed the presence of WO_2Cl_2 and $WOCl_4$ of which much the larger proportion was always WO_2Cl_2. While in certain cases some WCl_6 seemed to be formed, as evidenced by the purple color of the sublimate, the amount was never large and no attempt was made to separate and analyze it. From the fact that the $WOCl_4$ and WCl_6 were formed in relatively small amounts and only at the higher temperatures, it is quite probable that the reaction proceeds by steps, the amount of chlorine entering into the compound increasing with the temperature.

In observing the reaction mixture during the progress of an experiment, it was noted that as the reaction proceeded the surface of the mixture developed a pitted appearance with a particle of carbon at the bottom of each pit. On more careful examination, it became evident that the reaction proceeded most rapidly in the immediate neighborhood of the carbon particles but that the carbon did not seem to disappear. This suggested a catalytic action for the carbon. In order to obtain further information in this connection, a series of experiments was carried out to determine whether the reaction would proceed in the absence of carbon, whether there is an actual loss of carbon during the reaction and whether the ratio of carbon to tungstic oxide would influence the rate of reaction.

In the first of these experiments, chlorine was passed over the tungstic oxide in the absence of carbon. In all cases volatile chlorides of tungsten were formed, but only slowly and at much higher temperatures. A platinum–nichrome thermocouple placed in the reaction tube showed 700° as the lowest temperature at which any reaction could be detected. In the presence of carbon, the reaction was found to take place slowly at temperatures as low as 275°. The rate of reaction, however, increased rapidly with increasing temperature. At 500° the reaction was quite vigorous.

To determine whether or not there was any loss of carbon during the reaction, weighed amounts of tungstic oxide and carbon were intimately mixed on glazed paper and transferred quantitatively to a porcelain boat. The boat was then placed in the reaction tube, the air displaced by a stream of chlorine and the temperature raised to the desired point as rapidly as possible. In Table I are the results obtained from experiments selected more or less at random from a large number carried out in this manner. In each case the residue was tested for tungsten. In most cases the carbon was given no pretreatment, except powdering in the case of wood charcoal, though in a few cases it was heated to the temperature of the experiment before use. No difference in its effect was noted by this treatment.

TABLE I

EFFECT OF CHLORINE ON A TUNGSTIC OXIDE–CARBON MIXTURE

No.	WO_3, g.	C, g.	Residue, g.	Temp., °C.	Tungsten test on residue
1	0.2195	0.0109	0.0109	500	Neg.
2	.5438	.0274	.0272	500	Neg.
3	.5432	.0271	.0322	500	Pos.
4	.4985	.0249	.0299	550	Pos.
5	.9748	.0252	.0252	720	Neg.
6	.6795	.0702	.0548	745	Neg.

It will be noted that only in experiment No. 6 was there a loss of carbon. Later experiments showed that this was probably due to air that had not been removed from the system.

Increasing the proportion of carbon in the mixture resulted in all cases in an increase in the rate of the reaction at a given temperature. The evidence, therefore, seemed entirely to confirm the previous suggestion that carbon acts as a catalyst for the reaction between chlorine and tungstic oxide. If this view be accepted, the reaction should proceed according to the equation

$$2WO_3 + 2Cl_2 \longrightarrow 2WO_2Cl_2 + O_2$$

The question at once arose as to whether oxygen would be given off even if liberated in such close contact with hot carbon. To determine this it became necessary to devise a method for separating small amounts of oxygen from relatively large quantities of chlorine since the ordinary methods of gas analysis could not be used in the presence of chlorine. This was finally accomplished by absorption of the chlorine with mercury at room temperature. Experiment showed that chlorine is absorbed very rapidly if kept in contact with a fresh surface of the mercury while under the same conditions oxygen is unaffected.

The tungstic oxide–carbon mixture, contained in a porcelain boat, was placed in the reaction tube which was then swept free of air by means of a current of chlorine from the cylinder. The absence of air was determined by collecting a sample of the exit gases over mercury and noting whether it would be completely absorbed by the mercury. Following a reaction, the gaseous products were drawn into an absorption pipet where the chlorine was absorbed by mercury. Any residual gas was transferred to a measuring buret and analyzed for carbon dioxide, carbon monoxide and oxygen. The first experiments, carried out in a static atmosphere, showed considerable amounts of both carbon dioxide and carbon monoxide but gave no positive evidence of oxygen. When, however, a slow stream of chlorine was made to flow over the tungstic oxide–carbon mixture during the reaction, no carbon dioxide but definite quantities of oxygen were obtained. During these experiments, excess chlorine was absorbed by a fine stream of mercury flowing through the absorption pipet.

