Properties of X-Radiation

THE published accounts of unsuccessful attempts to find the *J*-phenomenon seem to call for some statement of the present position of investigations on the subject. Our experience of the phenomenon is now so extensive, that the comments and suggestions of experimenters are to us of little more than psychological, or shall we say philosophical, interest. Their results represent, at most, an almost negligible number of observations under conditions which we are able to reproduce at any time ; they add nothing to our knowledge.

These negative results, that is results showing no *J*-discontinuity, are neither more nor less accurate, neither more nor less real, than those which show the discontinuity. Results of one kind follow laws which are now familiar to physicists ; the others are governed by laws which are not as yet generally recognised. It is to the apparent violations of known laws and not to further confirmation under very precise and specialised conditions that we must look for advances in knowledge. The very rigid limitation of the number of variables, usually imposed upon the experimental conditions, is a most effective barrier to discovery in regions which have not been thoroughly explored. These limitations we have tried—indeed experience has taught us—to avoid.

The *reality* of a *J*-discontinuity can be established by an observer in an hour's time ; the wide generality of the phenomenon has however taken months and even years to establish. The laws which govern it have been studied for thousands of working days and certain general conclusions have been reached. How general these laws are, cannot, of course, be told. But they show with certainty that what have previously been regarded as the fundamental laws of X-ray action are not valid ; and they introduce us to entirely new conceptions of X-ray phenomena. It is quite evident that not only is the *J*-absorption-discontinuity conditional on some unidentified factor but that even the *K*-absorption edge (discovered by us some twenty-five years ago, and now perhaps too faithfully accepted) is conditional, and not perfectly general. In fact, the whole activity of a radiation in a substance is not governed solely by the wave-length of the radiation and the nature of the substance. Confirmation of this statement will be found in the work of Lindh and others on the absorption of X-rays by light substances—work which showed as alternative results absorption lines and absorption edges. It is such alternative results which we have frequently described in association with the *J*-phenomenon.

In this laboratory we have observed the disappearance of the *K*-absorption in a way so pronounced that there is no mistaking it.

It may be that many more years must pass before the results discovered can be attributed to one or two simple measurable quantities. The simplest interpretation has yet to be found. But it is important to know that current theories completely break down —that the quantum (or photon) may become impotent ; that an atmosphere of radiation (not independent quanta or harmonic constituents) is effective ; that superposed radiations act as a coherent whole ; that, so far as the radiation is concerned, something analogous to temperature of radiation is the dominant factor ; that the internal state (and history) of a substance (not simply the nature of constituent atoms) determines its behaviour under X-ray action. How far these conclusions apply to the *K* and *L* phenomena has yet to be determined, but even *their* conditional nature has been established. Detailed accounts will be published in other journals.

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Nov. 18.

Carbonyls of Lithium, Rubidium and Cæsium

THE carbonyls of certain alkali and alkaline earth metals have been prepared previously by the action of carbon monoxide on a solution of the appropriate metal ammoniate in liquid ammonia. In this way, Joannis[1] obtained sodium carbonyl, NaCO, and potassium carbonyl, KCO ; Gunz and Mentrel[2] barium carbonyl, $Ba(CO)_2$ and Roederer[3] strontium carbonyl, $Sr(CO)_2$. In the course of researches on the carbonyls proceeding in these laboratories, the corresponding compounds of lithium, rubidium and calcium have been obtained.

The carbonyls were prepared by condensing pure, dry ammonia on to a clean specimen of the metal in question by immersing the containing vessel in a bath at − 60°. After complete dissolution, which occupied about 45 minutes, the excess of ammonia was allowed to evaporate, a gentle stream of pure, dry carbon monoxide being meanwhile passed through the apparatus and continued until the metal ammoniate was wholly transformed into the carbonyl. Because of the highly reactive nature of the metals, ammoniates and carbonyls, all the operations were conducted with the rigid exclusion of both air and moisture.

Lithium carbonyl, LiCO, is a white pulverulent substance quantitatively synthesised by these means : found Li 18·80, 19·62, 21·05 per cent, mean 19·82 per cent ; calculated for LiCO, 19·86 per cent. It darkens on standing owing presumably to the liberation of minute amounts of carbon, and, on heating in a vacuum, it begins to decompose at 300° without detonation but with the separation of carbon. At about 500° this change is completed in a short time, the residue consisting of free carbon, carbonate and oxide, the amount of residual carbon indicating that the reaction takes the course,

$$4LiCO = Li_2CO_3 + Li_2O + 3C ;$$

ratio LiCO mol./C atoms, found 1·57, calculated 1·33 (the high ratio being probably due to the loss of carbon in the colloidal form). When treated with water the carbonyl detonated violently, with instant ignition of the gaseous products, a cloud of soot being produced and a residue of carbonate and carbon left. On the other hand, water vapour was absorbed quietly with the formation of a dirty brown liquid. The carbon from the detonation of the carbonyl gave ratios LiCO mol./C atoms lying between 2·5 and 3·5. These results together with those of Joannis, who showed that the gas from the detonation of sodium carbonyl with water contained 86 per cent hydrogen and 14 per cent carbon monoxide, indicate the probability of more than one reaction : the high proportion of hydrogen, together with the presence of carbonate in the residue accords well with a reaction of the type,

$$2LiCO + H_2O = Li_2CO_3 + C + H_2$$

involving the reduction of water by the carbonyl, which requires LiCO/C = 2.

