Adsorption Studies on Clay Minerals. III.
A Torsion Pendulum Adsorption Balance*

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by

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**Mr. Gelewitz died in a tragic automobile accident,
January 29, 1953, on a trip taken in connection with his
work. Chemistry has lost a young worker of great promise.

Many of the most important properties of the clay
minerals are in reality properties of the complex systems
clay-water. Since water enters directly into the equilibria
between clays and ionic solutions, determinations of the
water content of the minerals under specified conditions are
an obvious necessity in any complete study of these equilibria.
A formulation of the thermodynamics involved[1] indicates

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(1) George L. Gaines, Jr., and Henry C. Thomas, J. Chem.
Phys., in press.

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what information is necessary and how to take it into

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account. Furthermore, recent results of others[2] indicate that

2.   R. W. Mooney, A. G. Keenan and L. A. Wood, J. Am. Chem. Soc., 74, 1367 (1953); ibid., 74, 1371 (1953).

a knowledge of the water adsorption isotherms can profitably be used to help elucidate the structures of the clay minerals.

The determination of these isotherms by the usual experimental methods may be a slow and laborious process. Particularly with silicate minerals, because of their low heat conductivity, approach to equilibrium is likely to be slow and uncertain. The systems usually show hysteresis effects, which in part depend on the particular experimental technique in use. Much more work is necessary to delineate an isotherm when these effects are present than would otherwise be the case. Consideration of the large number of clay types and the extraordinary number of cases which may deserve investigation has led us to the development of a means for a more rapid determination of these isotherms still with the accuracy demanded by the problems involved.

Measurement of an adsorption isotherm of the type in which we are here interested involves merely a weighing after equilibration with a definite vapor. The weighing may be made indirectly through pressure measurements. If water vapor is in question, this method leaves much to be desired; the results are affected by adsorption on the apparatus as well as by uncertainties in the equation of state of vapor. We

must fall back on a direct weighing. This may be an "internal" weighing, such as with the McBain balance, or may depend simply on removing the sample to an analytical balance. The latter procedure is necessarily slow and tedious. The use of the McBain balance is subject to severe mechanical difficulties when one desires to obtain small changes on a rather massive sample.

Utilizing the well-known properties of quartz torsion fibers, we have therefore constructed a device for internal weighing which has many of the characteristics desired. In principle the method is of extreme simplicity. If changes in the moment of inertia of the swinging element of a torsion pendulum are due solely to changes in mass, and not to changes in geometry, these changes in mass can be determined with precision by measurements of the period. Preliminary calculations having shown that the demands of the experiment were well within the range of experimental feasibility, the apparatus was designed and constructed as described in the following paragraphs.

Our initial impression that we were embarked on a new application of the torsion pendulum was dispelled shortly after the work commenced when we found tha reports of the work of R. Seeliger[3], who used the method with success in the study

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3. R. Seeliger, Zeit. f. Physik., $\underline{4}$, 189 (1921).

Physikal. Z., $\underline{22}$, 563 (1921).

of the adsorption of a variety of gases on chabasite.

The requirements laid down for the apparatus were:
(1) an accuracy of 0.2 mg. on a 2 g. sample; (2) exposure to
the vapor of thin layers of the sample to expedite approach
to equilibrium as well as to minimize effects due to non-
uniform adsorption through the mass of the sample; (3) rapid
weighing to make possible observation of approach to
equilibrium; and, of course, (3) sufficiently accurate pressure
measurement and temperature control.

The essential parts of the apparatus are the torsion
pendulum, shown diagrammatically in Figures 1 and 2, the optical
system in the diagram of Figure 3, and the timing device
shown in the block diagram of Figure 4.

The sample under study is contained in the pan, .
Figure 1, which is pressed from 0.008 in. sheet aluminum.
The fibers, D, are joined centrally by a heavy piece of quartz.
To this piece of quartz is clamped an X-shaped rack of
aluminum which carries the pan. The pendulum is set
swinging by activating the solenoid F, which reacts on a bit
of soft iron carried within a glass tube fastened to the
silica block at the center of the fiber. In order to
avoid low frequency lateral vibrations of the pendulum the
quartz fiber is held in the brass framework   under a
tension of about 500 g.