The results, therefore, showed quite conclusively that the reaction proceeds according to the equation given above and that no carbon is lost if the reaction takes place in a current of chlorine. The extraction of tungsten from its ores by the action of chlorine, therefore, should be materially hastened by an intimate contact with carbon. This contact should be possible of accomplishment with a relatively small amount of carbon by keeping the mixture well agitated. In order to test this principle, samples of different tungsten ores including Scheelite, ferberite, wolframite and huebnerite were mixed with relatively small proportions of carbon, the mixtures were then introduced into the reaction chamber arranged so as to admit of constant stirring. In all cases complete extraction of the tungsten was obtained and the rate of reaction was very materially increased by the stirring.

Summary and Conclusion

1. The reaction tungstic oxide–carbon–chlorine has been studied and has been shown to proceed by steps with the production of WO_2Cl_2, $WOCl_4$ and probably WCl_6, oxygen being evolved.

2. The presence of free oxygen among the reaction products was confirmed by first extracting the chlorine by absorption with mercury followed by the usual methods of gas analysis.

3. The role of carbon is that of a catalyst which increases the rate of the reaction.

Reno, Nevada Received April 24, 1934

[Contribution from the Chemical Department, Michigan College of Mining and Technology]

The Surface Relations of the Xanthates

By C. C. De Witt, R. F. Makens and A. W. Helz

The mechanism of flotation of ores is one involving adsorption and other physico-chemical phenomena. Since there are many controversial views regarding various adsorption theories, it follows that the theories of flotation mechanism are equally unsettled.

This paper presents a correlation of the data on the surface relations of the various xanthates with the known performances of these xanthates in actual flotation practice.

Purification of Materials

The laboratory distilled water was redistilled once from an alkaline permanganate solution.

The solvents used, acetone, benzene, ether, were carefully dried and distilled. The carbon disulfide used in preparing the xanthates was redistilled, the middle portion being used.

Potassium hydroxide was recrystallized and made up as a solution containing 46.6% potassium hydroxide.

Metallic potassium was used in the preparation of the higher xanthates. The oxide coating was removed before use.

Thiophene-free benzene used for standardization purposes was distilled, the middle fraction was frozen, the mother liquor was poured off and the crystals were allowed to melt. After three recrystallizations the benzene was kept over fused calcium chloride and redistilled just before use.

The alcohols used in the preparation of the xanthates were obtained from reliable sources and were further purified by fractional distillation with a specially constructed 80-cm. Pyrex glass fractionating column sealed to a two-liter Pyrex flask. The corrected boiling points as obtained were: propyl alcohol, 97.06° (D), 97.2° (S) at 760 mm.; *n*-butyl alcohol, 117.70 ± 0.05° at 760 mm.; *n*-butylcarbinol 137.6 ± 0.3° at 760 mm.; isobutylcarbinol, 130.5 ± 0.05° at 760 mm.; *s*-butylcarbinol, 129.1 ± 0.2° at 760 mm.; methyl-*n*-propylcarbinol, 119.0 ± 0.2° at 760 mm.; diethylcarbinol, 115.8 ± 0.3° at 760 mm.; *n*-hexyl alcohol, 154.1 to 155.0° at 760 mm.; *n*-heptyl alcohol, 173.6 to 175.1° at 760 mm.; *n*-nonyl alcohol, 211.1 to 213.3° at 760 mm.

Preparation and Purification of Xanthates

Foster's[1] method as modified by De Witt and Roper[2] was used in the preparation of the xanthates. The additional precaution of having the solvents dry was found to give better yields of both potassium and sodium xanthates. The sodium ethyl xanthate was prepared by recrystallization of the commercial product. Normal propyl xanthate did not give clear water solutions even after five recrystallizations from acetone–ether solutions. Two samples of propyl alcohol were used: du Pont *n*-propyl alcohol was carefully dried and fractionated, converted to propyl acetate. The acetate was dried and then converted to the alcohol by hydrolysis with 25% sodium hydroxide. The propyl alcohol so obtained was dried with calcium oxide and finally distilled from metallic calcium. Synthetic propyl alcohol was made from ethylmagnesium bromide and formaldehyde.

The quality of the xanthate was judged by the amount of

---

[1] L. S. Foster, "Preparation of Xanthates and Other Organic Thiocarbonates," Utah Engineering Experiment Station, Technical Paper No. 2, 1928.

[2] De Witt and Roper, This Journal, **54**, 445 (1932).