On the other hand, the spectra of the hexagonal crystals are distinctly different from those of the monoclinic, the multiplets being much narrower and shifted toward higher frequencies (Table III). The spacings are also different and in some cases fewer lines are observed.[16] Since only one band from a triclinic crystal has been measured, no conclusions can be drawn, but preliminary observations on gadolinium acetate, which is triclinic, indicate that its spectrum is different from that of both the hexagonal and monoclinic types.

These results are in qualitative agreement with predictions made by Bethe[6] on theoretical grounds. Quantitative results, however, are not to be expected as he made many simplifying assumptions which do not apply here.

Summary

Absorption spectra of gadolinium ion in crystals consist of lines which arise from electronic transitions from a single basic level $4f^7$, $^8S_{7/2}$, to excited levels which are non-degenerate through the influence of the electric fields of the neighboring ions. The amount and nature of the splitting depend upon the symmetry and separation of the ions in the lattice with higher symmetry corresponding to smaller separations of the levels.

We are continuing this work, extending the number of compounds in each crystal system and including anhydrous as well as hydrated compounds.

(16) While hexagonal crystallographic symmetry does not necessarily mean that there is hexagonal symmetry about the gadolinium ion, it is likely that the symmetry in the hexagonal crystals is much higher than that in the monoclinic.

BERKELEY, CALIFORNIA

RECEIVED JULY 29, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Recording of Pressure and Time in Gas Explosions[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

Numerous investigations have been made of the increase in pressure during gas explosions in closed vessels. Generally, the instrument for indicating the pressure has been a thin metal diaphragm whose deflection is measured by a suitable optical arrangement. These diaphragms are, on the whole, very satisfactory for following rapid pressure changes. As they have been used, however, they possess at least two serious disadvantages. First, the tension of the diaphragm is dependent on the strength with which it is clamped into position. This clamping strength may be

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altered during explosions and so vitiate the calibration of the diaphragm. Second, these diaphragms usually possess apparent hysteresis, which, we believe, is to be attributed not so much to the diaphragm itself as to the inelastic clamping gaskets commonly used.

We have developed a diaphragm indicator which effectively overcomes these difficulties and which has been used successfully for the recording of ozone explosions from which the specific heat of oxygen has been obtained.[4] This diaphragm and a method of dynamic calibration, together with several other features, will be described in this paper.

A sketch of the diaphragm clamped into the opening of the bomb is given in Fig. 1 and Fig. 1a.

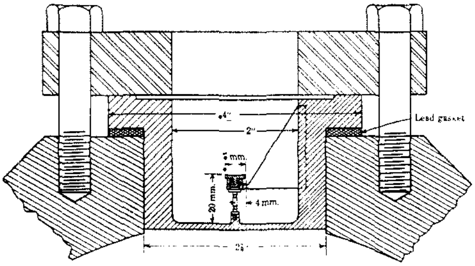

Fig. 1.

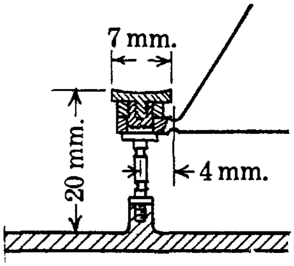

Fig. 1a.

A large cylinder of high-grade nickel steel is worked on the lathe to the shape given in the figure. The diaphragm itself forms the bottom of the piece and has a seat left in its center into which the piece carrying the mirror can be screwed rigidly by means of a conical thread. This piece consists of a thin rod of spring steel in which two necks have been cut to allow flexibility. Over the end of the central piece is fitted a thin ring which is kept rigid by means of a small nut. The ring is a part of a heavy piece of the same spring steel which is firmly dovetailed into the heavy wall of the diaphragm piece Immediately adjacent to the ring and part of the same piece, another flexible neck is cut The mirror, which is screwed into the top of the central piece by means of a conical thread, is concave and made of high-grade stainless steel. It was ground very accurately to a focal length of 1.5 meters by the astronomical instrument makers, John A. Brashear Co., Pittsburgh. Assembled, the whole mechanism was rigid as though made of one piece. When pressure is exerted on the back face of the diaphragm the center piece tends to move out and is forced to deflect to the right by reason of the necks. The mirror therefore moves about a circle with a radius of 4 mm., the distance between the center of the central rod and the center of the adjacent neck. The magnification of this system for a distance of 1.5 meters between the mirror and the film is about 1000. Thus only very small deflections of the diaphragm itself need take place for reasonable movements of the light point on the film. This has an obvious and important advantage, since the diaphragm can be made relatively thick and so possess a high natural frequency which is desirable in explosion experiments.

The whole piece was clamped rigidly into the opening of the bomb by bolts and a flange as shown in the figure. The strain was applied to the rim of the piece, leaving the diaphragm proper perfectly free. It was impossible for it to change its position as a result of explosions.

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[4] Lewis and von Elbe, THIS JOURNAL, 55, 511 (1933).