Light from a mercury arc is reflected from a plane
mirror (carried at the center of the pendulum) through the

optical system to a photomultiplier tube. This optical system produces an effective lever arm of about 100 meters. The pulse from the photomultiplier opens an electronic gate which admits the output of a 100 kc./sec. crystal-controlled oscillator to a scale-of-4096 counter. After a predetermined number of complete swings of the pendulum (usually ten) the pulse from the photomultiplier is allowed to close the gate and stop the counter. The record stored in the counter (in practice nearly two million counts) is proportional to the period of the pendulum.

The accuracy of the results depends, of course, on the constancy of the frequency of the oscillator. We have been unable to check the oscillator in the actual operating set-up; however, through the kindness of Professor Andrew Patterson of this laboratory, frequency measurements have been made on the oscillator with the following gratifying results. These tests were made by Professor Patterson at the U. S. Navy Underwater Sound Laboratory at New London, Connecticut, to which we are much indebted for the use of their equipment. The frequency of the crystal oscillator was measured with a Hewlett-Packard 524 A counting unit. Standard frequencies, which are compared daily or oftener with WWV, were obtained from an AN/FRH-3 Frequency Calibrator. During the tests the room temperature was between 26 and 27°. The power supply to the oscillator was obtained from a Sola transformer type regulator. The precision of the Hewlett-Packard unit is

better than one part per million. For the majority of the tests the unit was used with the ten second gate, so that the determinations were read to 1 in 10^6. The frequency stability of the AN/FRH - 3 is at least 1 in 10^7, hence the determinations were reliable to 0.1 cps. in the frequency of our crystal oscillator.

The frequency of the oscillator after a one-and-a-half hour warm-up was 99, 953.4 ± 0.1 cps. Over a period of six hours thereafter the frequency stability was within the precision of the measurement, 0.1 cps. (During the warm-up period the frequency decreased from 99, 955.8 to 99,953.4 cps.) The effect of changing the line voltage was just noticeable: lowering the voltage to 95 volts increased the frequency by 0.2 cps. Raising the voltage by 10 volts lowered the frequency 0.2 cps. This effect was immediate; time was not allowed for the temperature of the unit to change significantly as a result of the voltage changes. The influence of the ambient temperature was estimated by opening the top of the cabinet and adjusting a fan to blow directly into the instrument. Within twenty minutes the frequency rose to 99,955.2 cps.

It is apparent that under ordinary operating conditions the oscillator is reliable to within two parts per million, corresponding to four microseconds in the period of the pendulum now in use.

Many experiments have been made to determine the reproducibility of removing and replacing the pan on the pendulum as

well as to determine the reproducibility of a series of determinations done without disturbing the apparatus. In a series of determinations extending over fifteen hours the pendulum and framework were removed ten times from the glass container, the pan being each time removed from and replaced on its support. A total of thirty-six determinations of the period was made. The reproducibility within a single series (without disturbance of the apparatus) is illustrated by the following results: 1.743,174; -, 193; - , 196; -,199; -, 200 sec. The eleven periods (corresponding to the ten disturbances of the apparatus) varied from 1.743,192 sec. to 1.743,796 sec., eight of them lying between 1.743,369 sec. and 1.743,582 sec. The maximum difference of 0.000,603 sec. corresponds to a mass difference of 1.5 mg. However, such a discrepancy does not appear within a series of mass determinations on a single sample, placed only once on the pendulum. The discrepancy corresponds to a difference in the calibration of the instrument, and might be reflected in a displacement of an isotherm by 0.05% on a 3 g. sample.

The calibration of the instrument consists in the determination of the period with the pan empty, P_o, and a determination with a sample of known weight in place, P_1. As will be shown, the effect of damping under the adopted method of operation is negligible, so that we have simply:

$$P_o^2 = k r_o^2 m_o \quad \text{and} \quad P_1^2 = k(r_o^2 m_o + r_c^2 m_c)$$

in which the subscript c refers to the sample only; the r's and

m's are radii of gyration and masses, and k is determined by
the dimensions and dynamical properties of the quartz fibers.
The calibration constant is then:

$$K = 1/kr_c^2 = m_c/(P_1^2 - P_o^2)$$

and
$$m = K(P^2 - P_o^2)$$

is the mass of the sample for any period P.

