COMPRESSIBILITY OF GRAPHITE–FERRIC CHLORIDE COMPOUNDS

By Arthur F. Scott and Ronald F. Scheuerman

Department of Chemistry, Reed College, Portland, Oregon

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The compressibility coefficient of graphite–ferric chloride compounds has been measured at 30°. The compressibility of the compound is greater than that of pure graphite. An approximate relationship has been found which appears to represent the variation of the compressibility coefficient with density and composition of the lamellar compounds.

During the past few years the lamellar compounds of graphite have been the object of increasing attention. To gain further information regarding the nature of these compounds it seemed worthwhile to determine the compressibility coefficient of a typical compound of this type, *viz.*, graphite–ferric chloride.

According to Rüdorff, *et al.*,[1] who have made extensive studies of the graphite–ferric chloride systems, various compounds are formed depending on the temperature at which the reaction is allowed

(1) W. Rüdorff, *Z. anorg. allgem. Chem.*, **246**, 383 (1941); **254**, 319 (1947); W. Rüdorff and G. Rüdorff, *Ber.*, **80**, 417 (1947); W. Rüdorff and H. Schulz, *Z. anorg. allgem. Chem.*, **245**, 121 (1940).

to take place and on the subsequent treatment of the product. In the present experiments using Ceylon graphite we have been able to produce all but one of the products described by Rüdorff, although the conditions for our preparations do not agree exactly with those of Rüdorff.

The graphite–ferric chloride compounds for the present experiments were prepared by heating anhydrous ferric chloride and powdered graphite (80–100 mesh) in a Pyrex glass pressure tube at a known temperature for 48 hours, after which the excess ferric chloride was removed by sublimation A small sample of this initial product was taken for analysis; the bulk of the product in each case was

washed generally with 10% hydrochloric acid until the washings showed only a faint test with thiocyanate. The washed product was dried at 120° for 4–5 hours and finally dried in a desiccator over phosphorus pentoxide. A sample of this washed product was also analyzed. Analysis of the graphite–ferric chloride products involved, first, the perchloric acid digestion of the sample, followed by determination of iron by means of standard dichromate solution.

Densities of the washed samples were found by means of a pycnometer for solids, using benzene for the filling liquid.

The compressibility of the graphite–ferric chloride samples was determined by the Richards procedure for the case of solids.[2] Certain details, however, may be noted: a piezometer for solids was constructed from Pyrex glass; the liquid filling the piezometer was purified benzene except in one experiment with graphite when water was employed; in the experiments the pressure was varied over the range of 100–300 kg./cm.^{2}, approximately; all density and compressibility measurements were carried out at $30.00 \pm 0.01°$. In the compressibility experiments the solid samples were in the form of fine powder or pellets prepared from the powder material. The pellets were not found to be satisfactory.

The data pertaining to the preparation of the graphite–FeCl$_3$ samples are presented in Table I. Products Ia, Ib, IIa, IIb and III are believed to be similar to the compounds (72–56% FeCl$_3$) which Rüdorff obtained at 180–300°. From X-ray analysis Rüdorff deduced that in these compounds a layer of FeCl$_3$ appears between each layer of C atoms. Product IV is believed to be similar to Rüdorff's stage III compounds (37–30% FeCl$_3$) which he obtained at temperatures of 325–400°. For this type of compound Rüdorff adduced evidence to show that FeCl$_3$ is probably intercalated between every third layer of C atoms in the graphite. Our product III, incidentally, was the result

Table I

Information Regarding Preparation of Graphite–FeCl$_3$ Samples

Product	Conditions of preparation Wt. graphite, g.	Temp., °C.	% FeCl$_3$ Unwashed product	% FeCl$_3$ Washed product	Molecular ratio FeCl$_3$:C Unwashed product	Molecular ratio FeCl$_3$:C Washed product
Ia	1–2	250–260	71.3	62.7	1:5.4	1:8.0
Ib	10	255		52.3		1:13
IIa	3	360	58.1	54.9	1:9.7	1:11
IIb	10	355	63.4	55.6	1:8.0	1:11
III	3	400–410		61.5		1:8.5
IV	10	450	39.3	33.6	1:21	1:26

(2) T. W. Richards and W. N. Stull, Carnegie Inst. of Wash. Pub. No. 7 (1903); T. W. Richards and Grinnell Jones, J. Am. Chem. Soc., 46, 935 (1924).

of an unsuccessful attempt to prepare Rüdorff's stage II compound.

Table II

Data Pertaining to Compressibility Measurements

Substance	Density	$\beta \times 10^6$	Molar $\beta \times 10^6$
Water	0.998	40.28	
Grahite[a]	2.27	3.39[c]	17.5
[b]	2.69	47.6[d]	
Graphite–FeCl$_3$ samples			
Ib[b]	1.92	13.04	124
IIb[e]	2.37	10.12	117
IV[e]	2.36	10.32	80

[a] Graphite in the form of 1.5×5 cm. cylinders cut from large pieces of Ceylon graphite. [b] Pellets 1 cm. in diameter formed by pressing 80–100 mesh powder in a pellet press. [c] Water was used as the piezometer filling fluid. [d] The high value obtained for the compressibility of the graphite pellets is believed to be the compressibility of the pellet itself rather than that of the graphite particles making up the pellet. Apparently the pellet was not penetrated by the liquid filling the piezometer even under pressure. [e] Loose powder.

A summary of the data pertaining to the compressibility experiments is given in Table II. The compressibility coefficient β is expressed as the contraction (cc.) in unit volume per unit of pressure (kg. cm.$^{-1}$). The footnotes to the table give further details regarding the compressibility experiments.

As might be expected the graphite–ferric chloride compounds are more compressible than graphite itself. When values of the molar compressibility of these compounds (defined as the compressibility of that amount of compound containing one gram-atom of carbon) are plotted against per cent. ferric chloride, the plotted points fall closely on a straight line. If this relationship is accepted as valid one can derive the expression

$$\frac{\beta}{d} = 1.46 + 14.0f - 15.5f^2$$

Here β is the compressibility coefficient; d, the density of the compound; and f, the fraction by weight of ferric chloride in the compound. β/d, of course, can be viewed as the compressibility of 1.0 g. of the compound. This equation represents our experimental data satisfactorily for values of f over the range 0–0.56. It is noteworthy that the right-hand expression approximates zero when $f = 1$, suggesting that the changes in β/d with variation in f is due primarily to changes in the compressibility of the graphite structure rather than to an effect directly attributable to the ferric chloride present in the compound.