A STUDY OF HOMOGENEOUS COMBUSTION IN GASES

by

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ABSTRACT

Elucidation of the actual mechanism by which the chemical changes occur is the ultimate aim of a large fraction of the research on the combustion of fuels. A vast number of valuable investigations of the past have been directed towards no other goal and the same is true of numerous researches that are now being conducted in this field. Although these researches have yielded valuable information, it may be expected that, as in all other fields of scientific endeavor, there remains still a vast field for fundamental investigation. This work deals with a small phase of the problem, namely, the development of a method for studying the rates of reaction of gaseous fuels under homogeneous conditions. The study of rates under these conditions offers the only method of determining the mechanism of combustion of these fuels as it occurs in many important technical and industrial processes.

There are three methods in general use for the determination of the velocity of "homogeneous" reactions in gases: a) "static," b) "dynamic"; c) "pressure change." In all of these the gas is

brought to its reaction temperature by heat furnished from the externally heated reaction vessel. Since almost all gas reactions are catalyzed by hot surfaces, it is obvious that these methods do not determine the true homogeneous reaction rates. The observed rates are a combination of heterogeneous and homogeneous reaction. It may be stated therefore, that the fundamental requirement of any method for studying homogeneous reaction rate is that after mixing, the gases must be held out of contact with hot surfaces. Inasmuch as there is no suitable way of assuring good mixing and of following the reaction if the components are heated prior to mixing and allowed the react before coming into contact with hot surfaces, the only remaining choice is that of raising the temperature of the gas mixture in a <u>cold reaction vessel</u>. This can be done by suddenly compressing it in a cold cylinder. Under these conditions, with the assumption that no heat loss occurs during the compression, and no heat is produced by reaction of the mixture, the temperature at the end of compression is given by the relation

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{R/C_{v.}\ \mathrm{ave.}} \qquad (1)$$

where T_1 is the initial absolute temperature V_1/V_2 is the ratio of initial to final volume, C_v ave. is the value of Cv at the logarithmic mean temperature, if Cv is linear with temperature.

Actually the temperature will be lower than the theoretical value because of heat loss to the cold cylinder walls, unless the temperature has been raised to the point where the gas is self-heating from its own reaction.

The method that has been developed in this work to study the rate of homogeneous reactions uses the principle that has just been described for raising the temperature of a gas mixture to the point where reaction proceeds in the gas phase only. When such a mixture is compressed to a temperature below that of ignition, and allowed to cool at constant volume, its cooling rate, as determined by measuring the fall of pressure in the reaction vessel with time, will be less than the average for the separate components of the mixture. This slower cooling rate in the mixture is due to the heat liberated in the reaction and is a quantitative measure of it. The exact relations are expressed in the equation:

$$\frac{dP}{d\theta} = \left(\frac{RT}{V}\right) \frac{dNT}{d\theta} + \left(\frac{Rq}{VC_v}\right) \frac{dN}{d\theta} - \frac{R}{VC_v} \frac{dQ}{d\theta} \qquad (2)$$

where N = mols of combustible gas at time θ

N = total mols of " " "

q = heat evolved per mol change in combustible constituent at const. vol.

The term $\frac{R}{VC_v} \frac{dQ}{d\theta}$ expresses that portion of the pressure change which is due to loss of heat from the system externally, and may be evaluated by the use of a properly weighted average of the experimentally determined rates of cooling of the separate components of the mixture under similar conditions. A relation can be established between N'_T and N as soon as the reaction is specified.

Experimental realization of the simple principle that forms the basis of this method is one of great difficulty because it imposes such severe as well as stringent requirements upon the separate parts of the experimental apparatus.
These requirements are:

1) The gas mixture, introduced into a cold cylinder of fair size, must be suddenly compressed to a fixed final volume, determined by the final temperature required to cause a measurable rate of reaction without ignition.

2) The reaction cylinder must be of fair size to minimize heat loss and between a long narrow bore and short wide bore, the former offers greater advantages. Inasmuch as the cylinder receives the whole shock of the fast moving piston it must have great axial rigidity.

3) The piston must be suddenly accelerated

from a fixed initial position and more suddenly decelerated at the end of its stroke; its head must be sufficiently tough to receive severe impact against the top of the cylinder; it must be brought to a dead stop without the slightest rebound; and the constraining force on it must exceed that in the reaction cylinder. It must be packed loosely enough to prevent excessive friction; it must be leakless and so lubricated as not to contaminate the reactants.

4) A compressing force must be supplied of sufficient power to compress the gas in a period of time limited not by the force itself, but by the mechanical properties of the piston and other requirements stated under (3).

5) A sensitive indicator directly exposed to the pressure in the cylinder must respond faithfully to the pressure changes that occur in the reaction chamber itself, and only to these. Suitable timing and recording mechanisms must be provided with the indicator. The appearance of a wave of any description on the pressure record cannot in any way be associated with the expected changes in pressure in the reacting mixture, and is therefore an indication of improper performance of the apparatus, and of a questionable pressure record.

In satisfying the requirements that have been listed, the attempt was made to draw from the designs and experiences of other investigators with similar types of apparatus. Little information of real value could be obtained and the principal parts of the completed apparatus have resulted only after much experimentation. Almost all of these are therefore original.

The applicability of the apparatus that has been developed is determined by inspection of the pressure record to determine whether vibrational effects due to sudden impact of the rapidly moving piston are present and whether there is any indication of piston rebound. Both of these effects have necessitated much experimentation before being removed.

A specially designed manometer has been perfected for determining the initial pressure in the reaction cylinder, this together with an accurately calibrated measuring burette and mixing chamber for the gases, permits an accurate determination of the molal quantities of gas added to the cylinder, the volume of which is known.

A specially designed scaling device permits accurate reading of all pressure-time records.

PART I

INTRODUCTION

A. STATEMENT OF THE PROBLEM

Elucidation of the actual mechanism by which chemical changes occur is the ultimate aim of a large fraction of the research on the combustion of fuels. A vast number of valuable investigations of the past have been directed towards no other goal and the same is true of numerous researches that are now being conducted in this field. Although these researches have yielded valuable information, it may be expected that, as in all other fields of scientific endeavor, there remains still a vast field for fundamental investigation.

This research was begun under the grant of an Automotive Fellowship and has as its purpose the study of the mechanism of combustion in gases and vapors under slow as well as explosive conditions.

The magnitude and complexity of the problem of an investigation in this field is attested to not only by the vast amount of work on the constants of gaseous explosions, e.g., velocity of explosion, limits of inflammability, etc., but because in these are involved such questions as specific heats of gases (and vapors), composition of gases, heats of reaction, adiabatic compression, frequency of collision, emission and absorption of radiation, degree of ionization, critical increment of chemical reaction, velocity of sound, theoretical temperature of explosion, thermal conductivity, activation in front of wave, velocity of chemical reactions, size and shape of explosion vessel, catalytic surfaces, homogeneous catalysis, nature and effects of sparks, etc. - all of which are recognized as related to gaseous combustion.[1 *]

It is obvious therefore that the complex nature of the problem requires careful selection of experimental conditions if the exact mechanism is to be found. Indeed, for this reason it may be said that almost all of the researches in this field have failed to yield more than composite results.

Now, one of the best methods of determining the mechanism of any reaction is to determine its rate. But, rate is greatly influenced by the conditions under which the reaction is carried out. The logical starting

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*Refers to bibliography at the end.

point is to eliminate the specific actions of the surroundings and study the mechanism, or rate, under what is known as homogeneous conditions. Unfortunately, existing methods do not permit such a study, so that the initial requirement of this research is the development of a method for determining the rate of reaction of gases and vapors under homogeneous conditions. This method should be capable of such variation that many, if not all, of the variables contained in the general case may be added and their separate effects determined.

The problem may be stated, therefore, in the following brief manner:

A method is developed for studying the rates of gas reactions under homogeneous conditions. This method is more valuable because it is capable of including the separate factors, alone or jointly, that are superposed upon the homogeneous part of the reactions as they occur in many industrial and technical processes.

B. THE RATE OF CHEMICAL REACTION

The rate at which gas reactions proceed is of great interest from the standpoint of both theory and practice. Thermodynamics has made it possible to predict what chemical reactions can take place, namely those accompanied by increasing entropy, and it also permits a calculation of the extent of reaction before equilibrium is attained. The laws governing the specific rates for these reactions are, however, beyond the scope of thermodynamics. We are not in position to predict on the basis of thermodynamics therefore what will actually happen when chemical substances are mixed. Indeed there are many reactions which are accompanied by large increases in entropy that take place at extremely slow rates, while reactions with little thermodynamic tendency to proceed take place at speeds so great that they become difficult to measure.

The solution of the problem of reaction velocity must be looked for outside of the realm of thermodynamics, for it cannot be denied that the mechanism of chemical reaction is determined by the nature of the interacting molecules and atoms, and with these thermodynamics has not yet concerned itself.

It has been assumed that a complete survey of the literature of gaseous reaction kinetics is a necessary antecedent for the development of this research. As a result of this survey the following review will be given.

1. Classification of Chemical Reactions

Chemical reactions are subject to several methods of classification and, indeed, between classes there is much overlapping. A discussion of several of these classifications follows:

The order in which this discussion takes place is: homogeneous, heterogeneous or explosive, depending upon the location of the region of reaction in the system; catalytic and non-catalytic, depending upon the presence or absence of a substance necessary to the completion of the change; photochemical or thermal, depending upon the presence or absence of radiation from an outside source; isothermal and adiabatic; constant pressure and constant volume; the reaction order, and the number of steps in the transformation.

(a) The reacting substances in a homogeneous reaction are present in a single phase and the chemical change proceeds uniformly throughout the whole mixture. The universal criterion for a homogeneous reaction is that the surface of the container plays no part, and velocity is independent of the extent of this surface.

(b) In heterogeneous reactions, on the other hand, the actual chemical changestake place at the surface of discontinuity between two phases. Two types usually encountered are: (1) the interacting substances exist as separate phases; (2) the catalytic action of a surface is necessary to effect the change. Heterogeneous reactions are characterized by velocities that are directly proportional to the internal area of the vessel of the same material and volume.

(c) Explosive reactions are those in which the reaction zone propogates itself through a system originally homogeneous. It is sometimes convenient to disregard this difference between explosive and homogeneous reactions and view the moving reaction zone as a set of infinitesimal layers of mixture of varying concentration and temperature.

(d) Catalyzed and non-catalyzed reactions differ in that in the latter the chemical substances enter directly into the changes leading to the final products; in the former, however, one of the reacting substances must first interact with the catalyst either to form a chemical compound, or a lesser physical aggregate such as an adsorbed layer - the adsorbed layer being regenerated during the course of further change.

(e) Thermal and photochemical reactions differ by the circumstance that the latter occur under influence of an external source of radiation not in temperature equilibrium with the reacting mixture. On the other hand, thermal reactions are usually carried out under conditions such that the walls of the enclosure and reactants are more nearly in temperature equilibrium.

(f) Isothermal and adiabatic reactions differ in that the former are carried out at constant temperature by continuous interchange of energy between the walls of the vessel and the reactants; the latter, on the other hand, are completely isolated from the surroundings. Constant volume and constant pressure reactions are both common in studying gaseous reaction kinetics.

(g) In studying reaction velocities we must distinguish carefully between *order of reaction* and the *mechanism of reaction*. The order of reaction is determined by direct experiment, the mechanism, however, is a matter of uncertain theoretical interpretation.

The order of a reaction with respect to one of the reacting substances is defined as the power to which the concentration of that substance enters in the expression connecting rate of reaction with concentration. Thus, in a reaction between substances A, B, C, etc. which proceeds so that the rate can be expressed by the equation

$$-\frac{dC}{d\theta} = k\, C_A^X\, C_B^Y\, C_C^Z \quad . \; . \; . \; .$$

the reaction is of order X, Y, Z, etc. with respect to the substances A, B, C, etc., where C_A, C_B, C_C, etc., are the instantaneous concentrations of the reacting substances, and k is a constant.

The rate equations for gases are more conveniently expressed in molal concentrations which are proportional to the number of molecules present, or it is just as convenient to express concentrations as numbers of molecules per cubic centimeter, since the formulae of the kinetic theory can be applied immediately to calculate the number of collisions between molecules.

The specific reaction rate, k, in the equation is most conveniently expressed using time in seconds and concentrations in mols per cubic centimeter.

The mechanism assigned to any reaction is a representation of the individual processes occurring in the reaction mixture. If, as it sometimes happens, the order of a reaction does not agree with the stoichiometric equation, the mechanism chosen must satisfy the observed results, but it is well to keep in mind that some other hypothetical mechanism might serve just as well. The fundamental hypothesis of Guldberg and Waage is best satisfied if the attempt is made to resolve reactions into separate steps of simple order.

2. Thermodynamics and Reaction Rate

It has been stated previously that the general problem of chemical reactivity may be treated by two methods, the thermodynamic and the kinetic. The first one, as is well known, is capable of dealing only with the equilibrium state, and the conclusions are, therefore, independent of the mechanism by which such a state is attained. Van't Hoff[2] has shown by thermodynamics that

$$\frac{d\ln K}{dT} = \frac{Q}{RT^2} \qquad (1)$$

where K is the equilibrium constant and Q is the heat of reaction. This relationship between the equilibrium constant, the heat of reaction and the absolute temperature has proved to be one of the most valuable generalizations of modern chemistry. Stated in another form it will be shown later that this equation gives the relation between the temperature coefficient of a chemical reaction and the total energy involved in the reaction.

On the other hand, the kinetic point of view treats the problem of chemical reactivity by considering the method by which equilibrium is attained. Thus, the equilibrium state may be regarded as one in which the velocities of the two opposing reactions are equal. If, in addition, the Guldberg-Waage[3] law of mass action is taken into account the following relationships are observed

$$aA + bB + \dots\dots \rightleftharpoons xX + yY$$

and

$$-\frac{dC}{d\theta} = k_1 \, (C_A)^a \, (C_B)^b \dots - k_2 \, (C_X)^x \, (C_Y)^y$$

where C denotes the concentration, k_1 and k_2 the velocity constants. At equilibrium the actual velocity is zero and

$$\frac{k_2}{k_1} = \frac{(C_A)^a \, (C_B)^b}{(C_X)^x \, (C_Y)^y} = K$$

The determination of the factors which govern k_1 and k_2 is the role of kinetics and the aim of this research. Arrhenius[4] was the first to attempt an explanation of the factors which govern the reaction constant when he pointed out that the effect of temperature on the velocity of a reaction could be expressed by means of the <u>empirical</u> equation

$$\frac{d \ln k}{d\theta} = \frac{A}{RT^2} \qquad (3)$$

which is analogous to Van't Hoff's equation for the temperature-coefficient of the equilibrium constant.

In this equation, A is a constant for any given reaction. We may, for convenience, also express this equation in the following forms

$$\log k = -\frac{A'}{RT} + \text{Constant} \qquad (4)$$

or,

$$k = B\ E^{-A/RT}$$

3. The Concept of Activation

It will be valuable to inquire into this ordered relation between coefficient of reaction and temperature as Arrhenius did before he announced the following well-known hypothesis.

(a) The Arrhenius Hypothesis

Arrhenius interpreted his equation by suggesting that there exists an equilibrium between normal molecules and what he called "active" molecules, and that only the active molecules undergo chemical change. The active molecules were supposed to be formed endothermally from the normal molecules. The rapid increase in the rate of chemical change with rising temperature is therefore caused by the shift in the equilibrium between the two kinds of molecules, and, since k is proportional to the number of active molecules, the equation

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}$$

represents this shift in the ordinary thermodynamic way. A is the heat absorbed in the formation of an active molecule from a normal one and is therefore called the heat of activation.

This view, though indefinite, is accepted as correct for the most part. There is, however, no longer the belief that anything of the nature of a tautomeric change is involved in the conversion of an ordinary molecule to an active one. The active molecules are regarded simply as those endowed with exceptionally large amounts of energy. In this sense they are formed endothermally from the normal ones.

(b) The Physical Concept of Activation

The Arrhenius concept may be regarded as a chemical basis of activation. We retain the general idea in attempting to develop a more plausible mechanism, but it is necessary to resort to what may be called the physical basis of activation. In so doing it is well to point out again that the arguments for an activated state are based on the following facts:

1. Slow reactions. Reactions should take place instantly if all molecules are equally active.

2. The high temperature coefficient of almost all. This represents a much more rapid increase than could be accounted for by such factors as increased collision frequency.

3. The quantitative relation observed between temperature and the velocity constant.

The kinetic theory has been resorted to in establishing the physical basis of activation. The assumption is retained that the molecules that undergo chemical change are in special activated states, having a larger energy content than the average molecule. The quota of molecules in a given activated state is assumed to be replenished, as they are used up in the reaction by the striving of the molecules towards a statistical distribution which accords with the Maxwell-Batzmann distribution law, the large temperature coefficient of reaction velocity being due to the large increase with temperature in the tendency for molecules to assume high energy contents which is required by the distribution law.

There has been room, however, for much

speculation as to the actual mechanism of the processes by which the quota of activated molecules is maintained, since the Maxwell-Batzmann law states merely that there must be some tendency for the molecules to pass from unactivated states as the latter are used up by chemical reaction, but gives no immediate information as to the speed or mechanism with which this tendency towards statistical equilibrium will occur.

Indeed, the number of speculations on activation is so great that the mere reading of these becomes a laborious task. It is possible, however, to group them into the following four mechanisms:

(a) Activation by collision with another molecule of high enough kinetic energy (ordinary collision).

(b) Activation by collision with another molecule which is itself in an activated state, resulting in a transfer of energy of activation (collision of the second kind).

(c) Activation by the absorption of monochromatic radiation of the frequency calculated from the temperature coefficient of the reaction rate (simple radiation theory of chemical reaction).

(d) Activation by interaction with more than one frequency (elaborated radiation theory of chemical reaction).

This classification is to be regarded as transitory and even incomplete, for recent advances in the quantum theory on the nature of transfer of atoms and molecules from lower to higher quantum states opens new lines of verification or speculation.*

4. The Magnitude of the Energy of Activation

Before considering the various hypotheses it is necessary to determine first of all the magnitude of this energy for different types of reactions.

Considering the cases of uni - and bimoleculor reactions, the equations connecting rate of reaction and temperature are expressed in the usual form

$$-\frac{dC}{d\theta} = k\,C = \beta e^{-A/RT}\,C \qquad (6)$$

and

$$-\frac{dC}{d\theta} = k\,C\,C' = \beta' e^{-A/RT}\,CC' \qquad (7)$$

where C and C^1 are concentrations of the reactants, and k isthe Arrhenius coefficient from equation (5).

It is well to compare these equations with those deduced otherwise and to point out the significance

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*London, Naturwissenschaften 17,516 (1929).
Kassel, J. Phys. Chem., 32,225 (1928).

of the quantity A.

The problem of calculating the absolute value of the reaction velocity of a gas on the basis of kinetic theory was attempted first by Boltzmann.[5] He assumed that, in a bimoleculor reaction, collision between two reactant molecules was the only requirement for reaction, and velocity of reaction was therefore determined by collision frequency. This same idea has been advanced by Kruger.[6] Had Boltzmann and Kruger compared their theoretical treatment with experimental data, they would have realized that the collision frequency which is proportional to the $\sqrt{T}$ did not satisfy the exponential relationship that exists between reaction velocity and temperature. Collision frequency alone is, therefore, not a satisfactory criterion.

With this in mind Trautz[7] attacked the problem. His conception was that a molecule had to be in an active state in order to react, and he deduced,the fraction of the molecules in the active state at any temperature from the following considerations.

Combining equations 1 and 2, it follows that

$$d\,\frac{\ln K}{dT} = d\left(\frac{\ln k_1 - \ln k_2}{dT}\right) = \frac{Q}{RT^2}$$

$$= \frac{E_1 - E_2}{RT^2}$$

where $E_1 - E_2 = Q$

We may also write

$$d\frac{\ln k_1}{dt} = \frac{E_1}{RT^2}$$

$$d\frac{\ln k_2}{dt} = \frac{E_2}{RT^2}$$

and obtain a relation between temperature coefficient of the velocity constant and the heat of activation of the corresponding reactants. Furthermore, the difference between the heats of activation of the reactants and resultants is the thermochemical heat of reaction. It is to be noted that thermodynamics has been used to establish this relation but it cannot be used further in the study of reaction velocities.[8]

Now, if it is assumed that the molecules have to acquire an energy of activation given by E_1 before the reaction corresponding to k_1 can occur, it follows from Maxwell's law that the fraction, α, of molecules which at any temperature, T, possess this amount of energy is given by

$$\alpha = e^{-E_1/RT} \qquad (8)$$

where E_1 is the energy of activation at the temperature T.

Equation 8 leads at once to the relation

$$k = \beta'' e^{-E/RT} \qquad (9)$$

where k is the specific reaction rate. It is noted that this equation is identical in form with the Arrhenius equation.

Aside from the attempts of Arrhenius and Trautz, already mentioned, to develop satisfactory theoretical interpretations of equation 9, others have been made by Marcelin,[9] W. C. Mc Lewis,[10] Rice,[11] Perrin,[12] Dushman,[13] Tolman,[14] and others. These investigators have come to different conclusions as to the significance of the quantities β and E. Herein lies the ground for the speculation which has led to the four hypotheses, already listed, and to the vast literature on this subject.

It may be said, however, that the factor β differs in form according to the nature of the reaction. In a bimolecular reaction, for example, it must involve the number of collisions between molecules of the right kind; in unimolecular reactions, on the other hand, it may be independent of the collision number and may possibly involve the rate at which radiant energy is transferred. Similarly will E vary with the kind of reaction involved.

The method of determining E is based upon the measurement of the temperature coefficient of reaction velocity from which it is calculated by means of the Arrhenius equation.

Having determined the fraction of molecules possessing the required energy of activation, it is desirable to consider the speed with which activation must take place for a given reaction. As a minimum requirement it is evident that the number of molecules activated per second must be equal to the number which react in that time since otherwise the continuance of reaction would be impossible.

If the rate of activation is just sufficient to furnish the number of activated molecules necessary for the reaction, the overall rate of reaction will be determined by the rate of activation and will be affected by changes in concentration in a corresponding manner to the rate of activation. If, on the other hand, the rate of activation is high compared with the rate of reaction, a constant number of activated molecules determined by the Maxwell-Boltzmann law will be maintained, and the order of the reaction will be similar to the order of reaction in which the activated molecules take part. These considerations are necessary in applying this mechanism to simple reactions of different orders.

The methods of activation will now be considered.

5. Activation by Ordinary Collision

The hypothesis that molecules are activated only by collisions with other molecules has been advanced most especially by Lindemann[15] although, as has been mentioned, Trautz also considered this for one type of reaction. It is not possible to determine exactly the rate of activation due to collision since this would necessitate a knowledge of molecular behavior not possessed at present. The usual assumptions of kinetic theory must therefore be applied in calculating the amount of kinetic energy transferable into energy of activation through collision. If the molecules are regarded as rigid spheres of definite diameters the maximum kinetic energy transferable into other forms due to a collision between two molecules is $1/2 \frac{M_1 \cdot M_2}{M_1 + M_2} \cdot V^2$ where M_1 and M_2 are the masses of the two molecules and V is the component of relative velocity parallel to the line of centers of the two molecules at impact. Therefore the energy of activation is obtained only as a result of collisions in which V is greater than

$$\epsilon = 1/2 \frac{M_1 \cdot M_2}{M_1 + M_2} \cdot V^2 \qquad (10)$$

Langevin and Rery[16] have shown that the fraction of all collisions in which the component of velocity parallel to the line of centers is not less than V is given by the expression

$$e^{-1/2 \frac{M_1 M_2}{M_1 + M_2} \frac{V^2}{aT}}$$

The rate of activation per second from collision is therefore

$$\frac{d\,n}{d\,\theta} \text{ act} = Z e^{-\epsilon/aT} \qquad (11)$$

where Z is the number of collisions per second and the energy of activation per molecule. Jeans[17] shows that the collision frequency for this case is given by the relation

$$Z = n^2 \sigma^2 \sqrt{\frac{4\pi RT}{M}}$$

where n is the number of molecules per unit volume, σ the diameter of the molecules and M the molecular weight. Hence, changing from energy of activation per molecule ϵ to energy per mol E and changing to concentrations, equation (11) becomes

$$\frac{dC^*}{d\theta} = NC^2 \sigma^2 \sqrt{\frac{4\pi RT}{M}} \cdot e^{-E/RT} \quad (13)$$

where the expression gives the note of activation in moles per unit volume per unit time and N is Avagadro's number.

This equation is general and is readily modified if more than a single kind of gas is present. It can be applied to unimolecular and bimolecular reactions in the following manner. Since every collision between activated molecules is assumed to result in reaction we may write

$$\frac{dC^*}{d\theta} = \frac{dC^{**}}{d\theta}$$

However, a more reasonable point of view would require

$$\frac{dC^*}{d\theta} > \frac{dC^{**}}{d\theta}$$

It is generally agreed that activation by collision is inadequate to account for unimolecular reactions for two-reasons:

1) The velocity of a unimolecular reaction is independent of the pressure while collision-frequency

* acitivation
** reaction

is proportional to the pressure.

2. The calculated number of collisions is not fact enough to account for some observed rates of reaction.[18]

In bimolecular reactions one of three assumptions has been made by authors on the distribution of the energy of activation between two reacting molecules.

(a) One of the molecules entering into the reaction provides the whole energy of activation.

(b) Each molecule entering into reaction has been previously activated to the same extent.

(c) The molecules which react are not previously activated but obtain their energy of activation through the collision itself - collision therefore resulting in disruption of the two molecules involved.

Under these conditions equation 13 assumes the respective forms

a) $$\frac{dC*}{d\theta} = \phi \, e^{-E/RT} \qquad (14)$$

where E is the total energy of activation per mol

$$\phi = N C^2 \sigma^2 \sqrt{\frac{4\pi RT}{M}}$$

b) $$\frac{dC*}{d\theta} = \phi \, e^{-E/2RT} \qquad (15)$$

c) $$\frac{dC*}{d\theta} = 2\,\phi \cdot e^{-E/RT} \qquad (16)$$

It has usually been found that mechanism (a) is inadequate to satisfy the relationship

$$\frac{\text{Rate of Activation}}{\text{Rate of Reaction}} \geqq 1 \ ,$$ but

(b) or (c) can usually be applied.[7, 10, 19, 20]

We may conclude that bimolecular reactions may be satisfactorily explained by the mechanism of ordinary collision.

6. Activation by Collisions of the Second Kind - Chain Reactions

It was stated in the previous section that ordinary collisions will not account for the mechanism of activation for unimolecular reactions. Realizing this, Christiansen and Kramers[21] suggested that the mechanism of activation is explained by collisions of the second kind between activated molecules of the product formed in the reaction and unactivated molecules of the original reactant, thus raising these latter to an activated state and preparing them to enter the reaction, and establishing a reaction chain.

The schematic representation of the course of a unimolecular chemical change in which a molecule of reactant R breaks down into products P and Q would be

$$R \rightleftarrows R^1 \longrightarrow \begin{array}{l} P^1 \longrightarrow P \\ Q^1 \longrightarrow Q \end{array} \quad \text{decomposition} \quad (A)$$

$$P^1 + R^1 \longrightarrow P + R^1 \quad \text{collision of the second kind} \quad (B)$$

According to expression (A) the reactant can exist in two forms, the normal form R and an activated form R^1. The activated form breaks down spontaneously into activated forms of the products P^1 and Q^1 and these then change into the normal forms P and Q. This latter change, however, can take place, at least in the case of one of the products, through a collision of the second kind with a molecule of the reactant R, thus leading to the activation of a new molecule through the mechanism indicated by expression (B).

If the reaction deviates from a first -order course the number of such activations need not be the same as the number of molecules that decompose, but in case the reaction actually takes a first-order course Christiansen and Kramers introduce the special assumption that each decomposition in accordance with (A) is always immediately in accordance with (B). When this latter assumption is true the full quota of activated molecules, R^1, allowed by the Maxwell-Boltzmann law will be maintained.

The velocity of a chain reaction can be expressed in a general way by the formula

$$V = \frac{F\ (C)}{f\ (C,S)\ +\ A\ (1-X)} \tag{17}$$

where F (C) is a function of the concentrations of the reacting substances, to which the number of chains starting in unit time is proportional; f(C, S) is another function of the concentrations, or of the surface of the vessel, governing the rate of breaking of the chains; A is a constant which is as a rule many times greater than f(C, S); and X is a fraction which measures the number of activated molecules produced in each act of transformation.

We may distinguish between three cases:
1. $X = 1$, the velocity is stable and probably measurable; 2. X is much less than unity, V becomes very small because the term $A\ (1 - X)$ becomes dominant; 3. $f(C, S) = A\ (1 - X)$, the velocity is infinite.

It was first pointed out by Semenov[22] in his recent and valuable papers on the theories of chemical reaction velocity that X in equation 17 may vary with concentration, and when f(C, S) is small, a very small change in X may cause the reaction velocity to change suddenly from a finite magnitude to infinity. Consequently, a slight change in concentration may result in an abrupt transition from slow reaction to explosion.

Semenov pointed out, moreover, that explosions may be of two kinds:

1. Heat explosions, in which heat is liberated; by the reaction at the start faster than it is removed through the walls of the vessel, are characterized by cumulative increase in temperature with a corresponding increase in reaction velocity. These reactions are further characterized by the existence of a critical density below which the explosion will not take place for a given temperature.

2. Chain reactions, on the other hand, have a critical density which is independent of the temperature and is quite small.

In concluding this discussion on so-called collisions of the second kind, it may be stated that the concept of chain reactions, first suggested by Bodenstein in his work on photochemical reactions, offers for the first time a plausible explanation for homogeneous catalysis both positive and negative, in gas reactions. Positive catalysts are those substances, the addition of which, increase the number of "links" while negative catalysts decrease the number of links in the reaction chain. It is impossible, however, to develop a general theory on the assumption of chain reactions, It was mentioned that Christiansen and Kramers postulated exothermic reactions in developing their theory. There remain however, a large number of endothermic reactions which must be included by any theory which is at all general.

7. The Simple Radiation Theory of Reaction

The radiation theory of chemical reaction which was developed mainly by Perrin[23] and W. C. McLewis.[24] The theory was developed chiefly because the collision hypothesis was inadequate to account for unimolecular reactions as Trautz[25] had realized when he advanced the theory but in a rather obscure manner.

The theory takes the following simple form:

In the activation of molecules a narrow band of infra red frequencies is assumed to be operative.

All matter at constant temperature is in equilibrium with radiant energy, which is being continually absorbed and reemitted in quanta by the molecules.

A space entirely surreounded by material walls of sufficient thickness to be impenetrable to radiation is traversed in all directions by waves of every possible frequency. Unit volume contains a definite amount of radiant energy,- the radiation density, - determined only by the temperature of the walls, and distributed among the different frequencies in accordance with Planck's law.

This law states that if the quantity of energy lying between the frequencies ν and $\nu + d\nu$ be represented by $\rho_\nu d\nu$ where ρ_ν is the radiation density for the frequency ν then

$$\rho_\nu = \frac{8\pi h \nu^3}{C^3} \cdot \frac{1}{C^{h\nu/kt} - 1}$$

where c is the velocity of light, h is Planck's constant and k is the molecular gas constant.

Gas molecules exposed to this radiation absorb and emit quanta of magnitude $h\nu$, if their internal structure permits.

For the frequency which is effective in activating the molecules chemically $Nh\nu$ ought to be equal to E, the energy of activation. (N is Avogadro's number). From the heat of activation the activating frequency is calculated by the relation $\nu = E/Nh$. If the molecules really are activated by quanta of more or less monochromatic radiation the fact that a gas can absorb it should be manifested by the existence of an absorption band at this calculated frequency.

The temperature coefficient of the reaction is still given by the Arrhenius coefficient. It is assumed that the velocity constant is proportional to the radiation density. Observed chemical heats of activation correspond to frequencies in the short infra-red region, and for these values of ν the term $e^{h\nu/kT}$ in Planck's equation is large in comparison with unity. The expression for ρ_ν thus reduces to

$$\frac{8\pi h\nu^3}{c^3} \cdot e^{-h\nu/kT}$$

Thus $k^1 = \text{constant} \cdot e^{-h\nu/kT}$

Whence $\frac{d \ln k}{d\theta} = \frac{h\nu}{kT^2} = \frac{N h\nu}{NkT^2} = \frac{E}{RT^2}$

Numerous objections have been raised to the simple radiation theory. The first of these is the fact that the monochromatic radiation density is by no means sufficient to supply the energy demanded by some observed rates of reaction and there seems to be no doubt, as Christiansen and Kramers,[21] as well as Tolman[26] have shown, that the walls of the containing vessel fall short of giving sufficient radiation by at least a million fold.

A further objection results, however, because of the work by Daniels and Johnston.[27] The empirically determined energy of activation of a reaction in the equation $E = Nh\nu$ determined the frequency of light that should be photochemically active in bringing about that particular reaction. This was done for nitrogen pentoxide without effect. Furthermore, no absorption line or band could be found corresponding to the calculated frequency.

Numerous attempts have been made by investigators to account for the above discrepancies. These are pointed out in a review by Daniels 18.

In calculating this reaction it may be definitely stated, that the simple radiation theory, which assumes activation by passage from a single normal to a single activated state through the absorption of a quantum of radiation, cannot give a satisfactory account of unimolecular reactions, both because the rate of activation would be too small and because substances do not respond to radiation of the predicted wave length.

8. The Elaborated Radiation Theory of Reaction

This elaboration has been developed by Tolman[26] who discusses the following possibilities.

(a) Simultaneous absorption of several Quanta

If several quanta are involved in the passage from the normal to the activated state, the frequency of the activating light cannot be calculated by setting the energy of activation equal to $Nh\nu$, because several frequencies are involved. Such an explanation was advanced by Perrin to explain some of the failures in his simple radiation theory.

Two considerations militate against this view. In the first place, the quantum theory gives no reason to expect such coupled absorption. Secondly, there is no spectroscopic evidence that coupled absorptions ever occur. It is safe therefore to dismiss this possibility.

(b) The Successive Absorption of Quanta

It is quite possible that the molecule does not pass from a normal to an activated molecule in a single change, but rather, it passes through a series of intermediate stages. Several smaller quanta of different frequencies would then be required and this discrepancy between calculated and observed absorption bands, as well as the failure of reactions to respond to calculated frequencies, could be explained. However, the mere assumption of such intermediate states is of no help in getting around the difficulty of insufficient radiation density.

(c) The Absorption of a Continuous Range of Frequencies

The fact that there are photochemical reactions which are induced not by a single frequency but by the absorption of a continuous range of frequencies may be interpreted in terms of the quantum theory to mean that instead of a single activated state, there is a whole range of activated states of increasing energy content. Such a great increase in the number of activated states would greatly increase the rate of activation and thus account perhaps for the observed reaction rate, but it is not known if such increases are adequate.

(d) The Simultaneous Absorption and Emission of Quanta

If molecules could absorb and emit quanta simultaneously, rates of activation more in accord with observed rates of reaction would result, but there is no evidence to show that this mechanism is important.

9. Summary

In completing this survey of the literature on rates homogeneous of gaseous reactions it is well to point out first of all that the Guldberg-Waage law of mass action, and the fundamentals of the Arrhenius concept of activation are the basis of reaction kinetics.

Inasmuch as the Arrhenius equation expresses the temperature coefficient of the specific reaction constant, we may state that the rate of a reaction of any substance is proportional to its concentration and a function of its temperature.

The temperature function expresses the distribution of the molecules or pairs of molecules in the different states, or the distribution of energy of the system among the molecules.

The various mechanisms that have been suggested were prompted by the desire to find a theoretically sound basis for a relation that is observed to be ordered in the absence of disturbing influences.

No one of the mechanisms, including that of Arrhenius, is adequate to explain simple reactions. It may be stated, however, that there is no reason why all mechanisms may not contribute to the process of activation and, indeed, it is possible that the four will be included when the general mechanism is finally formulated.

10. The Homogeneous Reaction Between Hydrogen and Oxygen

The supposedly simple yet important nature of the reaction between hydrogen and oxygen has recommended its study in the initial applications that are to be made of this method. A survey of the literature of this reaction has been made therefore, and is contained in Appendix I.

PART II

STUDY OF HOMOGENEOUS REACTIONS

A. EXPERIMENTAL PROCEDURE

In the general review that has been given of homogeneous rates of reaction in gases no mention was made of the methods by which rates are determined. This phase of the subject will now be considered.

1. The General Experimental Methods

There are three methods in general use for the determination of velocity of "homogeneous" reaction in gases:[28] "static," "dynamic," and "evacuated bulb." Descriptions of these methods follow.

(a) Static Method. - A known quantity of mixture is placed in a previously evacuated vessel at a temperature where reaction is negligible. The vessel is quickly placed in a heated thermostat where it is held for a known time, it is quickly removed and cooled; its contents are then analyzed. The process is repeated with different times of heating, concentrations, etc. to establish the rate and mechanism.

(b) Dynamic Method. - The cold gas mixture is passed through a heated tube at a known rate, and analyzed. The process is repeated at different rates of flow with the same initial mixture, thus varying the time.

(c) Evacuated Bulb Method. - The cold gas mixture is allowed to flow quickly into a thermostatically heated evacuated bulb. The course of the reaction is followed by an attached manometer. This method can be used only in those reactions where there is a change in the number of mols.

2. Defects of the General Methods

Apart from any particular defect, it is recognized that these three methods have one defect in common, namely, the walls of the vessel are heated and we may therefore expect to get surface, action as well as gas phase reaction, unless the particular gases are not catalyzed by hot surfaces. It happens, however, that almost all gas reactions are affected by hot surfaces so that it is questionable if homogeneous reaction rate can be determined by any of these methods.

There are, however, two methods by which the temperature of the reactants may be raised, and the reaction may proceed, without the disturbing influence of hot walls. The first of these is the method of heating the reactants separately and allowing them to mix and react before they reach a heated surface, as is done in the concentric tube method of Dixon[29] or the jet method of Wartenburg and Kannenburg.[30]

The second method is that of sudden compression of the gas mixture, the rate of compression being so rapid that the gas temperature is raised above that of the container.

Both of these methods were devised originally for determining ignition temperature of gases without wall effect. The concentric tube method is well adapted to this but cannot be used for determination of rates of reaction. On the other hand, the method of sudden compression is well suited to the determination both of ignition temperatures and of velocity of reaction. Indeed, it is well suited for the study of many phases of reaction phenomena which will be pointed out subsequently. It is because of its wide application that it has been selected for this research.

3. The Method of Adiabatic Compression - Its Uses

The principle of the method of adiabatic compression can be understood readily if the equations for the adiabatic change in state for perfect gases are derived. Following this a review will be made of some of the applications that have already been made and other possible uses pointed out.

(a) Adiabatic Compression

The fundamental equation for the change in state of a non-reacting gas is given by

$$dQ = C_V\, dT + PdV \qquad (1)$$

Since the process is adiabatic, $dQ = 0$

and

$$C_V\, dT = -PdV \qquad (2)$$

For the gases to be dealt with, the specific heat, C_V, will be assumed to vary linearly with temperature, giving the form

$$C_V = \alpha + \beta T \qquad (3)$$

The perfect gas law will be assumed to hold over the range of temperature and pressure that will be used.

$$P = \frac{RT}{V} \qquad (4)$$

Substituting from (3) and (4) into equation 2, and integrating between limits, we have

$$\int_{T_1}^{T_2} \alpha \frac{dT}{T} + \int_{T_1}^{T_2} \beta \quad dT = -R \int_{V_1}^{V_2} \frac{dV}{V} \qquad (5)$$

$$\alpha \ln \frac{T_1}{T_2} + \beta (T_1 - T_2) = -R \ln \frac{V_1}{V_2} \qquad (6)$$

Dividing by $\ln T_1/T_2$,

$$\alpha + \beta \frac{(T_1 - T_2)}{\ln T_1/T_2} = -R \quad \frac{\ln (V_1/V_2)}{\ln (T_1/T_2)} \qquad (7)$$

But $\alpha + \beta \frac{T_1 - T_2}{\ln T_1/T_2}$ = value of C_v at log mean of the temperature limits.

therefore

or

$$\frac{\ln(V_1/V_2)}{\ln(T_1/T_2)} = - \frac{C_{v\,ave}}{R} \qquad (8)$$

$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{C_{v\,ave}/R} \qquad (9)$$

and

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{1+R/C_{v\,ave}} \qquad (10)$$

It is seen from equation 9 that the temperature of a gas mixture can be raised to any desired value by compressing it adiabatically. Actually, the true adiabatic conditions are never attained because of heat loss to the walls of the vessel. The general case, in which heat interchange with the walls of the vessel is taken into account, is treated in Appendix II.