The damping due to the internal viscosity of the silica
fiber suspension is negligible by many orders of magnitude.
For our pendulum the time for damping to half-amplitude due to
this cause is easily computed to be approximately 10.7 days.
(In this connection see Strong[4].) Our pendulum actually

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4.   John Strong, "Procedures in Experimental Physics",
     Prentice-Hall, New York, 1941, p. 193.

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requires 69.5 seconds to reach half-amplitude in air at
atmospheric pressure. Since the motion of the pendulum is
relatively slow, we may assume that the air drag in
proportional to velocity in order to estimate the effect of
damping on the determinations. The effect may show itself in
two ways: first by a change in the fundamental frequency and
second by the more important effect due to the impossibility
of opening and closing the gate when the pendulum is exactly
at center.

A series of measurements on the pendulum swinging in air,
with period P = 1.806 sec., gave as the time for half-amplitude
69.5 sec., (corresponding to an average number of cycles of

38.5). The damping constant for the pendulum is, then, $\lambda = 0.693/69.5 = 0.010 \text{ sec}^{-1}$.

If we take as the equation of motion of the damped pendulum,

$$I \frac{d^2\theta}{dt^2} = -k\theta - b\frac{d\theta}{dt}$$

then:

$$\frac{2\pi}{P} = \sqrt{\frac{k}{I} - \frac{b^2}{4I^2}} = \sqrt{\frac{k}{I} - \lambda^2}$$

or for our pendulum in air:

$$m \simeq \frac{k}{4\pi^2 R^2}\left(1 - 0.0001\frac{P^2}{4\pi^2}\right)P^2$$

$$= \frac{k}{4\pi^2 R^2}(0.99999)P^2$$

Thus the use of the simple formula, for the undamped pendulum, introduces an error of only 0.001% in a mass determination.

The damping of the pendulum introduces another possibility of error which may be much larger than that just considered. Since it is impossible to line up the optical system so that the gate is opened and closed just at the maximum velocity of the pendulum, we must have an estimate of the tolerance in this adjustment. To a first approximation, we get this estimate as follows. If the angular position of the pendulum is given by:

$$\theta = A e^{-\lambda t} \sin\left(\frac{2\pi}{P} t + \varphi\right)$$

then, at $t = 0$ and at $t = nP + \Delta t$, $\theta_0 \sim A \sin\varphi$ is the angular position at which the measurement is started and stopped. Now if the apparatus is properly adjusted, φ is small, and so also are Δt and $n\lambda P$. One can then easily show that:

$$\Delta t \simeq \frac{n\lambda P^2}{2\pi \cot\varphi - \lambda P}$$

The operating conditions we have chosen make $A \simeq 15°$ so that for small θ_0, $\cot\varphi = 1/\sin\varphi \simeq 1/A\theta_0$. If we demand that Δt be no greater than 50 μ sec., we find for θ_0 the value 2×10^{-4} radian as the maximum tolerable value. Now the effective lever arm of the optical system is about 10^4 cm. and we estimate the accuracy of setting the position of the leading edge of the spot of light to be about 1 cm. Hence when the optical system is lined up with the mirror at rest, θ_0 is less than 0.5×10^{-4}. This value is only a rough estimate: the gate is opened by the rate of rise of the signal from the photomultiplier, and this is determined not only by the relative position of the mirror and photomultiplier but also by the diffuseness of the edge of the beam of reflected light. In an actual experiment the period was determined for 10-swing intervals and found to be 1.596,946

± 0.000,002 sec. (5 determinations); for 1-swing intervals the period was found to be 1.596,99$_4$ ± 0.000,005 sec. The difference of -50 μ sec. is of the magnitude expected and indicates that the photomultiplier is actuated before the mirror reaches dead center. This timing error corresponds to about 0.1 mg. in mass, is a nearly constant effect, and so is negligible in an isotherm determination.

The pendulum and its frame are contained in a large cylindrical glass jar equipped with a plane window. The frame of the pendulum is surrounded by a shield of sheet aluminum to facilitate temperature equilibrium. The glass jar is attached to a conventional vacuum system (fore pump and mercury diffusion pump). Pressure measurements are made with a simple manometer containing vaccum pump oil. An engraved glass scale is rigidly fastened in the manometer frame and the manometer is read through a telescope. The sensitivity of the pressure measurement corresponds to 0.01 mm. Hg, although discrepancies of several times this amount, have been observed. We are still searching for a more satisfactory manometer fluid.

