

series coincides with the bands investigated by Kistiakowsky at 2300A but this may be accidental as those bands appear at much higher pressures.

All the observed facts go to show that one of the valence electrons between the two carbons is excited and that the two series are due to the different coupling of its orbital momentum with the internuclear axis. Thus the upper levels of class I can be provisionally designated as *P*II levels and those of Class II as *P* $\Sigma$  levels.

As many as ten vibrational transitions accompany some of the fundamental electronic transitions. Their analysis is greatly simplified by the magnitudes of the isotopic shifts. It appears that the CC bond is weakened considerably in the upper states whereas the CH bond remains practically unaltered. This is in agreement with the fact that no CH vibration is excited by absorption from the normal state and also that the shift in zero point energy is only about 20 cm<sup>-1</sup>. All the bands of appreciable intensity are included in our classification.

The band system at 1520A shows strong predissociation. The next system at 1340A is slightly diffuse whereas all the

bands at shorter wave-lengths appear to be sharp. If it is assumed that the predissociation is due to interaction with the normal state, then the heat of dissociation of C<sub>2</sub>H<sub>2</sub> into CH+CH must be slightly less than 8.1 electron-volts or the energy of the triple CC bond is slightly less than 187 Cal./Mol.

The situation is similar in ethylene. The bands are somewhat more diffuse and only one Rydberg series is observed. Predissociation occurs at 1750A giving the heat of dissociation corresponding to C<sub>2</sub>H<sub>4</sub>→CH<sub>2</sub>+CH<sub>2</sub>≡7.05 electron-volts or the strength of the C=C bond ≤162 Cal./Mol.

The bond strengths are in good agreement with the best chemical data. It is thus clear that the work is going to be of considerable value in the recently developed chemistry of free radicals.

The early part of the work was done in collaboration with Dr. G. B. Collins.

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#### The Orientation of the CO<sub>3</sub> Groups in Ammonium Bicarbonate Crystal

Ammonium bicarbonate, (NH<sub>4</sub>)HCO<sub>3</sub> crystallizes in the orthorhombic system and its structure has recently been analyzed by x-ray methods by Mooney.<sup>1</sup> He finds that the CO<sub>3</sub> groups in the crystal are all oriented with their planes parallel to *a*(100), and that the dimensions of the CO<sub>3</sub> groups are practically the same as in the normal carbonates.

Measurements on the magnetic anisotropy of the crystal confirm these conclusions. Denoting by *x*<sub>a</sub>, *x*<sub>b</sub> and *x*<sub>c</sub> the principal gram molecular diamagnetic susceptibilities of the crystal along its *a*, *b* and *c* axes, respectively, it is found that

$$x_b - x_a = 5.0; \quad x_c - x_a = 4.5$$

in 10<sup>-6</sup> c.g.s. e.m.u., *x*<sub>b</sub> and *x*<sub>c</sub> are thus nearly equal and greater than *x*<sub>a</sub> by about 4.7 × 10<sup>-6</sup>, which is practically the same as the value of the magnetic anisotropy of the CO<sub>3</sub> group in calcite, aragonite, strontianite and witherite, obtained by Krishnan, Guha and Banerjee.<sup>2</sup> This shows

that the CO<sub>3</sub> planes in ammonium bicarbonate crystal are oriented parallel to one another in the *a*(100) plane, and that the magnetic anisotropies of these CO<sub>3</sub> groups, and hence presumably their structure also, are the same as in the normal carbonates quoted above.

In strong contrast to the magnetic behavior of ammonium bicarbonate is that of potassium bicarbonate. The latter crystal (which is monoclinic) exhibits a much feebler anisotropy, which shows that the planes of the different CO<sub>3</sub> groups in the unit cell of this crystal must be considerably inclined to one another.

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<sup>1</sup> Mooney, Phys. Rev. **39**, 861 (1932).

<sup>2</sup> Krishnan, Guha and Banerjee, Phil. Trans. **A231**, 235 (1933).

#### Two New Phenomena at Very High Pressure

It has long been surmised that there should be another modification of bismuth, denser than the liquid phase, stable only under high pressure, in analogy to the high pressure modifications of ice. Attempts to produce this new phase by the application of pressures up to 20,000 kg/cm<sup>2</sup> have, however, been unsuccessful. I have recently found that this modification is produced reversibly from the ordinary solid phase at room temperature at about 25,000 kg/cm<sup>2</sup>. The transition is accompanied by a volume decrease of about 9 percent. By extrapolation, the liquid should be about 5 percent more dense than the ordinary solid at the reversible melting point under 25,000 kg/cm<sup>2</sup>, so that we may expect the new solid to be formed from the

liquid with a contraction of the order of 4 percent. The next obvious step is to raise the temperature in order to find the location of the triple point between the two solids and the liquid, but this must wait for modifications in the present apparatus.