It is convenient to express (9) and (10) in general form by means of plots. This has been done in Figures 1 and 1-A where values of C_p/C_v cover the whole range from monatomic gases down. In addition, the temperature variation of the molal heat capacities # at constant volume for the common gases are given Figure 2; and in Figure 2-A, the values of C_v at the logarithmic mean of 298° K(25° C) and T° are given. (When $C_v = \alpha + \beta T + \gamma T^2$, the proper mean value to use for C_v in equations 9 and 10 is given in Appendix II).

(b) Some Applications of the Method of Sudden Compression

It is well to review some of the methods that have been used in applying this principle to gas reaction phenomena.

The method originated with Nernst who pointed out its principles and advantages to Falk[31] for determination of the ignition temperatures of gases. Falk's method consisted of driving a piston into a steel

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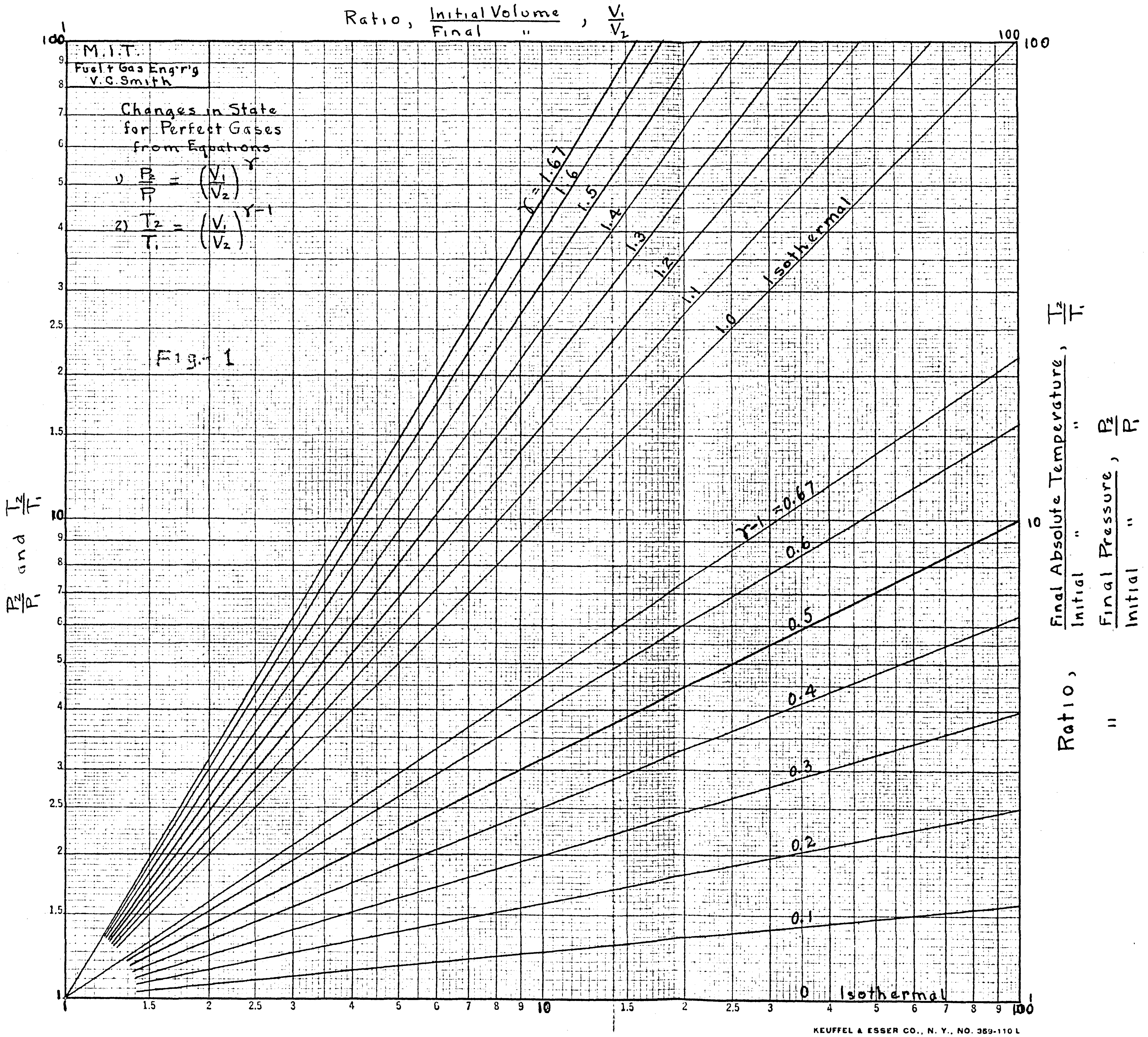
Data from Partington and Shilling "Specific Heats of Gases"



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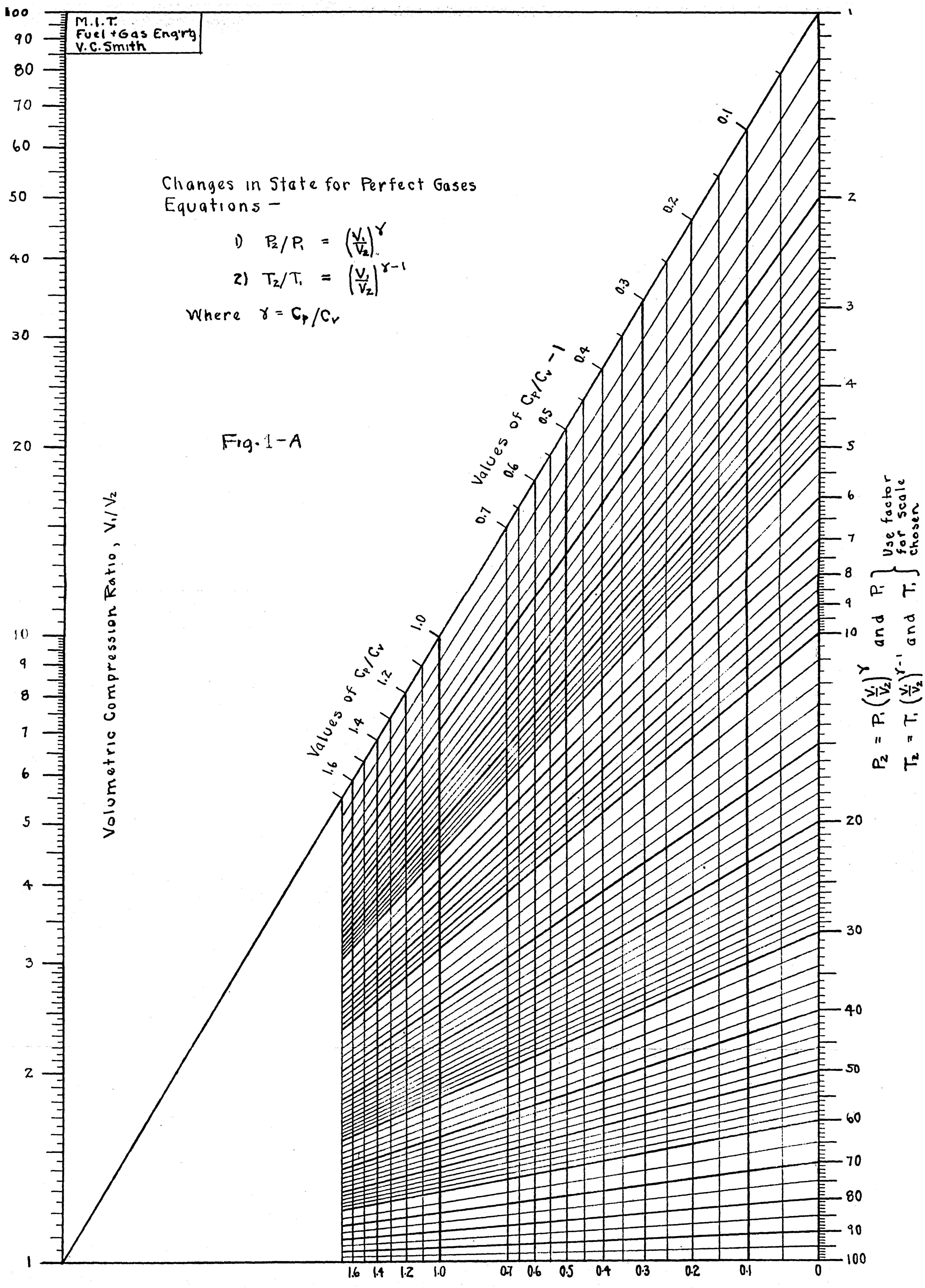
Changes in State for Perfect Gases from Equations

1) $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$

2) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

Fig. 1

KEUFFEL & ESSER CO., N. Y., NO. 359-110 L
Logarithmic, 2 × 2 Cycles.



Changes in State for Perfect Gases

Equations −

1) $P_2/P_1 = \left(\frac{V_1}{V_2}\right)^{\gamma}$

2) $T_2/T_1 = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

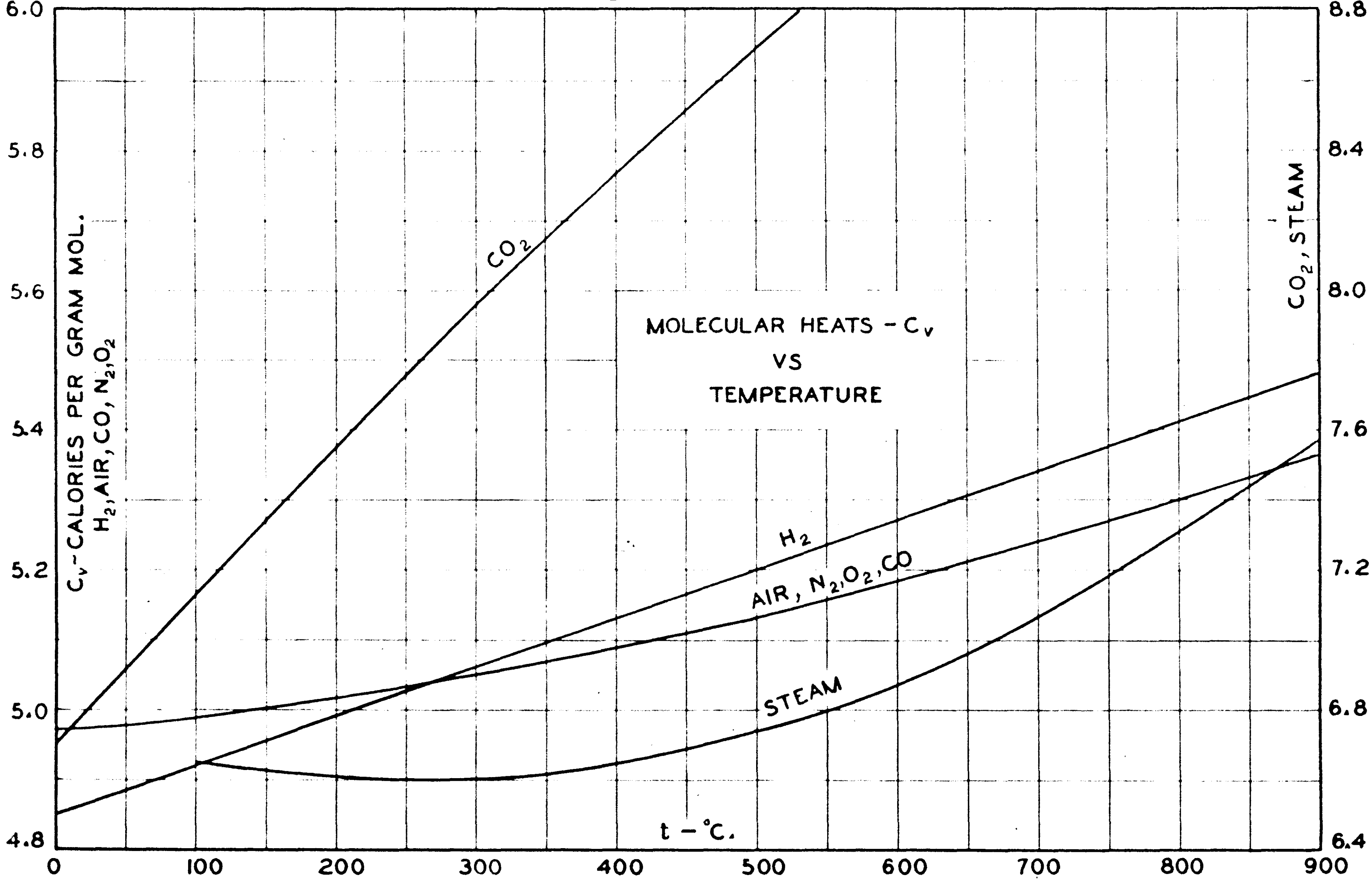
Where $\gamma = C_p/C_v$

$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma}$ and P_1

$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ and T_1

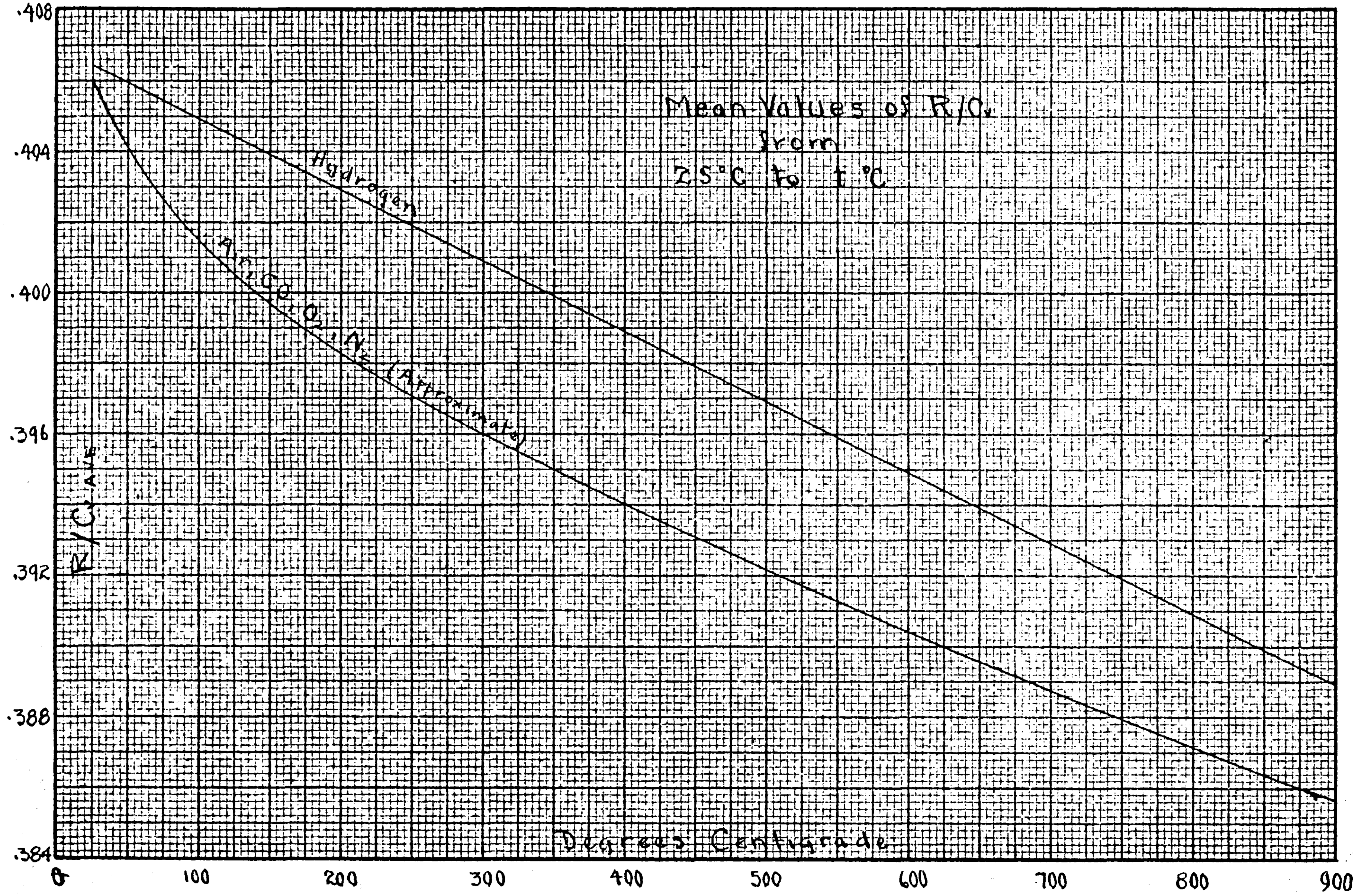
Fig. 1-A

Figure 2



MOLECULAR HEATS – C_v
VS
TEMPERATURE
C_v–CALORIES PER GRAM MOL.
H_2, AIR, CO, N_2, O_2
CO_2, STEAM
CO_2
H_2
AIR, N_2, O_2, CO
STEAM
t – °C.
6.0
5.8
5.6
5.4
5.2
5.0
4.8
8.8
8.4
8.0
7.6
7.2
6.8
6.4
0
100
200
300
400
500
600
700
800
900

Fig. 2 - A


Mean Values of R/Cv
from
25°C to t °C
Hydrogen
Air, CO, O2, N2 (Approximate)
R/C ave
Degrees Centigrade
.408
.404
.400
.396
.392
.388
.384
0
100
200
300
400
500
600
700
800
900

cylinder containing the gas mixture by means of a falling weight, until the descent of the piston was arrested by the explosion. Falk assumed that the mixture was heated adiabatically and unifromly throughout its whole mass until it reached the ignition temperature, - the temperature at which the rate of heat development in the gas mixture was equal to its dissipation to the walls of the vessel. The further assumption was made that it then detonated instantly and arrested, at the moment of ignition, the downward movement of the piston. The temperature of ignition was calculated from the equation of adiabatic compression of gases by noting the initial temperature and volume, and volume corresponding to piston position at explosion.

Dixon and his co-workers[32] had no difficulty in showing, however, that the assumptions of Falk were untrue. Indeed, by photographing the explosion produced by adiabatic compression of combustible mixtures, Dixon found that, although the flame does not start from a point, yet in the more slowly burning mixtures, it takes an appreciable time to spread through the whole of the gas, so that only in the case of fast burning mixtures can the time factor be regarded as negligible. In other words, Dixon concluded that explosive gaseous mixtures do not usually detonate when fired by adiabatic compression, and that the real ignition point usually does not synchronize with the appearance of flame. Hence, it is evident that the pre-flame period is not negligible, and, therefore, that in any determination of ignition temperatures by this method, the piston should be stopped at the beginning of the pre-flame period, a precaution which Falk had neglected.

These experiments indicated, then, what modifications of Falk's apparatus would be desirable in order to determine the ignition-point of gases by adiabatic compression. The cylinder must be sufficiently wide and long to prevent appreciable cooling by the walls of the central mass of gas during compression; it must be sufficiently long to give a final volume that can be measured with accuracy; the piston must be driven in rapidly, and must be gas-tight without the lubricant's coming into contact with the explosive mixture; and the piston must be stopped the moment it has compressed the gas to the true ignition-point.

Dixon and Crofts[33] therefore constructed the apparatus shown in Figure 3. The ignition temperatures were calculated from the minimum observed

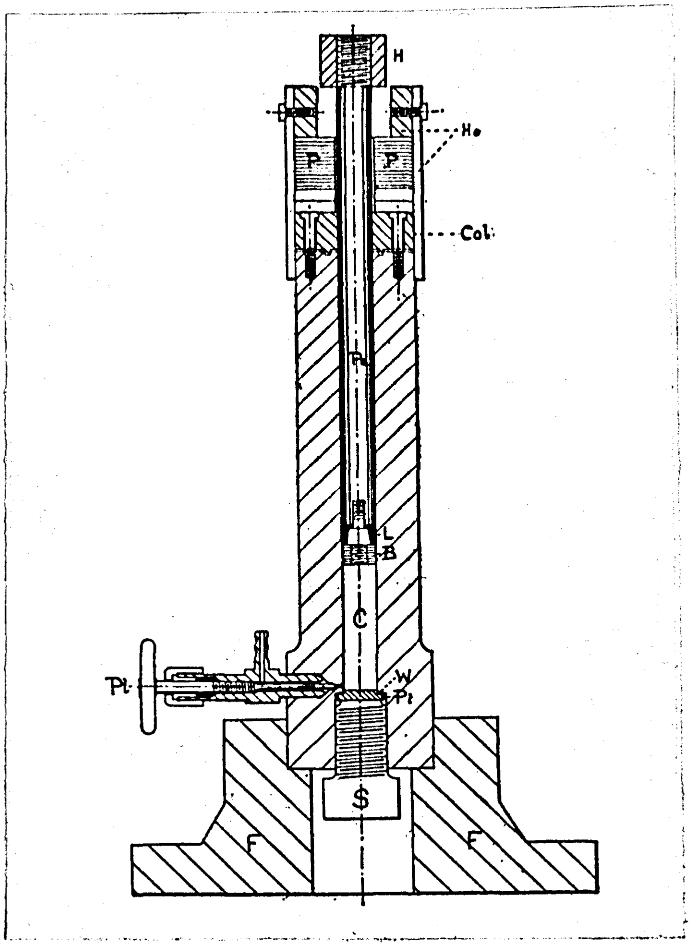


Fig. 3.

Dixon and Crofts' Apparatus

Description. - The cylinder is steel with a 3 cm. bore; the plunger, also steel, with a maximum stroke of 40 cm. is driven in by a 250 pound weight falling from a height of 5 feet on to the head (H); the piston, of phospher bronze, is packed with a leather annular washer and lubricated with lanoline; the hardened steel plates (P) of various thicknesses allow variation in compression ratio.

compression ratio necessary to cause ignition.

Dixon has improved his apparatus recently as a result of a suggestion by Tizard and Pye who pointed out that if the piston is only arrested and not held in place when the ignition compression is reached, the gas during the self-heating pre-flame period may do work against the piston and so be cooled. Especially might this happen when, owing to the sudden collision of the steel head of the piston with the steel collar that stops it, there is a tendency for the piston and weight to rebound. The error was corrected by placing a lead cylinder on the piston head, the cylinder being held between the weight and the piston until the latter is stopped by the collar; the momentum of the weight then squeezes the lead into a flat disc maintaining the pressure on the piston while strong clamps slide over the top of the weight and hold it at its lowest point.

Tizard[35] and later Tizard and Pye have determined the ignition temperatures of hydrocarbon-air mixtures under conditions which correspond closely to those in an engine cylinder. It was pointed out that the interval between the end of compression and the occurrence of ignition might be of the order of one second in the case of hydrocarbons, and, indeed, this lag is a property of the gas mixture unable to be eliminated by any change of experimental conditions which does not change the gas temperature. They attempted to correlate the delay before ignition at different temperatures with rate of combustion, i.e., with the temperature coefficient of reaction. For this purpose it was necessary to attach an indicator to the apparatus and record quantitatively the pressure variation during and after compression as a function of the time. A fan was enclosed in the cylinder so that the rate of heat loss could be varied. A sketch of the apparatus appears in Figure 4.

From the experimental observations it was concluded that ignition occurs very locally and at these points the temperature is above the mean as determined by the pressure record, a view in accord with Dixon's photographic results. However, the rate at which these hotter parts lose heat bears some relation to the average rate for the whole gas. It is shown also that the temperature at the end of compression is much less than calculated for adiabatic compression, and the assumptions of Dixon in calculating ignition temperatures from volumetric compression ratios is not justifiable.

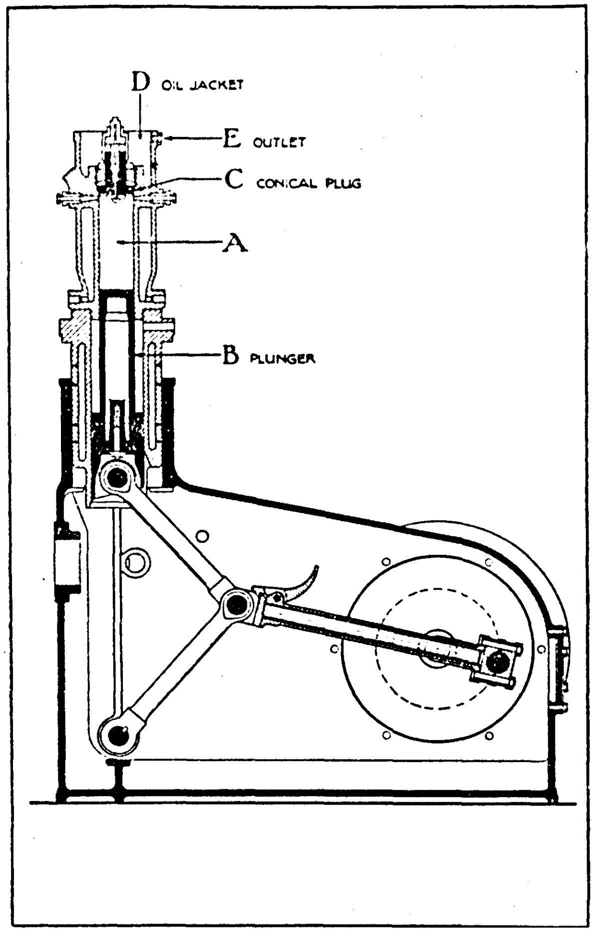


Fig. 4.

Tizard and Pye's New Apparatus

Description. - Apparatus consists of oil-jacketed cylinder in which gaseous mixture can be heated to any desired temperature up to 180° C. before compression; temperatures higher than 60° C destroy leather washers, hence, two cylinders are arranged in tandem and the lower one kept at room temperature; upper cylinder is fitted with close-fitting plunger, piston for lower cylinder is fitted with double leather cup washers with castor oil seal; it is assumed that on compression, pressures in the two cylinders balance and there is no tendency for gas to leak from upper cylinder; plunger of 3-inch diameter and 8-inch stroke is actuated by a heavy fly wheel, spinning at 350 r. p. m., so constructed that the Ricardo toggle engages when it is desired but releases and locks piston in place automatically at end of compression; compression ratios are 6:1 or 9:1 and pressures are determined with a Collins micro-indicator; a time of compression not less than 0.14 sec. is necessary to prevent fracture from inertia.

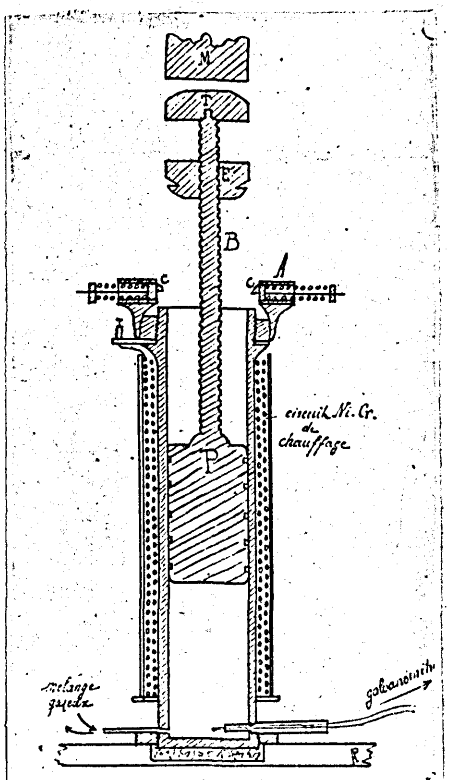
Among the few researches in which the adiabatic compression method has been used we may also mention that by Cassel,[36] who continued Falk's work and after introducing improvements in the original apparatus was able to correct some of Falk's data on ignition temperatures of oxygen-hydrogen mixtures; the relation between ignition temperature and pressure was studied, as well as the time of explosion as an index of the reaction rate for different mixtures of hydrogen and oxygen but no definite conclusions could be drawn from these results because of the crudeness of the experimental method.

Aubert and Pignot[37] have published some preliminary results that have been obtained with an adiabatic compression apparatus shown in Figure 5. Their researches have dealt with the following questions.

1. Determination of the initial temperature necessary to produce ignition of a fuel-air mixture, both as function of mixture ratio and compression ratio for several paraffin, aromatic and naphthenic hydrocarbons.

2. The effect of compression ratio on the final pressure attained after autoignition, on the time of inflammation, on the ratio of maximum to initial pressure, on the lag before inflammation, and the effect of tetraethyl lead on these, for specific air-fuel mixtures of the hydrocarbons benzene, cyclohexane and hexane.

Finally, we may refer to the work of Duchêne[38] on the photographic study of the flame characteristics of homogeneous gas mixtures, ignited by a spark after adiabatic compression; the following phases were studied: influence of ignition spark, of mixture ratio, of initial temperature, of degree of compression, of tetraethyl lead, of tube length, on the flame



— Appareil de M. Pignot, pour la mesure des températures d'inflammation.

Fig. 5.

Pignot's Apparatus

Description. - No dimensions of cylinder bore or stroke are given; a 35-pound weight, M drops from a maximum height of 8 feet onthe head of the plunger which is stopped when adjustable collar E, reaches cylinder; two oppositely placed tongues, CC, engage in the recess in E and prevent cooling of gas from rebound of plunger at impact, and also prevent piston from being thrown back by explosion in the cylinder; compression ratio is varied by adjustment of collar, E, on threaded piston rod.

properties of benzene, cyclohexane, cyclohexene, and hexane.

A sketch of the apparatus appears in Figure 6.

(c) Summary

The researches that have been reviewed in the previous section constitute, as far as is known, all that have made use of the method of adiabatic compression in the study of combustion phenomena in gases. Two of them have been published since the start of the present work.

It is well to summarize these researches from two points of view, - (a) requirements of the apparatus; (b) uses of the method for combustion studies.

i. Requirements of the Apparatus

1. The gas mixture, introduced into a cylinder of fair size, must be rapidly compressed to some final definite volume.

2. The piston must be capable of moving at high speed without affecting the gas mixture because of frictional heat, contamination from a lubricant, or leakage; it must possess mechanical properties that allow it to be decelerated rapidly at the end of its stroke; it must in some way be prevented from

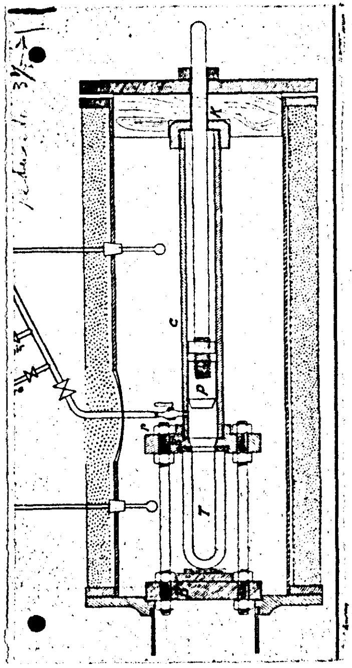


Fig. 6.

Duchêne's Apparatus

<u>Description</u>. - Cylinder, C, is steel with a 3 cm. bore; explosion chamber, T, is thick glass or quartz; steel piston with cast segments is packed with washers between segments; maximum stroke 26 cm ; apparatus enclosed in thermostat with openings for exposing tube and manipulation of stopcock; piston forced in by falling weight which also sparks mixture at end of stroke.

rebound due to elastic impact and, if the course of a reaction is to be followed under constant volume conditions, the constraining force on the piston must at least equal that resulting from the reaction.

3. The temperature and pressure do not correspond to the calculated adiabatic values because of cooling; this discrepancy depends chiefly upon the rate of compression, being zero for infinite rate; for finite rates it depends upon the quantity, surface/volume, condition of surface, temperature difference between gas and surface, quantity of gas, thermal properties of the gas, and turbulence.

4. During the course of an experiment correct information on temperature and pressure in the cylinder can be obtained only by measurement with an instrument of high precision designed for the purpose; since the changes are rapid the record must be made automatically.

ii. The Uses of the Method

1. Ignition temperatures can be determined without the disturbing influence of hot walls common to almost all other methods; the variation of ignition

temperature with composition of the gas mixture, the effect of diluents, the lag before ignition, variation of ignition temperature with pressure, all these are readily studied under homogeneous and well defined conditions.

2. The pre-flame period can be studied under thermodynamically well defined conditions, to obtain quantitative data on reaction rate and mechanism; it may be mentioned that this possibility is little appreciated and has therefore been but little investigated.

3. The investigation of fuels under conditions corresponding to those in internal combustion engines is made easy and the results made definite by this method. Indeed, in addition to the superficial investigation of such factors as the effect of compression ratio on the final pressure attained after auto-ignition, etc., as crudely conducted by Aubert and Pignot, the additional relations between compression ratio, mixture composition, (including of course contents of ordinary unscavenged gas), size and shape of combustion space, presence of hot spots, etc., when the mixture is sparked at the end of the stroke, have yet to be quantitatively studied from

the standpoint of lag before inflammation , rate of inflammation, ratio of maximum to initial pressure, and tendency to detonate. The method herein described seems to have qualifications which permit its adaptation to the study of many of these problems.

4. Finally, we may indicate a further application to which the first phase of this work is devoted. As has been stated already, the firing of gases by sudden compression can be qualitatively explained by the theory that at the temperature of compression the gas reacts at such a rate that heat is evolved by the reaction faster than it is lost by conduction to the walls of the vessel; therefore, the slope of the temperature-time curve of the mixture is zero at the ignition temperature. At temperatures a little less than ignition there is a small negative slope, less, however, than that in a non-reacting mixture, and the measurement of the difference between the two offers a convenient method of studying not only the mechanism of the reaction and its rate, but the temperature coefficient as well. This idea is more readily explained by a plot.

Let a non-reacting gas mixture or a single gas be compressed suddenly to a temperature, t_1, in

Figure 7, and let this temperature be below the ignition temperature of the gas being studied; also let the gas be held at constant volume after compression. The gas will cool along some line t_1 t_1^1. Now let a combustible gas be compressed to the same temperature and volume. Since heat is being evolved, the slope of the cooling curve will be different; the gas will cool along some line t_1 t_1^{11}. This initial difference in slope may be taken as a measure of the heat being evolved by the reacting gases. If the process is repeated at the same temperature but with different concentrations, it is possible to study the mechanism of the reaction and, following this, to evaluate the reaction constant at this temperature. The same process repeated at different temperatures will give the effect of temperature on the reaction constant.

A new set of conditions may then be imposed as regards condition of vessel, diluent gases, knock suppressors and inducers, etc., and their effect upon the rate of reaction determined.

A more complete discussion of the detailed procedure will be given in the next section.

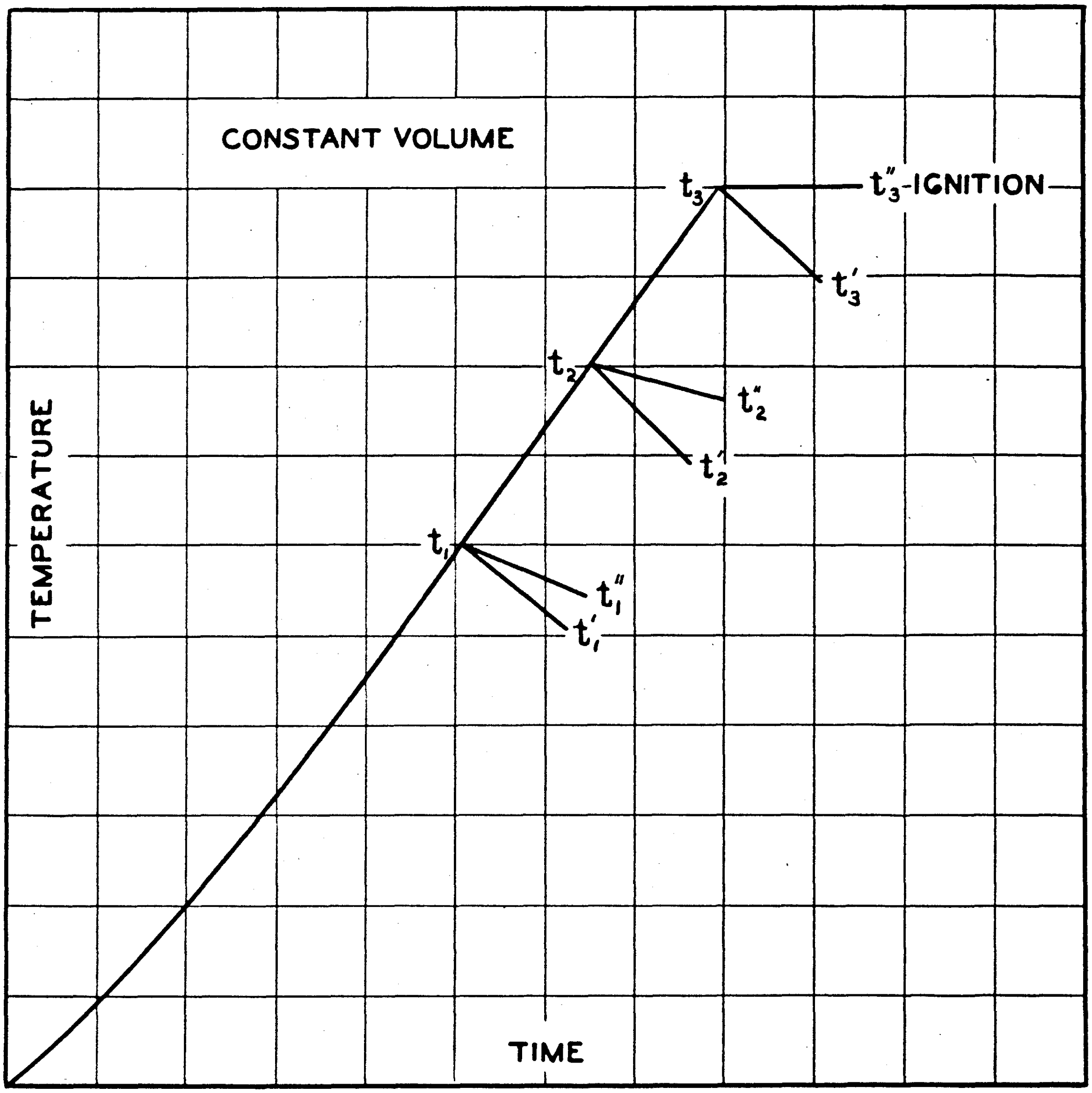

CONSTANT VOLUME
t_3
t''_3-IGNITION
t'_3
t_2
t''_2
t'_2
t_1
t''_1
t'_1
TEMPERATURE
TIME

Figure 7

4. Determination of Reaction Rate by Method of Sudden Compression

The qualitative relations that exist when combustible and non-combustible gas mixtures have their temperatures suddenly raised have been explained in the previous section; the quantitative relations will be developed in this section.

Given a gas mixture of N_T mols, the relations between temperature, pressure, and volume are given by the gas equation

$$PV = N_T RT \qquad (1)$$

If V is constant,

$$VdP = RTdN_T + NRdT \qquad (2)$$

Dividing by $d\theta$,

$$\frac{VdP}{d\theta} = RT\frac{dN_T}{d\theta} + N_T R\frac{dT}{d\theta} \qquad (3)$$

Where θ is the time.

The utility of (3) for determination of reaction rate will depend upon the type of reaction as the following considerations will show.

Consider the following conditions.

(a) Isothermal reaction - $dT = \theta$

Rate of reaction can be determined from a pressure-time relation only if the number of mols in the reaction changes.

(b) Adiabatic reaction - $dQ = 0$

$$N_T C_V dT = q \cdot dN \qquad (4)$$

where q is the heat of reaction per mol change in combustible constituent and N isthe number of mols of combustible gas, as distinguished from N_T, the total mols present.

C_V is the molal heat capacity.

