

Fragments of the solidified melt containing $3\text{LiF}:\text{InF}_3$ were studied microscopically and by powder X-ray diffraction. Some grains showed a negative Bxa figure from which the optic axial angle was estimated to be about 60° . Approximate values of the refractive indices for white light at room temperature are $\gamma = 1.43$, $\alpha = 1.41$ and $\beta = 1.422$. No lines in the X-ray diffraction pattern could be attributed to the starting materials (Table I). The compound decomposed in water to form lithium fluoride and a product resembling that obtained from the hydrolysis of aqueous indium fluoride solutions.¹⁰

Discussion

The failure to obtain fluoro-indium complexes of the majority of cations studied is in marked contrast to the behavior of most elements closely related to indium, particularly gallium. The larger size of the indium ion may be largely responsible for this behavior. Although the reversible color change from pink to blue, which is observed when the cobalt salt is heated, is strongly indicative of the presence of hexahydrated cobalt(II) ions and hence of the

formulation $[\text{Co}(\text{H}_2\text{O})_6][\text{InF}_6(\text{H}_2\text{O})]$, the possibility of formulating the compound as a fluoro-complex of cobalt(III) is not conclusively eliminated. Such a structure would require oxidation of the cobalt and the experimental conditions were not favorable for this. The stability of the ammonium salt can be attributed to hydrogen bonding and the absence of steric interference which could become important with the larger ions.

Thermal analysis of the lithium fluoride-indium fluoride system shows conclusively that only one compound exists in this system. The empirical composition is Li_3InF_8 and the compound melts congruently at 867° . The decomposition of the compound when it is placed in water is further confirmation that the fluoroindate ion is less stable than the hydrated indium ion or hydroxy-fluoro-indium complexes, a conclusion which is also deduced from the studies in aqueous solution.

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Rare Earth Graphite Intercalates

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Intercalation in graphite of the whole series of rare earth chlorides has been investigated and some disagreements found with pre-existing incomplete studies. Only yttrium and gadolinium chlorides are found to intercalate consistently and in appreciable quantities. The light lanthanons do not intercalate, and inconsistent intercalation of heavy lanthanons appears attributable to variable degrees of hydration of the parent chlorides. Hall coefficient and magnetic susceptibility measurements confirm that the intercalates are ionic, while X-ray studies appear to confirm beliefs that the ions are located at imperfections in the graphite lattice. There appears some foundation for believing that ionic size and electronic structure are the major factors influencing intercalation.

Introduction

Croft¹ recently listed the varying reactions to intercalation in graphite of many elements in various ionic states and attempted to explain variations in degree of intercalation on the basis of interaction of vacant valence orbitals which could accept paired, but not single, electrons from 2-p- π orbitals of graphite atoms. Several criticisms of Croft's work² have developed but, theoretical aspects notwithstanding, his qualitative findings suggested immediately a new technique of rare earth separation potentially capable of applications to both gross and refined systems. Thus, yttrium and dysprosium appeared to be readily separable from erbium; similarly, ytterbium and scandium demonstrated differences in behavior which might well be the basis for a separational technique effective enough to supplement or supplant conventional amalgam-reduction techniques. Samarium apparently reacted differently from neodymium, while europium appeared separable from both gadolinium and samarium by graphite intercalation.

These pre-existing studies, however, were incomplete, the intercalation of terbium, holmium

and lutetium not having been examined. In a generalized examination of these rare earth graphite intercalates we have now filled this deficiency while simultaneously checking the intercalation effects of the whole rare earth series. Results obtained, in comparison with those of Croft, are concisely shown in Table I. Table II records the results of some separations attempted.

TABLE I
INTERCALATION OF RARE EARTH CHLORIDES, %

Ion ³⁺	Croft ¹	Present work
Sc
Y	43	25.5
La
Ce
Pr
Nd
Sm	38	4.9
Eu	3	..
Gd	16	19
Tb	n.i. ^b	2.5
Dy	22	2.0
Ho	n.i. ^b	.. ^a
Er
Tm	n.i. ^b	0.9
Yb	9	4.0
Lu	n.i. ^b	3.4

^a See text. ^b n.i., not investigated.