Clay-water isotherms have thus far been measured only in a preliminary way, without temperature control. Further results will be reported elsewhere.

This work is being done as part of work under contract between Brookhaven National Laboratory and Yale University. We wish to acknowledge our indebtedness to the Department of Nuclear Engineering of Brookhaven Laboratory for their continued interest.

Figure 1

Torsion Pendulum and Frame

A   Frame

B   Levelling Screw

C   Circular Spirit Level

D   Silica torsion fiber

E   Calibrated springs

F   Solenoid for starting oscillations

G   Leads to 12 volts

H   Soft iron finger enclosed in glass

I   Mirror

J   Sample in pan

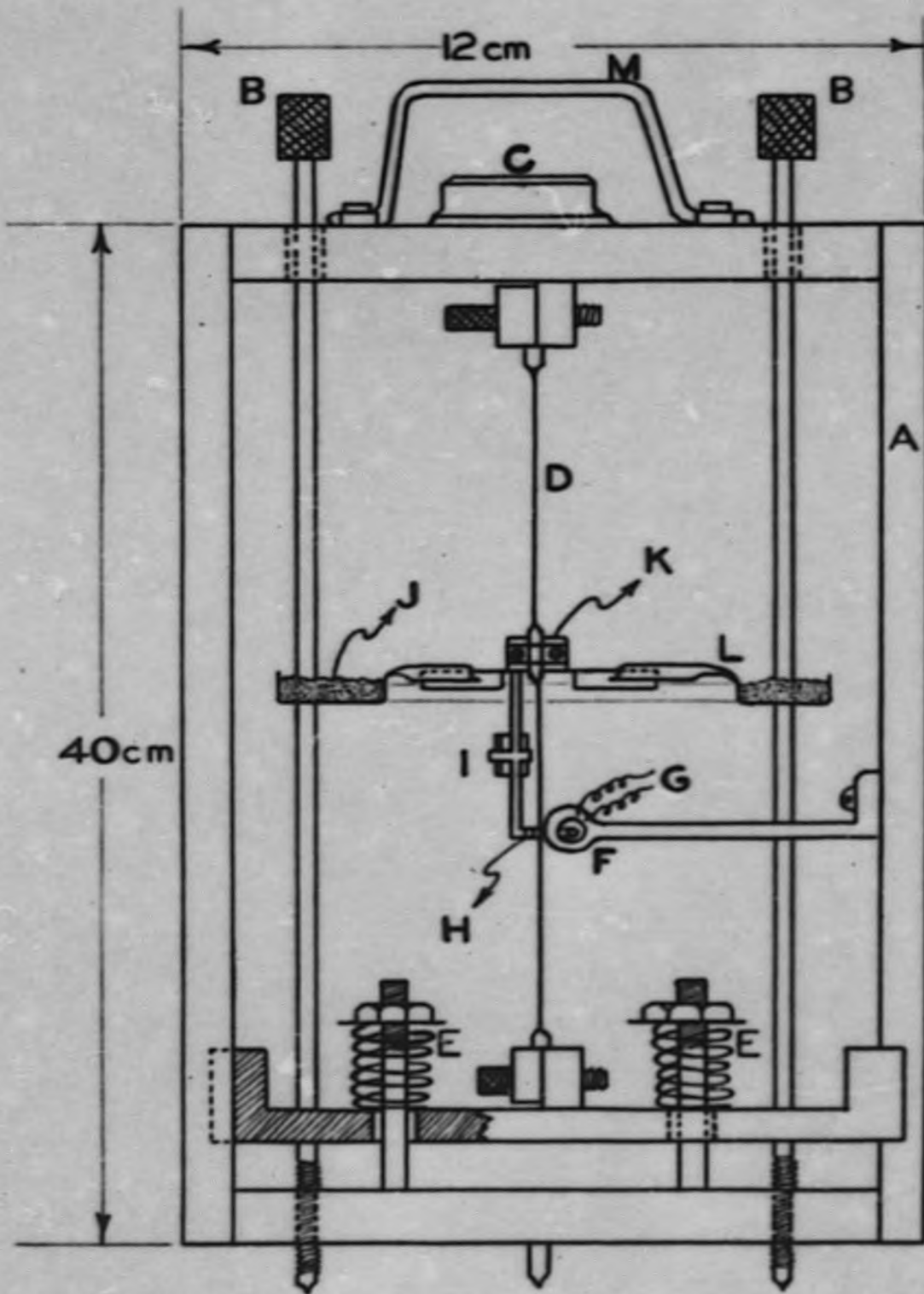K   Pan support fastened to torsion fiber