Calibration of Diaphragm.—Calibrations were made in two ways, dynamically and statically. In the dynamic method the pressure was applied to the diaphragm in a time interval of about 0.01 second, which was about the same order as the time during which the pressures were released in explosions under investigation. The results showed that with this type of diaphragm there was no difference between the two methods of calibration. This strongly indicates that hysteresis effects are negligible for the deflections employed.

For the dynamic calibration, the device shown in Fig. 2 was used. It was fitted into the bomb through a hole directly opposite the hole carrying the diaphragm. The distance between the end face of the calibration cylinder and the face of the diaphragm was about $^1/_{16}$ inch. It is essential for correct results that no part of the diaphragm piece be touched by the calibration cylinder. The space between was sealed from the rest of the bomb space by means of a rubber gasket. The cylinder was filled with hydrogen gas at a known pressure, which was suddenly released onto the diaphragm by quickly turning a quadruple screw which opened a needle valve. A large accurately calibrated gage of the Bourdon type was in the system all the time. The time during which the total pressure was released on the diaphragm depended on the gas used and not on the above manipulations. This was made clear by calibrations with carbon dioxide gas, which showed conclusively that the time required to reach the final pressure in the calibration was a function of the viscosity of the gas used. The line on the film representing the pressure increase coincided with the final pressure line on the film for both carbon dioxide and hydrogen in a time of the order of 0.01 second from the commencement of pressure increase.

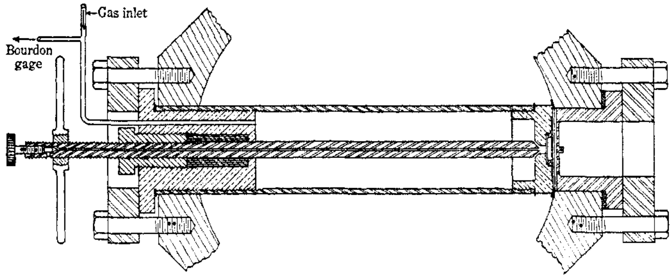

Fig. 2.

The calibration cylinder is easily removed and replaced whenever it is desired to make a new calibration. It may be stated, however, that the diaphragm described above showed the same calibration after it was removed from the bomb and replaced again on several occasions.

Recording on the Film of Instant of Passage of Explosion Spark.—Since it was desired to make time–pressure analyses of the explosions taking place in the bomb,[5] a device was used which essentially is not new but which deserves description. An auxiliary spark was placed at the focus of a parabolic mirror which was built into the housing covering the rotating film. This spark was in series with the main spark at the center of the bomb. By means of a slit the auxiliary spark made a sharp narrow line on the film at right angles to its movement. Both sparks passed when contact was broken by a switch operating with the moving shaft. The procedure was to hold the film stationary and to record the fine light point from a carbon arc and the line from the auxiliary spark on the film. (The bomb spark was disconnected during this operation.) The film was now allowed to rotate at a constant speed and both sparks allowed to pass. The original distance between the auxiliary spark line and the light point made when

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(5) Lewis and von Elbe, in preparation.

the film was stationary, measured back from the new auxiliary spark line made with film in motion, located the point on the film at which the light point was when the spark passed in the bomb.

Summary

A diaphragm indicator for measuring the pressures developed in explosions is described. Its essential advantages are sensitivity, freedom from hysteresis for the deflections employed, and constancy. A method of calibrating dynamically, without removing the diaphragm from the explosion chamber, is described in which pressures are released against the diaphragm in a time interval of the same order as in explosions. It is shown that for this type of diaphragm the observed deflections for a given range of pressures investigated are the same for dynamic as for static calibration.

PITTSBURGH, PENNSYLVANIA
RECEIVED AUGUST 4, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Thermal Equilibrium between Oxygen Molecules and Atoms[1]

BY GUENTHER VON ELBE[2] AND BERNARD LEWIS[3]

During the course of experiments carried out at the Pittsburgh Experiment Station of the U. S. Bureau of Mines on the direct determination of the specific heat of oxygen at high temperatures by exploding mixtures of ozone and oxygen,[4] it was necessary to know the degree of dissociation in order to obtain accurate values of the specific heats. Since this information is not available in the literature, we have set up an equation for the equilibrium constant of the reaction $2O \rightleftharpoons O_2$ expressed as

$$K_p = \frac{[p_{\text{at.}}]^2}{p_{\text{mol.}}} \tag{1}$$

One commences with the well-known fundamental thermodynamic equation

$$\Delta F = \Delta H - T\Delta S \tag{2}$$

For the condition of equilibrium between atoms and molecules of oxygen $\Delta F = 0$, and therefore

$$0 = (\Delta H/T) - \Delta S \tag{3}$$

The entropy per mole of each participant in the reaction is given by

$$S = C_{p_0} \ln T + \int_0^T \frac{C_{\text{vib}}}{T}\,dT - R \ln p + Ri + C_{p_0} \tag{4}$$

where C_{p_0} is the constant part of the specific heat at the temperature T,

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(4) Lewis and von Elbe, THIS JOURNAL, **55**, 511 (1933).