(1) R. C. Croft, *Nature*, **168**, 32 (1951); **172**, 725 (1953); *J. Appl. Chem.*, **2**, 557 (1952); *Australian J. Chem.*, **9**, 184 (1956).

(2) G. R. Hennig, Proc. Second. Conf. on Carbon, June, 1955, pp. 108, 111, Pub. 1956, University of Buffalo; W. Rudolf, V. Sils and R. Zeller, *Z. anorg. allgem. Chem.*, **283**, 229 (1956).

TABLE II
 SEPARATION OF RARE EARTH PAIRS

Reactants	Temp., °C.	Time (hr.)	Rare earth chloride in reacted graphite, %	
0.52 g. Madagascar graphite	550	1		
.79 g. ErCl ₃			ErCl ₃	None
.89 g. YCl ₃			YCl ₃	25.5
.35 g. graphite	550	1		
.5 g. SmCl ₃			SmCl ₃	4.9
.5 g. NdCl ₃			NdCl ₃	None
.34 g. graphite	550			
.48 g. YbCl ₃			YbCl ₃	4
.49 g. ScCl ₃			ScCl ₃	Trace

Experimental

As far as may be ascertained, the procedures established by Croft¹ in intercalation studies were adhered to rigidly except in the nature of the graphite employed. Croft employed a South Australian graphite after purification by hydrochloric and hydrofluoric acid treatment, but pointed out that this material had the same structure as Ceylon or Madagascar graphite. Madagascar graphite, similarly treated, was employed in the studies now reported. Although Dzurus and Hennig³ have shown that the source of graphite has little influence upon intercalation of ions, it may, of course, be taken that the nature of any impurities in the material may well have some influence, particularly where they have high vapor pressures.⁴

With the exception of scandium, the rare-earth oxides employed as starting materials were all of spectroscopical purity, obtained from Johnson Matthey and Co., London, England. The scandium oxide employed had been extracted from South Australian davidite and purified by ion-exchange techniques to 99.9+^o% purity.⁵

The hydrated rare earth chlorides were prepared, as by Croft, by repeated evaporation with concentrated hydrochloric acid, and reaction was effected in Carius tubes at the temperatures and for the times used by Croft. No difference in reactivity was found, whether the tubes were filled with nitrogen or evacuated before heating.

In examining separational applications, mixed chloride pairs were heated with graphite and treated in the same way as in normal intercalation; rare earths in the leach solution and washings were precipitated as oxalates which were ignited to oxide for spectrographic and/or X-ray fluorescence analysis. The graphite intercalate was ignited directly to oxide and similarly analyzed.

Discussion

Mulliken⁶ indicated that, for intercalation of compounds in graphite, fulfillment of two conditions appeared necessary—electronic interaction between graphite and the cations and an adequate electron affinity of the cations. The work of Orgel,⁷ Rabinowitch and Stockmayer,⁸ Dainton,⁹ and Weyl¹⁰ lends additional support to the influence of cationic valence states, while Croft¹ believes that electron affinity of the cations is not solely responsible for intercalation, there being a minimum value for the electron affinity of the cations below which intercalation does not occur.

However, none of the arguments submitted

(3) M. L. Dzurus and G. R. Hennig, *THIS JOURNAL*, **79**, 1051 (1957).

(4) A. Taylor and T. Laidler, *Nature*, **146**, 130 (1940); J. S. Lukesh, *J. Chem. Phys.*, **19**, 1203 (1951).

(5) R. C. Vickery, *Australian J. Sci.*, **16**, 113 (1953); *J. Chem. Soc.*, 245 (1955).

(6) R. S. Mulliken, *THIS JOURNAL*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(7) L. E. Orgel, *Quart. Rev. Chem. Soc. (London)*, **8**, 422 (1954).

(8) E. Rabinowitch and W. H. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

(9) F. S. Dainton, *J. Chem. Soc.*, 1533 (1952).