Substituting in (3)

$$\frac{VdP}{d\theta} = \frac{RT\ dN_T}{d\theta} - \frac{Rq\ dN}{d\theta} \qquad (5)$$

or
$$\frac{dP}{d\theta} = \frac{P}{N_T} \cdot \frac{dN_T}{d\theta} + \frac{RqdN}{VC_V\ d\theta} \qquad (6)$$

Again, the reaction rate $dN/d\theta$ may be obtained from P vs. θ record when the reaction is specified, since a relation may then be obtained between N and N_T and all the other arguments are of known magnitude.

(c) Reactions intermediate between cases (a) and (b) - $dQ \neq 0$

$$N_T C_V\ dT = -dQ + qdN \qquad (7)$$

Substituting the value for dT from (7) into (3) we obtain

$$\frac{dP}{d\theta} = \left(\frac{RT}{V}\right) \frac{dN_T}{d\theta} + \left(\frac{Rq}{VC_v}\right) \frac{dN}{d\theta} - \frac{R}{VC_v} \quad \frac{dQ}{d\theta} \qquad (8)$$

Again, the reaction rate $\frac{dN}{d\theta}$ may be obtained if we can evaluate $\frac{dQ}{d\theta}$ in terms of arguments of known magnitude.

If we assume that $\frac{dQ}{d\theta} = hA\ (T - T_W)$, in which h is a constant, A is the area of the container, and T_W is the wall temperature, then

$$\frac{dP}{d\theta} = \frac{P}{N_T} \frac{dN_T}{d\theta} + \frac{Rq}{VC_v} - \frac{R}{V} \frac{hA}{C_v} \frac{PV}{N_T R} + \frac{RhAT_W}{V\ C_v} \qquad (9)$$

$$\frac{dP}{d\theta} = \frac{P}{N_T} \frac{dN_T}{d\ \theta} + k_1 \frac{dN}{d\theta} - k_2 \frac{P}{N_T} + k_3 \qquad (10)$$

Where

$$k_1 = \frac{R\ q}{VC_v}$$

$$k_2 = \frac{h\ A}{C_v}$$

$$k_3 = \frac{RhAT_W}{VC_v}$$

To obtain a value for h, the different pure components of the mixture are compressed individually, each following an equation of the type,

$$\frac{dP}{d\theta} = -\frac{R}{VC'_v} \cdot \frac{dQ'}{d\theta} \qquad (11)$$

obtainable from equation (8) when no reaction occurs. Primed terms are used to indicate a gas composition different from that of the reacting mixture. The values of h so obtained may then be weighted to determine h.

The solution of (9) is obtained by determining the value of $dP/d\theta$ at the beginning of the cooling period, at which time the value of N is No, P is Po, the values of these at the maximum pressure. This neglects of course any reaction that might have occurred while the gas was being brought to the pressure P_o. It was indicated that this is accomplished by sudden compression, in which case the time during which the gas is at an elevated temperature prior to the maximum is extremely short, and it is probable that no appreciable reaction can occur. Therefore, equation (9) may be expressed in the form

$$\left(\frac{dP}{d\theta}\right)_{P_o} = \frac{P_o}{N_o}\,\frac{d\,N_T}{d\theta} + k_1\,\frac{dN}{d\theta} - k_2\,\frac{P_o}{N_o} + k_3 \qquad (15)$$

which may be used to determine $dN/d\theta$ as soon as we know the relation between N and N_T.

With the principle of the method of adiabatic compression explained, and its numerous applications pointed out, the particular apparatus that has been used in this work will now be considered.

Part III

THE EXPERIMENTAL APPARATUS

A - THE DESIGN OF THE APPARATUS

In designing the apparatus that has been used it was considered advisable to follow previous designs except where obvious improvements could be made. Of these designs, only those of Dixon and Tizard and Pye were considered worthwhile for the investigation that was being made; and, between these two, the method of Dixon, with a long cylinder of not too narrow bore, offered advantages over the other method. It was decided, therefore, to construct an apparatus of similar type. This decision did not mean, however, that Dixon's method was to be followed entirely. For example, the dropping of a weight was never favored and there is no doubt whatever that if Dixon had attempted to record the pressures in the cylinder by methods then available, the vibration produced by the impact of this weight would have made his records meaningless.

1. The Factors to be Considered in the Design

Careful study of the problem revealed the following factors that had to be considered in the design of the apparatus:

a) Pressures and temperatures to be studied

b) Compression ratio necessary to (a)

c) Desirable size of bore and length of stroke to give reliable results

d) Necessary force to produce desired rate of compression and to hold piston in place over the period studied.

e) The sudden stopping of the piston at the end of compression

f) A piston and packing with little friction but leakless

g) A sensitive indicator capable of recording the pressure changes in the cylinder with minimum lag, and which would have such high frequency that its own vibration due to any shock given the apparatus would not interfere with the pressure record.

2. Conclusions on the Design

Concerning the factors in the design, the following conclusions were reached:

a) Reactions would be studied with initial pressures below atmospheric, and final pressures at, or not much above, atmospheric. The initial pressure must be determined with great accuracy.

b) Compression ratios would be varied to produce different final temperatures and the cylinder wall would be left at room temperature; compression ratios would be varied by placing hard steel plates on the cylinder head; the initial volume would remain constant.

c) The reaction cylinder would be of 2-inch bore and capable of giving a volumetric compression ratio of 20:1 and a minimum value of the quantity surface/volume at this compression ratio; its wall thickness must be sufficient to give rigidity under impact when the head of the piston rod strikes it.

d) The force of compression could be furnished best by connecting a cylinder in tandem with the reaction cylinder, and suddenly releasing compressed air at such pressure, and from a container of such volume, that the desired rate of compression, as well as sufficient residual pressure at the end of compression, could be obtained; the use of compressed air, instead of a heavy weight, and a light piston, gives power without inertia.

e) The upper piston also serves as the stopping head at the end of compression, therefore its lower surface must be of hard tough metal; rupture of the piston rod would be likely if the piston is brought to a sudden dead stop when traveling at very high speed, therefore, some kind of shock absorber must be provided which will operate rapidly and positively, always stopping the piston at a definite and predetermined point.

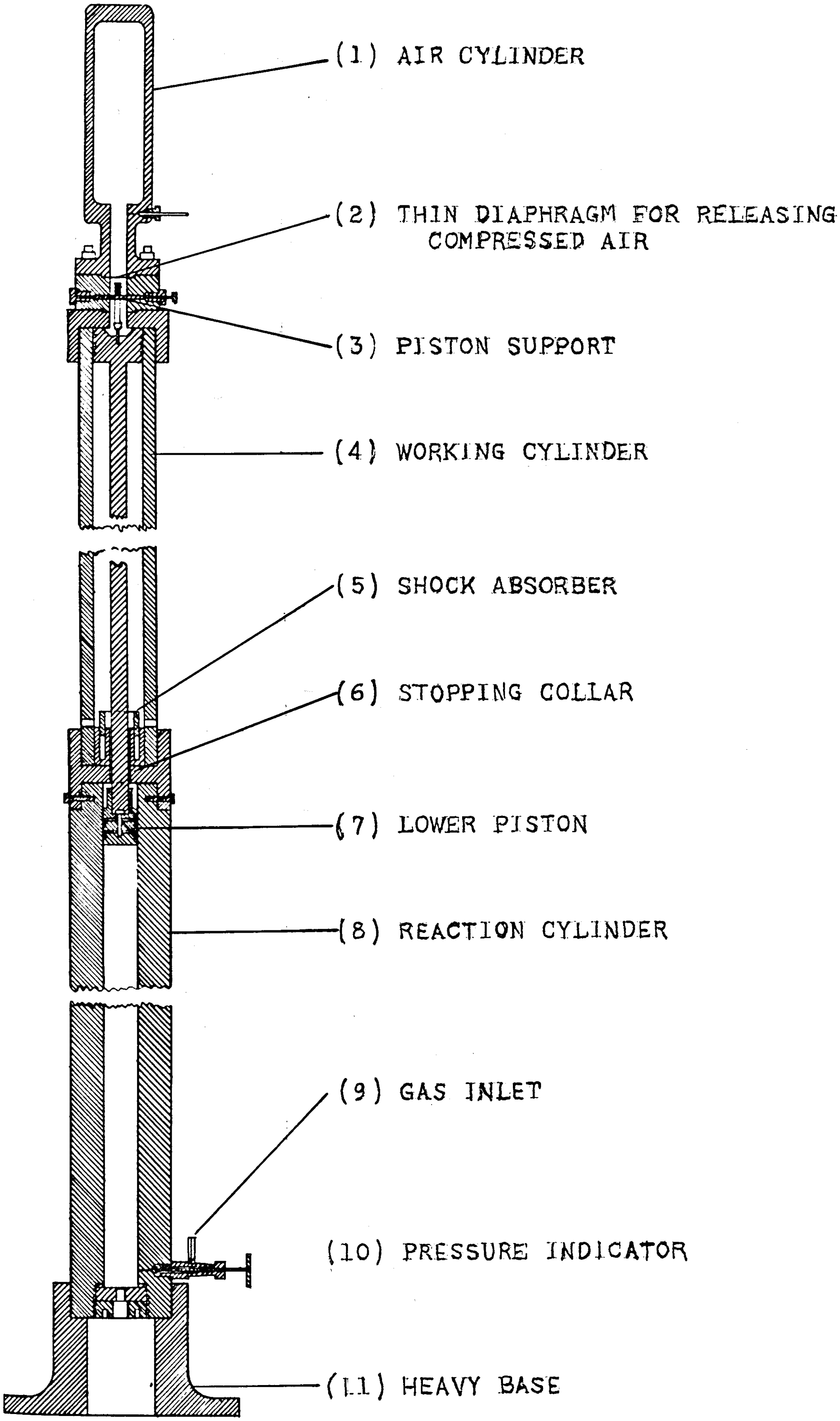
f) For the reaction cylinder a soft metal piston provided with flexible packing of rubber or leather is best; these packings preclude heating the cylinder wall above 60-70°C.

g) Electrical indicators are best suited for this type of work since the recording mechanism can usually be located at some point away from shock or vibrations that might otherwise vitiate the record; if a good electrical indicator could not be obtained, an optical indicator of some type would be used.

h) A heavy base must be provided to withstand and distribute the shock produced by the striking of the piston.

3. Sectional View of Apparatus

The conclusions expressed in the previous section are represented in the sectional view of the apparatus as shown in Fig. 8. Details of the parts are given in succeeding sections.



SECTIONAL VIEW OF APPARATUS

FIG. 8

B - DETAILS OF THE APPARATUS

The parts of the skeleton view of the apparatus shown in Fig. 8 must be gone into in much detail inasmuch as almost every part of the present equipment has, of necessity, been made satisfactory only after much experimentation. In presenting these details two methods can be followed: first, the development might be shown from the standpoint of the whole apparatus in the chronological order of its occurrence; secondly, the parts might be considered separately and in the order of their development. Of these two methods, the latter is adopted because it offers better advantage for comparing similar parts, it avoids needless repetition, and gives more continuity to the entire presentation.

The order in which the parts are presented is, for the most part, arbitrary, but the attempt is made to use the one which seems most logical, and which makes presentation of the difficult phases occur at the end. The parts are discussed, therefore, in the following order:

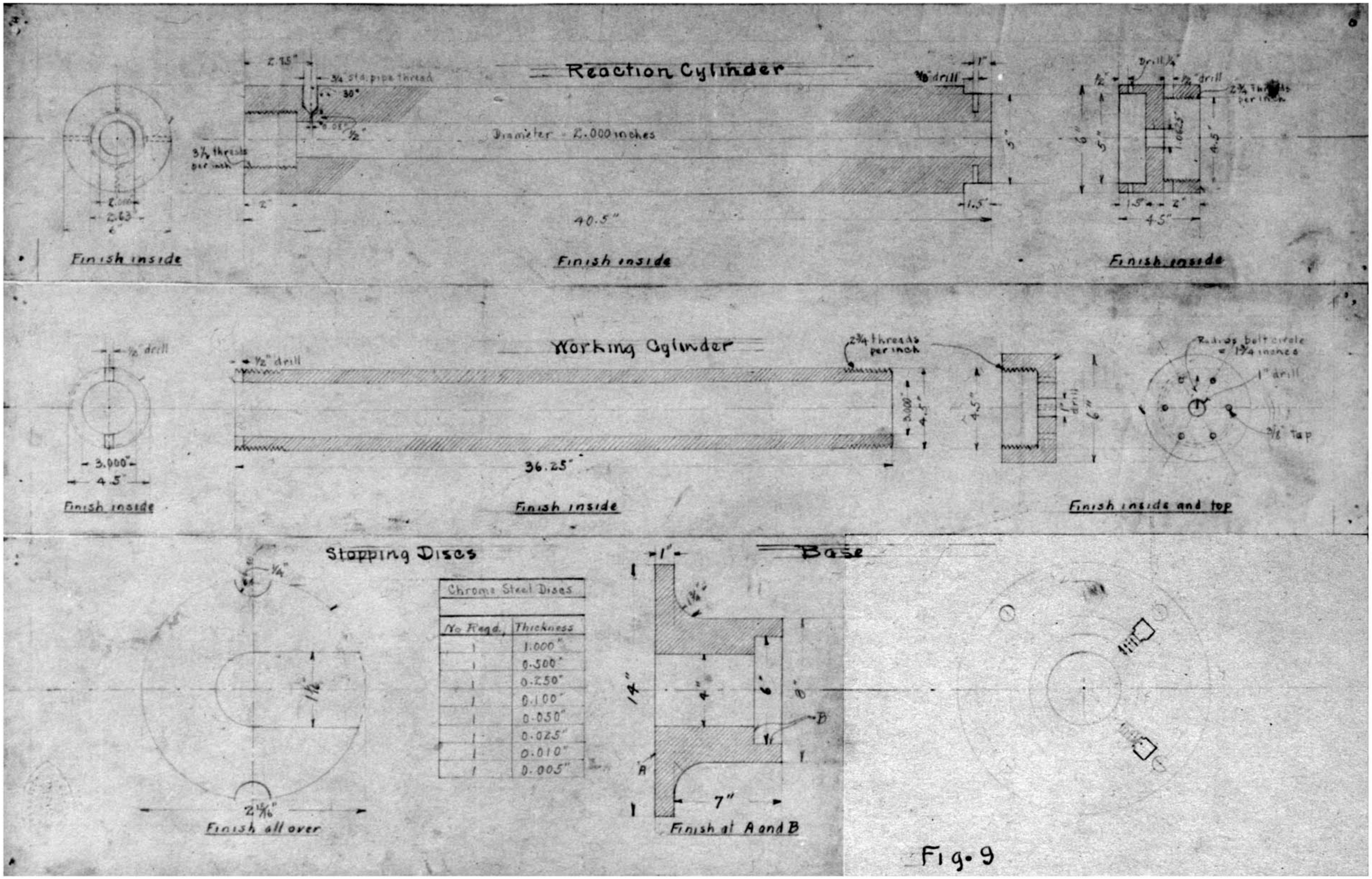
1) Cylinders, base, stopping plates
2) Pistons
3) Power for compression
4) Indicators, and recording mechanism
5) Shock absorbers for plunger

1) Cylinders -

The apparatus requires two long cylinders in tandem, capable of being separated readily after an experiment, and of such strength that the pressures and forces that come into play are amply provided for. The reaction cylinder must be very carefully bored, and suitably designed for attachment of a pressure indicator and its subsidiaries.

These conditions are met by the designs shown in Fig. 9 where, in addition to the cylinders, the connecting collar, cap, and heavy base and stopping plates are also shown.

The reaction cylinder is bored from a heavy nickel-chromium steel ingot, and its 2-inch wall, along with its natural hardness, makes it well-suited to receive severe axial impact when the piston is brought to a stop. The bottom of the cylinder is closed by the indicator so that it is exposed to cylinder pressure without circuitous connections, and the indicator is securely held by a heavy screw. The cylinder is evacuated, charged and closed by means of a specially designed valve shown in Fig. 8. One opening in the lower end allows light to reach the optical indicator, and



Chrome Steel Discs

No Reqd.	Thickness
1	1.000"
1	0.500"
1	0.250"
1	0.100"
1	0.050"
1	0.025"
1	0.010"
1	0.005"

Fig. 9

another is provided for supplying damping liquid to the indicator if such is needed.

The upper cylinder of 3-inch bore is made from seamless steel, and its 3/4-inch wall is amply thick inasmuch as it must withstand only relatively low air pressure. Openings at its lower end allow air to escape readily when the piston moves down.

The base into which the reaction cylinder fits is made from cast iron and is fastened to a concrete base by means of heavy bolts. Set screws prevent the reaction cylinder from moving on the base. This latter is a necessity if an optical indicator is used, inasmuch as slightest motion throws the system out of alignment.

The compression ratio is varied by means of the stopping plates. Their location subjects them to the shock and impact of the striking piston. These plates have therefore been made from hard chrome steel.

2) Pistons

The demands placed upon the pistons and rod in this work are quite severe and much work has been necessary to produce the correct type.

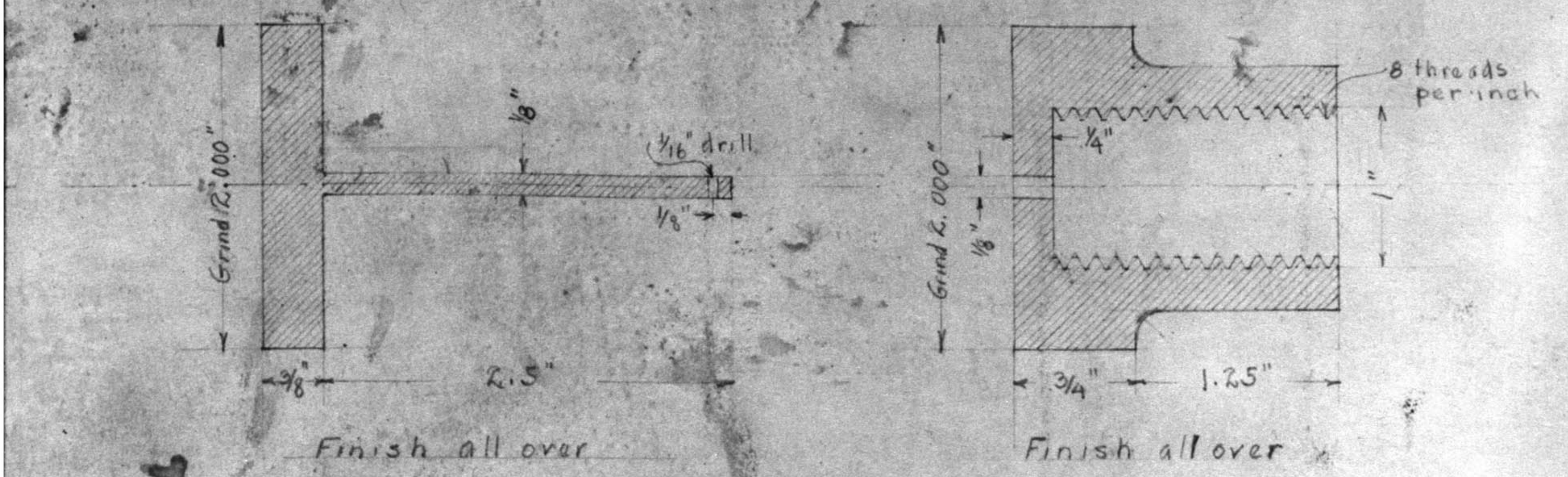
The requirements of the pistons and rod set forth in the general requirements of the apparatus indicated that the following conditions must be met:

The piston for the reaction cylinder must not only be leakless to pressure and vacuum, but it must also be loose-fitting so that it may operate at high speed, and without undue friction. Friction would not only require higher power for operation, but, worse, it might influence the reaction from the heat effect of this friction. A more rigid requirement, however, is that the parts of the piston must remain together, or the piston itself remain on the rod when its velocity is suddenly reduced from a high value to zero. This same requirement applies as well to the piston rod where, as a result of inertia, the rod would tend to elongate first of all, and then to rupture at its upper end. Another severe requirement is that the upper piston must stand the hammering impact against the stopping plates without distortion.

The above requirements have been satisfied with remarkable success, but only after much experimentation. The different types of pistons tested will now be given.

a) Flexible disc piston

The first piston tested in the reaction cylinder was designed after the method used by P. W. Bridgman[39] for high pressure experiments. Details of the piston appear in Fig. 10. The principle of this type of piston is that a flexible disc packing, with a central hole held between the upper portion of the piston and its floating end, is subjected to stress in proportion to the pressure against which the piston operates. Inasmuch as the area of the packing is less than the area of the piston by an amount equal to its central hole, the packing is under proportionally higher unit pressure than the lower end of the piston. Now, if the packing behaves at all like a fluid, i.e., if the pressure is the same in all directions, it may be expected that the pressure per unit area which it exerts against the cylinder wall must also be greater than the pressure



Flexible Gasket
Piston

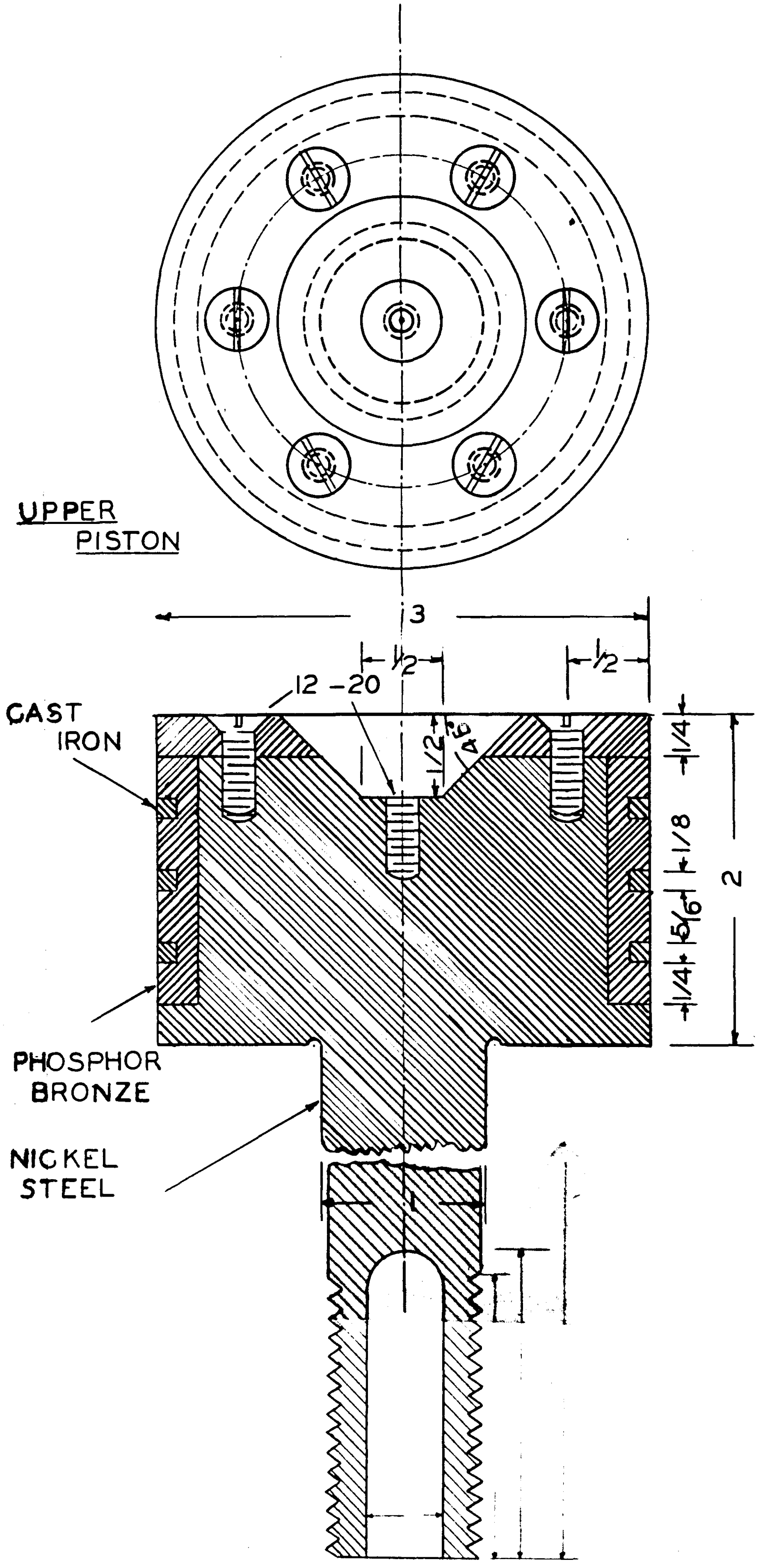
Fig. 10

in the cylinder. Therefore, a differential is maintained at all pressures, and theoretically, at least leakage cannot occur. Practically, however, these pistons had been used only on high-pressure, slow-speed work where friction is not a factor, and the packing can be made very tight initially. For high-speed work there was no precedent, but it was decided to use one of these because of the good results that had been obtained at the lower speeds.

Both parts of the piston (Fig. 10) were made from phosphor bronze. Several kinds of packings were tried in the course of the tests. These consisted of molded tread-stock rubber discs, 1/8-and 1/4-inch thick, or discs cut from different kinds of Garlock rubber, or rubber composition packing. The discs were lubricated with anhydrous lanoline, and as many as three were used at one time. The initial pressure on the packing was controlled by a compression spring as shown in the drawing. The method of testing will be indicated after the upper piston and the rod are described.

The combined upper piston and piston-rod are shown in <u>Fig. 11</u>. The rod is turned from 3 1/2% nickel steel; the piston carries a phosphor-bronze sleeve

Figure 11



Upper Piston and Piston Rod

to prevent scoring the cylinder and is packed with three cast-iron rings. In addition to these, it was necessary to use a leather cup washer (not shown in drawing) as the piston head to prevent excessive leak of air.

The method of testing the lower piston for leaks consisted merely of applying gas pressure to the reaction cylinder while the piston was held at different points throughout the height of the chamber. A failure of the piston to hold its pressure when the packing was highly compressed initially by the spring,was regarded as sufficient ground for the belief that this type of piston was not suited to this work. This decision does not mean that this type of piston cannot be used for work of this kind, but merely that with the comparatively poor condition of cylinder wall, and the maximum pressure that could be exerted with the strongest spring that could be used, the piston could not be made gas-tight even when as many as three discs in series were used.

b) Leather cup-washer piston

The second type of piston was designed to use two leather cup-washers. These washers could oppose the pressure in the cylinder only, or one could oppose the cylinder pressure and the other the pressure of the atmosphere, if excessive leakage occurred during and after evacuation of the reaction cylinder. These pistons are shown in Figs. 12 and 12-A. Again the body is made from phosphor bronze but the two parts are held together by a steel screw. Both these pistons fit the rod previously described.

The results obtained with these cup-washer pistons have been completely satisfactory as far as gas-tightness is concerned. Lubrication with a small amount of lanoline before each run is the only attention that is needed. Not only can the cylinder be evacuated readily, but an absolute pressure of a centimeter of mercury is easily held. The same is true for pressures above atmospheric. Four atmospheres is as high as the apparatus has as yet been used, but there is no difficulty in holding such a pressure indefinitely.

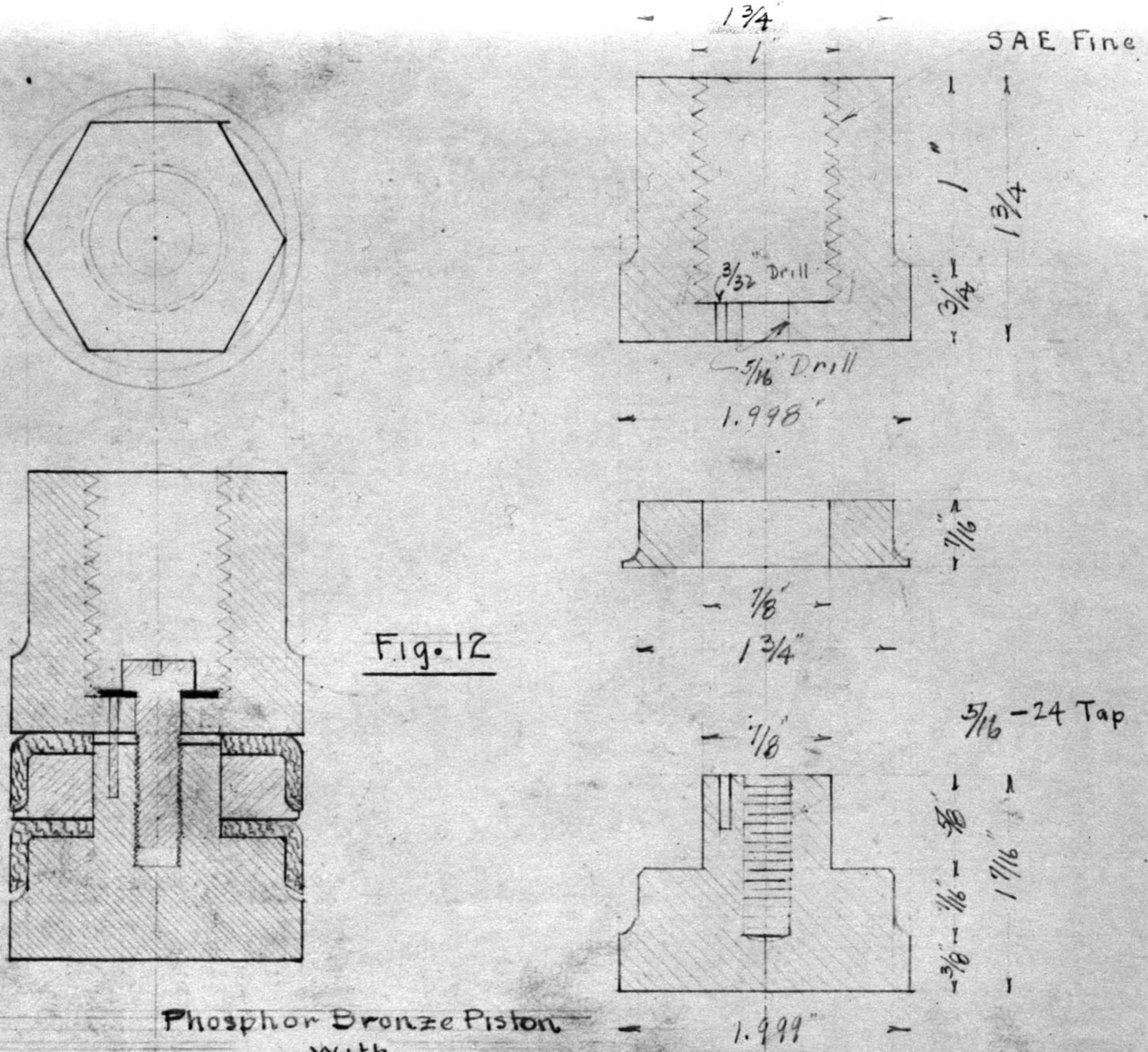


Fig. 12

Phosphor Bronze Piston
with
Leather Cup Washers

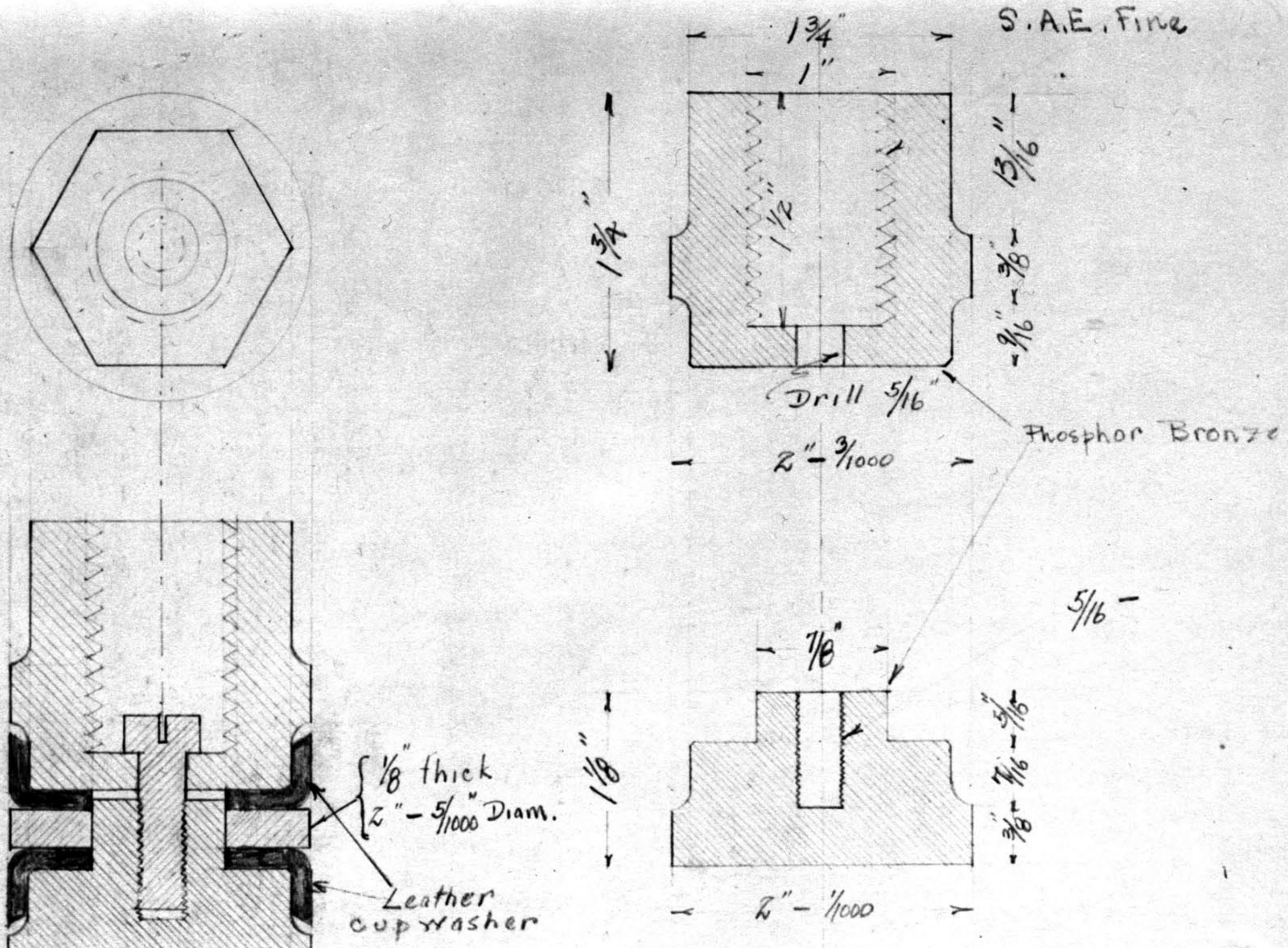


Fig. 12-A

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The results of static tests mentioned in the previous paragraph are valuable, but it is also desirable to test the piston for any leaks that might occur during rapid compression. Fig. 12-B is a portion of a record from a test run on air, (any non-reacting gas may be used). In addition to the base line for initial pressure, p_i, and the theoretical adiabatic upper line, p_f, a third line, p_e, is recorded. Line p_e corresponds to isothermal conditions, or the end pressure, after the gas has cooled from the temperature attained during compression to the temperature of the cylinder walls. Two minutes are allowed for cooling before the final pressure is recorded.

The initial pressure and initial and final volume of the gas are know. Therefore, the final pressure, p_e, may be calculated. Also, the load-deflection curve of the indicator is a straight line and we may write

$$p_f - p_i = \alpha (d_f - d_i)$$

where $(d_f - d_i)$ is the measured distance between the upper and lower lines and α is a proportionality constant.

Therefore,

$$p_e = \alpha (d_e - d_i) + p_i$$

The calculated and observed values of p_e are shown under Fig. 12 - B and are seen to check within 1/2%.

Experimental results soon demonstrated that not only must the piston be gas-tight, but, because the pistons and rod must be suddenly accelerated and more suddenly decelerated, they must possess minimum mass and maximum shock resistance. The significance of this requirement was impressed by two occurrences: the first, when the steel screw which holds the parts of the lower piston together was fractured by the high stress produced when the piston was suddenly stopped; the second, when, on substituting a larger screw which would not fracture, the screw pulled through the supporting shoulder in the upper portion of this piston, and this, despite the fact that a steel washer was distributing the load of the screw head.

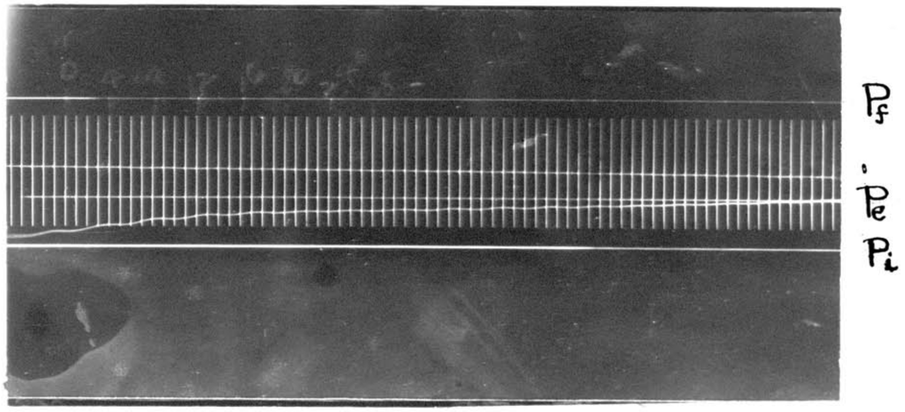


Fig. 12-B.

Test for Piston Leak.

Calculated Pe = 106.5 cm. Hg

Calculated Pe = 106 " "

These occurrences made it necessary to change radically the design of the piston and rod as shown in the next section.

c) Duralumin Piston and Rod

The high tensile strength of duralumin and its low density recommended it as a substitute for the steel and phosphor bronze used in the previous combinations. A comparison of these properties for the three metals will make this plain.

Physical Properties

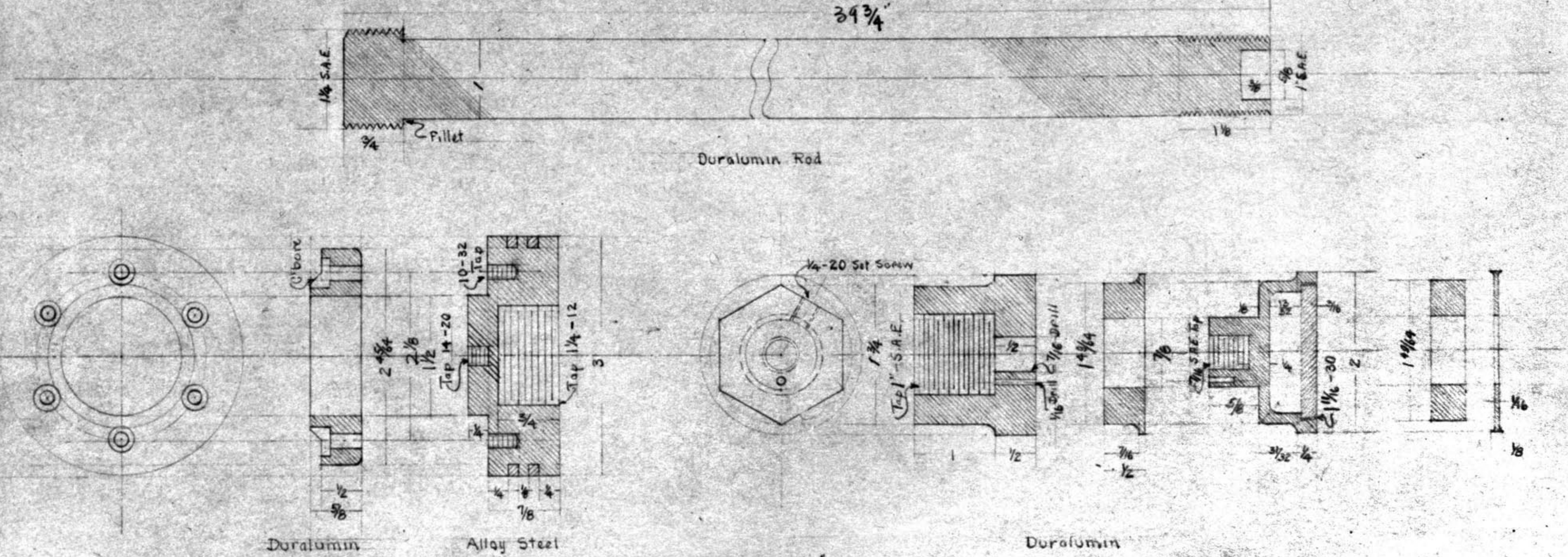
	(a)		(b)	
Metal	Tensile Strength		Sp. Gravity,	$\frac{(a)}{(b)}$
	(approximate values)			
3 1/2% Ni Steel	80,000	#/sq.in.	7.8	10.3×10^3
Phosphor Bronze	40,000	"	8.0	5×10^3
Duralumin	60,000	"	2.8	21.4×10^3

The table makes clear the advantage that duralumin offers for piston and piston rod construction where, as it has already been indicated, a maximum strength with minimum mass is required. The latest piston and rod design has, therefore, made use of as much duralumin as expedient. Unfortunately, it could not be used throughout because its relative softness made it unsuitable for the lower, or striking, portion of the upper piston. For this part, a hard nickel-chromium steel has been used. Also, the steel screw and washer for the lower piston have been retained. The complete design is shown in Fig. 13.