Hitherto the irreversible transition from white to black phosphorus has not been produced at temperatures below 200°C, where the pressure necessary is about 12,000 kg/cm<sup>2</sup>. I have just made black phosphorus from white at room temperature by the application of about 35,000 kg/cm<sup>2</sup>. In appearance to the eye the mass is indistinguishable from regular black phosphorus, but there was no trace of any red phosphorus on the exterior surfaces;

such has always been found before. However, the transition from white to black is apparently not quite as complete under the new conditions as at higher temperature and lower pressure, for on breaking the freshly formed mass open with a knife there were a few flashes of flame, indicating nuclei of still untransformed white phosphorus. The density is only 2.59 against 2.69 for the regular black phosphorus. It is furthermore to be remarked that at room temperature the transition takes place from that modification of white phosphorus which is stable at atmospheric pressure only below  $-80^{\circ}\text{C}$ , instead of from the normal form of white phosphorus stable at room temperature. It is

therefore possible that the new black phosphorus is not exactly the same as that known before.

The two experiments described above were instigated by the recent development of a new grade of steel considerably stronger than any steel yet available to me. With this I have reached pressures well over 40,000 kg/cm<sup>2</sup>. A number of interesting questions suggest themselves for rough qualitative examination in this extended pressure range.

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May 14, 1934.

### Beta-Radioactivity of Neodymium

In a previous publication<sup>1</sup> Professor W. M. Latimer and the present author mentioned evidence for the radioactivity of neodymium in connection with a report of work on the alpha-activity of samarium and the possible activity of other rare earths. Since that time, additional evidence for a beta-ray neodymium activity has appeared which seems to be sufficiently interesting and conclusive to justify publication.

A sample of Nd<sub>2</sub>O<sub>3</sub> originally prepared by Professor James was carefully purified to remove lead, bismuth, barium, thorium and their radioactive homologues, and its activity measured. After having allowed it to stand for seven months the activity was measured again and was found to be the same within fifty percent. In addition, absorption experiments showed 5 mm of air could completely stop the radiation. Magnetic deflection experiments were then completed. It was found possible to bend the hardest of the radiation into circles of 7.5 mm radius, or less, by a field of 500 gauss. Finally, purification of a Nd<sub>2</sub>O<sub>3</sub> sample prepared by Professor B. S. Hopkins revealed a residual activity of the same intensity and properties.

These data seem to make the presence of any of the known radioactive series in significant amounts extremely improbable. The possible presence of a rare earth impurity which might emit such a radiation was checked by deflection experiments done on samarium, lanthanum, and praseodymium, none of which showed a deflectable radiation of intensity greater than one-third of that of the neodymium. The intensity of the alpha-radiation from the samarium was about ten times that from the neodymium in the absence of a field.

The apparatus used was essentially a Geiger-Müller counter with a wall of copper screen having five No. 28 wires to the cm. The deflection measurements were made by surrounding the counter with a concentric cylinder having the Nd<sub>2</sub>O<sub>3</sub> on its inner surface, 15.0 mm from the counter wall, and with a solenoid wound around it. The charge determination consisted of observing the effect of field reversal when slanting metal vanes were placed between the sample and counter cylinder.

Fig 1. shows the magnetic deflection data. The abscissae are the  $H_{\rho}$  values of particles which would just miss the counter under the most favorable conditions of emission and the given field. The maximum  $H_{\rho}$  value apparently is

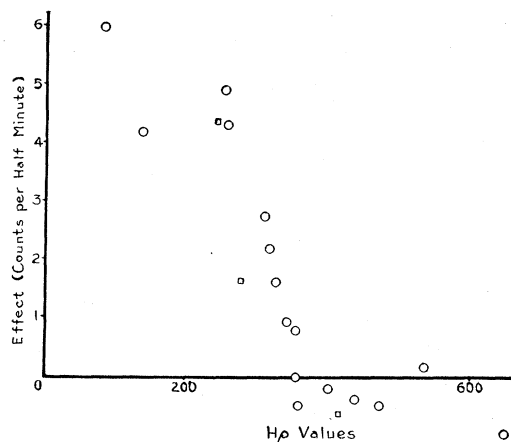


FIG. 1. Circles, James sample; squares, Hopkins sample.

close to 355 which agrees well with the observed range according to the data of Schonland<sup>2</sup> on cathode rays. This means a range of 2.4 mm in air. Table I shows the data from the charge determination experiment. The direction for negative charge was checked by using KCl and by geometrical calculation.

Each of the four values given is the mean of about 900 readings. The runs with sample present and sample absent were made on different days and the absolute values are of little significance. The effect,  $+0.90 \pm 0.22$ , of the addition of the sample appears conclusive. The effect indicating low energy positives from the wall in the absence of the sample remains unexplained but definite. The table shows that the

TABLE I.

	Count per half minute with field so negatives pass	positives pass	Effect
Sample present	$23.37 \pm 0.108$	$23.07 \pm 0.107$	$+0.30 \pm 0.15$
Sample absent	$23.38 \pm 0.108$	$23.98 \pm 0.11$	$-0.60 \pm 0.15$

<sup>1</sup> W. F. Libby and W. M. Latimer, J. Am. Chem. Soc. **55**, 433 (1933).

<sup>2</sup> Schonland, Proc. Roy. Soc. **A104**, 235 (1923); **A108**, 187 (1925).