(10) W. A. Weyl, *J. Phys. Chem.*, **55**, 507 (1951).

particularly explain intercalation of the rare earths and, particularly, of yttrium and gadolinium. According to Croft, rare earth chlorides can only interact with graphite by means of vacant valence orbitals which may accept paired but not single electrons from 2-p- π orbitals of graphite, this probability being somewhat confirmed by the failure to intercalate the tetrachlorides of silicon, germanium, tin and lead. The application of this theory to rare earth chloride intercalation is, however, somewhat hypothetical, suggesting as it does that intercalation results from transfer of electrons from graphite to depleted 4-f orbitals in the rare earth atom. Since, according to Croft, gadolinium and dysprosium are capable of intercalation, the belief is promulgated that these elements are potentially multivalent. There is no cogent evidence to support this theory. Indeed, existing knowledge of nuclear and electronic structures of the rare earths would militate against such an analysis. Again, one would expect on this basis intercalation of cerium, praseodymium or terbium—none of which are in fact intercalated.

Our general survey has shown several deviations from Croft's findings (Table I), and we have found that mode of preparation of the chloride has great influence upon degree of intercalation. Croft himself, in examining chromium and copper chlorides, observed that the anhydrous compounds intercalated much less readily than when free chlorine or hydrochloric acid was present. We have found 13, 9 and 6% of holmium chloride to intercalate, depending upon an increasing degree of dehydration. Generally, the figures given in the third column of Table I represent consistently obtained intercalation values. Data for HoCl₃, being very inconsistent, have been reported separately in this text. Predominantly, however, we have been unable to confirm intercalation of DyCl₃. Some of Croft's findings for minor intercalation, *i.e.*, of europium and ytterbium, might conceivably be attributable to impurities such as samarium or yttrium in his metals. Impurities of this close nature were absent in our studies. However, the lack of agreement in intercalation of DyCl₃ cannot be ascribed to impurities, and this non-conformity has been continuously confirmed in these laboratories.

Dzurus and Hennig¹¹ have pointed out that development of "spacers" within the graphite lattice permits the entrance of many substances into graphite which do not enter spontaneously and that chloride functions as such a spacer with, *e.g.*, aluminum chloride. We believe such "spacing" to be the reason for the minor quantities (2-5%) of lutetium, terbium, etc., which can be inserted in graphite, the chlorine being derived from minor excesses of acid present as such in the chlorides or as produced by their hydrolysis. Intercalation of HoCl₃ is considered a specific example (*vide supra*). It should be noted, however, that these minor intrusions occur only within the heavy-earth group, the ionic radii of which are somewhat smaller, and the electron affinity somewhat higher, than those of the light earths. But this does not explain the

(11) M. L. Dzurus and G. R. Hennig, *Bull. Am. Phys. Soc.*, **29**, No. 7, 12 (1954); *J. Chem. Phys.*, **20**, 1438 (1952).

intercalation of gadolinium but not europium, nor of yttrium but not dysprosium. Indeed, if ionic size and electron affinity be the sole criteria, then scandium would also intercalate. There appears likewise no correlation between thermodynamic properties of the rare earth chlorides (H_t , S_b , ΔF , etc.) and the extent of their intercalation in graphite.

It is apparent that the rare earth chlorides reside in the graphite lattice ionically without covalent bonding. Croft reports as much from his preliminary magnetochemical studies, and we have confirmed this from magnetic susceptibility measurements on the gadolinium and holmium intercalates. That the rare earth cation accepts electrons from graphite is confirmed by preliminary Hall coefficient studies which we have made. As with intercalated aluminum chloride,³ positive coefficients have been obtained.