In designing these pistons the attempt was made also to reduce the dimensions of all parts to a minimum consistent with satisfactory operation. The result of this cutting down in dimensions and substitution of duralumin reduced the total weight to six pounds as compared with fifteen pounds in the previous case.

Other features of the latest design are: a) the second cup washer may operate for pressure or vacuum on the same piston. b) the piston rod is not integral with the upper piston and yet its design is such that it possesses the same strength as though it were integral; c) the shoulder which fractured in the phosphor-bronze piston is now twice as thick as before and the lower portion

Reduce to 8½ x 11 (Bind here)



Total Overall Length = 43½"

Fig. 13

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School of Fuel and Gas Engrg.
Details of Piston for Compression App.
December 25, 1929; V. G. Smith

of the piston is reduced to its minimum allowable mass; d) the upper piston is provided with a leather cup washer in addition to the piston rings.

The results obtained with this piston have been satisfactory in every way. The predicted decrease in force required to operate the piston, as well as the diminished shock effect for the same time of compression of the previous case, have been observed.

d) Piston Support

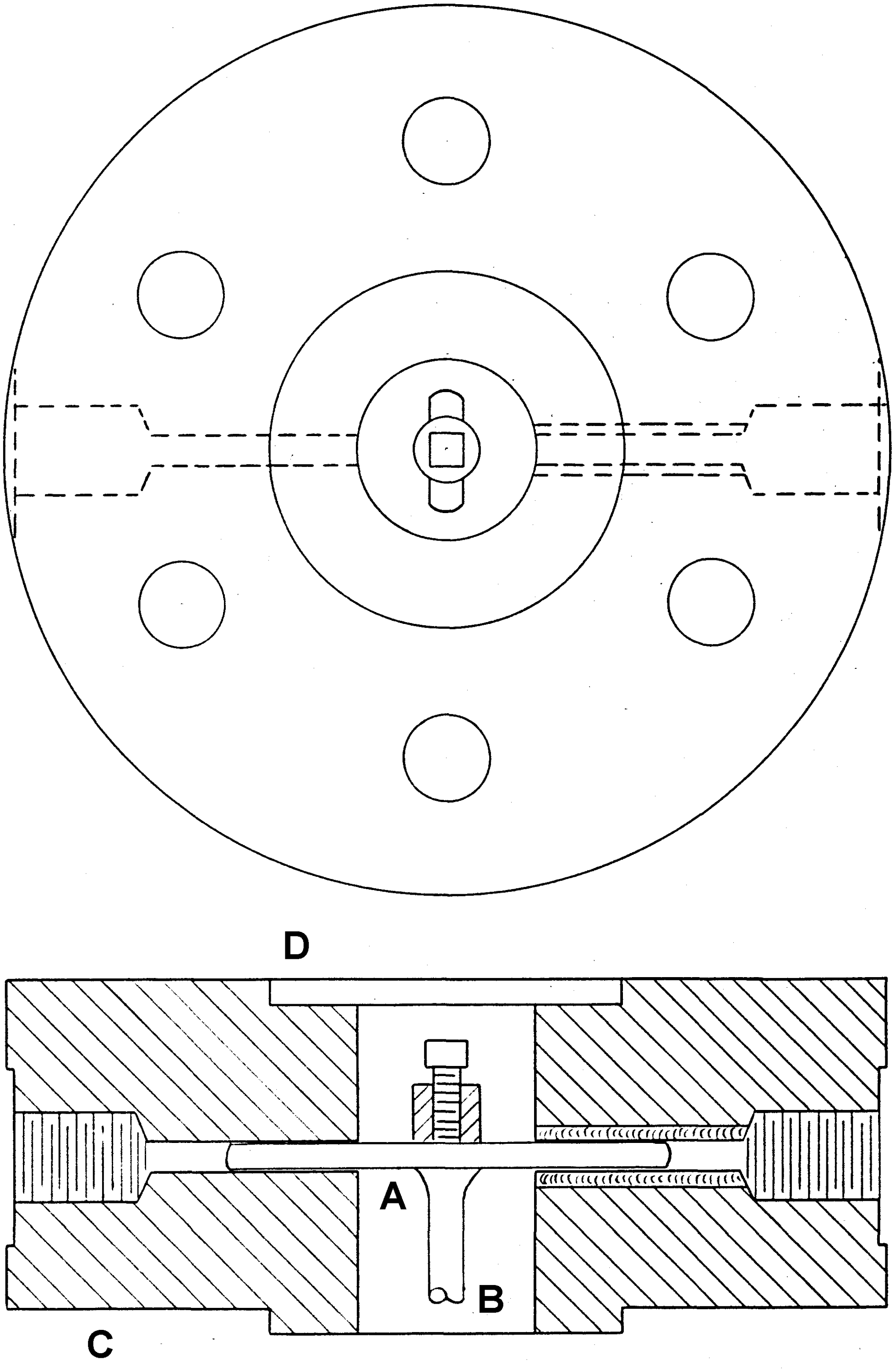
The initial position of the piston is so critical for final pressure and temperature that it must be well defined. The method by which this is done is described in this section.

The equations for adiabatic change in state have indicated that volumetric compression ratio determines the temperature and pressure ratio for the gases being compressed. This requires exact determination of both initial and final volume. Now, the free running pistons do not remain in a fixed position for pressure differences in excess of three-fourths of an atmosphere. Consequently the piston would move to the end of its stroke on evacuating the reaction cylinder if some method were not provided for supporting it. Equally as important as piston support, however, is the requirement that the piston be released from its support suddenly on application of compressed air at the beginning of an experiment.

The above requirements are met in the manner shown in Fig. 14, a drawing of a steel collar which fits between the cap of the upper cylinder and the air cylinder. A screw in the head of the piston terminates as the swivel for a turnbuckle, B, in the other end of which is a set screw. A 3/16-inch cast iron rod, A, supported on its ends by the steel collar, C, also passes through the loop of the turnbuckle. Tightening of the set screw pulls the piston hard against the upper collar; so that its initial position is always defined.

Cast iron has been chosen for the supporting rod because of its property of breaking without bending. There is every reason to believe that as soon as the thin diaphragm, D, bursts the cast iron

Figure 14



Stopping Collar

rod is snapped and the piston gets under way without false start. The following figures support this belief: a 3/16-inch cast iron rod supported as shown will carry a maximum central load of 60#; the minimum pressure applied when the diaphragm breaks is 75#/sq.in.; and, the area of the upper piston is 7.06 sq. in. The initial force is, therefore, more than eight times the breaking strength of the rod, and this neglects the indefinite initial load which is always placed on the rod by the set screw.

In addition to supporting the piston, the scheme shown in Fig. 14 permits accurate indication of the start of compression on the pressure-time record. This will be described in a later section.

3) The Compressing Force

One of the conditions necessary for adiabatic compression of the gas in the reaction cylinder is that the piston complete its stroke in the shortest possible time. The method of application, and the magnitude of the force required to effect this motion will now be discussed.

It has been stated already that the method used by Dixon and others to force the piston into the cylinder was unsatisfactory because of the inertia effect of the weight when the latter was suddenly stopped. More detailed consideration will indicate that there are other factors which rule out the drop-weight method for this work, where it has definitely been possible to reduce the time of compression to the order of magnitude of 0.05 second.

Let it be assumed that the gas is compressed by a weight falling on the piston head, and that the time of compression for a 2 1/2-foot stroke is 0.05 sec. A minimum value may be readily obtained for the height from which a weight must fall to effect compression in the required time, by assuming that the weight follows the law of a freely falling body, both before and after striking the piston.

For the conditions just stated, the weight would have to fall 37.5 feet before striking the piston.

Actually, the height would be greater than that calculated for free fall by the amount necessary to compensate for the resistance offered by the air as well as the piston and gas. It is seen, therefore, that for this reason alone a falling weight is not a practicable method for forcing the piston into the long cylinder that is being used.

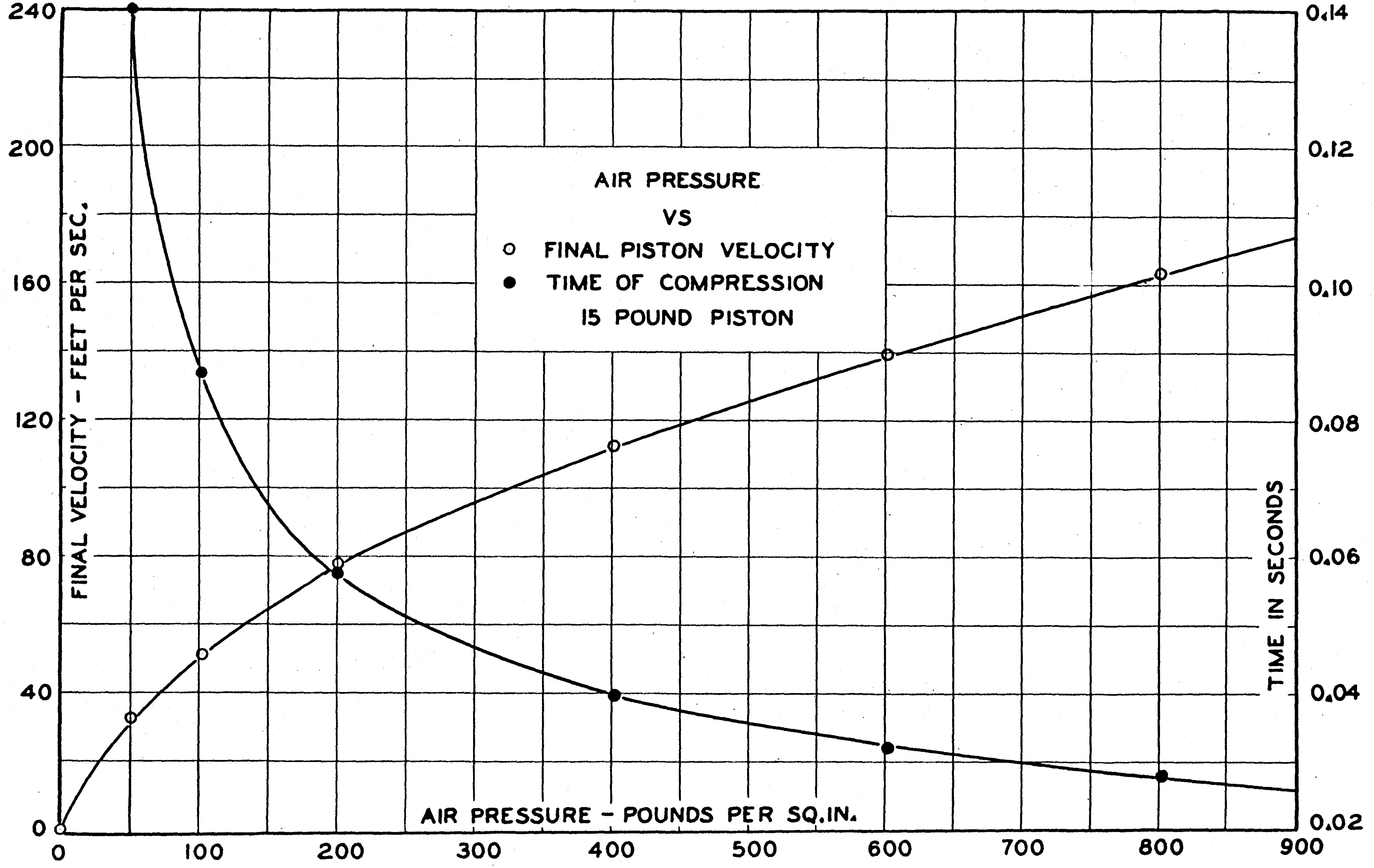
We turn now to a description of the method that has been perfected for this work. A compressed air bottle placed on top of the apparatus as shown in Fig. 8 is filled from a commercial cylinder to some pressure which may, or may not, burst the thin diaphragm that separates the air cylinder and upper cylinders. During the early stages of the work the pressure was actually increased until the diaphragm burst; in later experiments, the pressure was increased to the desired point and the diaphragm pierced by releasing a spring-operated, internal sleeve. In either case, the release of the air forces the piston down, and the rate at which it is forced down is determined entirely by the pressure-volume relations in the working and reaction cylinders, the mass of the pistons and rod, and piston friction.

The velocity of the piston at any part of its stroke, and the elapsed time from the beginning of its stroke, are readily calculated for any given conditions. The final piston velocity is especially important, as will be seen later; and, a knowledge of its variation, as well as variation of the total time for different combinations of the factors enumerated in the preceding paragraph is in many instances desirable. As an example, the time of compression, and the final piston velocity, for different air pressures have been calculated for the following conditions:

Weight of piston =15#
Ratio, V_f/V_i, air cylinder = 3.1 : 1
" V_i/V_f, reaction " =20 : 1
Final pressure, p_f = 1 atmosphere
Friction (constant) =50#

The results of the calculations are shown in Fig. 15. The observed time of compression agrees well

Figure 15


AIR PRESSURE
VS
○ FINAL PISTON VELOCITY
● TIME OF COMPRESSION
15 POUND PISTON
FINAL VELOCITY - FEET PER SEC.
TIME IN SECONDS
AIR PRESSURE - POUNDS PER SQ.IN.
240
200
160
120
80
40
0
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
100
200
300
400
500
600
700
800
900

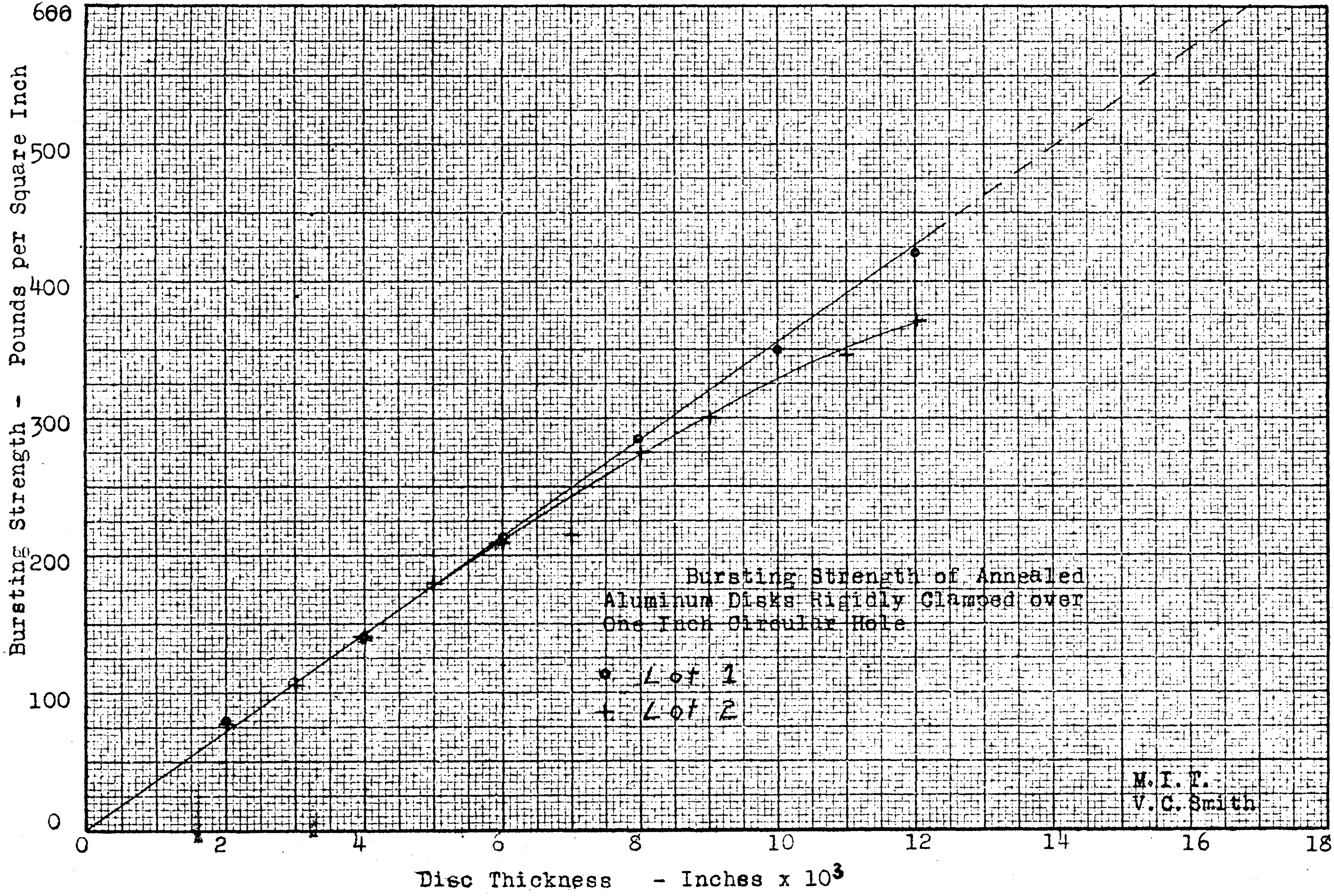
with the calculated time for conditions approximately the same. Further, the shape of the time curve agrees with the observed result of changing the air pressure. It is seen that in one range of pressures the time of compression changes very little with the pressure, while in the other range, small changes in pressure correspond to large changes in time of compression. This property also accounts for a difficulty that was experienced with aluminum discs--one thickness causing too slow compression and the next thickness causing too rapid compression.

a) Bursting Strength of Aluminum Discs

In many of the experiments that have been performed, accurate knowledge of the bursting strength of aluminum discs was necessary.

A method was developed, therefore, for testing these diaphragms under conditions similar to those in actual use. The results of the tests are shown in Fig. 16. They were made on dead soft sheet, (Aluminum Co. of America, 2 SO) cut into discs which were clamped rigidly at the edges over a one-inch circular hole, and loaded gradually with compressed air.

Figure 16



Bursting Strength - Pounds per Square Inch
600
500
400
300
200
100
0
0
2
4
6
8
10
12
14
16
18
Disc Thickness - Inches x 10³
Bursting Strength of Annealed Aluminum Disks Rigidly Clamped over One Inch Circular Hole
○ Lot 1
+ Lot 2
M.I.T.
V.C.Smith

For the thinner sheets it is seen that the relationship is linear and may be expressed by the following equation:

$$P_b \doteq 35000\ t$$

where P_b = bursting pressure - #/sq.in.

t = thickness - inches

b) Spring-Operated Air Release

Releasing the compressed air by loading a diaphragm to its bursting point was unsatisfactory. A better method is the one described here.

The method of applying the compressed air by slowly building up pressure in the air bottle until the diaphragm broke was not only time consuming and tedious, but the occurrence of the break with reference to the ends of the recording film was entirely a matter of chance; so that the record was, in most instances, made difficult to analyze by this circumstance. Moreover, as already mentioned, the difference in bursting strength between different thicknesses of discs was too great to give the desired changes in time of compression. Usually, if one diaphragm produced too rapid compression, the substitution of the next lower thickness would produce too slow compression. While the volume of the air cylinder could be changed to produce the desired rate, such a method is inconvenient. This effect was magnified, of course, when the weight of the piston was reduced from 15- to 6 pounds. Another difficulty which accompanied the reduction in weight, and made a change necessary, was the fact that the required diaphragm thickness was now reduced from 0.005 in. to 0.003 in., and the clamping of such thin diaphragms not only became difficult but their bursting strength became most erratic. Thus, the remarkable regularity in the bursting strength of these aluminum discs that had been observed, and relied upon, to give comparable results between similar experiments, was no longer observed. A more effective method was now not only desirable, but necessary.

The different types of solenoid, or lever, quick-acting valves were considered as substitutes for the thin diaphragms. However, all of them possess a possibility of leak into the space above the piston that might cause premature release of the latter; and are open to the further objection of slow opening. It was decided therefore, to retain the diaphragms and provide some method of piercing them. The manner in which this has been done is shown in Fig. 17 and may be briefly described: The flange between the air bottle and upper cylinder has been retained, but lengthened by a coupling and nipple. The steel sleeve, A, is held against a powerful screw, C, by the hardened steel pin, B; upon release of the lever, F, by the solenoid-operated trip-lever, G, the former is made to operate the pin by another heavy spring, E; after release, the sleeve strikes the diaphragm at D and pierces it. The sizes of parts are such as not to obstruct the air passage greatly.

This mechanism, though complicated in appearance, is simple and effective in operation. Its advantages may be pointed out briefly.

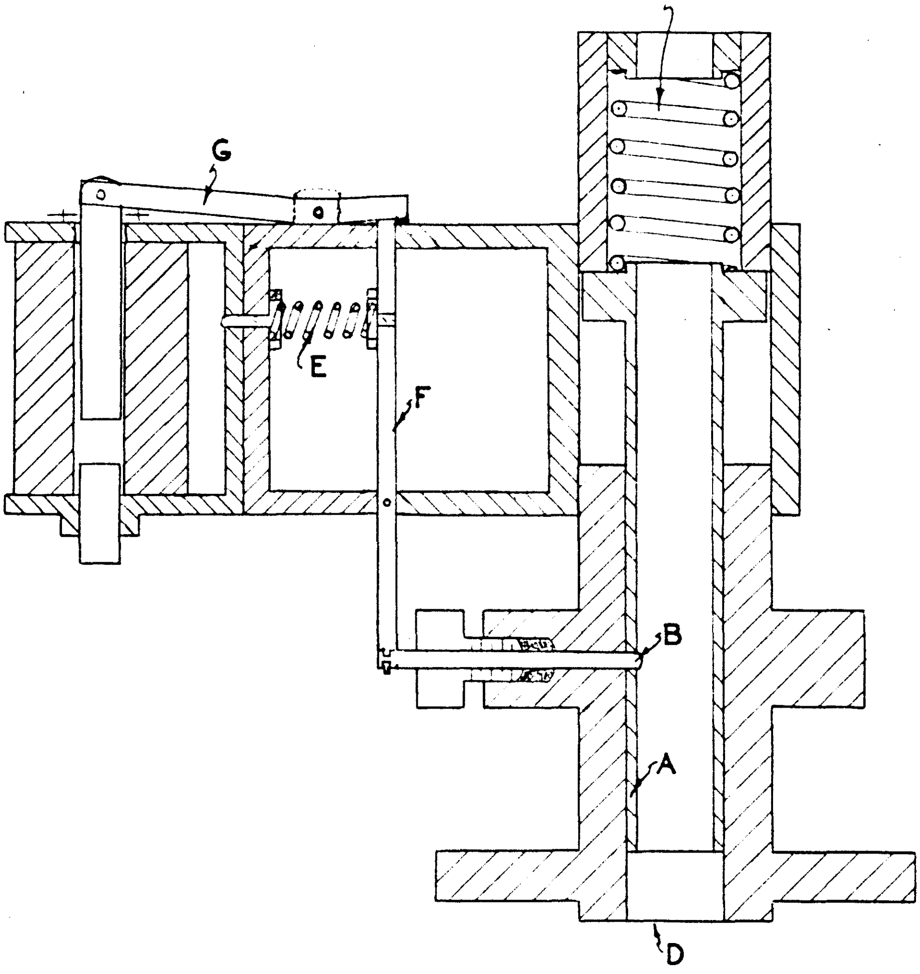
a) It greatly reduces the difficulty of operating the apparatus.

b) The compressing force may be regulated as closely as it is possible to measure with pressure gages.

c) The operation of the sleeve is instantaneous and positive.

d) It permits synchronization of the recording mechanism with piston motion so that the record may be

Figure 17



SPRING - OPERATED
AIR RELEASE

placed on any desired portion of the photographic film.

e) Finally, by using a solenoid to trip the main lever, the operation of the whole apparatus has now been reduced to the mere act of throwing a switch.

4) Indicators for Rapid Pressure Changes

The accurate measurement of the pressure or temperature changes in the reaction cylinder is one of the primary requirements of this work. Experience has indicated that it is impossible to follow the temperature changes, and we must therefore depend entirely upon pressure measurements.

A realization of the above fact has necessitated a rather exhaustive study of the theory of measurement of rapid changes in pressure and the methods by which this can be done. It was discovered that little information existed that pertained to the theory of indicator design. Some of this theory has been developed during this work and will be presented during the course of this discussion.

Almost all publications on indicators have appeared since the advent of the high-speed engine. Inasmuch as the requirements of indicators for research on these engines are much the same as those in explosion research, it follows that a good engine indicator may also be well adapted to this work. Among the publications pertaining to engine indicators those by Judge,[40] Schlink,[41] Morgan and Rubbra,[42] and Martin and Caris[43] have been found valuable.

In addition to the large number of indicators that have been developed for engines, there are some that have been developed during investigations on gaseous explosions. These, as well as those above, will be referred to later; for the moment, it is well to enumerate the requirements which are common to both.

a) Properties of a Good Indicator

There is general agreement on the characteristics of indicators as listed below.

1) Flush mounting--that part of the indicator to which pressure is applied should be mounted flush with the inner wall of the cylinder or combustion chamber. Narrow connecting tubes from the combustion chamber to the indicator element introduce errors in the pressure record.

2) High Natural Frequency--To give a true record, an indicator should have a natural frequence several times that of the phenomenon recorded. In general, thick pressure elements have high natural frequencies, but low sensitivity, so that in selecting a pressure element these opposing properties must be kept in mind.

3) Low Inertia--The pressure element and its attached members should be of small mass, and the inertia forces should be negligible in comparison with those resulting from the changes that are to be recorded.

4) Proper Damping--To prevent superposition upon the record of its own natural frequency, the indicator should be properly damped. This damping is best accomplished by fluid friction. Electrical, or eddy-current damping may also be used, but mechanical or rubbing friction should be avoided.

5) Minimum Friction--Indicators depending upon the action of a small piston usually give trouble from friction. Friction introduces hysteresis, and therefore makes faithful recording impossible.

6) Accuracy--The indicator must be readily calibrated and must retain this calibration over the period of use. A linear relation between load and deflection is desirable. Disturbing influences of temperature should be avoided.

b) Classification of Indicators

There are a large number of indicators in use at the present time, but it is found that they may be grouped into the following classes: 1) mechanical indicators; 2) electrical indicators; 3) optical indicators. Some of the typical indicators from each group will now be discussed.

1) Mechanical Indicators

All indicators in which the connecting linkage between the pressure element and the recording stylus or pencil is purely mechanical are called mechanical indicators. Most of them suffer from friction, lost motion, low natural period, and inertia.

Among the indicators in this class may be mentioned the micro-indicator of Mader[44] in which a stylus traces the record on a smoked glass. The Collins Micro-indicator is a second example; a modified form of this indicator was used by Tizard and Pye. Fig. 18 shows two views of this instrument. The pressure displaces a piston with an oil seal of which the movement is controlled by a stiff cantilever spring. The record is traced by a pointed stylus on polished celluloid wrapped round a uniformly rotating drum. The normal maximum deflection is 1-2 mm. Deflections can be read under a microscope to about 1/500 mm. The time record is given by a stylus attached to a tuning-fork. The natural frequency is 1300 cycles per second.

2) Electrical Indicators

Those indicators in which an electric current is employed in producing the record are called electrical indicators. They have the advantage that it is usually unnecessary to mount the recording apparatus near the explosion apparatus. This is a big advantage where the experiment is likely to produce some shock or vibration for in such cases these effects may appear on the record and make its interpretation difficult or impossible.

It is convenient to separate electrical indicators into the following classes: (a) piezo-electric; (b) resistance; (c) induced e.m.f.; (d) electron tube.

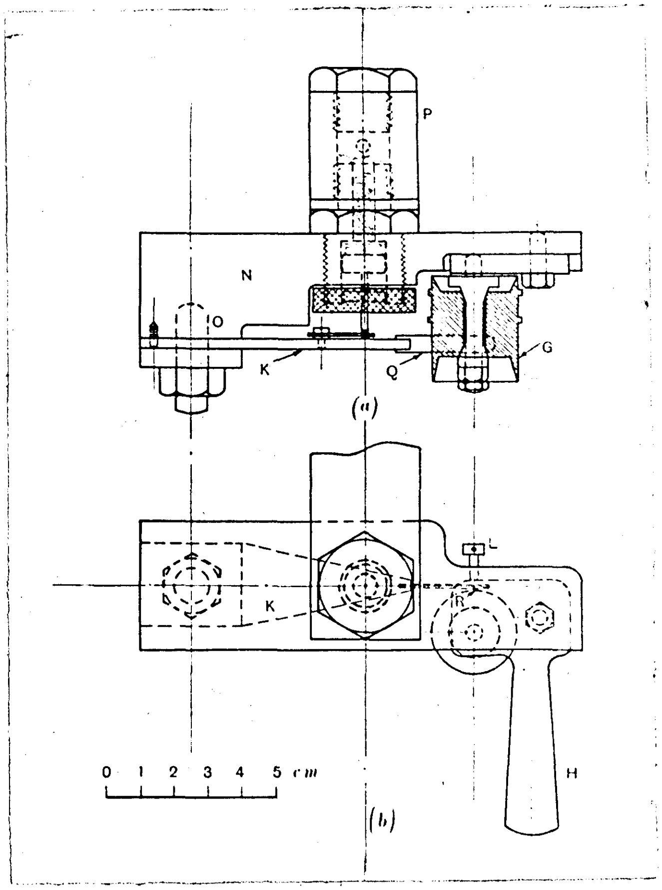


Fig. 18

Modified Collins Micro-indicator

Description:- The free end of the cantilever-spring carries a stylus which traces (not a scratch) a fine line on celluloid wrapped around a uniformly rotating drum. The parts are: N, body and spring seat; K, stiff cantilever spring; P, support with drilled hole connecting oil cavity to cylinder; Q, steel stylus support; R, stylus; G, drum for celluloid.

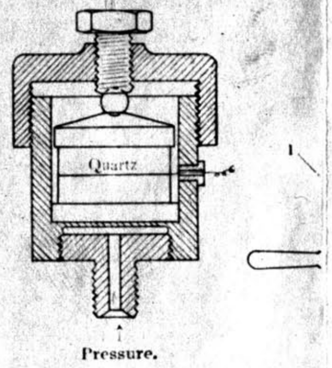
a) Piezo-electric Method

As is well known, the piezo-electric effect is an electro-elastic property of certain crystals. It involves conversion of mechanical into electrical energy, and also the converse effect. It is a property of those crystalline minerals which have a symmetric molecular arrangement: for example, quartz and tourmaline.

The use of the piezo-electric effect to determine diagrams of explosions and for recording pressure variation with time has been attempted by several investigators; among these may be mentioned J. J. Thompson[46], D. A. Keyes[47], and J. C. Karcher[48]. This method recommends itself for recording rapid pressure changes because of the absence of inertia effects. The recorded effect depends only in a secondary manner upon displacement and the displacements involved are solely due to the elastic yielding of the materials. This becomes even more affective if a cathode ray oscillagraph is used, as is customary, in the recording.

A quartz indicator for measuring pressures in internal combustion engines, as well as pressures in bomb explosions, has been developed recently by Watanabe.[49] In addition, a cathode-ray oscillograph has been developed for use with this instrument Fig. 19 shows a sketch of the indicator.

The principles of the quartz indicator may be described as follows: A thin plate of quartz with its faces plane and parallel, cut from a quartz crystal so that the plane of the plate is perpendicular to an electric axis of a crystal, when subjected to a compressional force in the direction of the electric axis and normal to the faces, will liberate a quantity of electricity at these faces the magnitude of which is proportional to the force applied. This proportionality has been found to remain linear over the tested range of 50,000 #/sq.in. The usual construction consists of a stack of these plates with their metal electrodes between adjacent plates to increase the charge due to greater plate area. The manner of construction is similar to that of a mica condenser with metal foil electrodes, except the quartz plates possess polarity and must be assembled so that the faces of the two plates in contact with the same electrode develop charges of the same sign when force is applied.



Piezo-electric pressure gauge.

Fig. 19

Piezo-Electric Pressure Indicator

Description: Two quartz plates with electrical axis in direction of force applied, faces of similar polarity separated by thin foil; these plates held between metal blocks; pressure from explosion transmitted by thin diaphragm; lead wires from foil and housing connect with deflecting plates of oscillograph.

Moreover, quartz, unlike tourmaline, yields no charge when exposed uniformly to hydrostatic pressure so that the plates must be in a gas-tight housing and pressure applied by a diaphragm or piston.

b) The Resistance Method

An indicator has been introduced recently by Martin and Caris[43] which makes its record from variation between the resistances of two carbon-piles. The resistances forming the branches of a Wheatstone bridge. As is seen in Fig. 20 the pressure element is a thin diaphragm flush with the inner walls of the housing. This is connected by an invar rod to a cantilever spring, the displacement of which reduces the resistance in the other. The record is made by an ordinary oscillograph or a cathode-ray oscillograph. The natural frequency is about 3000 cycles per second.

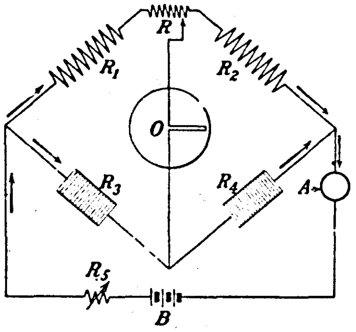
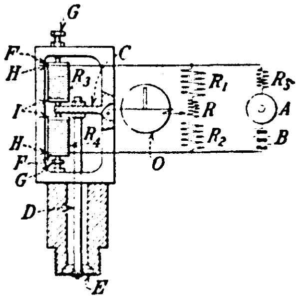


FIG. 3—DIAGRAM OF WHEATSTONE BRIDGE WITH CARBON STACKS

The Units Are: *A*, Ammeter; *B*, Storage Battery; *O*, Oscillograph; *R*, 40-Ohm Copper-Wound Balancing-Rheostat; R_1 and R_2, 40-Ohm Resistance; R_3 and R_4, Carbon Stacks; R_5, 40-Ohm Variable Rheostat



—INDICATOR AND CIRCUIT

C, Tongue Acting as Cantilever Spring; *D*, Invar Push-Rod; *E*, Diaphragm; *F*, End Pressure-Plates; *G*, Adjusting Screws; *H*, Copper Connection-Plates; *I*, Central Pressure-Plates. Other Letters Are the Same as for Corresponding Parts in Fig. 3

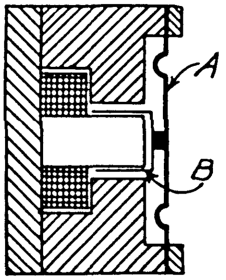
Fig. 20

Resistance Type of Electrical

Indicator with its Circuit

(b) Induced E.M.F. Method

A pressure measuring device introduced by Trowbridge[50] is shown in Fig. 21. It consists of an indicator body which is fastened to the cylinder, and which carries a thin steel diaphragm exposed on one side to the cylinder pressure and on the other to the atmosphere.



Pressure Measuring Device.

Fig. 21

Trowbridge Pressure Indicator

Description: A small coil of fine wire, B, wound on a form attached to the center of the diaphragm, and moving with the diaphragm, is so placed that it moves between the poles of an annular electromagnet. By connecting the terminals of the coil B to an oscillograph the e.m.f. induced in the coil by a motion of the diaphragm may be recorded on a moving photographic film. The oscillograph deflection is proportional to the velocity of the coil in the field; if the field is kept constant. This velocity is in turn proportional to the rate of change of pressure on the diaphragm. The record produced by this indicator is a curve of $dP/d\theta$ vs θ where P is pressure in cylinder at time θ. The pressure-time curve is therefore the integral curve of the recorded curve.

d) Electron Tube Method

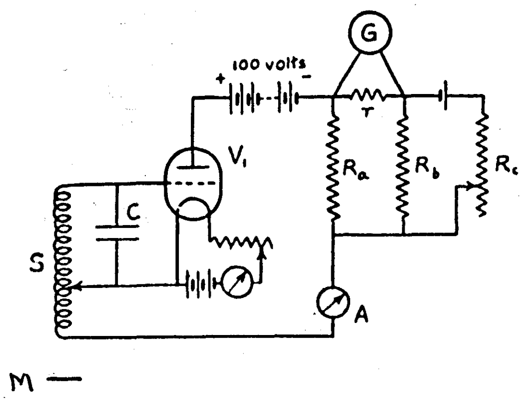
The use of electron tube circuits for pressure measurement has been given much study. Two methods may be used: a) capacity change; b) eddy-current change. In both cases an electrical oscillation, having a frequency of some 600 kilocycles per second, is started in a circuit containing a thermionic valve, and the displacement produced by the pressure is made to produce a corresponding change in the anode current of the valve. This change in the anode current is measured or recorded by means of a galvanometer or an oscillograph. The novel feature of these methods lies in their extreme sensitivity.

Papers have been published by Whiddington,[51] Dowling,[52] Thomas,[53] Obata,[54] and many others relating to the utilization of generating valve circuits for pressure measurements. The method devised by Whiddington utilizes the beat between two generating valve circuits and is the so-called "heterodyne" method. On the other hand, Dowling and Thomas work with only one generating circuit, and the pressure to be measured is made to produce a corresponding change in the anode current of the thermionic valve. In Dowling's method this change in anode current is caused by the change in a capacity in the circuit, while in the Thomas' method it is produced by a change in the eddy-current loss. Obata's circuit uses one generating valve, and it is so constructed that either the capacity or the eddy-current method may be used.

A more detailed description of Obata's method will be given in view of the fact that the first work on indicators, when this research was begun, was an attempt to use Obata's method. Consequently an indicator was constructed according to Obata's specifications. The results were not promising, however, and the method was dropped. A description of the method follows:

i) The capacity--change--method

In its usual form the instrument consists of a tuned grid circuit as shown in Fig. 22 (in this case M has no bearing with the circuit).



V_1: Tōkyō Electric Co. thermionic valve, "Cymotron" 201 A.
G: Einthoven string-galvanometer.

Fig. 22.

An electric oscillation is started in the circuit by changing the total number of turns of the oscillation coil S, as well as the number of turns of the part of the same coil contained in the grid circuit.

These adjustments are made by means of the sliding contacts (a) and (b). The circuit has a natural frequency calculable from the capacity of the condenser C and the inductance of the coil L by the formula $N = 1/(2\pi\sqrt{LC})$ where the capacity, C, and inductance, L, are expressed in farads and henries, respectively. When the circuit is operating a certain definite direct current is flowing in the plate circuit, on which will be superposed the alternating current of the oscillations whenever the tube starts into oscillation. This d.c. component of the plate current varies with the frequency of oscillation. In other words, if the coil, S, be of fixed inductance, then the d.c. plate current will alter with any change in the capacity of the condenser, C. If C is so constructed that a diaphragm connected to the pressure to be measured serves as one side of a plate condenser, any motion in the diaphragm due to pressure change, produced a change in capacity and thus alters the plate current. Inasmuch as it is the change in anode current, and not the anode current itself, that needs to be measured, the latter is balanced out by means of a potentiometer.

ii) The eddy-current method--A similar generating valve circuit is used. M represents a diaphragm in the explosion cylinder. A change in the distance between M and the oscillation coil S causes a change in the eddy-current loss and consequently a change in the anode current results.