Rubidium carbonyl is a pure white solid possessing as ordinarily prepared a nacreous lustre and dissolving readily in water to give a pale yellow solution. Quantitative synthesis gave Rb 76·55, 74·89 per cent; mean 75·72 per cent; calculated for RbCO, 75·35 per cent. The lilac colour attributed to some of these carbonyls only appears when the conversion from ammoniate to carbonyl is incomplete, and is undoubtedly due to a fine dispersion of the former material. When rubidium carbonyl is heated in a vacuum, the usual dissociation sets in about 350°, and proceeds with increasing rapidity as the temperature is further raised, carbonate, carbon and oxide being produced.

Calcium carbonyl is a dirty, cream coloured, pulverulent powder: found Ca 40·75, 43·66 per cent; mean 42·21 per cent; calculated for $Ca(CO)_2$, 41·70 per cent. With water, it darkens in colour and partially dissolves with the evolution of heat, but without detonation. When heated in a vacuum it gives carbon, carbonate and oxide, the reaction commencing about 200° and increasing in velocity as the temperature is raised.

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[1] *C. R. Acad. Sci.*, **116**, 1518; 1893.
[2] *Bull. Soc. Chim.*, (3), **29**, 585; 1903.
[3] *Ibid.*, **35**. 715; 1906.

Systems of Four Immiscible Liquid Layers

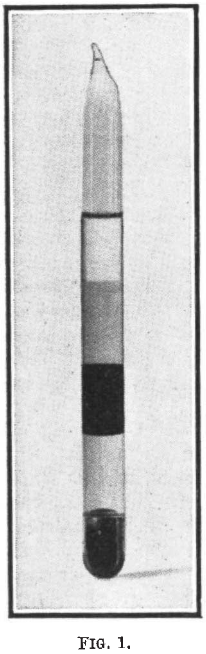

FIG. 1.

IN a recent letter Prof. J. R. Partington[1] states that the system of four immiscible liquid layers described by me[2] does not appear to be stable, inasmuch as a specimen, that originally separated into the four layers, now forms two only. A little more than two years ago I prepared a sealed tube containing this system, plus mercury. It has been shaken repeatedly, but still separates into five layers. Moreover, there has been no noticeable tendency for any one of the layers to decrease in volume, much less to disappear. A recent photograph of this tube is reproduced as Fig. 1. A second specimen, made about the same time, behaved in precisely the same way.

It is difficult to account for the instability of Prof. Partington's specimen, unless indeed impure materials were used (for example, the best oleic acid obtainable commercially is impure) or unless precautions were not taken to exclude atmospheric oxygen and carbon dioxide. The latter will decompose the soap, and the four layers will become three. This might conceivably happen within two years through the action of atmospheric carbon dioxide if the specimens were stoppered with cork or rubber; but then under such conditions the hexane might evaporate away. The suggestion that some decomposition has occurred, or that impure materials were used, is supported by the fact that the two layers of the unstable specimen are reported to be brown in colour.

The phase rule does not demand that systems shall remain in equilibrium in the presence of reactive substances not included among the components. Indeed, it is applicable even when slow interaction between the components occurs. For example, Schreinemakers' studies of the system succinic nitrile, water,[3] and my own of the system sodium oleate, sodium chloride, water, ethyl acetate,[4] are not invalidated because the nitrile and the ester respectively are slowly hydrolysed by the water. These systems would certainly not remain in equilibrium for two years, but as it happens the system under consideration is not of this type. Provided that it is prepared with pure materials and suitably sealed, it seems likely that it will remain unchanged indefinitely, thus constituting the first example of a system of four immiscible liquid layers in permanent true equilibrium. This claim is sufficiently established by the single example illustrated in the accompanying photograph, and is not weakened by the fact that the same phenomena may not be manifested under slightly different conditions.

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[1] NATURE, **130**, 967, Dec. 24, 1932.
[2] NATURE, **127**, 91, Jan. 17, 1931.
[3] *Z. Phys. Chem.*, **23**, 418; 1897.
[4] *J. Phys. Chem.*, **36**, 2455; 1932.

Vacant Positions in the Iron Lattice of Pyrrhotite

PREVIOUS investigations on the solubility of sulphur in iron sulphide (FeS) have led to the conclusion that the solid solutions of sulphur in iron sulphide are formed by substituting some of the iron atoms in the original lattice by sulphur atoms. Assuming that the radius of the sulphur atoms is smaller than that of the iron atoms, this hypothesis explains the fact that the lattice dimensions decrease with increasing sulphur content. It seems, however, doubtful if this relation between the radii of iron and sulphur atoms agrees with reality, and the difficulties are still more increased when one has to explain the analogous (only more pronounced) lattice variations in solid

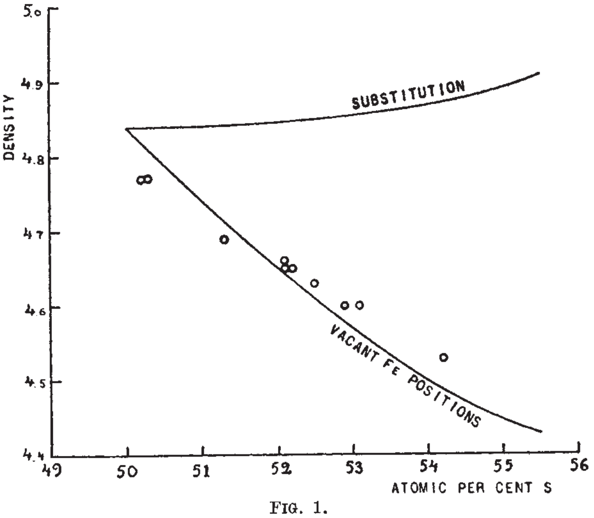

FIG. 1.