L   Pan

M   Handle
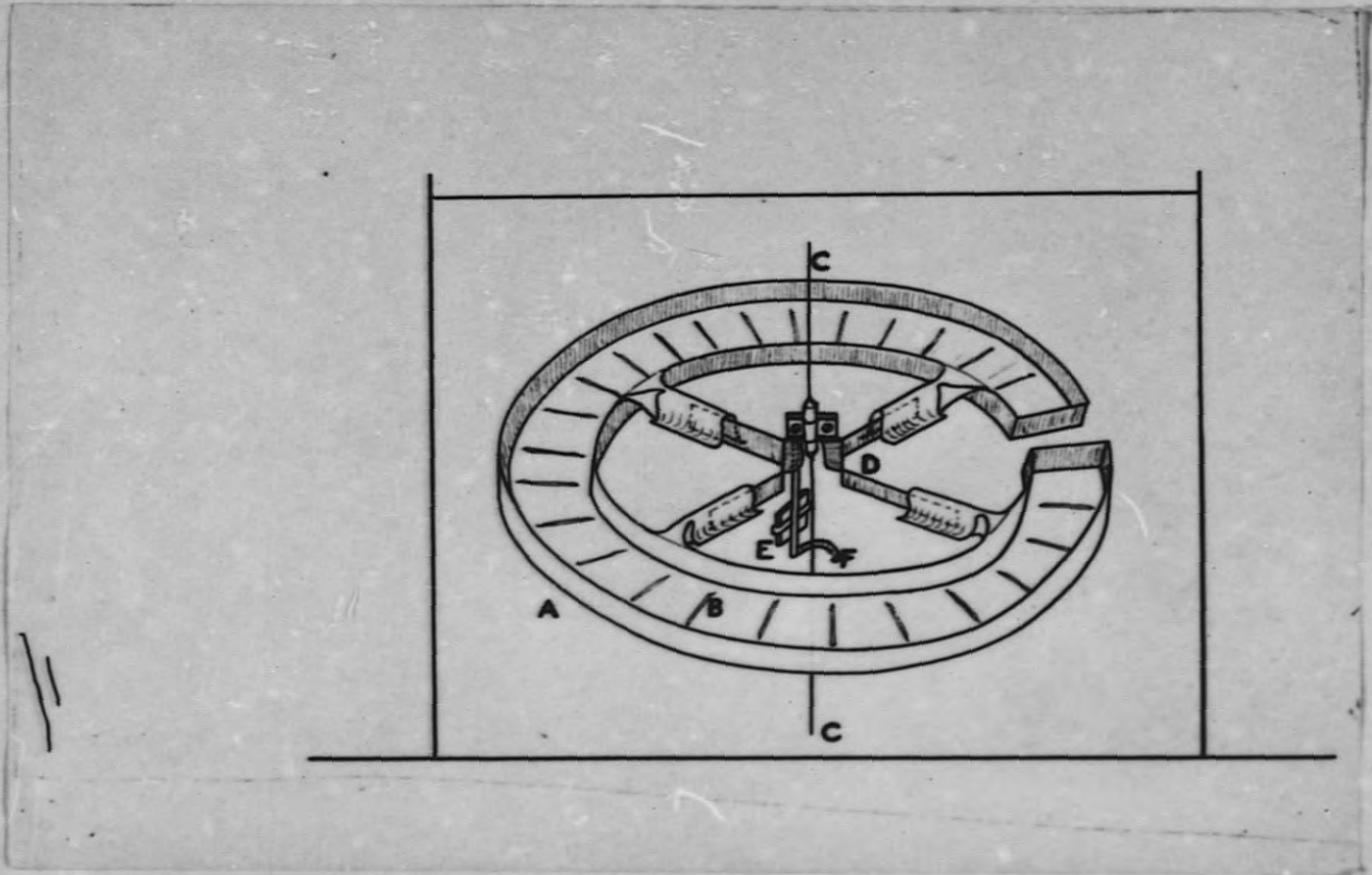
Figure 2

Pan and Detail of Pan Suspension

A   Removable pan

B   Ribs in pan bottom for stiffness

C   Silica torsion fiber

D   Pan holder attached to torsion fiber

E   Mirror

F   Soft iron finger enclosed in glass

Figure 3

Optical System

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Lamp	H 100 4A Mercury vapor lamp.
L_1	Coated achromatic objective, f.l. 192 mm., 52 mm. diameter.