For obtaining records by means of an oscillograph, it is necessary to add one or two stages of amplification.

The serious drawback, apart from the expensive equipment necessary, is the difficulty in maintaining the anode current constant for the required period of time. It was chiefly this factor that necessitated its abandonment in this work.

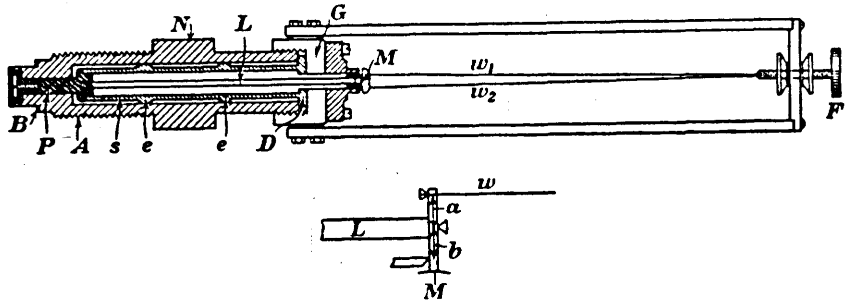
3) Optical Indicators

Optical indicators are by far the largest group used for pressure measurement. They are characterized by the use of a beam of light as the means of amplifying the motion of the pressure element, which may be either a small tight-fitting piston, or a diaphragm. Properly designed, an optical indicator can produce large amplification without great displacements of the pressure elements, thereby giving high natural frequencies.

These indicators require some kind of camera for obtaining a record of the pressure changes and usually some external method of superposing a time record. The important factor in taking records with these indicators is that there shall be no relative motion between the film or plate and explosion vessel due to shock or vibrations. This requirement is at times difficult to meet and it is here where optical indicators meet their greatest setback as pressure recording instruments. A more complete discussion of this is reserved for a later section.

The well-known engine indicators in this class are; a) Hopkinson;[55] b) Burstall;[56] c) Midgley;[57] d) Dalby-Watson.[58] The first three are the piston type while the last is a diaphragm type.

The optical indicators that have been used exclusively for explosion research have been chiefly the original, or some modification of the original, Petavel[59] indicator. The original indicator (Fig. 23) is suitable only for very high pressures, but its optical magnifying arrangement is found on all of the modified forms for lower pressure work. Modified forms have been used by Fenning,[60] Fig. 24, and Klusener,[61]



.—PETAVEL MANOMETER.

Fig. 23

Petavel Optical Indicator

Description: Spring, S, tubular, 5 inches long fits closely in N at e, e to prevent buckling. End D held rigidly by nut G, while other end is free and screwed into piston P. Compressions of spring transmitted by rod L to mirror M, shown diagrammatically in subsidiary sketch. Distances a and b about 1.6mm., but could be reduced to 1/4 mm. for extreme sensitiveness. Zero adjustment made through steel wires W_1, W_2 with screw F.

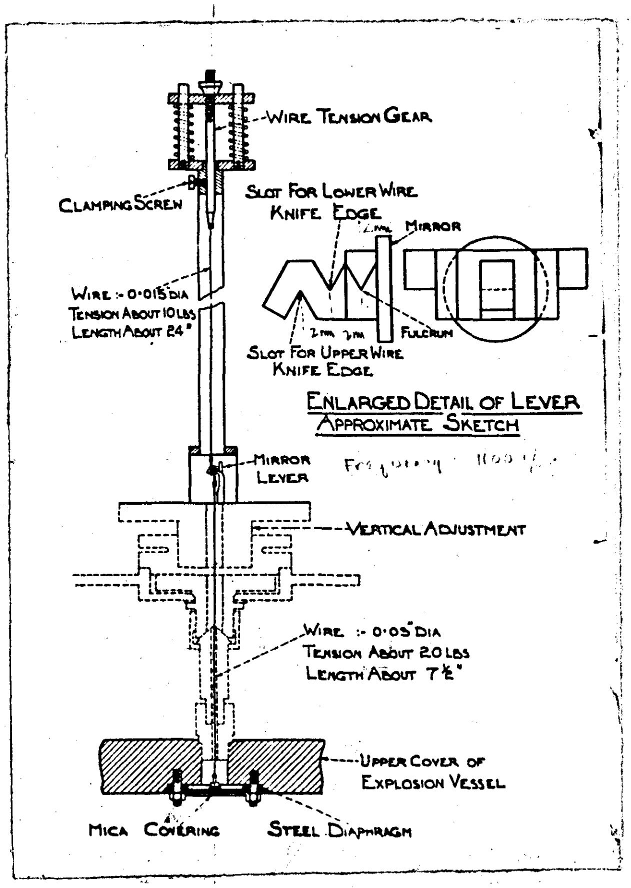


Fig. 24

Fenning Optical Indicator

Diaphragm turned from a solid steel plate is 0.07 in. thick and 1 1/2 in. diameter; a rim is left at edge for clamping and a boss at center for fastening tension wire.

Other satisfactory types of indicators have been developed by Ellis and Wheeler,[62] and Pier.[63] The latter uses a corrugated steel diaphragm as the pressure element; a pedestal located upon s ridge near the mid-radius serves as mirror support. Motion imparted to the diaphragm causes a rotation of the mirror and consequent deflection in a light beam focussed upon it.

With this review completed it is well to consider next some of the theoretical aspects of indicator design.

c) Contribution to Theory of Indicator Design

Despite the numerous papers on indicators, and the universal agreement on the requisite properties, little has been written from either the theoretical or the practical standpoint that is usable for design purposes. The indicators that have been perfected have resulted from repeated experimentation. Such a method is not to be derided necessarily, but repeated experimentation with indicators is tedious and time-consuming. The attempt has been made, therefore, to develop some of the theory of indicator design and to present this in such form that an indicator may be designed arbitrarily to satisfy the usual demands that are placed upon it.

The most important properties of an indicator are: a) frequency; b) sensitivity; c) damping. If an optical indicator is to be used, a further requirement is a properly designed optical system and a suitable apparatus for recording. These requirements will be discussed in order, and application made where data are available. In addition, there will be presented three optical indicators, together with the recording mechanism, that have been developed for pressure recording in this work.

1) Frequency of Vibration of Indicator Systems

If a body is held in position by supports in which it causes strains within the elastic limit, the elastic forces of the supports are just such as will produce equilibrium of the body. If the body receives linear or angular displacement, say, due to an impact or the sudden application of an additional force, the elastic forces of the constraints in the disturbed position will not generally be such as will produce equilibrium, and vibrations ensue. Such vibrations, maintained by the action of the elastic forces of the constraints alone, are called free or natural vibrations. The frequency depends upon the inertia of the system and the stiffness of the elastic constraints, and their amplitude upon the magnitude of the initial disturbance. If no subsequent disturbance occurs the vibrations continue until gradually damped by frictional resisting forces, which may be small, but are always present.

Generally an elastic system can perform vibrations in several modes and have what is known as several degrees of freedom. In the simplest case, however, the system is determined completely by one quantity and is therefore described as having one degree of freedom. The elastic forces will be proportional to the displacement, and the character of the motion will be simple harmonic.

a) System with one degree of freedom

dq = displacement of system measured in any coordinate system.

ds_1 = corresponding linear displacement of particle m , in system.

a = $\sum m \left(\frac{ds}{dq}\right)^2$

c = $\frac{\text{Total energy due to displacement dq}}{1/2(dq)^2}$

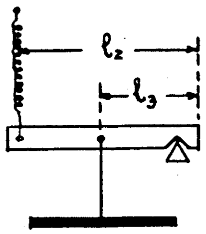
N = frequency of vibration $=\frac{1}{2\pi}\sqrt{\frac{c}{a}}$

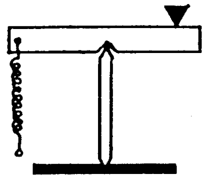
If a = mass of system, c equals force per unit linear displacement from equilibrium, equals stiffness of system.

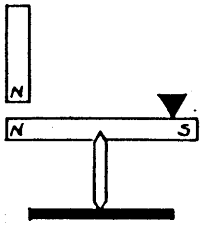
If a = moment of inertia of system about a fixed axis, c equals modulus of torsion about that axis i.e., torsional couple per unit angular displacement around axis, or stiffness times square of distance from fulcrum.

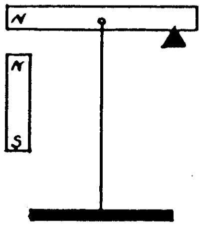
d) General Classification of diaphragm-spring combinations

Let there be a diaphragm linked at its center to a pivoted beam carrying a mirror, the beam being held rigidly by a spring or magnet operating in conjunction with the diaphragm. Apply to the beam a couple the same in sign as the couple exerted by the spring or magnet or whatever is used. There are three possible cases: (1) As the beam is moved under the action of the applied force, the couple exerted by the spring or magnet decreases. All spring combinations and some magnetic combinations fall in this class. Type combinations are:









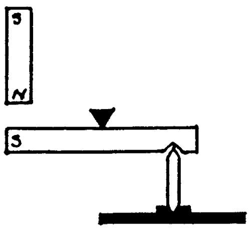
As will be shown later, the frequency is given by

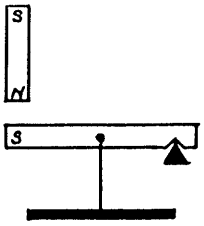
$$N = \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2 + K_s l_2^2}{I}} \qquad \text{for springs}$$

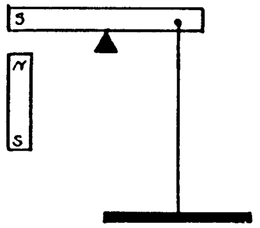
$$= \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2 + \frac{F_1}{f_1 + \alpha} \cdot l_2^2}{I}} \qquad \text{for magnetic combinations}$$

Kd and Ks are stiffness coefficients of diaphragm and spring, respectively, and I is the moment of inertia of the system about the fulcrum.

Case 2 . As the beam is moved under the action of the applied force, the couple exerted by the magnet increases. No spring combinations and some magnetic combinations come under this class. Type combinations are:







The frequency is given by $N = \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2 - \frac{F_1}{f_1 + \alpha} \cdot l_2^2}{I}}$.

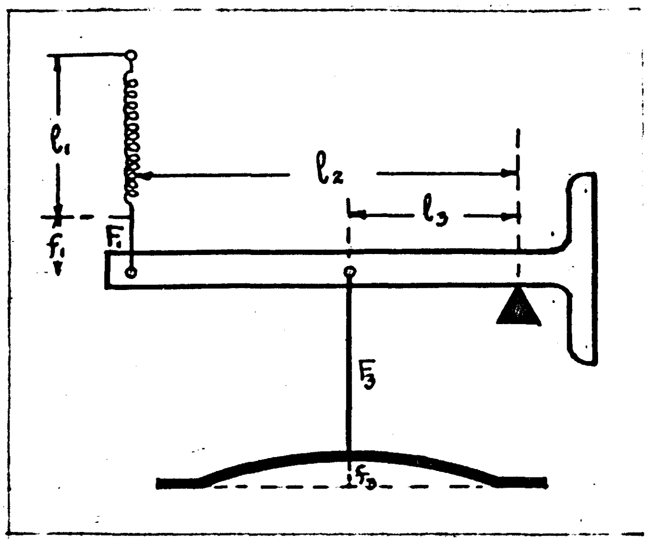
These combinations consequently act as though the magnetic portion had negative stiffness, i.e., a term is subtracted from that one involving diaphgram stiffness.

Case 3. The couple exerted by the magnet or spring does not change. This is a limiting case for weak springs or magnets or for the case of a weight hung on the beam. The effective stiffness of that part of the system is then 0, and the equation for frequency is:

$$N = \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2}{\Sigma I}}$$

It is obvious that Case 1 is the desirable one. It will be noticed that the frequency of a magnetic system under Case I is a function of the distance to the magnet, i.e., its natural period will be different for different values of disk deflection. It is improbable that a magnet could be made strong enough to compete with a spring for effective stiffness, altho it has the advantage of adding no term in the denominator of the expression giving N. All magnetic systems falling under this case involve repulsion. Consequently the beam must be a permanent magnet. A permanent magnet with like poles adjacent to like loses its magnetism quickly.

Case I for springs



Let K_s and K_d = stiffness coefficients of spring and diaphragm, respectively, out of the system, i.e., distorting force divided by corresponding distortion.

$$F_3 = K_d \cdot f_3$$
$$F_1 = K_s \cdot f_1$$
$$F_1 \cdot l_2 = F_3 l_3$$

Apply a downward force F at l_3. Call resulting displacement q. Let primed letters represent new conditions.

$$F_3' = K_d\,(f_3 - q) = F_3 - K_d q = F_1 \frac{l_2}{l_3} - K_d q$$

$$F_1' = \left(F_1 \frac{l_2}{l_3} - K_d q + F\right)\frac{l_3}{l_2} = \frac{l_3}{l_2}\,(F - K_d q) + K_s f_1$$

$$f_1' = \frac{l_3}{l_2}\left(\frac{F}{K_s} - \frac{K_d}{K_s} \cdot q\right) + f_1$$

$$\text{But } \frac{f_1' - f_1'}{q} = \frac{l_2}{l_3}$$

$$\therefore\ q = \frac{l_3}{l_2}\,(f_1' - f_1) = \left(\frac{l_3}{l_2}\right)^2 \frac{F - K_d q}{K_s}$$

$$\frac{F}{q} = \frac{K_d l_3^2 + K_s l_2^2}{l_3^2}$$

In the eq. $N = \frac{1}{2\pi}\sqrt{\frac{c}{a}}$, $c = \frac{F}{q} \cdot l_3^2$

$\therefore\ c = K_d l_3^2 + K_s l_2^2$

$a = I_m + M_s l_2^2 + M_d l_3^2$

$$N = \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2 + K_s l^2}{I_m + M_d l_3^2 + M_s l_2^2}}$$

In the above, M and M are effective masses of spring and diaphragm, to be taken as 1/3 and 2/3, respectively, unless a cantilever spring

$$N = \frac{1}{2\pi}\sqrt{\frac{K_s l_2^2 + K_d l_3^2}{I_m + M_s l_2^2 + M_d l_3^2}} \qquad (1)$$

From this we infer that the frequency is high for high values of "stiffness" of either spring or diaphragm, for low values of their masses and for a low value of the moment of inertia of the mirror system. The frequency is not affected by the tension placed on the spring before starting the vibration (providing the diaphragm has not been so much distended as to change its stiffness). The effects of l_2 and l_3 on N are not so readily determined, being dependent on relative magnitudes of the other factors involved.

The stiffnesses of the spring and diaphragm may be determined:

$$K_d = \frac{h^2 E}{.0275\, a^2}, \quad (2)$$

in which h equals semi-thickness
a " radius
E " modulus of elasticity (force units, not mass units)

this is for load applied at center

for a straight wire spring $K_s = \frac{E\pi d^2}{4l}$ (3) in which d = diameter of wire
l = length of wire

for a cantilever spring uniform rect. cross-section $K_s = \frac{Ebh_s^2}{4l_s^3}$ in which b = width
h_s = thickness of spring
l_s = length

(use 1/4 true mass as effective mass)

for a cantilever spring triangular in shape $K_s = \frac{Ebh_s^2}{6l_s^3}$ (Use 1/5 true mass as effective mass)

In substituting the above values for stiffness into the equation of frequency to determine what gives maximum N, it must be remembered that the further condition of high deflection per unit uniform load on the diaphragm is desired.

If straight wire spring is used we have, on substituting values for K and for M's in terms of dimensions and density, :

$$N = \frac{1}{2\pi}\sqrt{\frac{\frac{E\pi d^2}{4l_1} \cdot l_2^2 + \frac{Eh^3}{.0275\ a^2} \cdot l_3^2}{I_m + \frac{d^2 l_1}{12.}\rho\, l_2^2 + \frac{4}{3}\pi a^2 h \rho \cdot l_3^2}} \qquad (4)$$

$$D = \frac{.0214\ a^4}{h^3\ E} \qquad (5)$$

deflection per unit pressure applied to inside of disk, cm/(dyne /sq.cm.)

$$N = \frac{1}{2\pi}\sqrt{\frac{K_d l_3^2 + K_s l_2^2}{\sum I}}$$

R = range of desired pressure record, atm.

ϕ = deflection of bar carrying mirror, measured in radians per unit load on disk, or in degrees per atmosphere. (proper value of ϕ is determined by distance to photographic drum, and by R.) It is to be remembered that the light beam is turned through twice the angle of the mirror.

L = Necessary initial elongation of spring or wire to permit some residual tension at end of pressure rise.

F = initial load on wire from diaphragm.

D = initial distension of diaphragm

In deciding on a combination to use, N,R, D may be fixed at some desired values. L,F, S are fixed by the nature of the combination.

$$\phi = \frac{.0214\ a^4}{E\ h^3\ l_3}\text{, radians per dyne per sq. cm.} = \frac{1.242\ a^4 \mathrm{x} 10}{E\ h^3\ l_3}\ \text{deg. per atm.}$$

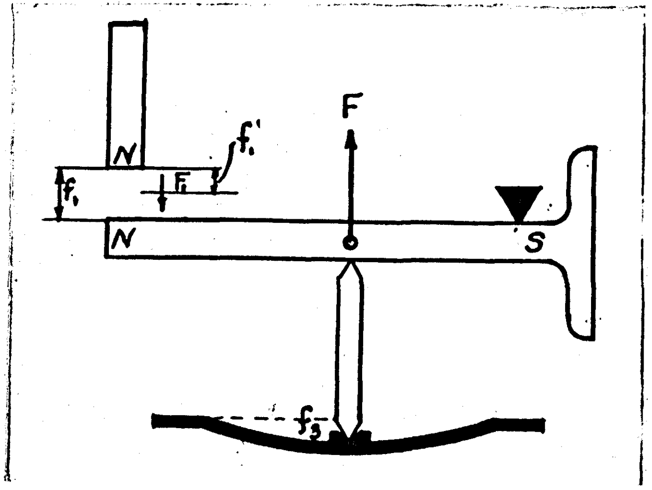
$$N = \frac{1}{2\pi}\sqrt{\frac{\dfrac{h^3 E\ l_3^2}{.0275a^2} + k_s l_2^2}{I + \frac{1}{3}\, M_s l_2^2 + \frac{4}{3}\pi a^2\ h \rho\, l_3^2}}$$

$$L = \alpha\,(R\phi l_2) \qquad \text{in which } \alpha \text{ is about } \tfrac{4}{3}$$

$$F = K_s R \phi l_2 \cdot \frac{l_2}{l_3}$$

$$D = \frac{F}{K_d} = \alpha \frac{K_s R \phi l_2^2\ .0275\ a^2}{l_3\ h^3 E}$$

ii) Case 1 for Magnets



Assume $F = \frac{k}{f+\alpha}$; $f = \frac{k}{F_1} - \alpha$

From other case (5)

$F_1' = \frac{l_2}{l_2}(F - K_d q) + F_1$; $f_1' = \frac{k}{\frac{l_2}{l_2}(F-K_d q) + F_1} - \alpha$

$\frac{f_1 - f_1'}{q} = \frac{l_2}{l_3}$; $q = \frac{l_2}{l_2}(f_1 - f_1')$ $q = \frac{l_3}{l_2}\left(f_1 + \alpha - \frac{k}{\frac{l_3}{l_2}(F - K_d q) + \frac{k}{f_1+\alpha}}\right)$

Call $\frac{l_3}{l_2}(f+\alpha) = \phi$ $q = \phi - \frac{k}{F - K_d q + k/\phi}$

$q = \frac{F\phi - K_d q\,\phi}{F - K_d q + k/\phi}$; $1 = \frac{(F/q - K_d)\phi}{F - K_d q + k/\phi}$

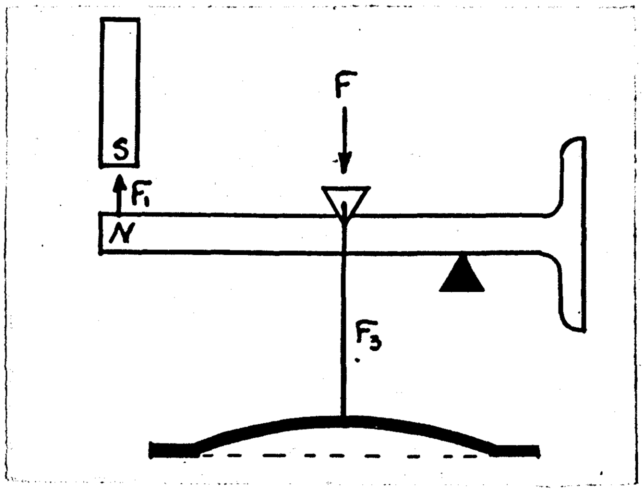
Let F and q = 0 $\frac{k}{\phi} = \frac{F}{q}\,\phi - K_d\phi$

$\frac{F}{q} = K_d + \frac{k}{\phi^2} = K_d + \frac{k l_2^2}{l_3^2(f_1+\alpha)^2}$ $C = \frac{F}{q}.l_3^2 = K_d l_3^2 + \frac{k}{(f_1+\alpha)^2}.l_2^2$

$= K_d l_3^2 + \frac{F_1}{f_1+\alpha}.l_2^2$

From which we conclude that this magnetic combination has an effective stiffness which adds to that of the disk in determining the numerator of N.

iii) Case 2



Assume $F_1 = \frac{k}{f_1 + \alpha}$. First 2 steps are same as in Case 1.

$$f_1' = \frac{k}{\frac{l_3}{l_2}(F - K_d q) + F_1} - \alpha$$ But 3rd step has sign changed

$$\frac{f_1' - f_1}{q} = \frac{l_2}{l_3} \; ; \qquad q = \frac{l_3}{l_2}\left(-(f + \alpha) + \frac{k}{\frac{l_3}{l_2}(F - Kdq) + \frac{k}{f + \alpha}}\right)$$

Following through from here as in Case 1, we obtain

$$\frac{F}{q} l_3^2 = C = K_d l_3^2 - \frac{k}{(f + \alpha)^2} \cdot l_2^2$$
$$= K_d l_3^2 - \frac{F}{f_1 + \alpha} \cdot l_2^2$$

From which we conclude that such a system has for the numerator of the term determining N, the difference rather than the sum of two terms, i.e., this magnetic combination acts as though it had "negative" stiffness.

2) Circular steel plate clamped rigidly at edge

$$\text{Frequency, } N = \frac{5.963}{2\pi} \left(\frac{E'}{\rho}\right)^{1/2} \cdot \frac{h}{a^2} \qquad (6)$$

where $E' = E/(1-\sigma^2)$ E = Young's modulus = 2.139×10^{12}

σ = Poisson's ratio = 0.310

h = semi-thickness - cm.

a = radius

ρ = density = 7.85

$\sqrt{E'/\rho} = 5.5 \times 10^5$

Deflection under load

$$f_u = 3/16 \, \frac{(m^2-1)pa^4}{Em^2 \, t^3}$$

$$f_u = o.17 \, \frac{a^4 p}{t^3 E} \quad (7)$$

f_u = deflection at center due to uniform load on disc clamped at edge

where $m = 1/\sigma$

a = radius

p = pressure per unit area

t = thickness

E = Modulus of elasticity

(8) $$S_{max} = \frac{0.75}{t^2} r^2 p$$

where S_{max} = Maximum radial stress - lb./sq.in.

r = radius - inches

t = thickness- "

p = pressure - lbs./sq.in.

3) Application of Indicator Frequency Analysis

The validity of the previous analysis as well as its usefulness will be demonstrated in two ways:

1) Calculation of the frequency of vibration of the Fenning indicator (Fig.24) which is classified under Case I for springs.

2) Calculation of frequencies of vibration for several arbitrary dimensions of diaphragms, etc. under Case I for springs.

ii) Calculation of Vibration Frequency for Arbitrary Dimensions

The great length of the tension wires in Fenning's indicator eliminated it immediately as a prospect for use in the apparatus designed for this work. Shorter dimensions may be chosen however, and calculations made as before.

Case I for Springs - Arbitrary Dimensions

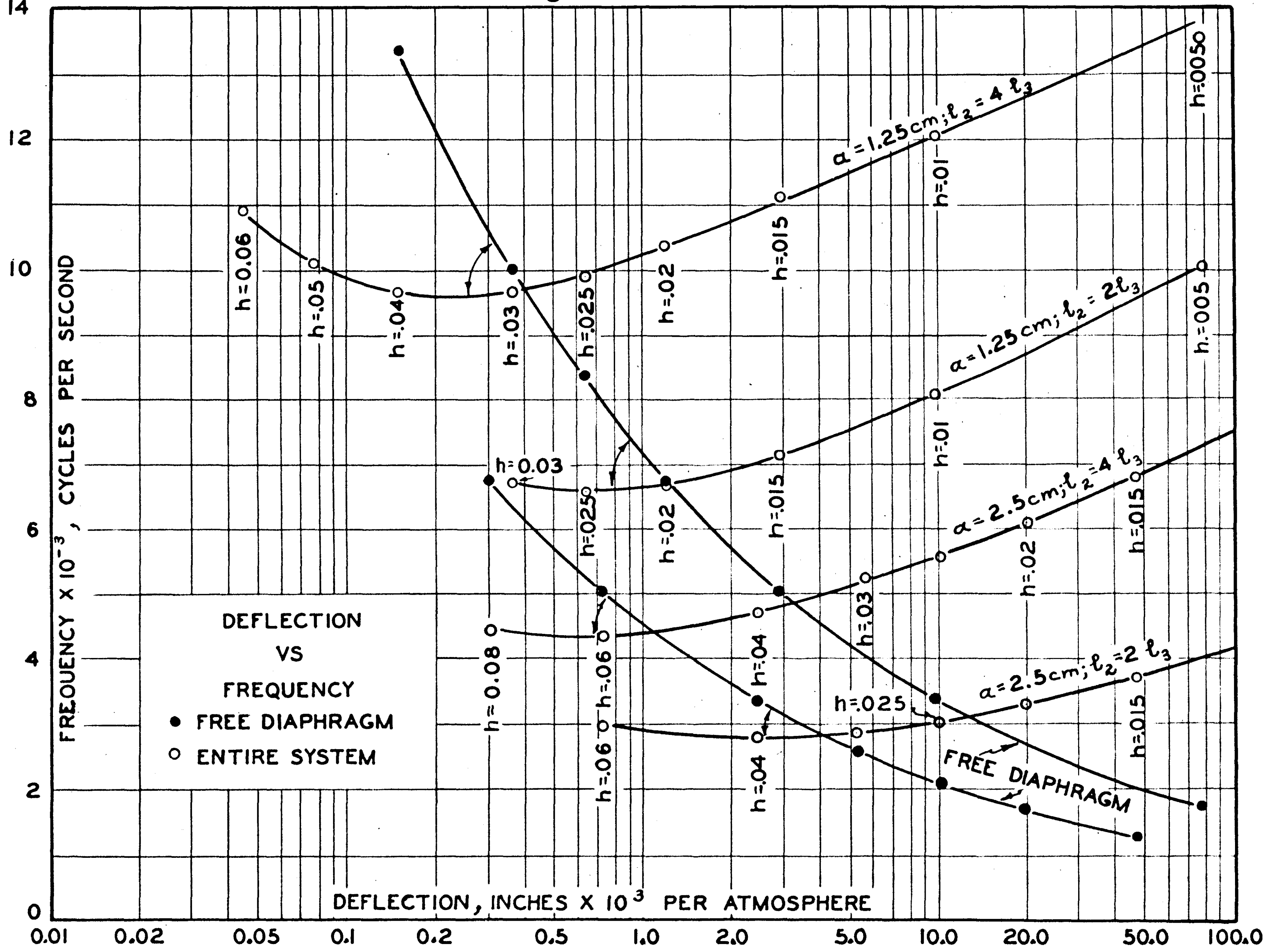
		Case A	Case B
Diameter of disc	=	5 cm	2.5 cm
l_2	=	0.020 cm	0.2 "
l_3	=	0.10 "	0.05 "
l_1	=	2.54 "	2.54 "

The results are presented in Fig. 25 where deflection per atmosphere is shown as a function of frequency for - a) system as a whole; b) free diaphragm. It is noteworthy that the frequency of the system passes thru a minimum as the diaphragm thickness increases. Prior to this the frequency of the system is controlled by the properties of the spring; beyond this point, the frequency is controlled by the diaphragm.

The location of this minimum may be determined readily by eliminating h from the equations for frequency and deflection, differentiating and equating the first derivative to zero in the usual manner.

The fact that a coupled system permits design of an indicator in which the pressure element enters but little

Figure 25


DEFLECTION
VS
FREQUENCY
● FREE DIAPHRAGM
○ ENTIRE SYSTEM
FREQUENCY X 10^{-3}, CYCLES PER SECOND
DEFLECTION, INCHES X 10^3 PER ATMOSPHERE
14
12
10
8
6
4
2
0
0.01
0.02
0.05
0.1
0.2
0.5
1.0
2.0
5.0
10.0
20.0
50.0
100.0
a = 1.25 cm; l_2 = 4 l_3
a = 1.25 cm; l_2 = 2 l_3
a = 2.5 cm; l_2 = 4 l_3
a = 2.5 cm; l_2 = 2 l_3
FREE DIAPHRAGM
h = 0.06
h=.05
h=.04
h=.03
h=.025
h=.02
h=.015
h=.01
h=.005
h= 0.03
h=.025
h=.02
h=.015
h=.01
h=.005
h= 0.08
h=.06
h=.04
h=.03
h=.02
h=.015
h=.06
h=.04
h=.025
h=.015

into the stiffness of the system is little appreciated by indicator designers. Much has been written about the effect of temperature on elastic properties of diaphragm metals, and while such effects may be serious with poor designs, it is usually possible to place the controlling stiffness where it is free from these temperature effects.

u) Calculations of Frequency of Vibration, N, for Fenning's Indicator.

Diaphragm radius = a = 1-1/2 x 2.54/2 = 1.905 cm.

" semi-thickness = h = .035 x 254

Modulus of elasticity = E = 2.139×10^{12}

Upper wire, .015" diam. x 24" long

Lower wire, .030" diam. x 7-1/2" long

$l_3 = 2$ mm.

$l_2 = 2 + 2 = 4$ mm.

$$K_d = \frac{h^3E}{.0275a^2} = \frac{(.035 \times 2.54)^3 \times 2.139 \times 10^{12})}{.0275 \times 1.905^2} = 1.504 \times 10^{10}$$

$$K_s = \frac{2.139 \times 10^2 \times 3.1416 \times (.015 \times 2.54)^4}{4 \times 24 \times 2.54} = 4.003 \times 10^7$$

$$I_m = .2 \times .2 \times .6 \times 8 \times .3^2 = .01729$$

$$M_s \text{ effective} = \frac{1}{3}\left(\frac{\pi(.015 \times 2.54)^2}{4} \times 24 \times 2.54 \times 8\right) = 0.186$$

$$M_2 \text{ effective} = \frac{2}{3}\left(\frac{\pi \times 3.81^2}{4} \times .07 \times 2.54 \times 8\right) = 10.81$$

$$N = \frac{1}{2\pi}\sqrt{\frac{4.0 \times 10^7 \times .4^2 + 1.50^4 \times 10 \times .2^2}{.0173 + .186 \times .4^2 + 10.81 \times .2^2}} = \frac{1}{2\pi}\sqrt{\frac{60.8 \times 10^7}{.4795}}$$

$$= \frac{1}{2\pi}\sqrt{12.68 \times 10^8} \quad ; \qquad N = \underline{5520}$$

$$N, \text{ disk alone}, = \frac{5,963}{6,283} \times 10^6 \times \sqrt{\frac{2.37}{8}} \times \frac{.035}{.75^2 \times 2.54} = \underline{12,620}$$

The value of 5520 does not take into effect the distortion of the lower wire connecting the diaphragm to the beam. Its effect is to reduce the effective stiffness coefficient of the diaphragm.

$$K_d = \frac{\text{distorting force}}{\text{corresponding distortion}}$$

corresponding distortion of diaphragm = $\frac{F}{1.504 \times 10^{10}}$

$$\text{distortion of wire} = \frac{F}{K_{wire}} = \frac{F}{2.139 \times \frac{10^{12} \times 3.1416 \times .03^2}{4 \times 7.5 \times 2.54} \times 254^2}$$

$$= \frac{F}{5.13 \times 10^8}$$

$$K_d = 1.504 \times 10^{10}$$

$$K_{wire} = 5.13 \times 10^8$$

$$\Sigma q = q_d + q_w = \frac{F}{K_d} + \frac{F}{K_w} = \frac{F(K_d + K_w)}{k_d \; k_w}$$

$$K_{Res.} = \frac{F}{\Sigma q} = \frac{K_1 \; K_2}{K_1 + K_2} = \frac{1.504 \times 10^{10} \times 5.13 \times 10^8}{1.555 \times 10^{10}} = 4.96 \times 10^8$$

This value is much lower than the stiffness of the diaphragm alone

$$\text{Then, } N = \frac{1}{2\pi}\sqrt{\frac{4.0 \times 10^7 \times .4^2 + 4.96 \times 10^8 \times .2^2}{.04795}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{26.24 \times 10^6}{.4795}}$$

$$= \frac{7.4}{2\pi} \times 10^3 \quad = \underline{1178}$$

The frequency 1178 is obviously very different from that obtained by considering the disk alone (12,620) or even considering the whole system, but forgetting the effect of the lower wire (5520). Experiments by Fenning with this indicator show a ripple superimposed on the explosion pressure-time record, the ripple having a frequency of between 1100 and 1150, which checks the present calculated value closely. Fenning's system, therefore, could have been made much better by using a shorter or thicker wire connecting the diaphragm to the beam. Due to the superimposed record of the diaphragm vibration on that of the desired pressure-time relation, the latter is of questionable value for exact analysis.

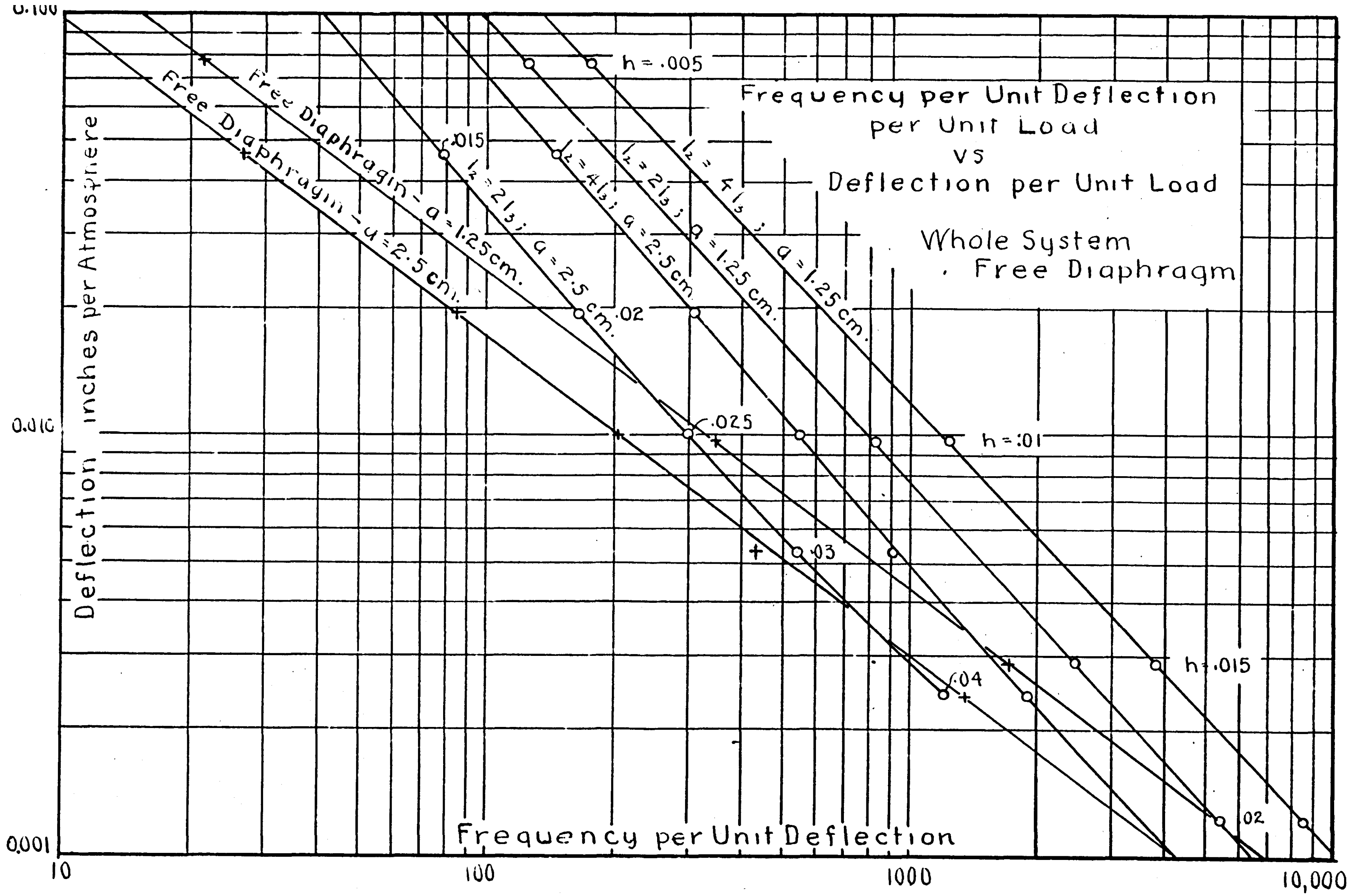
4) The Sensitivity of Indicator Systems.

Aside from having high frequency of vibration an indicator should be sensitive. The definition of sensitivity, and some data taken from the calculations of the arbitrary system in the preceding section are presented here.

The curves in Figure 25 showing frequency of vibration versus deflection per unit load for different thicknesses of diaphragms are not the true test of an indicator system. A better test would be the determination of frequency per unit deflection per unit load as a function of deflection per unit load. Thick diaphragms have high frequencies but cannot be used for determination of small variations in pressure. Thin diaphragms have high deflections per unit load but low frequency; the thinnest possible diaphragm for a given frequency requirement is usually the best choice.

The arbitrary system used in the previous section has been investigated further on the basis of its sensitivity. The results are presented in Figure 26. It is seen that frequency per unit deflection increases rapidly as diaphragms increase in

Figure 25


Frequency per Unit Deflection
per Unit Load
vs
Deflection per Unit Load
Whole System
Free Diaphragm
Deflection inches per Atmosphere
Frequency per Unit Deflection
0.100
0.010
0.001
10
100
1000
10,000
h = .005
.015
.02
.025
.03
.04
h = .01
h = .015
.02
Free Diaphragm - a = 1.25cm.
Free Diaphragm - a = 2.5 cm.
$l_2 = 2l_3$; a = 2.5 cm.
$l_2 = 4l_3$; a = 2.5cm.
$l_2 = 2l_3$; a = 1.25 cm.
$l_2 = 4l_3$; a = 1.25 cm.

thickness. This rapid increase is due not so much to increase in frequency with thickness but to rapid increase in stiffness (decreasing deflection) with increasing thickness.

