

and naphthacene molecules fluoresce. Our experimental results that light of wave-lengths 460, 475, 490 μ , which cannot be absorbed by anthracene molecules, can produce enhanced fluorescence of naphthacene, is against Bowen's hypothesis.

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MR. GANGULY'S observations, which are in complete accord with those of several other workers on the subject¹, can scarcely be said to refute the idea of energy transfers in crystals. Solid naphthacene fluoresces with its characteristic band emission, though rather faintly; when dissolved in solid anthracene it also fluoresces, as Mr. Ganguly notes, if illuminated by light which is directly absorbed by naphthacene molecules (4350–4000 Å.). The vital question in the matter of energy transfer is what happens when shorter-wave light is used. If the mercury line at 3650 Å. is used for excitation, the green fluorescence of naphthacene is visible in solid solutions containing only one molecule of naphthacene in 10^6 molecules of anthracene; at 1 in 10^4 this green fluorescence is strong, and above about 5 in 10^4 the green is brilliant while the violet anthracene fluorescence has disappeared. At 3650 Å. anthracene absorbs much more strongly than naphthacene; the extinction coefficients in liquid solution are 1600 and 400 respectively, so that unless the ratio of extinction coefficients changes by a factor of about 10^4 in passing from solution to solid, the light must be absorbed by the anthracene molecules.

This being so, an explanation must be found for the emission by the naphthacene and the quenching of the anthracene emission. One possibility is that the anthracene emits its fluorescence (4450–4030 Å.) and that this is reabsorbed by the naphthacene, the bands of which are in this region. However, the *maximum* extinction coefficient of naphthacene in (liquid) solution is 12,000²; this possibility is likely to be effective therefore only at molar ratios of anthracene to naphthacene of $12,000/1,600 \approx 10$ (again assuming that the solid absorption ratios are not greatly different from those of liquid solutions). Since the maxima of the naphthacene absorption bands do not overlie the maxima of the anthracene fluorescence bands, this ratio must be an overestimate, probably by a factor of 10.

We are therefore forced to assume an 'exciton'³ mechanism. The electronic energy in an excited anthracene molecule must be mobile and capable of moving from molecule to molecule in the crystal by resonance. In pure anthracene the career of the exciton is terminated by fluorescence at some point. When naphthacene is present in solid solution, the exciton is trapped owing to the lower energy level of the excited state of the molecule below that of anthracene; the excess energy is lost as heat, and the fluorescence afterwards emitted is that of the naphthacene. Liquid solutions (as in benzene) of anthracene containing minute amounts of naphthacene fluoresce like pure anthracene instead of the green of naphthacene, the 'handing on' process being inhibited by lack of molecular proximity and orientation. For this reason impurities in crystals in general often

profoundly alter the fluorescence properties while exerting no such effect when the whole is dissolved up in a liquid.

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¹ For example, Dufraisse and Horlois, *Bull. Soc. Chim.*, 1888 (1936).

² Clar, *Ber.*, 65, 503 (1932).

³ Franck and Teller, *J. Chem. Physics*, 6, 861 (1938).

Reaction Between Solids

IN reactions between solids the transport of the reactants through the reaction-product is rate-determining if the formation of the new compound on the surface of the reactants proceeds fast enough. The rate is then closely connected with the mobility of the 'reacting constituents', that is, ions and electrons, in inorganic substances. The behaviour of the reaction product as a semi-conductor is indicative of this mobility.

Experimental verification of recent theories¹ on this subject has nearly all been confined to simple reactions between a metal and a metalloid, such as in the corrosion of metals, and has been mainly carried out at temperatures not much above room temperature.

We have investigated the formation of spinel, $MgAl_2O_4$, from magnesia and α -alumina above 1,000° C. This reaction is probably characteristic of others encountered in the refractory and ceramic industries, and also in the production of many metals from their oxides by reduction with aluminium. Unpublished investigations in this laboratory have shown that spinel is an intermediate compound formed during the production of magnesium vapour by reduction of magnesia by aluminium *in vacuo*.

Alumina² and magnesia³ are both 'reduction' semi-conductors⁴, that is, substances the conductivity of which increases when heated in a reducing atmosphere (for example, hydrogen) or vacuum. By this treatment they lose oxygen and the excess metal is left behind as positive ions in interstitial positions, electrons being trapped in the ionic field⁴. Very probably the same applies to spinel⁵.

If this is so, and if the reaction on the phase boundary proceeds fast enough, spinel should be formed at a higher rate in a reducing atmosphere or *in vacuo* than in air. To check this theory two sets, of four cylindrical briquettes, one inch in diameter and one inch high and each weighing 25 gm., were made up of powdered magnesia and α -alumina (passing 200 mesh, $r \leq 0.037$ mm.) in stoichiometric proportion. The briquetting pressure was 11.4 tons per sq. in. To one set there was added 5 per cent of metallic magnesium powder.

The briquettes containing the magnesium powder (set *a*) were heated to 1,000°, 1,050°, 1,100° and 1,150° C., respectively, in a high-frequency vacuum furnace evacuated to a pressure of 0.1 mm. of mercury and maintained at temperature for one hour. The briquettes of the other set (set *b*) were heated in the same furnace, and under exactly the same conditions of temperature and time as set *a*, but without evacuation of the furnace.

Debye diagrams (copper $K\alpha$) were then made from powder from each briquette and compared qualitatively with those of spinel and the original reaction mixture. In all the magnesium gettered specimens