Our X-ray studies have shown little or no measurable variation to occur in dimensions of the graphite lattice upon intercalation; this is in accord with Hennig's observations¹¹ and reopens the concept of effect of ionic size upon intercalation. If, as Hennig suggests, intercalation occurs only at crystal imperfections, then the ionic size of the cation should be a major factor, not only in the entrapment of the rare earths but also in their removal. This approach can best be exemplified by postulating that rare-earth ions greater than, *e.g.*, gadolinium (1.11 Å.) cannot enter these lattice imperfections, while those ions smaller than, *e.g.*, yttrium (1.06 Å.) cannot be retained on subsequent washing out or treatment with dilute acid. Hennig has calculated that imperfections are approximately 10 μ in length—if the present postulate is correct, a limit of *ca.* 1.11 Å. is therefore set upon the width of the imperfection. This physical entrapment is, we consider, the primary facet of intercalation but still leaves unexplained the differing reactions of yttrium, dysprosium, gadolinium, holmium, terbium and erbium, all between 1.04 and 1.11 Å. ionic radius.

Distinction may be found, however, in considering electronic structures of the consistently intercalated yttrium and gadolinium. Both are trivalent, yttrium has no incomplete inner electron shell, gadolinium has seven 4-f electrons. The

gadolinium configuration is generally taken to be of appreciable stability, and the multivalence of samarium, europium and terbium attributable to a tendency for the trivalent ions of these elements to attain the stable 4-f configuration.¹²

Being "internally" stable, the Y^{3+} and Gd^{3+} ions can only be expected to accept electrons into their valence shells, and then only where sufficient ionic interaction exists between them and the anion (Cl^-) such that a resonating structure or hybridization can occur. Where incomplete ionic shells exist, it may be expected that any graphite-chlorine-rare earth resonance or hybridization will so unduly affect the lower lying electrons¹³ as to render the whole coordinated structure unstable.

There appear, therefore, the two requirements for intercalation of ionic size (or, most probably, hydrated ionic or associated ion size) and possession of a stable internal electronic structure. These requirements, considered together with those postulated by Mulliken,⁶ would appear to establish the model for intercalation of rare earth chlorides in graphite lattices.

Adverting to separational aspects: several rare earth pairs have been examined for preferential intercalation but, from the results obtained, the adequacy of such an approach is found only for yttrium-erbium mixtures (Table II), and this intercalation technique appears suitable for large-scale application. In normal separational systems, even those involving ion-exchange techniques, yttrium adopts a serial position close to dysprosium, holmium and erbium and many precise techniques have been suggested for its removal from these lanthanons—or *vice versa*. Use of this intercalation technique would now appear to render unnecessary anything more than crude separation down to conservative systems before complete extraction of the yttrium can be made; any gadolinium present will accompany the yttrium, but these two elements are so generally separable by, *e.g.*, ferricyanide precipitation that this refinement is of minor importance.

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(12) J. K. Marsh, *Quart. Rev. Chem. Soc. (London)*, **1**, 126 (1947); R. C. Vickery, "Chemistry of the Lanthanons," Butterworth, London, 1953.

(13) R. C. Vickery, *J. Chem. Soc.*, 421 (1952).

[CONTRIBUTION FROM THE MAIN LABORATORY, SOUTH AFRICAN COAL, OIL AND GAS CORP., LTD.]

Appearance of FeC in a Hydrocarbon Synthesis Catalyst

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The normal equilibrium catalyst in our type of Fischer-Tropsch synthesis reactor contains Hägg iron carbide as a significant component. During the course of a synthesis run a new crystalline phase was discovered in the Debye-Scherrer X-ray diffraction diagram. A deposit from the wall of the reactor was found to consist mainly of this new phase and this material was studied by X-ray diffraction and wet chemical analyses. The X-ray diffraction pattern showed this phase to be identical to the iron carbide previously reported by Eckstrom and Adcock (1950) and designated by them as FeC. Wet chemical analyses support the conclusion drawn from X-ray analyses. Thermomagnetic studies of this material have not yet been possible.

In our hydrocarbon synthesis plant the active catalyst is produced by the action of CO and H₂ at about 20 atmospheres pressure and 315° on pro-

moted and reduced magnetite, analyzing about 95% total iron, in a circulating fluidized bed according to the Kellogg process.