5) Maximum Allowable Deflection for Diaphragms

Figure 25 is incomplete in as much as no indication is given on the limiting deflection that a diaphragm may undergo without permanent deformation. This value is readily determined by eliminating from equations 7 and 8 to obtain

$$f_e = 0.226\, S_e \frac{a^2}{Et} \qquad (9)$$

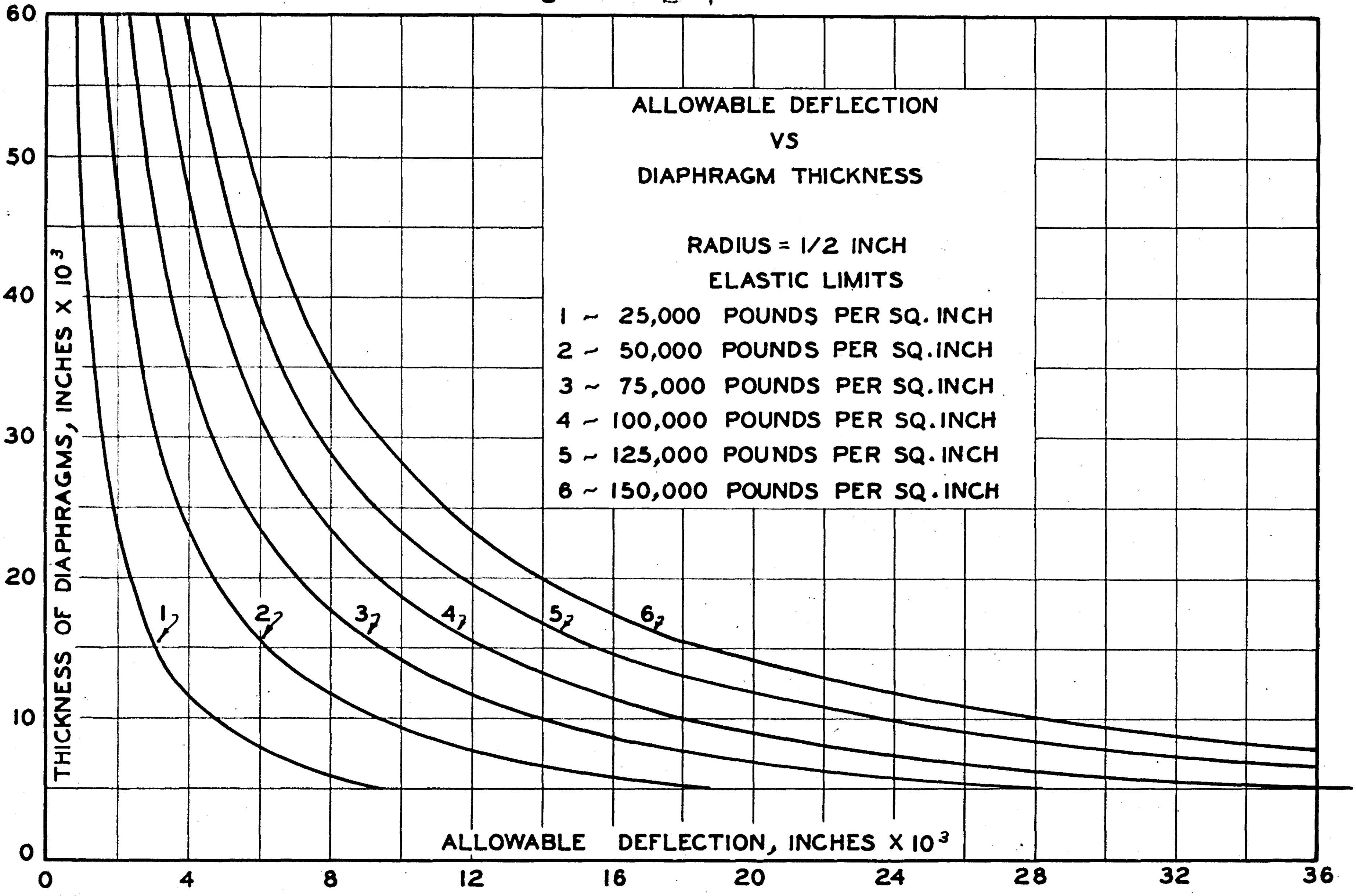
Where Se is the allowable elastic stress

f_e is the allowable deflection

Allowable deflections have been calculated with(9)for diaphragms of one-and two-inch diameters, for varying thicknesses and elastic limits. The modulus of elasticity is taken as 30×10^6 #/sq.in . These data are presented in Figure 27 and Figure 28.

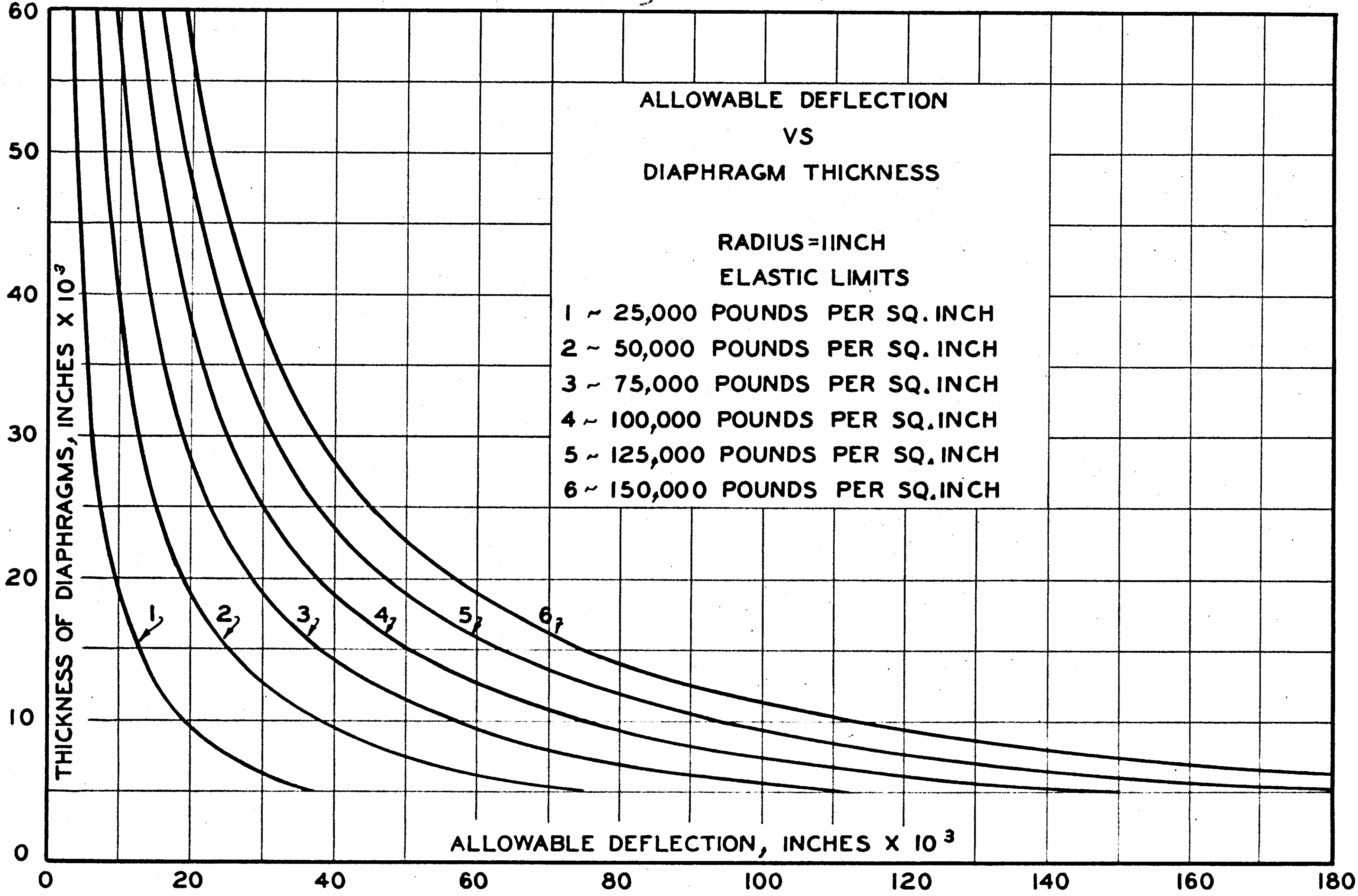
A curve may be divided into two parts. In one, the allowable deflection is almost independent of

Figure 27



ALLOWABLE DEFLECTION
VS
DIAPHRAGM THICKNESS
RADIUS = 1/2 INCH
ELASTIC LIMITS
1 ~ 25,000 POUNDS PER SQ. INCH
2 ~ 50,000 POUNDS PER SQ. INCH
3 ~ 75,000 POUNDS PER SQ. INCH
4 ~ 100,000 POUNDS PER SQ. INCH
5 ~ 125,000 POUNDS PER SQ. INCH
6 ~ 150,000 POUNDS PER SQ. INCH
THICKNESS OF DIAPHRAGMS, INCHES X 10³
ALLOWABLE DEFLECTION, INCHES X 10³
0
10
20
30
40
50
60
0
4
8
12
16
20
24
28
32
36
1
2
3
4
5
6

Fig 28



ALLOWABLE DEFLECTION
VS
DIAPHRAGM THICKNESS
RADIUS=1INCH
ELASTIC LIMITS
1 ~ 25,000 POUNDS PER SQ. INCH
2 ~ 50,000 POUNDS PER SQ. INCH
3 ~ 75,000 POUNDS PER SQ. INCH
4 ~ 100,000 POUNDS PER SQ. INCH
5 ~ 125,000 POUNDS PER SQ. INCH
6 ~ 150,000 POUNDS PER SQ. INCH
THICKNESS OF DIAPHRAGMS, INCHES X 10³
ALLOWABLE DEFLECTION, INCHES X 10³
1
2
3
4
5
6
0
10
20
30
40
50
60
0
20
40
60
80
100
120
140
160
180

thickness; in the other, slight changes in thickness correspond to large changes in allowable deflection. Almost all pressure indicators lie in the former range. The proportional advantage of high elastic limit is also apparent in the plots..

6) Maximum Allowable Elongation for Wire

In addition to the allowable deflection of diaphragms, the allowable deflection of the spring wire must be considered. Indeed, the allowable deflection of the wire may be the controlling factor in a system where short lengths of these must be used.

It is seen from (3) that

$$\frac{P}{e} = K_s = \frac{E\pi d^2}{4l} = \frac{E\,A}{l}$$

Where e is strain

P is force

Therefore,

$$\frac{e}{l} = P_e/E\,A = S_e/E$$

Where Pe = allowable elastic stress.

e/l = allowable elastic strain per unit length

Values of $^{e}/_{1}$ vs Se have been calculated, assuming $E = 30 \times 10^6$ #/sq. in., and are presented in Figure 29. It is seen that these values are quite small, and explain why it is necessary to use long tension wires on indicators like the Petavel.

7) Maximum Allowable Load for Plane Diaphragms

In addition to allowable deflection, it is necessary to know the allowable load for diaphragms. This is readily calculated from 8 where it is seen that

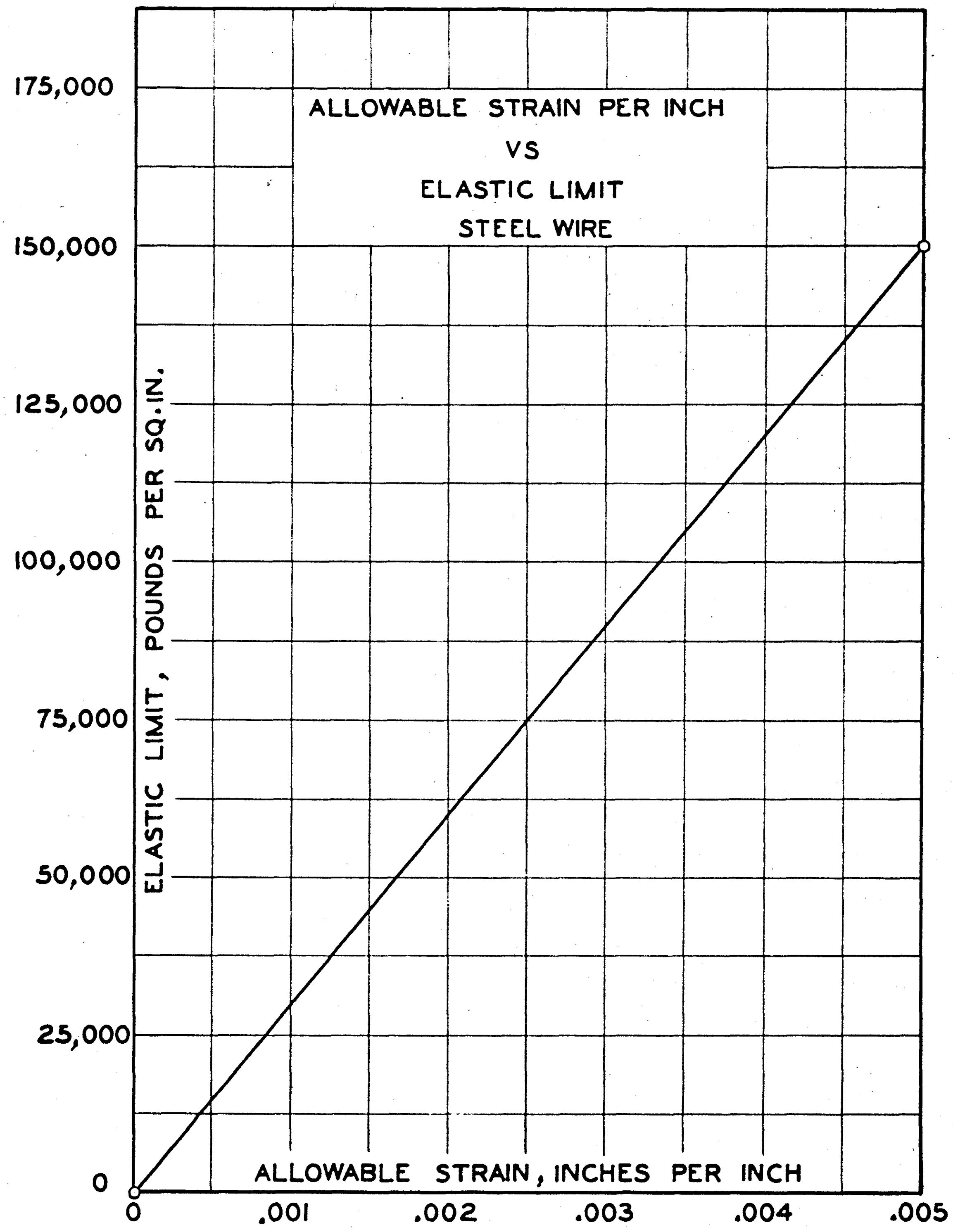
$$P_m = \frac{4}{3} \frac{t^2}{r^2} S_e$$

Where $P_m =$ allowable pressure - #/sq. in.

$S_e =$ stress at elastic limit - #/sq. in.

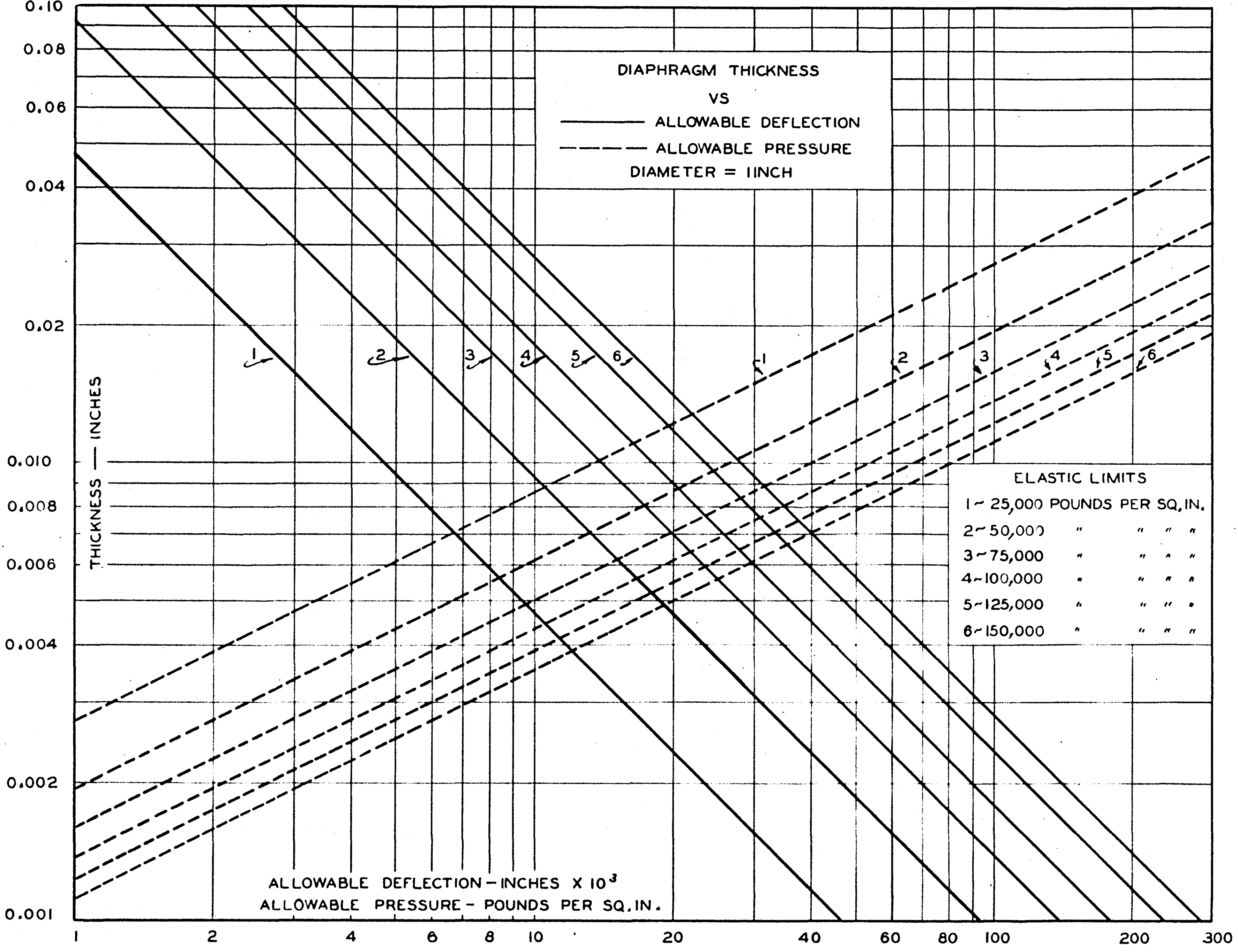
With this equation the maximum pressures for 1-inch diaphragms of different thickness and elastic limits have been calculated. Inasmuch as the equation is parabolic, it is more convenient perhaps to plot the data on log paper. This has been done in Figure 30, where, in addition to allowable pressure, the data for allowable deflection from Figure 27 are also shown.

Figure 29



ALLOWABLE STRAIN PER INCH
VS
ELASTIC LIMIT
STEEL WIRE
175,000
150,000
125,000
100,000
75,000
50,000
25,000
0
ELASTIC LIMIT, POUNDS PER SQ.IN.
ALLOWABLE STRAIN, INCHES PER INCH
0
.001
.002
.003
.004
.005

Figure 30


DIAPHRAGM THICKNESS
VS
ALLOWABLE DEFLECTION
ALLOWABLE PRESSURE
DIAMETER = 1 INCH
ELASTIC LIMITS
1 ~ 25,000 POUNDS PER SQ. IN.
2 ~ 50,000 " " " "
3 ~ 75,000 " " " "
4 ~ 100,000 " " " "
5 ~ 125,000 " " " "
6 ~ 150,000 " " " "
THICKNESS — INCHES
0.10
0.08
0.06
0.04
0.02
0.010
0.008
0.006
0.004
0.002
0.001
ALLOWABLE DEFLECTION – INCHES X 10^3
ALLOWABLE PRESSURE – POUNDS PER SQ. IN.
1
2
4
6
8
10
20
40
60
80
100
200
300
1
2
3
4
5
6
1
2
3
4
5
6

8) Load-deflection Properties of Corrugated Diaphragms

Corrugated diaphragms are common pressure elements for indicators. In the course of this work it has been necessary to use some of these, but only after determining their properties. The results of this investigation are given below.

The theory of corrugated diaphragms has not been developed and it is not possible to calculate, as in the case of plane diaphragms, the stiffness, maximum allowable load, etc. No data were available that could be used, and it is unwise to attempt to use data from one set of these diaphragms to determine properties of another unless both sets are geometrically similar in surface contour. The properties of these diaphragms can be determined only by experimentation. However, with sufficient experimental data it may be possible to establish the general relations by the method of dimensional analysis, in which case the same variables that have been used in the theoretical treatment of plane diaphragms would be assumed to hold for a corrugated diaphragm.[64] Insufficient data have been

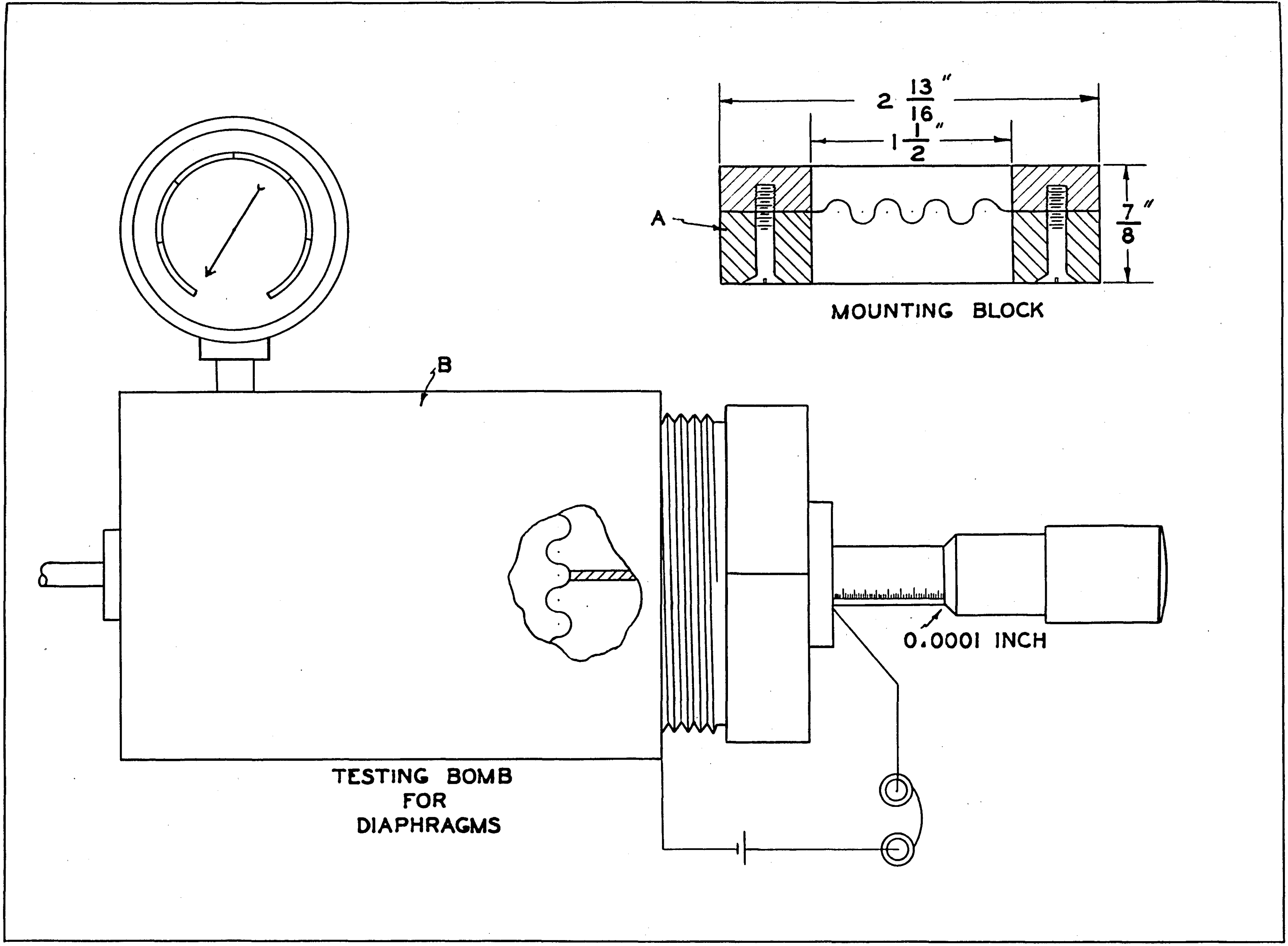

2 13/16"
1 1/2"
7/8"
A
MOUNTING BLOCK
B
0.0001 INCH
TESTING BOMB
FOR
DIAPHRAGMS

Figure 31

collected in this work for the establishment of such relations. However, a simple method has been developed, and this method with the data obtained will now be given.

i) Experimental Method

Diaphragms to be tested are mounted between suitable clamping surfaces as shown at A, Figure 31. The block is then clamped securely in bomb - B by means of a heavy hollow screw. A micrometer head, fastened to the center of the screw, carries a projection rod which contacts with the center of the diaphragm. Ear phones are arranged so that contact between rod and diaphragm produces a click. Diaphragms are loaded by means of compressed air and deflections corresponding to these loads are determined with the micrometer.

ii) Results

By means of the method just described, the following results have been obtained for a set of corrugated diaphragms.

The following data apply to the diaphragms:

Metal - French Finish Swedish Spring Steel (sheet).

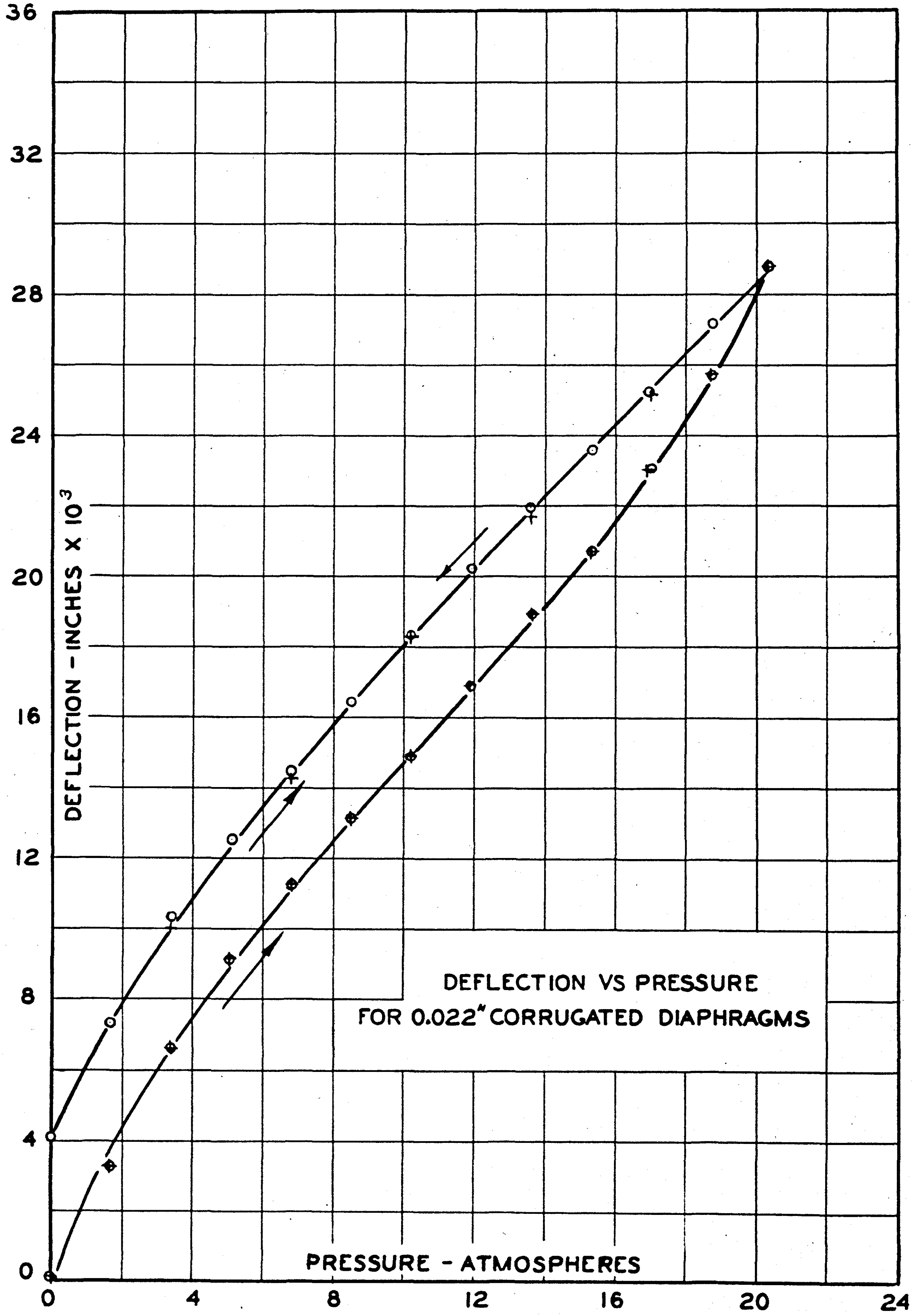
Method of Corrugating - Metal was spun in a lathe on a wooden die for the thinner - and a steel die for the thicker sections. The die face contained eight equi-spaced circular depressions and seven ridges on its 1 1/2-inch face.

Heat Treatment - After the spinning process the diaphragms were blued at 600° F. Such treatment usually increases the elastic limit as much as 100% after a metal has been severely cold-worked.

The experimental results are presented in a series of plots. Figure 32 shows a typical load-deflection curve for these diaphragms. If the initial loading does not exceed the elastic limit, the curve returns along the same path that it followed during loading; when the elastic limit is exceeded in the loading a deformation results, the return path is different, and corresponds, as would be expected, to a higher stiffness factor than before. Again, in loading and unloading the diaphragm the load-deflection curve is the same provided the initial maximum is not exceeded. This maximum is now the elastic limit for the diaphragm.

The shapes of these typical curves do not agree with the frequently made assertion that

Figure 32



DEFLECTION VS PRESSURE
FOR 0.022" CORRUGATED DIAPHRAGMS
DEFLECTION - INCHES X 10^3
PRESSURE - ATMOSPHERES
36
32
28
24
20
16
12
8
4
0
0
4
8
12
16
20
24

corrugated diaphragms give linear load-deflection curves. The source of the belief is not known, but it is certain that it is based on no theoretical investigation of corrugated diaphragm properties.

This investigation was not aimed primarily at determining the shape and slope of the load curves, but at a determination of the maximum allowable load for these diaphragms, or the load at the elastic limit. The determination of the elastic limit is so difficult that it is better to adopt the proportional limit, or the limit of application of Hooke's law. This has been done for a series of diaphragms, ranging in thickness from 8 to 30 thousandths of an inch. The load-deflection curves for initial loading are given in Figure 33. The proportional limits have been estimated and are given in Figure 34.

It is interesting to compare the proportional limits observed with the elastic limits for plane steel diaphragms that are calculable by (8). These results appear also in Figure 34. It is seen that corrugated diaphragms fall in a range of plane diaphragms of very high elastic limit. This may be due to the high elastic limit of the heat-treated

Figure 33

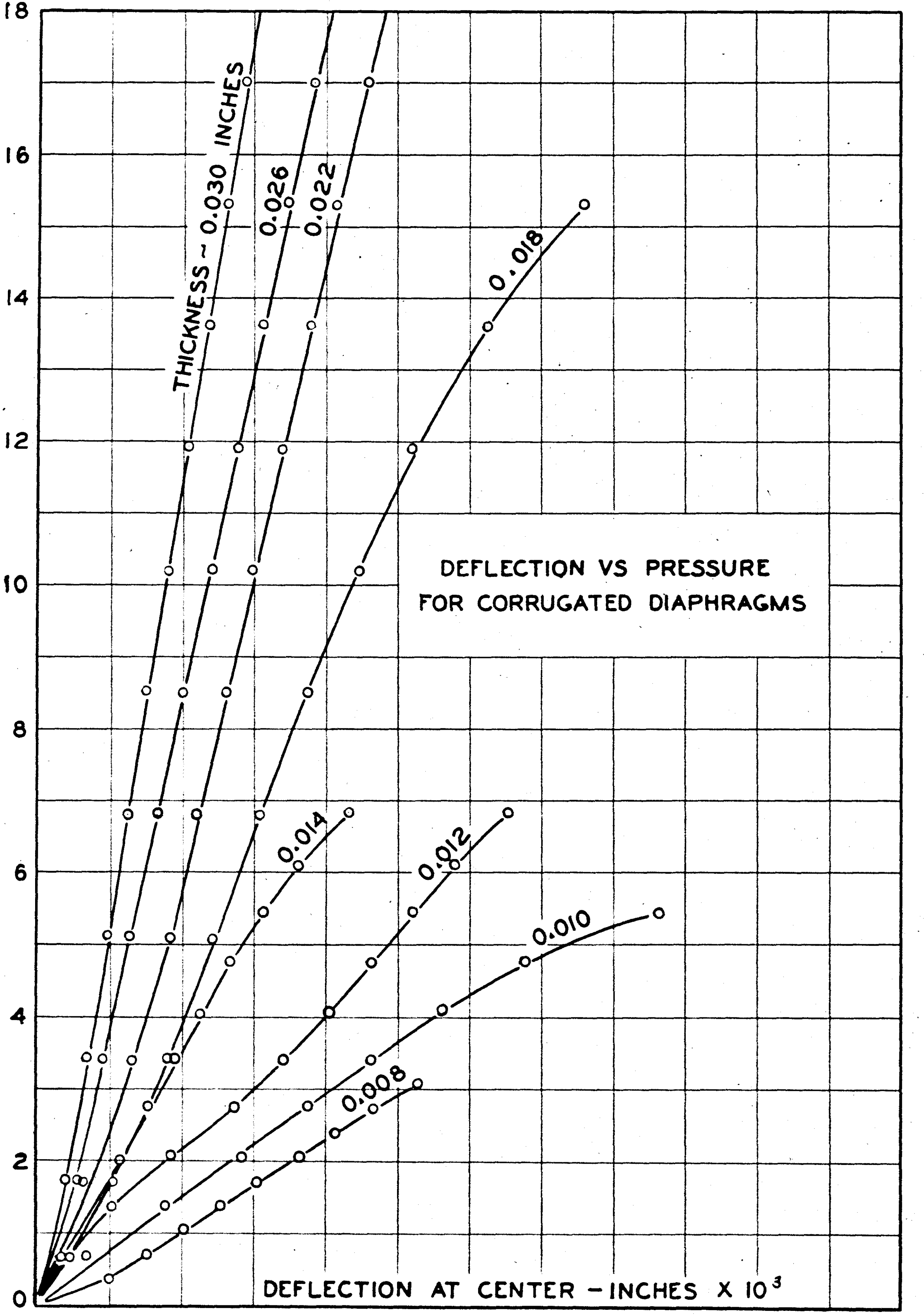
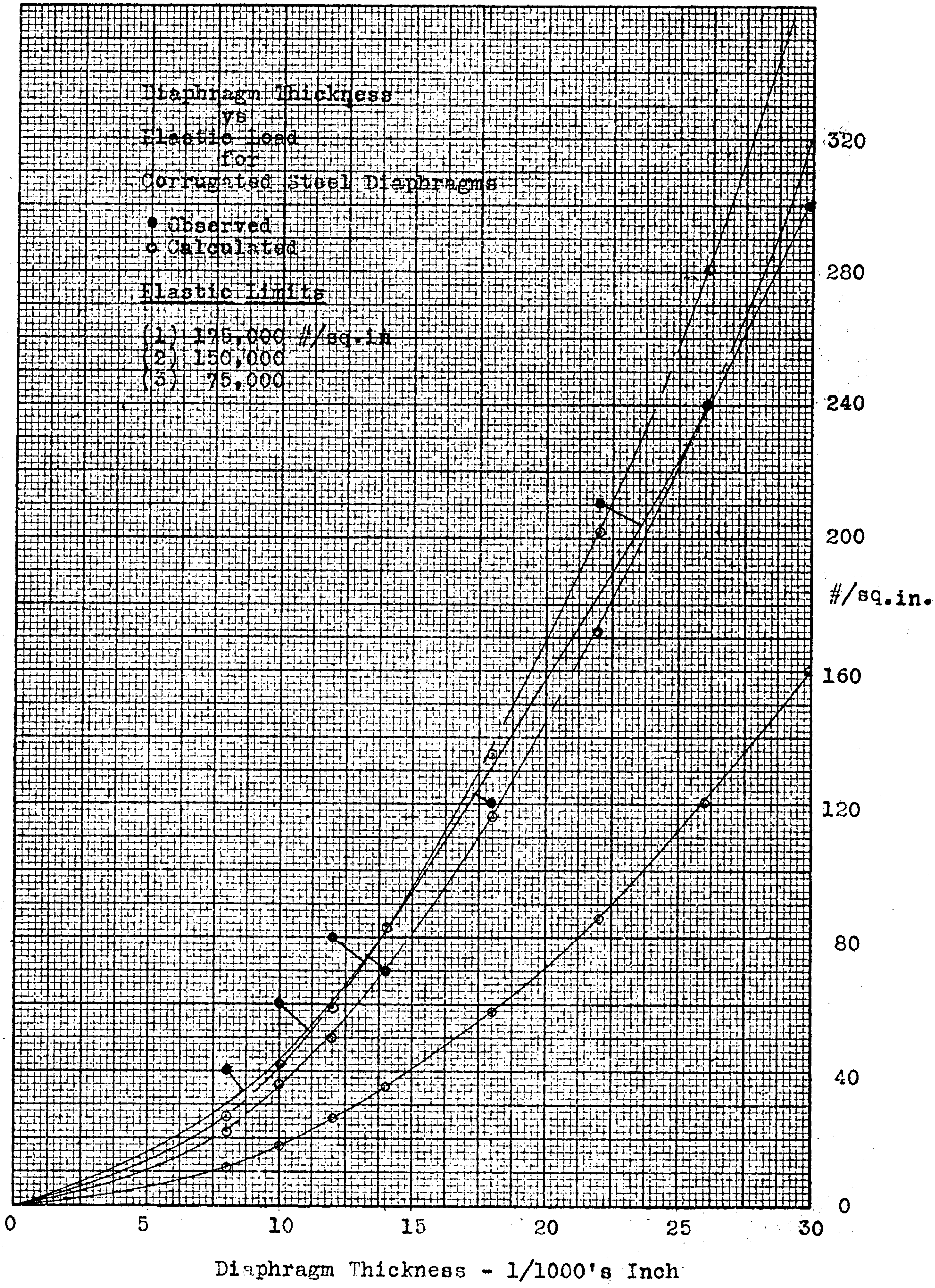

18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
DEFLECTION VS PRESSURE
FOR CORRUGATED DIAPHRAGMS
THICKNESS ~ 0.030 INCHES
0.026
0.022
0.018
0.014
0.012
0.010
0.008
DEFLECTION AT CENTER - INCHES X 10^3

Fig. 34



Diaphragm Thickness
vs
Elastic Load
for
Corrugated Steel Diaphragms
● Observed
○ Calculated
Elastic Limits
(1) 175,000 #/sq.in
(2) 150,000
(3) 75,000
320
280
240
200
#/sq.in.
160
120
80
40
0
0
5
10
15
20
25
30
Diaphragm Thickness - 1/1000's Inch

diaphragms, but it is more probably due to the increase in effective diameter that corrugation always produces.