S_1	Razor-blade slit, about 0.5 mm. wide.
Mirror	First-surface mirror, on pendulum, 1 X 1 cm., 0.5 mm. thick.
L_2	Same as L_1.
A	Plane of real image of S_1 produced by L_2.
L_3	Microscope objective, 10X.
L_4	Microscope ocular, 15X.
S_2	Razor-blade slit, about 0.2 mm. wide. (Plane of real image of S_1 produced by L_4).
Phototube	Photomultiplier 931 A.
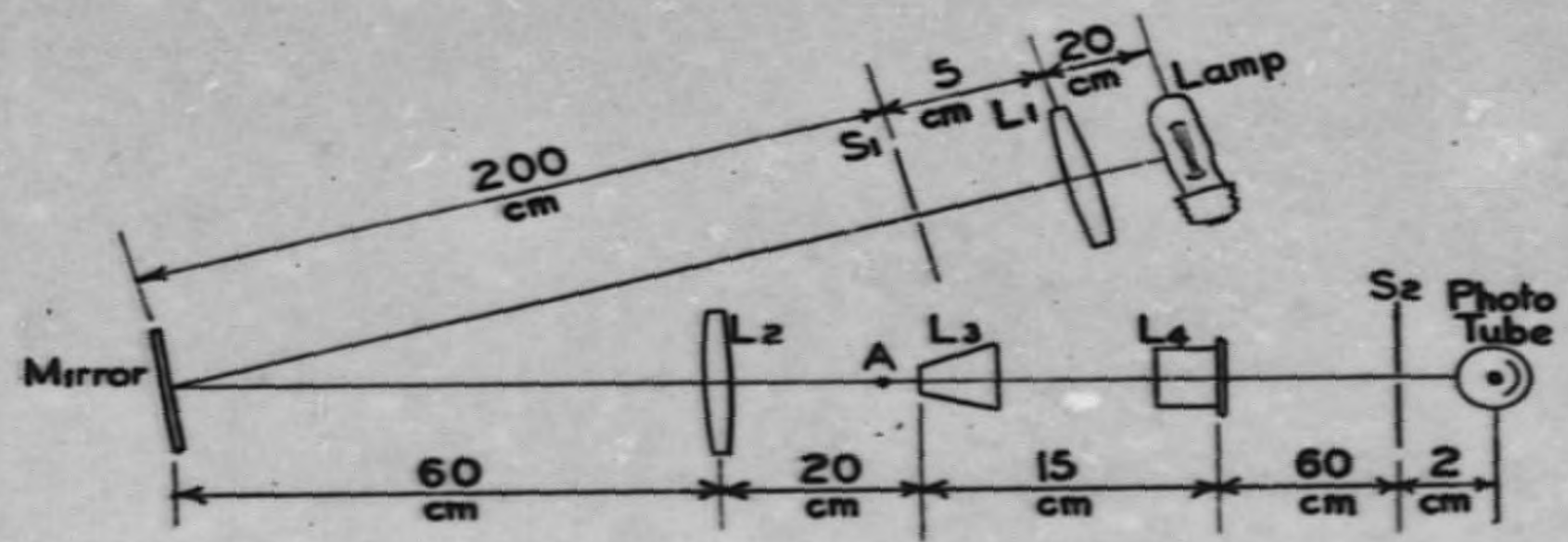
Figure 4

Block Diagram of Timing Device