A further analysis of the data obtained consisted of applying the theoretcial equation for plane diaphragms to the observed load-deflection data. Rewriting equation (7),

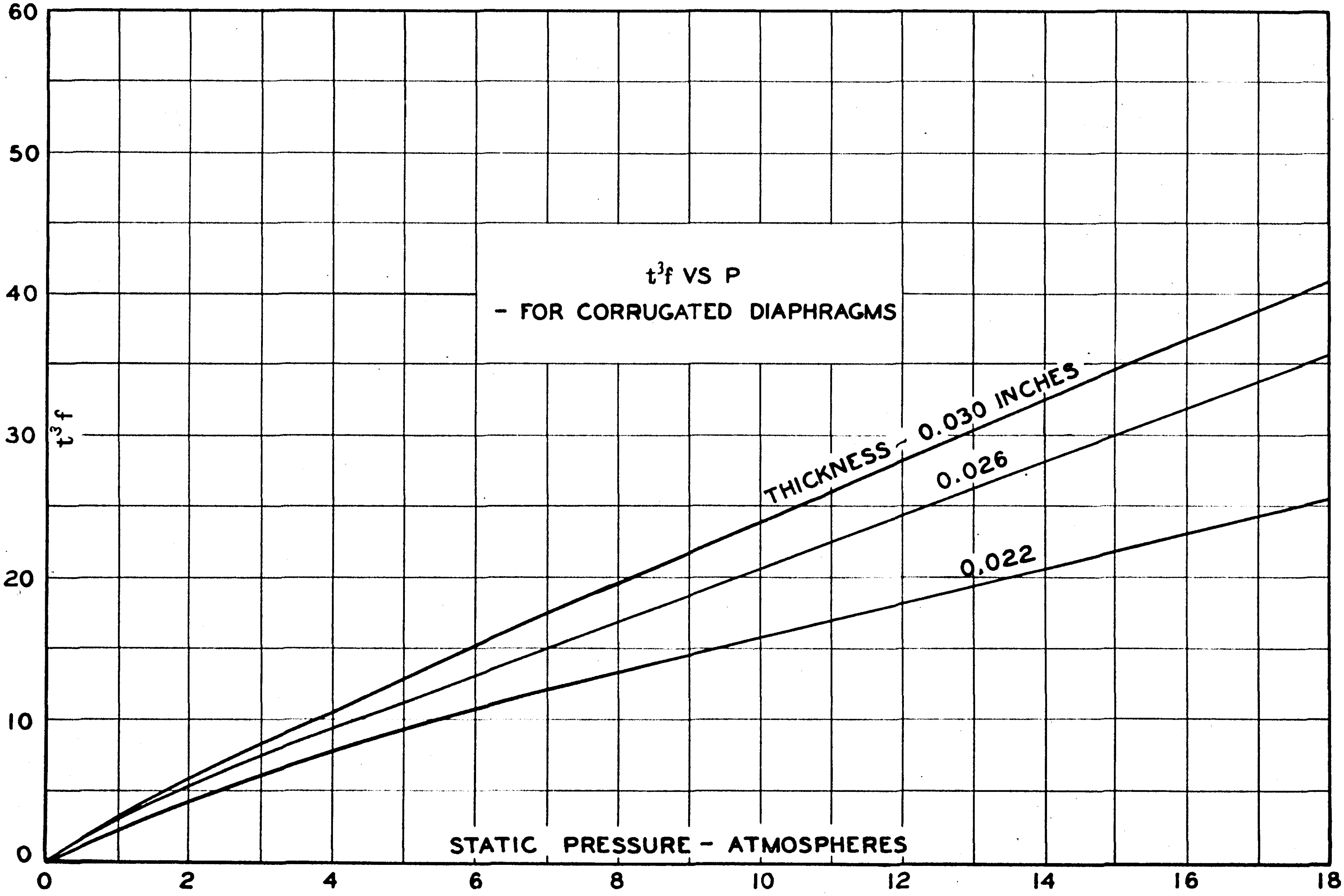
$$f_u = 0.17 \frac{a^4 p}{t^3 E}$$

so that the product $t^3 \times f_u =$ constant. P for diaphragms of the same material and diameter. If this relation is the true one, the data for diaphragms of different thickness should lie in the same straight line. The data for three thicknesses have thus been computed and are given in Figure 35. It is seen that the relation expressed by (7) is not the true one.

d) Choice of a Suitable Indicator

The analysis that has been made of some of the important properties of indicators makes it possible to determine whether any indicator among the group that have been listed is suitable for this work. The only specifications that are made are that the

Figure 35


t^3f VS P
- FOR CORRUGATED DIAPHRAGMS
t^3f
THICKNESS - 0.030 INCHES
0.026
0.022
STATIC PRESSURE - ATMOSPHERES
0
10
20
30
40
50
60
0
2
4
6
8
10
12
14
16
18

frequency be high (5-10 kilocycles/sec.), deflection a maximum within the capacity of the indicator, and that the indicator be reliable. The different types will now be examined with regard to these specifications.

1) Mechanical Indicators

This type of indicator is not regarded as practicable because of the usual small size of record obtained, and further, its piped connections to the source of pressure, or use of a piston, make it unreliable.

2) Electrical Indicators

It has been stated previously that electrical indicators are the most desirable kind of this work, and that the electron tube type had to be abandoned after repeated experiments showed that it could not be stabilized for satisfactory recording. Of the other types of electrical indicators it may be stated that: the induced e.m.f. type is awkward because it measures rate of change of pressure, and, neglecting this, it is hardly suited to the slow changes in pressure in the cooling portion of the curve;

piezo-electric indicators are not yet perfected; the resistance type requires carbon piles for which a satisfactory method of producing has only recently been found.

3) Optical Indicators

Optical indicators offered the only types that held any promise for immediate selection for this work, and even in this group, the standard types could not be applied. It has been shown already that the modified Petavel type did not suit the spatial arrangement of the apparatus; a cantilever spring type might possibly be used without difficulty in construction or operation. The indicators that have actually been used are not the usual types and their development has required much original design and painstaking effort. These indicators will be described in the order of their development.

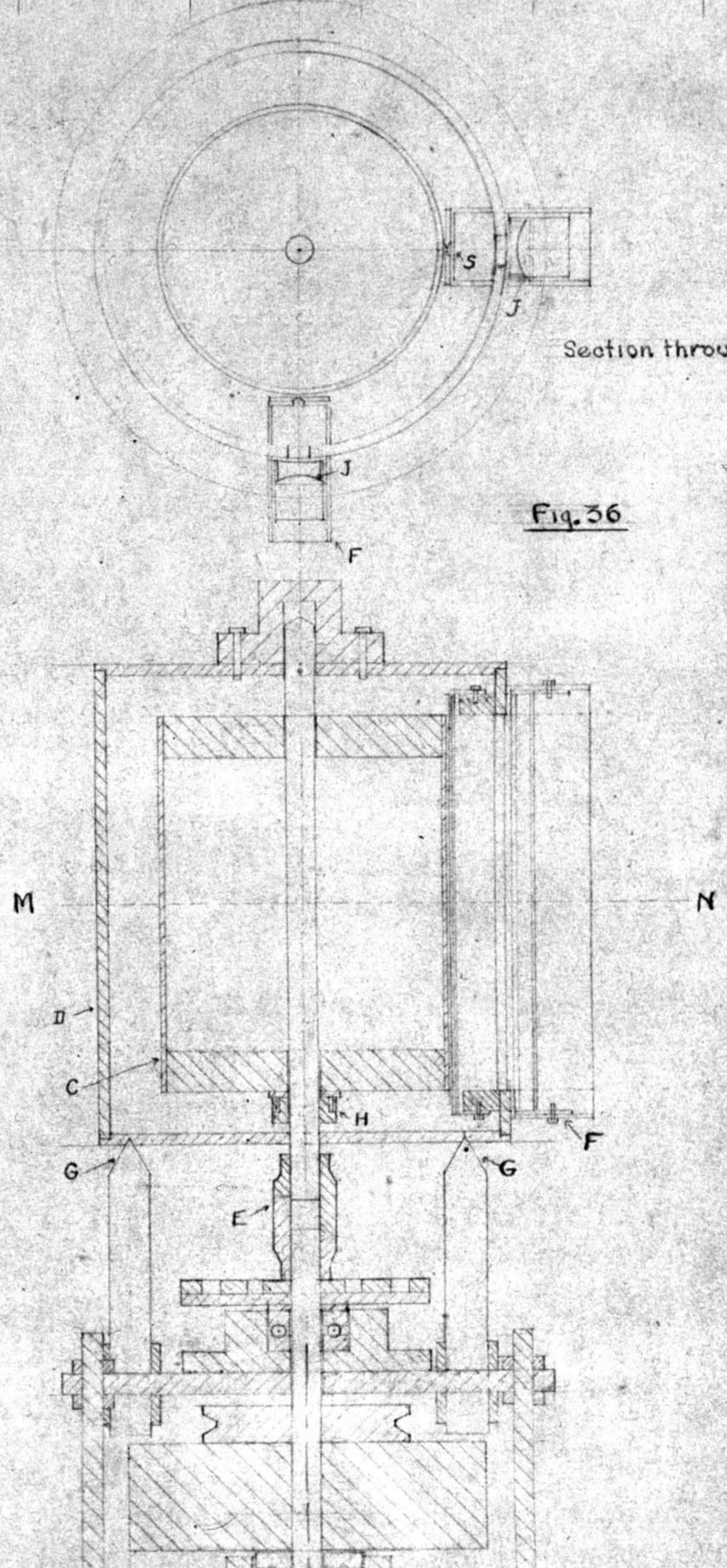
Before describing the optical indicators that have been developed it is advisable to describe the method of recording the indicator motion. All optical indicators require cameras for recording, and when it was decided to use an optical indicator for this work, a special camera had to be designed for the purpose. In addition to the camera, some method of timing had to be provided, and for this purpose a tuning fork mechanism had to be designed and constructed. Also, a suitable light source is an essential factor for optical indicators. These had to be developed before an indicator could be tested and they are described in the order given above.

a) Camera

The camera is the drum type as shown in Figure 36. Its housing, D, the top of which is removable, and shutters, F, together with the flexible coupling, E, and the 3-point supports, G, (or a flange and groove) make it readily portable so that it may be loaded or unloaded in the dark-room, but used in the light. The film drum, C, is keyed to the shaft by means of collar, H, and carries a film 11 inches long and any width not exceeding 4 inches. A special seam clamp is provided to hold the film tightly to the drum. Two cylindrical lenses, J, J, are built into the housing; one of these receives light from the indicator, the other from the tuning fork. Slits, S, S, are provided for auxiliary purposes. The drive mechanism carries a heavy flywheel, M, to assure uniform rotation, and a spiral, L. The spiral is an essential part of the timing mechanism to prevent superposition of time lines. It is arranged so that series connection with the electric tuning-fork shutter permits the latter to remain open only when the circuit is closed through the spiral. Electric contact once made in spiral itself, is automatically broken and, in any case, can occur for not more than one revolution of the camera drum, so that the tuning fork marks occur on the film for one revolution or less.

b) Timing Apparatus

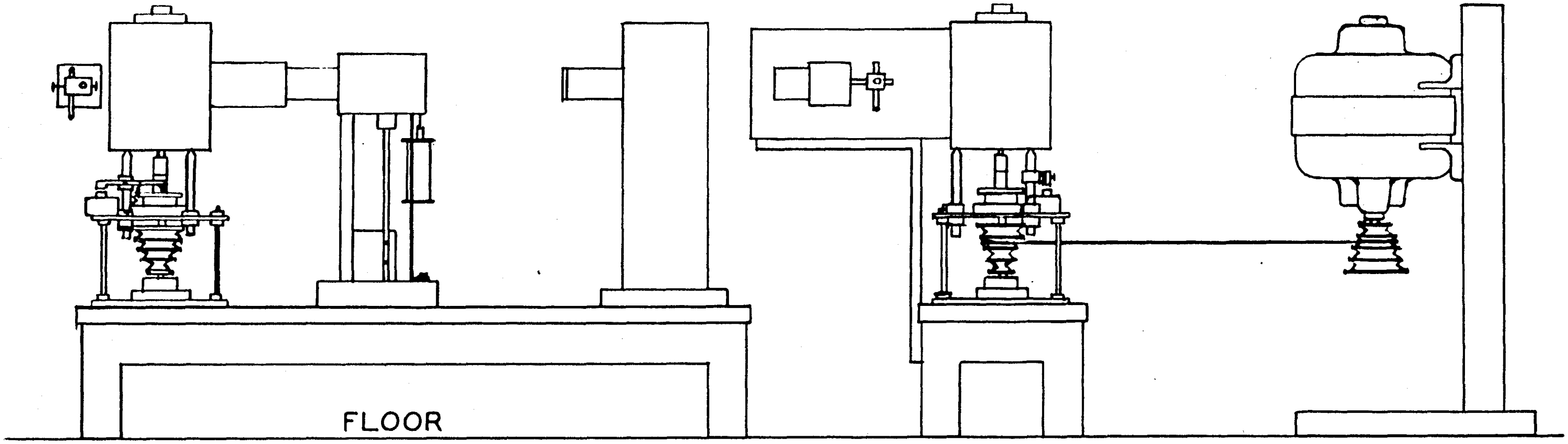
The tuning fork was adopted as the most reliable means of superposing the time record upon the pressure record. Driving the fork by the usual methods of make and break, or the microphone hummer, did not appear satisfactory from experiences of other investigators. The latest and excellent method involving the use of vacuum tubes was therefore adopted. This method is briefly described.



Section through MN

Fig. 36

Photographic Camera
M.I.T - Fuel and Gas Eng'r'g.
V. C. Smith - 5-1-28



CAMERA ASSEMBLY

Figure 36-A

i) Electron Tube Tuning Fork Drive

The maintenance of vibrations of tuning forks by vacuum tubes was first introduced by Eccles.[65] The method has since superseded all other methods from the standpoint of constancy and ease of maintenance. Since Eccles' publication, other methods, the complete theory of operation, and the weight of all factors involved in satisfactory operation, have been published in papers by Butterworth,[66] Eckhardt and others,[67] Dye,[68] Pack,[69] Klein and Rouse,[70] and Quayle.[71]

The method of Eckhardt, Karcher and Keiser, though differing in arrangement from the other types, appeared simplest. A diagram of the arrangement of the circuit appears in Figure 37, together with the size of tube, condenser, and turns of wire on the laminated yokes in the grid and plate circuits. The circuit is a regenerative, mechanically-coupled type so that variation of the distance between the yokes by moving the grid coil makes possible an adjustment of the circuit to give the desired amplitude for any one fork and the use of the same circuit for different forks.

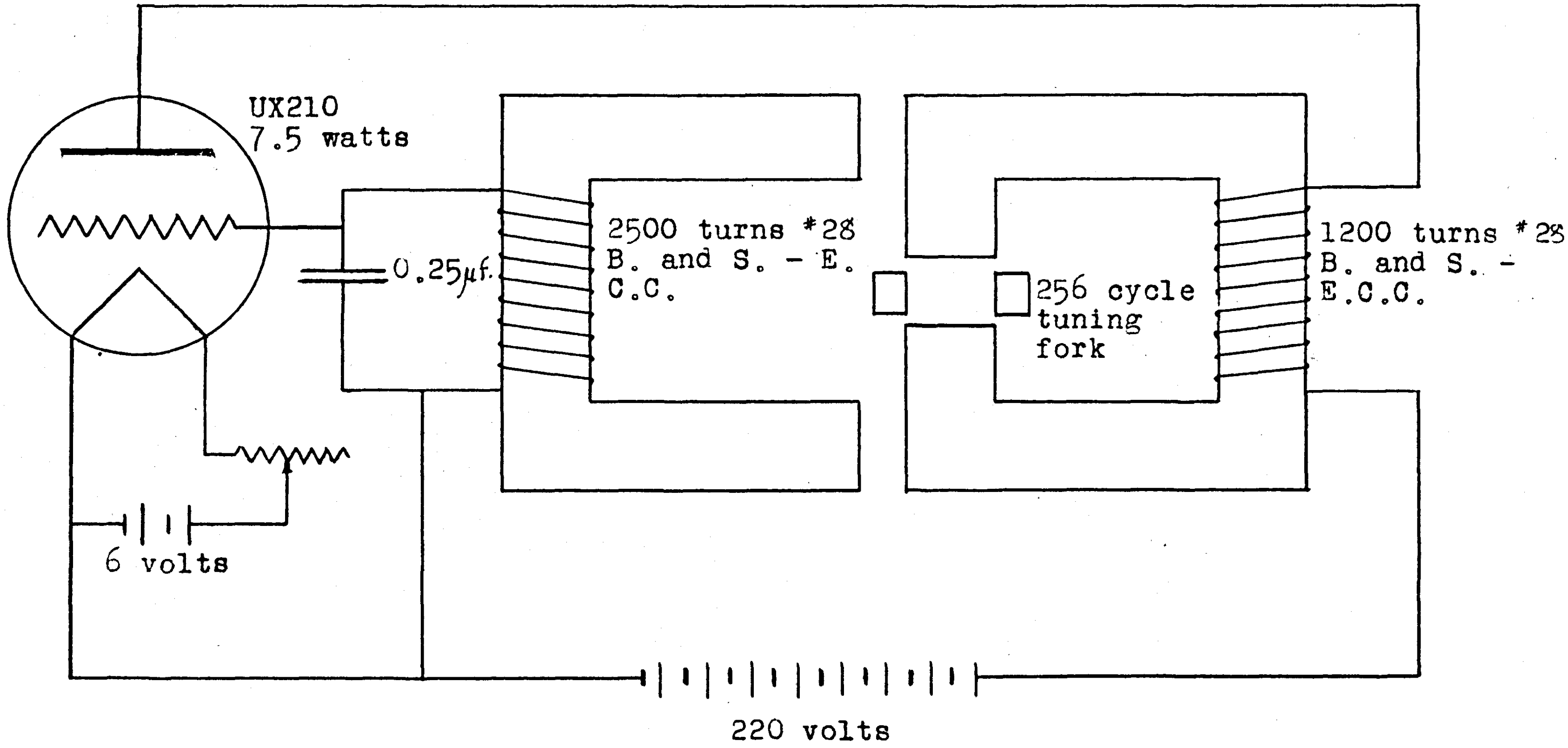


Fig. 37

Electron Tube Tuning Fork Drive

School of Fuel and Gas Engineering

Mass. Institute of Technology

ii) Functioning of the Circuit

Closing the plate circuit with the filament bright starts the plate current through the driving electromagnet. The fork prongs are pulled together and thereby vibrate feebly. This feeble motion of the fork has relatively large effect upon the reluctance of the magnetic circuit. The reluctance changes are determined by the free period of the fork. Corresponding changes in plate current result, which by virtue of the coupling existing between the plate and grid circuits are regeneratively amplified. The a.c. component of the plate current, as it increases, causes the fork to vibrate with greater amplitudes, accelerating regenerative action. This continues until limited by the tube.

While adjusting the circuit, singing of the tube is a valuable guide. As the free period of the fork is approached, beats between the two frequencies are heard. Adjustment is carefully made until all beats disappear when the two frequencies synchronize.

The 256 cycle fork shown in the diagram has attached to its prongs two thin pieces of aluminum through which narrow slits (0.005" x 0.75") have been made. With the fork at rest these slits are made to coincide. When the fork vibrates, a beam of light from a long helical-filament lamp focussed on and flooding the slit passes through to the photographic drum. A double convex lens attached to the frame supporting the fork focusses the beam on the cylindrical lens at the drum and is in turn focussed to a fine line on the film. If the film moves at a uniform rate and the slits are exactly opposite when the prongs are at rest, the lines will be equi-spaced and parallel on the film. Usually, however, the exact adjustment is difficult and it is better to consider distances between every other line where, in any case, the lines are parallel and equi-spaced. Also, since the slits are opposite twice during each cycle there will be two lines per cycle.

This method of maintaining vibrations has been found satisfactory and convenient. Further, the time lines that are obtained make it easy to analyze a record with high precision. This is obvious from Figure 12-B, as well as other records to be presented.

c) Light Source

A suitable light source is a necessary part of an optical indicator and if a record is to be made of the pressure change, the source must be of sufficient intensity to affect the film. The source that is used in this work and some of its properties are discussed below.

In almost all work of this kind, the rate of change of pressure in the system is highly variable so that while the photographic film is moving at constant speed the actual exposure may differ widely during an experiment. If the intensity of the source is increased so that the record is discernible in the least exposed parts, fogging usually occurs in the other parts. The ideal condition constitutes uniform exposure of the minimum required amount. This requirement naturally rules out such sources as carbon or tungsten arcs which are not readily varied in intensity. On the other hand, tungsten filament lamps can be varied in intensity without difficulty and if the required intensity is greater than the rated capacity of the lamp, overloading is easily and safely effected without serious consequence to the life of the lamp, provided the time of overload is short.

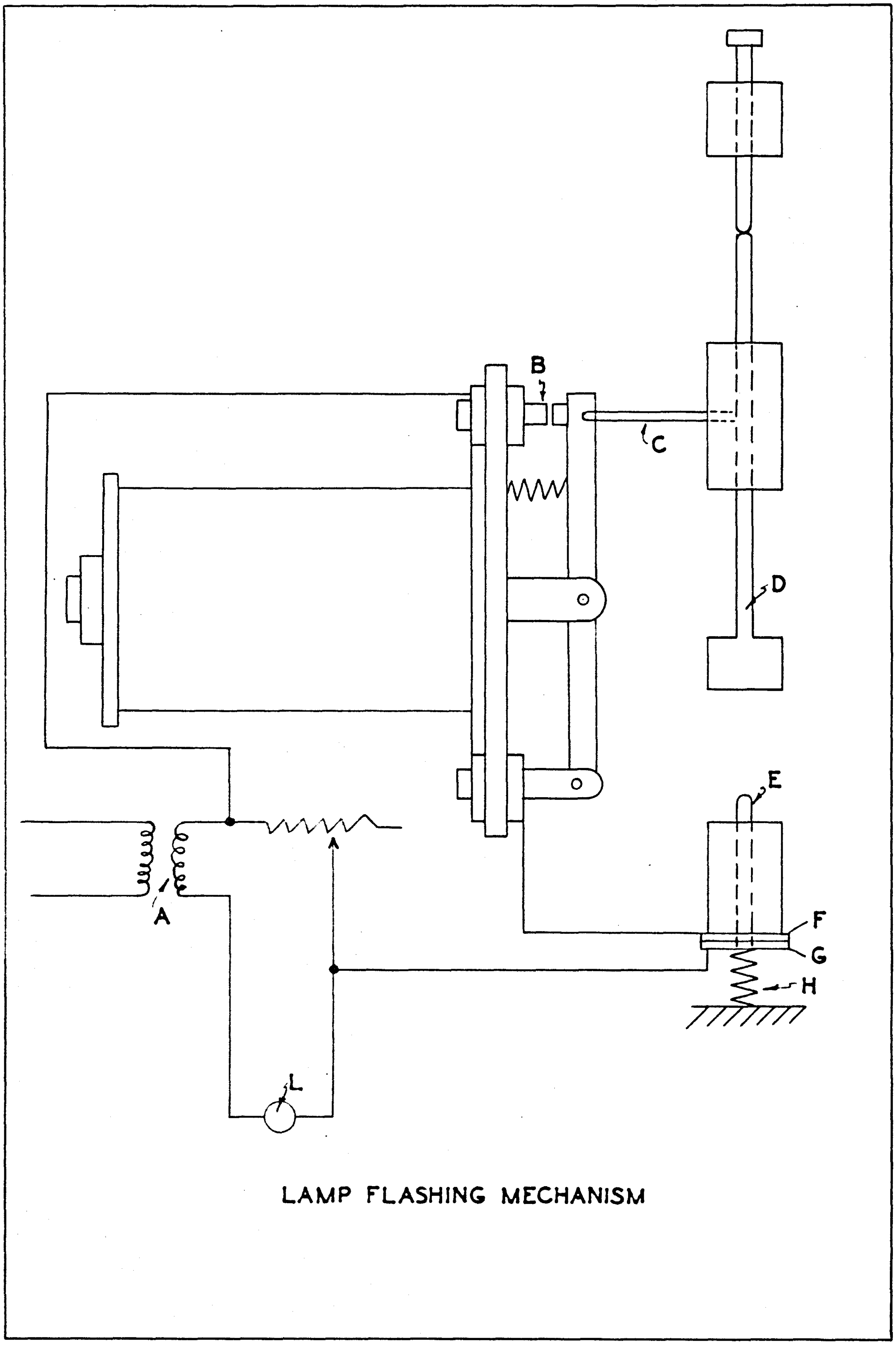
Another factor which influences the choice is the geometrical shape of the source. Obviously, if the image of the source is to be focussed on the film, the source must conform to the requirements of the image. Usually this is a fine dot or very fine line, so that unless the source is itself a dot or very fine line in the usual optical system it must be made so by an initial focussing on a slit or pin hole.

For this work a straight filament, gas-filled lamp manufactured by Westinghouse Manufacturing Company for use in their Osiso Oscillograph has been used. The filament is sufficiently thin to give a narrow image with proper focus at unit magnification.

The rate of pressure change is such that the lamp has to be flashed from a capacity a little below rated and this is done in the manner shown in Figure 38.

Current from the transformer, A, flows, normally, through the lamp and variable resistance, R. When contact is made between the solenoid-operated lever and binding post at B, the resistance is short-circuited. However, the operation of the lever causes the pin, C, to release the weight, D, which falls freely, and strikes stem, E, connected with disc, G, breaking electrical contact between the latter and

Figure 38



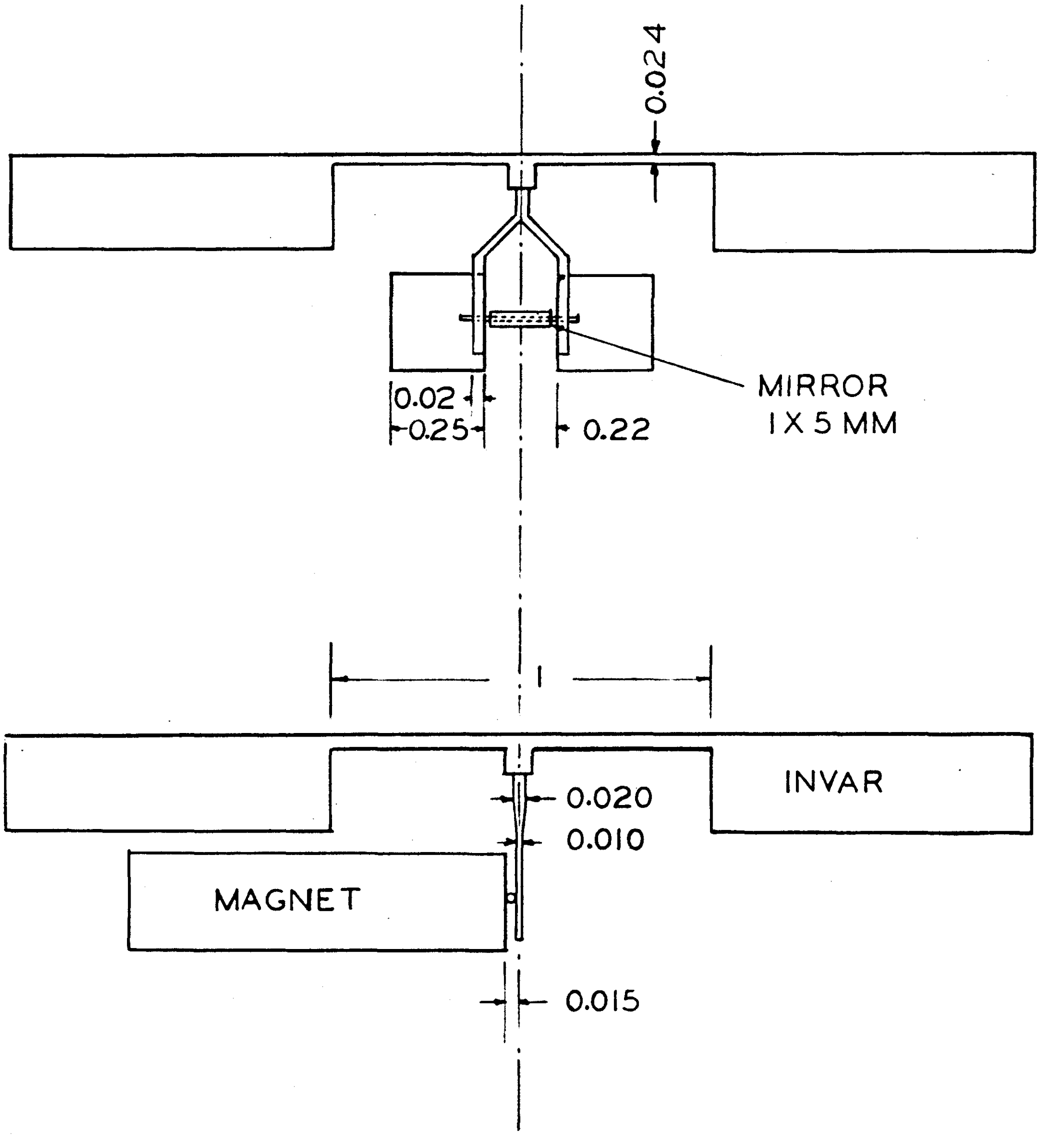
LAMP FLASHING MECHANISM

disc, F. The time of flashing is thus determined by the time required for the weight to fall and the height of fall is controllable by screw, J.

d) Magnet Indicator

The first indicator developed receives its name from the fact that a horseshoe magnet is an essential and distinctive feature. It offered a simple method of obtaining a highly sensitive indicator and was selected over a cantilever spring type for this reason.

A diagrammatice sketch of the indicator is shown in Figure 39. A disc of Invar steel has a central portion turned leaving a thin diaphragm 1-inch in diameter and 0.024 inch thick. A boss left in the center of the diaphragm carries a steel fork, the prongs of which pass in front of the poles of a horseshoe magnet; a small spindle of 0.010 inch drill rod carrying a small plane mirror lies between the fork prongs and magnet faces; the latter are ground, and they form the bearing surfaces over which the spindle rolls when the fork moves. Small motion of the diaphragm produces large angular motion in the spindle so that a light beam focussed on the mirror attached



DIAGRAMMATIC SKETCH
OF
OPTICAL INDICATOR

Fig. [redacted] 39

to the spindle also executes correspondingly large deflection for small diaphragm motion.

A cylindrical lens of 12-inch focal length is securely fastened in the indicator housing close to and in front of the mirror. This lens, the straight filament lamp, the mirror, and the cylindrical lens in the camera housing, constitute the whole optical system of the indicator. Hardy,[72] by considering the limitations imposed by diffraction from the edge of the mirror, has shown that the width of the spot on the film for this optical system can never be less than is indicated approximately by

$$W_1 = 0.0009 \frac{v}{W_2}$$

Where W_1 = width of the spot

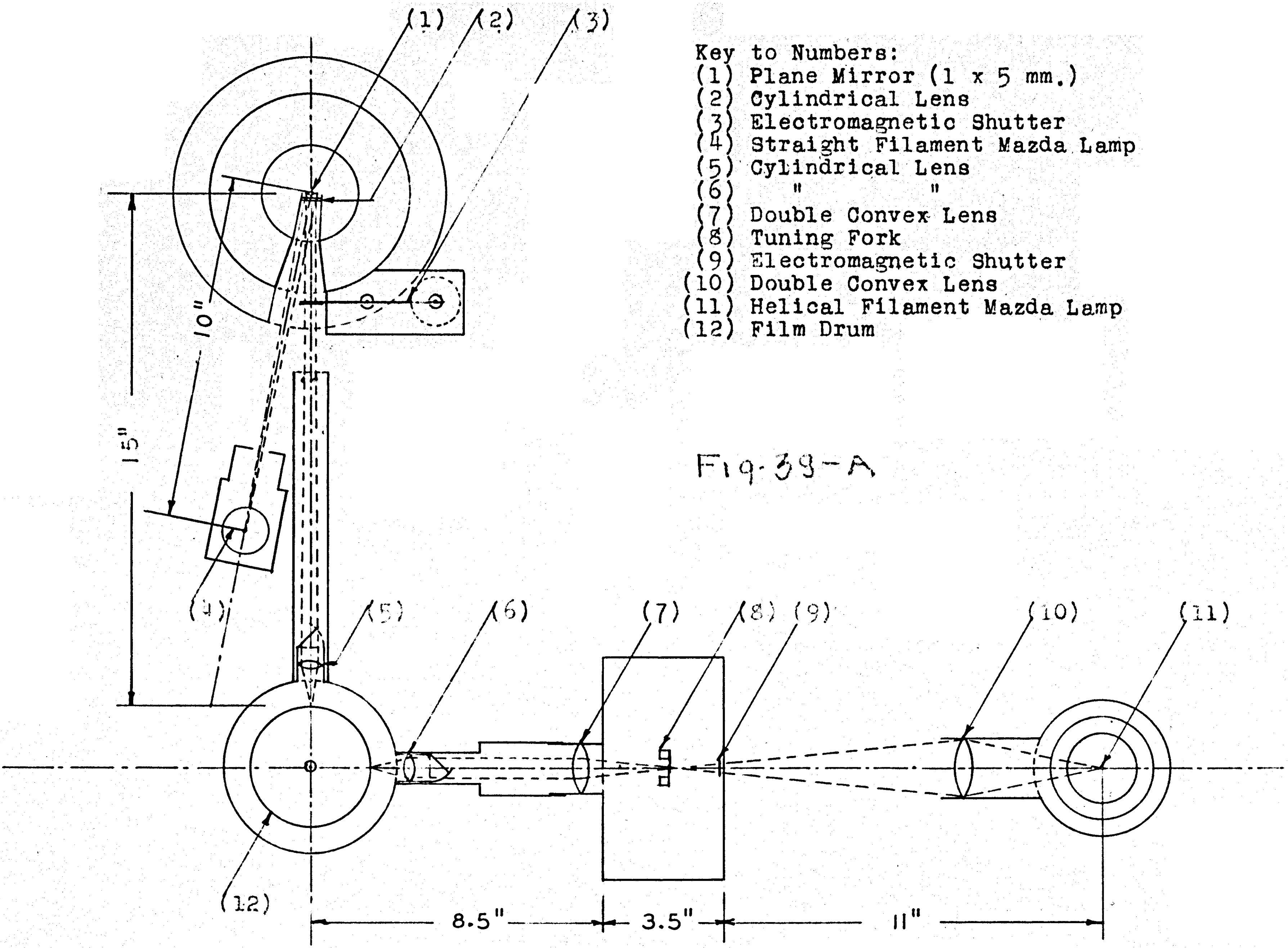
W_2 = width of the mirror

v = distance from the lens to the film.

If a desirable value of W_1 is assumed to be 0.1 mm. the optimum distance per millimeter width of the mirror is 11 centimeters.

A complete diagrammatic sketch of the recording system is shown in Figure 39-A where the actual dimensions as well as the names of the parts are given.

DIAGRAM OF OPTICAL SYSTEM



Key to Numbers:

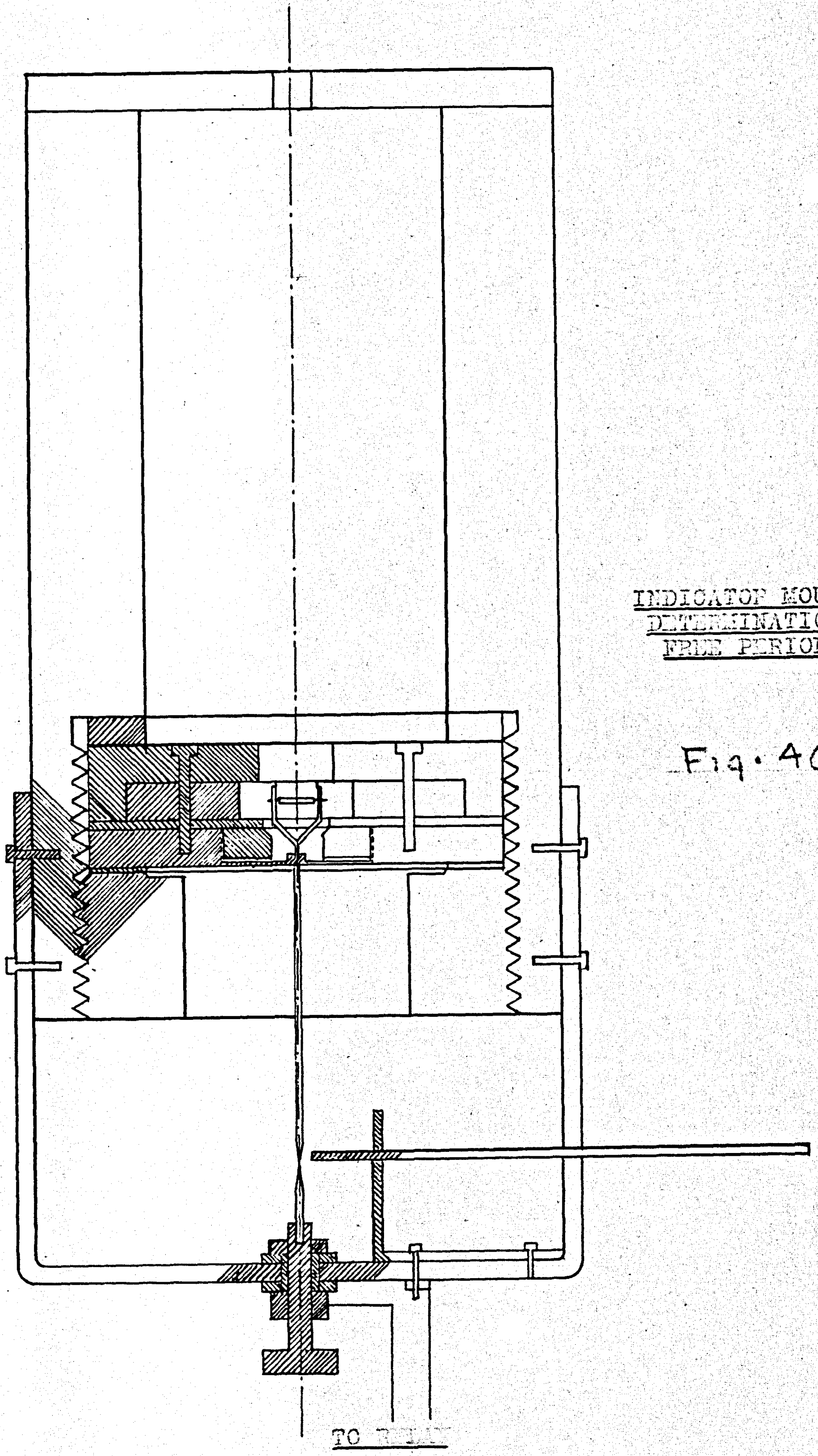
(1) Plane Mirror (1 x 5 mm.)
(2) Cylindrical Lens
(3) Electromagnetic Shutter
(4) Straight Filament Mazda Lamp
(5) Cylindrical Lens
(6) " "
(7) Double Convex Lens
(8) Tuning Fork
(9) Electromagnetic Shutter
(10) Double Convex Lens
(11) Helical Filament Mazda Lamp
(12) Film Drum

Fig. 39-A

In order to determine the fitness of the indicator for this work the following properties had to be investigated: a) frequency of vibration and damping; b) load-deflection characteristics; c) resistance to shock. The results are presented below.

i) Frequency of Vibration

The diaphragm thickness was chosen for a frequency of 10,000 cycles per second neglecting the weight of the fork. The actual frequency was about 8,200 cycles per second, and the amplitude of the vibrations diminished rapidly, indicating good damping. The method of producing the vibration is shown in Figure 40. The indicator is held in the bomb, D, and arranged so that its deflection can be recorded with the camera. Rod, B, is made to place a tension on the diaphragm, A; when rod B is touched by another rod, C, the tension is relieved and the diaphragm vibrates under its own elastic forces. A time record photographed with the vibrations permit determination of the frequency. This method eliminates the jarring that is inherent in the usual method of striking the diaphragm to initiate vibrations.



INDICATOR MOUNTED FOR DETERMINATION OF FREE PERIOD

Fig. 40

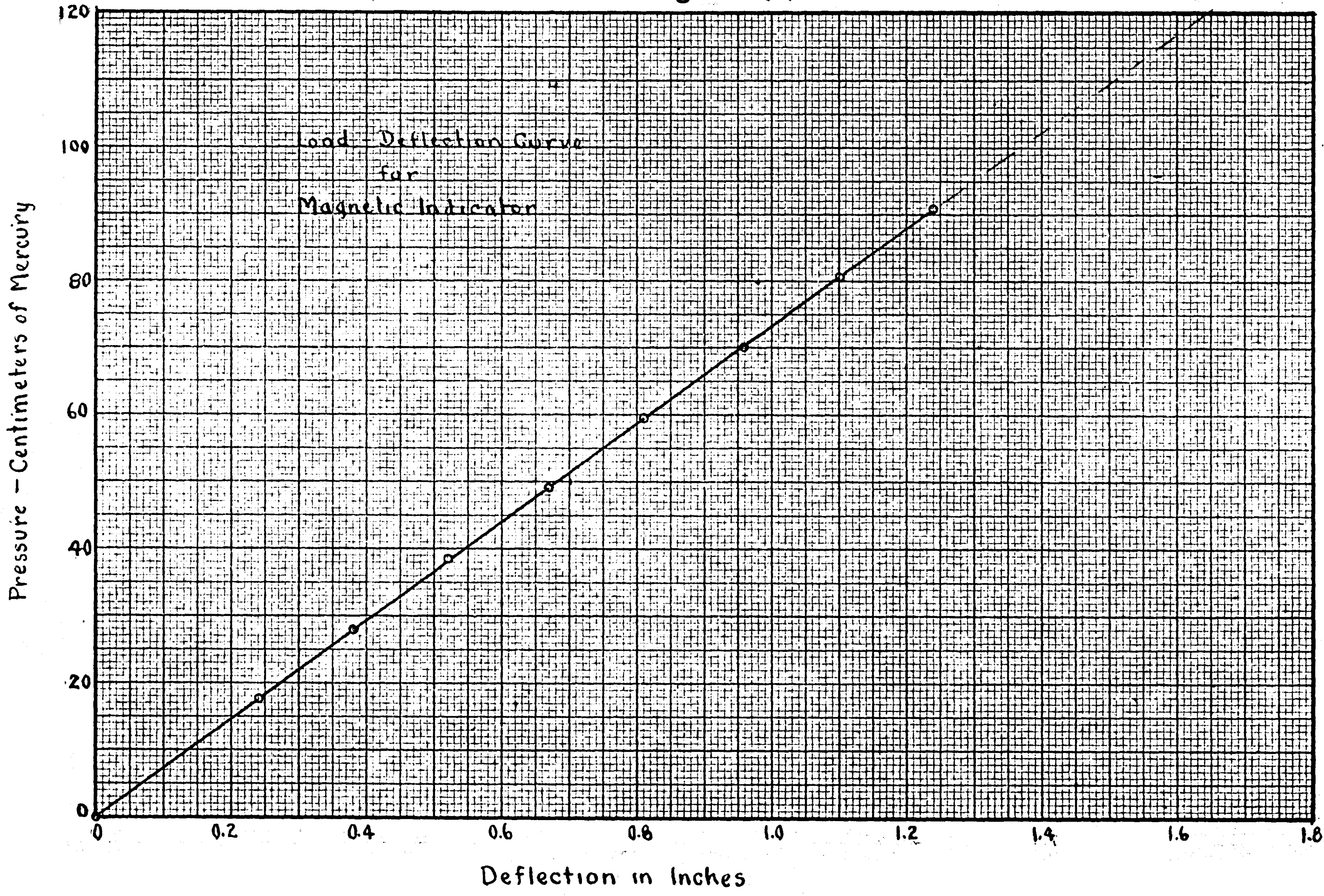
ii) Load-deflection Curve

Figure 41 shows the load-deflection curve for this indicator. It is seen that the relation is a linear one.

c) Resistance to Shock

The one failing of this indicator for the present work is its failure to withstand the shock that is produced by the piston when the latter strikes the stopping mechanism. An actual record of this failure is shown in Figure 42. The base line, B, represents an initial air pressure of 1.05 cm. of Hg, and the upper of 76 cm. of Hg. Compression began at A as indicated by a spark produced when the cast iron support rod snapped. This latter occurrence also controls the opening of the shutter that admits light to the indicator; thus, the initial portion of the compression does not appear on the first part of the record. The shutter opened at C and the compression is recorded until the optical system was thrown out of alignment by the shock.

Figure 41



Load - Deflection Curve
for
Magnetic Indicator
Pressure - Centimeters of Mercury
Deflection in Inches
0
20
40
60
80
100
120
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

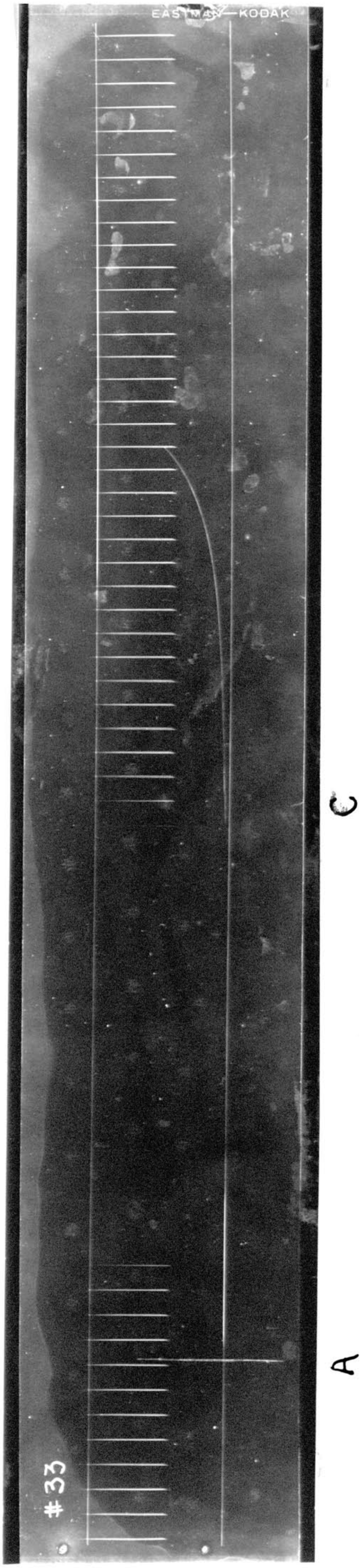


Fig. 42

Run 33.

$P_i = 1.05$ cm.

$P_f = 76$ cm.

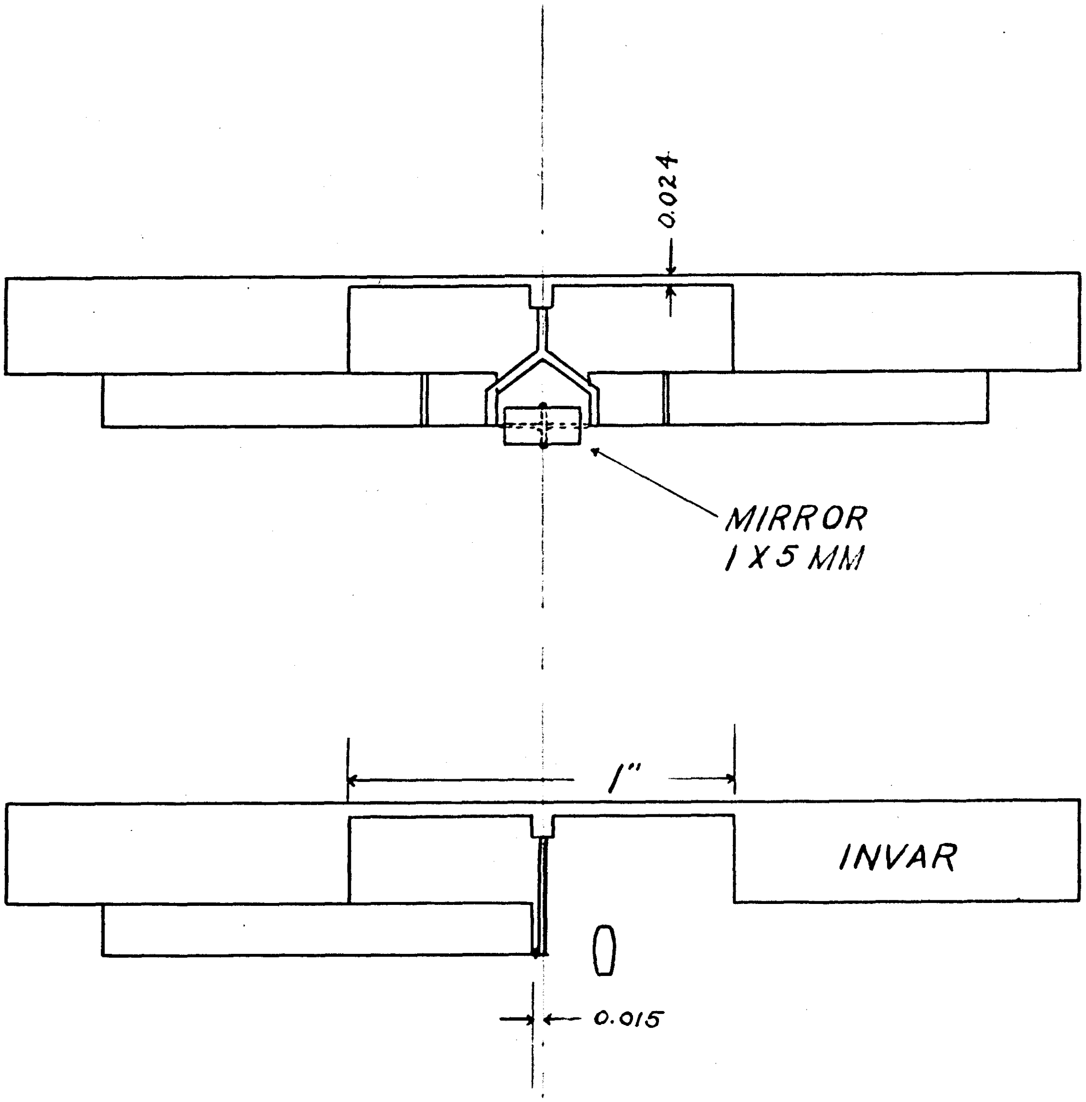
Magnet Indicator

d) Fixed Fulcrum Indicator

The magnet indicator had to be altered radically to make it suitable for this work. The alterations were effected in a manner indicated below.

The fact that the deflection per unit load, the frequency, and the damping were so good led to the retention of all parts of the magnet indicators except the magnet and spindle. A fixed shoulder was substituted for the magnet as shown in Figure 43 and the fork was cut off to the level of the shoulder. A very light spring-steel cross was slung between the fixed support and the prongs of the fork by means of 0.003-inch constantan wire with very careful soldering. The attempt was made to keep the distance between the support and the prongs as small as possible in order to retain the previous high deflection per unit load.

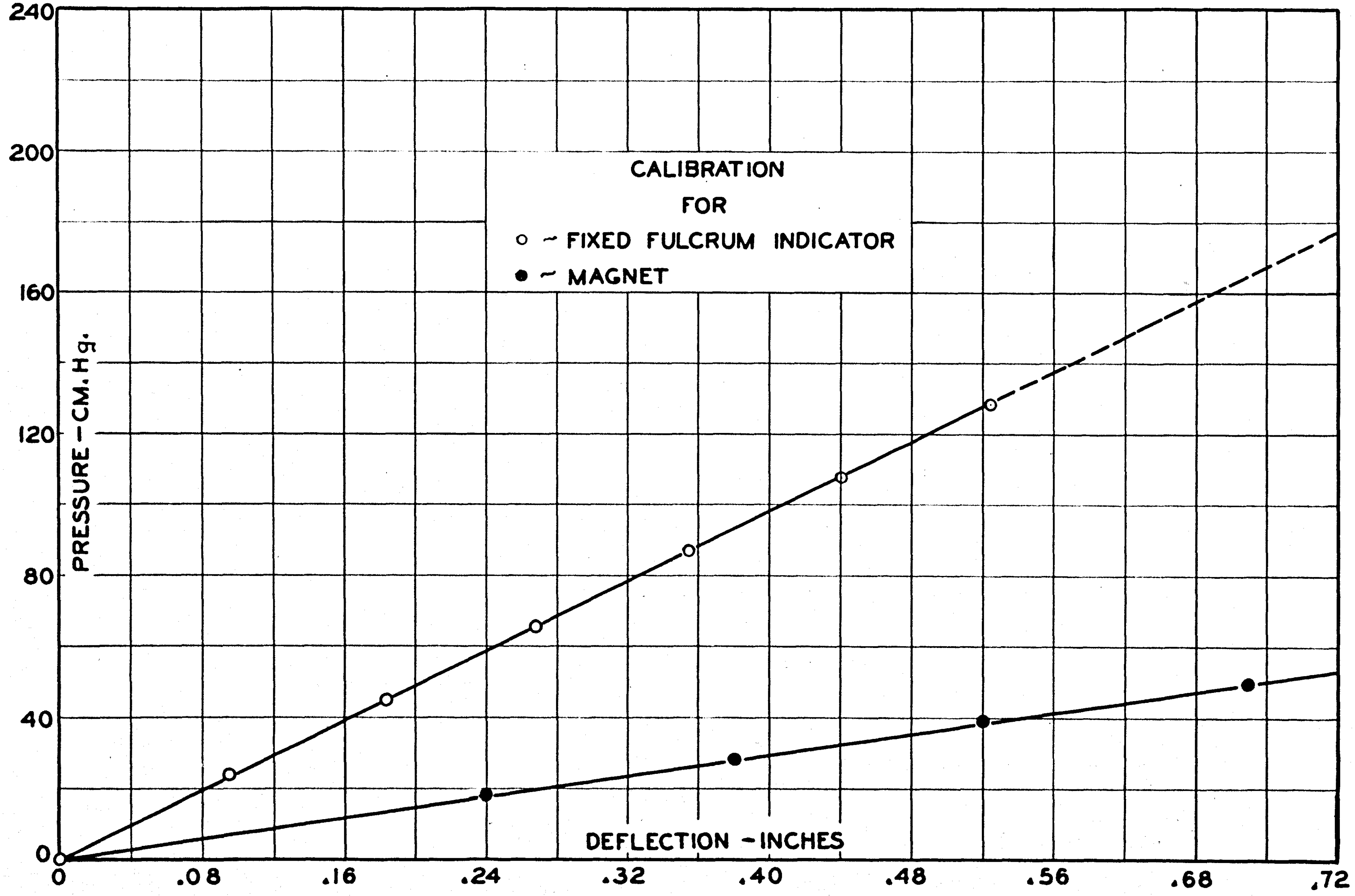
The load-deflection curve for this indicator is given in Figure 44, and for comparison, the data for the magnet indicator are replotted. The deflection per unit load of the latter is more than three times that of the former. This is not a serious matter for



DIAGRAMMATIC SKETCH
OF
OPTICAL INDICATOR

Fig. [redacted] 43

Figure 44



CALIBRATION
FOR
○ ~ FIXED FULCRUM INDICATOR
● ~ MAGNET
PRESSURE – CM. Hg.
DEFLECTION – INCHES
240
200
160
120
80
40
0
0
.08
.16
.24
.32
.40
.48
.56
.68
.72

it was necessary at any rate to increase the final theoretical gas pressure from one atmosphere to four atmosphers in order to prevent excessive loss in pressure due to cooling during compression. The deflections under these conditions are ample. A pressure record recently taken with this indicator is shown in Figure 45.

e) Corrugated Diaphragm Indicator

Another type of indicator that has been developed and which has given the best results is the corrugated-diaphragm type that is discussed here.

The corrugated diaphragm indicator with the mirror attached to the diaphragm was used first by Perry,[73] later by Pier,[74] and by Wohl and von Elbe.[75] A stud is fastened to the surface of the diaphragm somewhat as shown in Figure 46. Pier placed his stud on the crest of the corrugation at about the mid-radius of a diaphragm with less corrugations than are shown in the diagram. By actual experiment the optimum location of this stud with reference to the corrugation was found to be in the trough as shown and a little to the side. Also, the location of the

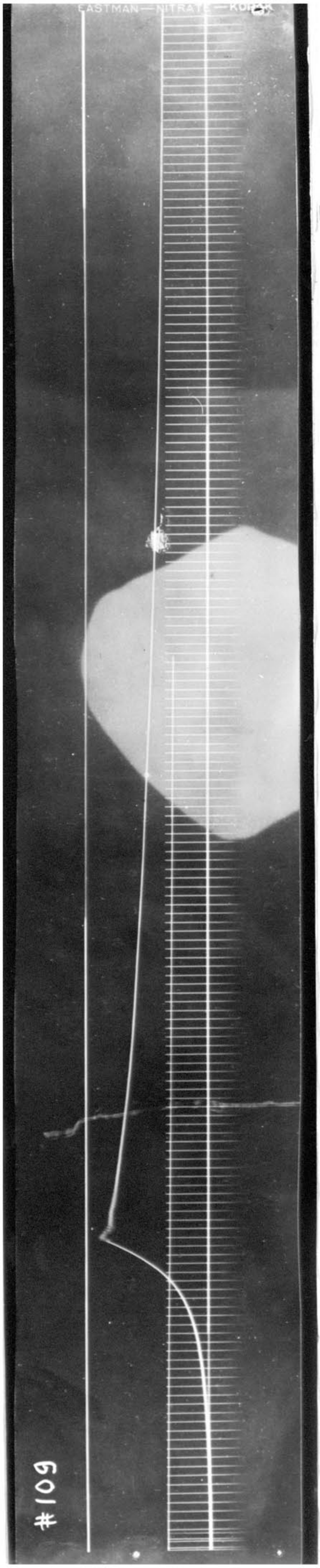


Fig. 45

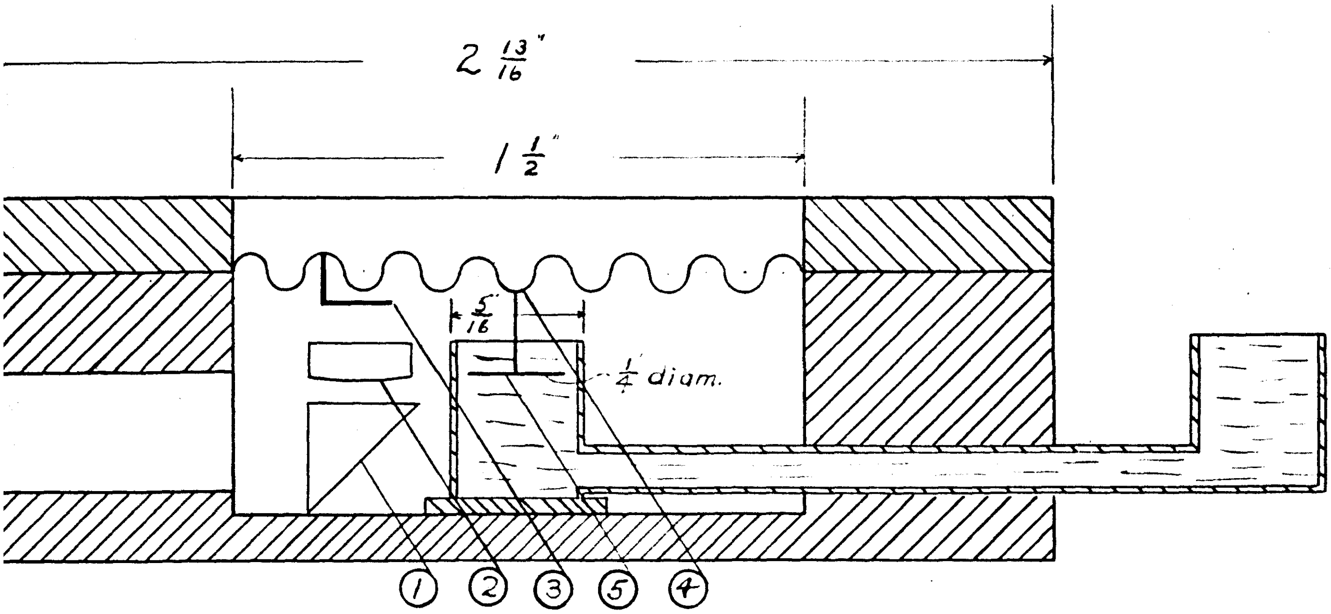
Run 109

$P_i = 6.7$ cm. Hg

$P_f = 304$ cm. Hg

5 lead cones, 3.66 mm. clearance

Fixed fulcrum indicator



CORRUGATED DIAPHRAGM INDICATOR
DIAGRAMMATIC SKETCH

1. PRISM
2. CYLINDRICAL LENS
3. PLANE MIRROR
4. STEEL DIAPHRAGM
5. DAMPER

Fig. [redacted] 46

stud is confined within rather narrow limits. The stud is made from spring phosphor bronze sheet,, or annealed spring steel, bent L-shaped. It is soldered securely in place. The diaphragm material, the method of clamping, etc., have been described in an earlier section.

The optical parts of this indicator are the mirror, which is cemented to the stud, the cylindrical lens and a 90-degree prism. The latter two are securely housed, and are fastened to the body of the indicator.

i) Oxygen-Hydrogen Bomb Tests

An important part of this indicator is the disc damper which is connected to the center of the diaphragm by a small stem, the whole being as light as is consistent with strength. The significance of this damper can be demonstrated best by eliminating any vibrations due to mechanical shock. Consequently in the original testing, explosions of hydrogen-oxygen mixtures were used. The rate of explosion of equal volumes of these gases is so rapid that the damping properties of the indicator are subjected to extreme test.

The bomb used in these tests is the one that has been used in so many of the tests that have been necessary on the different parts of this apparatus; it is shown in Figure 40. For the present tests the compression apparatus was removed from its base and the bomb mounted in its place. Thus, advantage could be taken of the recording and all other parts of the apparatus necessary for the tests, including the gas mixing apparatus.

The results of the tests may be demonstrated by two of the photographs. Figure 47 shows the result obtained with the diaphragm and no damper when equal volumes of hydrogen and oxygen are exploded. An initial pressure, P_1, was chosen so that with an assumed ratio of final to initial pressure of eight, the final would not exceed four atmospheres absolute. The short heavy portion of the line represents the initial pressure; ignition occurs and the pressure rises suddenly, then suddenly falls due to cooling. The sudden rate of change on reaching the maximum sets up the free vibrations in the indicator and although the frequency is too high to be discernible, the envelope is visible. Further, the fact observed in the compression apparatus that the vibrations in this indicator do not damp out readily are borne out in this record.

Figure 47-A demonstrates the effect of the damper that has been described when the damping liquid was a light lubricating oil and the damper was 1/4" inch in diameter. The wide envelope is seen to have disappeared and a thin line remains. The effectiveness of the method is demonstrated and these dampers have been used on all subsequent corrugated diaphragm indicators.

Inasmuch as the indicator must be mounted before the bomb or compression apparatus is in place, the liquid must be added later. Arrangements are thus made for screwing the stem of an auxiliary liquid chamber, through the cylinder wall into the indicator housing after the latter is in place, and the cylinder is in its base. A predetermined quantity of liquid is then added to the auxiliary reservoir.

In addition to liquid damping, eddy-current damping, such as is used in many electrical instruments, might be effectively applied to these indicators.

The load-deflection properties of this type

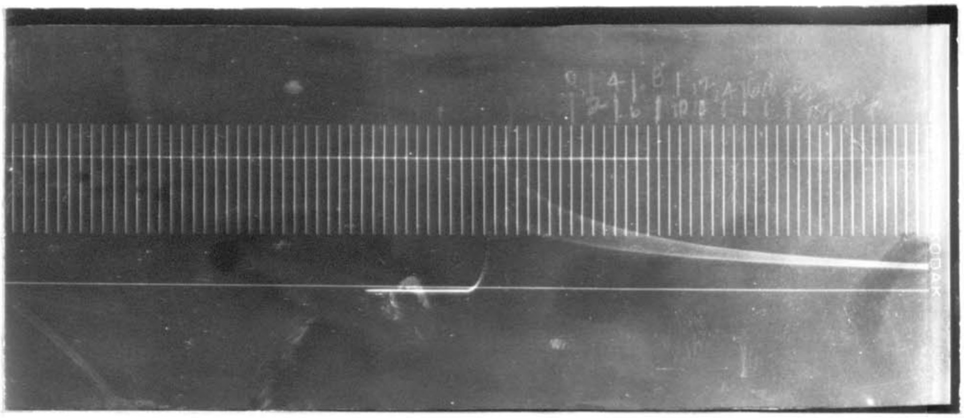


Figure 47

Explosion of Equal Volumes of Hydrogen and Oxygen without Damping the Indicator.

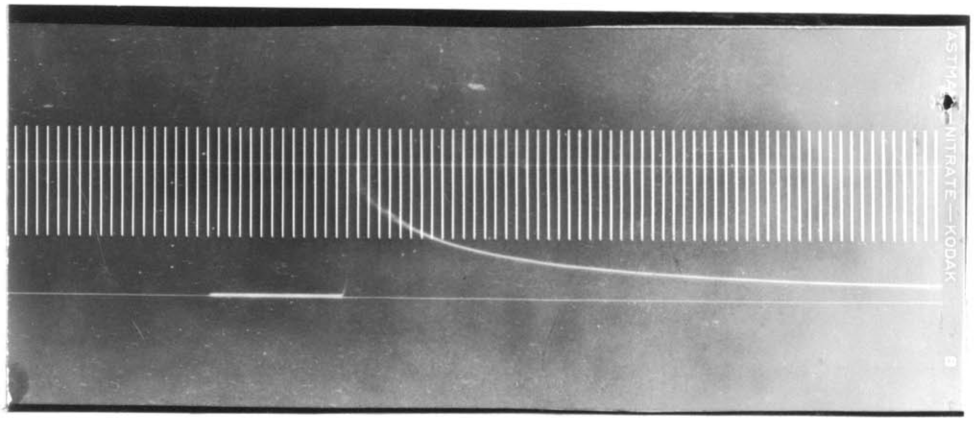


Figure 47-A

Explosion of Equal Volumes of Hydrogen and Oxygen with Liquid Damping of the Indicator.

of indicator have also been plotted, as in the previous types, in Figure 48. The relation is again a linear one.

The explosion records just given show that as far as the time lines and indicator lines are concerned, the optical properties of this indicator are exceptional. Indeed, it may be stated that in none of the indicators discovered during the exhaustive investigation of the literature on this subject, were the optical properties as good as those that have been developed in this type. This will be observed also in other records to be given.

5) The Vibration Effects of the Experimental Method.

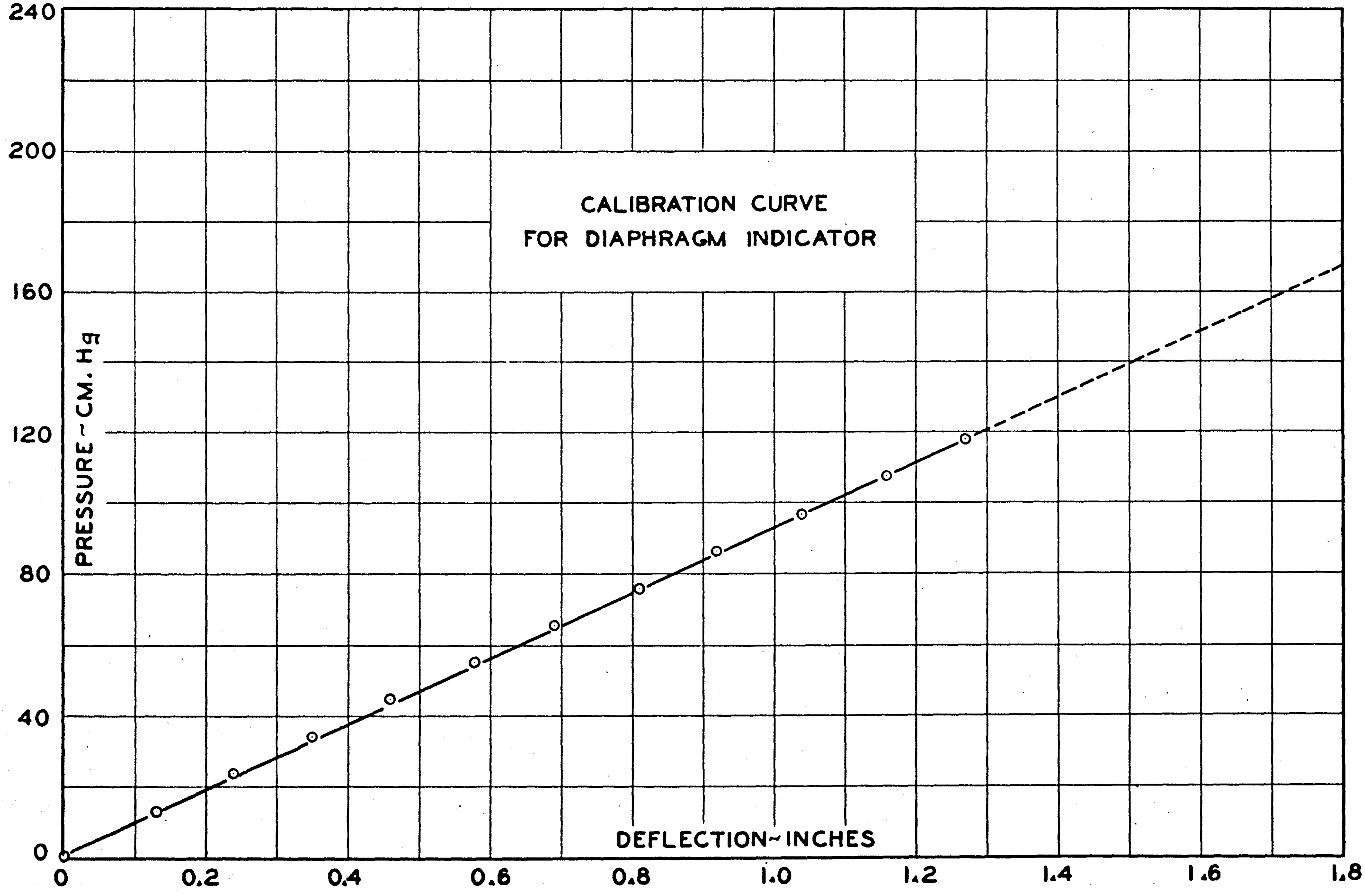
The fundamentals of this experimental method require that the pressure-time record be free from all vibration effects during compression, but most especially at the end of compression and at the beginning of cooling. Vibration and similar effects which have been found to attend the sudden release of the compressed air on the piston and the more serious effects of the kinetic energy in the plunger when the latter strikes the stopping collar will be discussed as follows:

a) Piston rebound;
b) Other sources of vibrations.

a) Piston Rebound.

One of the most disturbing effects of suddenly

Figure 48



CALIBRATION CURVE
FOR DIAPHRAGM INDICATOR

stopping the plunger in this apparatus is the tendency of the piston to rebound. This will be discussed as follows:

i) The factors that influence rebound;
ii) The methods of eliminating rebound.

i) Factors that Influence Rebound.

The factors that determine the magnitude of the rebound of the piston are the mass of the plunger, its velocity at the end of its stroke, and the nature of the impact between the plunger head and the stopping mechanism. The energy in the plunger at any instant is proportional to its mass and to the square of its velocity. The magnitude of the energy to be dissipated therefore increases rapidly with the velocity. The tendency to rebound is influenced also by the nature of the impact, i. e., to what extent the plunger and stopping collar approach perfectly inelastic conditions. Being of steel, they are considerably elastic and if the base and cylinder are considered stationary, there will always be some rebound as a result of impact. Fortunately this rebound may be controlled without decreasing the velocity at impact. The methods of doing this are considered in the next section.

ii) Elimation of Rebound.

There are many methods of preventing rebound after impact between two bodies. A discussion of some of these methods and their suitability to the present work follows.

Rebound is prevented by dissipating the kinetic energy by means of a shock absorber of some kind, or by applying a resisting force of sufficient magnitude at the proper instant. For the problem at hand, the method used must fit into the experimental apparatus and be suited to the method of operating the apparatus; it must operate in a manner not to place too much stress in unsupported ends of the plunger when the whole is suddenly stopped.

The average stress in any transverse section of the lower piston and rod when the plunger is suddenly stopped, is given by the relation

$$P = \frac{M V_1^2}{2 S} = \frac{W}{2g} \cdot \frac{V_1^2}{S}$$

Where, W is the total weight between any transverse section and the unsupported end.

V is the velocity of the plunger at impact.

S is the stopping distance.

The value of P is a maximum at the upper end of the rod and increases with decrease in the stopping distance, being theoretically infinite when $S = 0$. The above relation indicates also that there is advantage in making the lower piston and rod light.

As to the necessity for making the stopping distance finite and appreciable, it may be said that the attempt to stop the plunger moving at high speed without any kind of absorber has only resulted in fracture of the lower piston and excessive rebound. The magnitude of this rebound under such circumstances is severe as is shown from Fig. 49, where the time of compression was about 0.05 second. The sudden dip in the curve at the end of compression is a result of rebound with consequent reduction in pressure; the pressure rises again as the piston is forced down until the latter reaches the stopping collar; from this point, the cooling follows the normal course.

The record also shows that there are severe vibrations in some parts of the apparatus produced as a result of this severe shock.

The record that has just been discussed shows that some method of absorbing the energy in the plunger is necessary. The methods that have been tried and the results obtained are given in the following discussion.

In supplying an absorber for the plunger, it must be realized, as has already been stated, that the

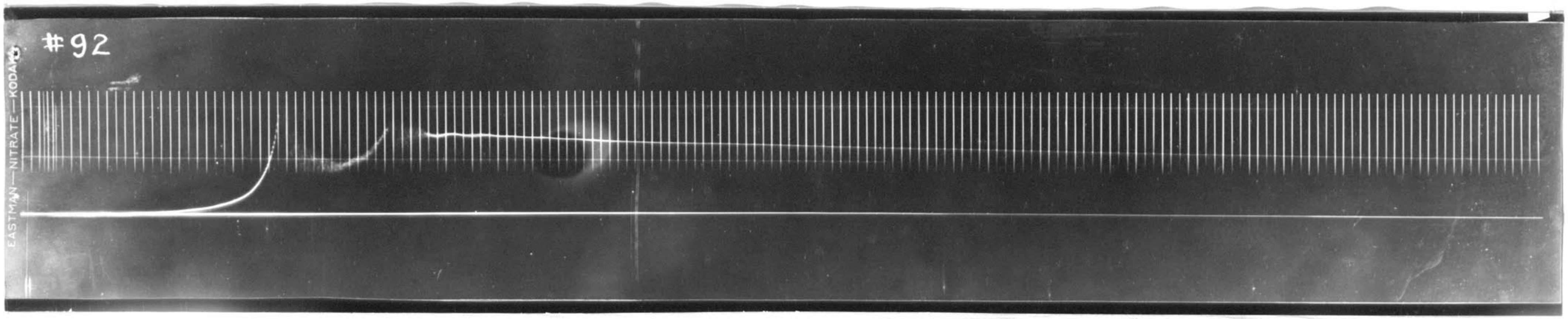


Figure 49

Run 92

Air Pressure = 100 gage.

Pi = 6.7 cm. Hg;
P_f = 304 cm. Hg.

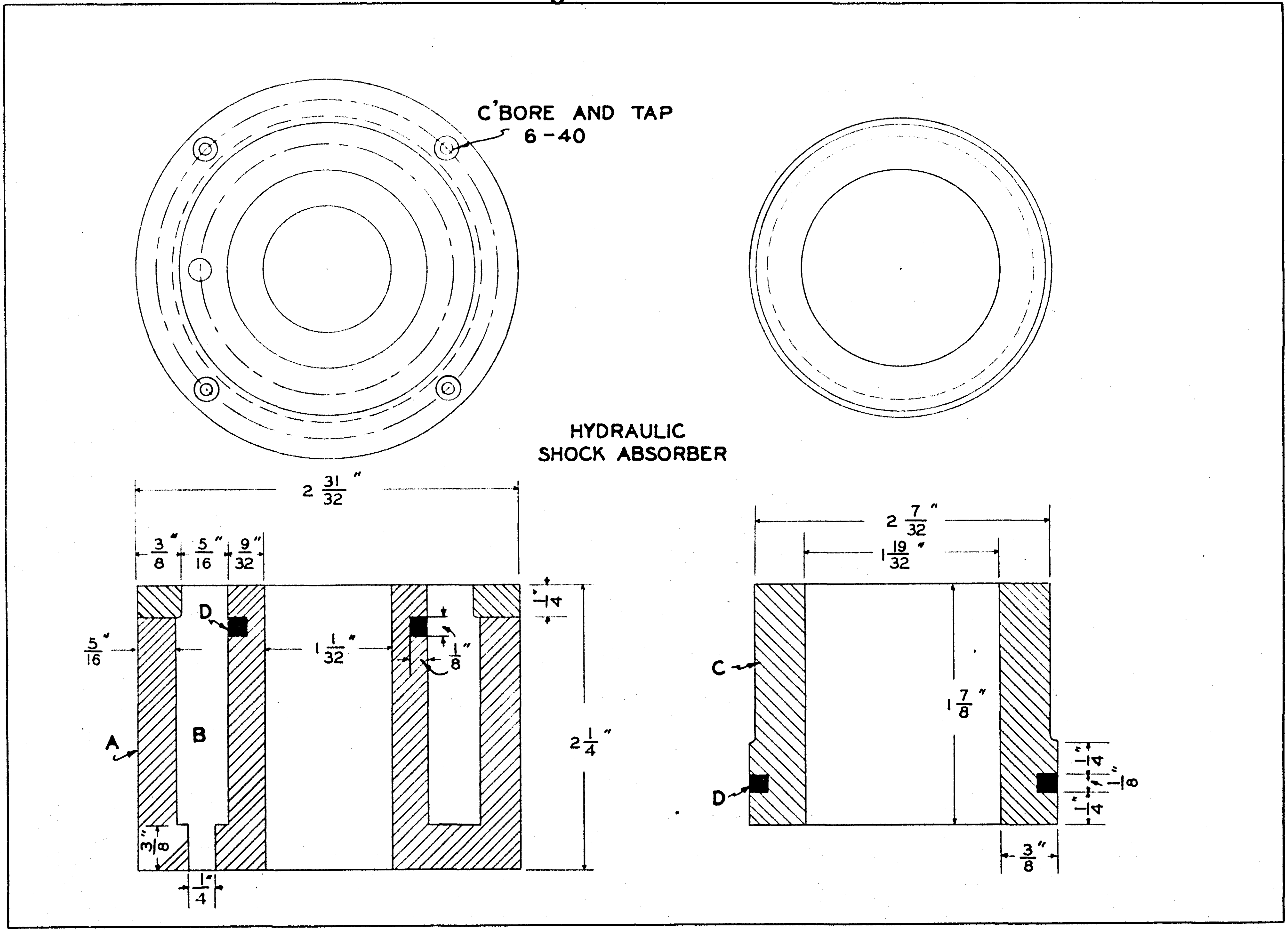
No shock absorber
Time of compression =
0.054 sec.

Corrugated diaphragm indicator (0.014" thick) gas in the reaction chamber has to be compressed to a final volume suddenly and there must be reasonable definiteness as to the magnitude of this volume prior to the experiment. Thus the absorber must be quick-acting as well as constant in its range of action. However, the impact velocity of the plunger may vary and the absorber must adapt itself to this variation. No less than five types of absorbers have been considered, and two types actually used in the experimental work. In addition to the use of absorbers, the attempt was made to eliminate rebound either by changing the velocity at impact without changing the time of compression, or by increasing the resisting gas pressure, or both. These modifications and the absorbers will be taken up in the order in which they were tested.

.1) Hydraulic Shock Absorber.

This type of absorber is the first that was tried and the arrangement is that shown in Fig. 50. The cylinder, A, with a central hole, for the piston rod and an external diameter such that when it is securely fastened to the stopping collar with screws the upper cylinder can be screwed readily into the collar has an annular cavity, B, extending almost its whole length. A sleeve,

Figure 50


C'BORE AND TAP
6-40
HYDRAULIC
SHOCK ABSORBER
2 31/32"
3/8"
5/16"
9/32"
1/4"
D
5/16"
1 1/32"
1/8"
A
B
2 1/4"
3/8"
1/4"
2 7/32"
1 19/32"
C
1 7/8"
1/4"
1/8"
1/4"
D
3/8"

C, slides in the annular space and has a range of one inch total motion. A hole in the bottom of the annular space connects through a hole in the collar to the outside of the latter so that liquid from a reservoir that is fastened to the collar may be forced in or out of the annular space as the sleeve is moved. Cast iron piston rings, D, D, are usedfor packing and the sleeve is held by an offset on its outer surface and a collar on the top of the main cylinder. Glycerine is used as the liquid for the brake.

The results obtained with this brake were not satisfactory because there appeared on all of the records a wave of very low frequency such as is shown in Fig. 51, and which persisted unchanged regardless of attempts to vary it by making slight changes in the recording mechanism, or in other parts of the apparatus. The general shape of the curve suggests, however, that it is a piston-rebound effect. This type of absorber is subject to little control for work of this kind. The fixed orifice necessarily imposes a variable rate of deceleration with a very high initial pressure. A better type would have a variable orifice and an absorber of this kind was designed but never constructed. The details are shown in Fig. 50-A.

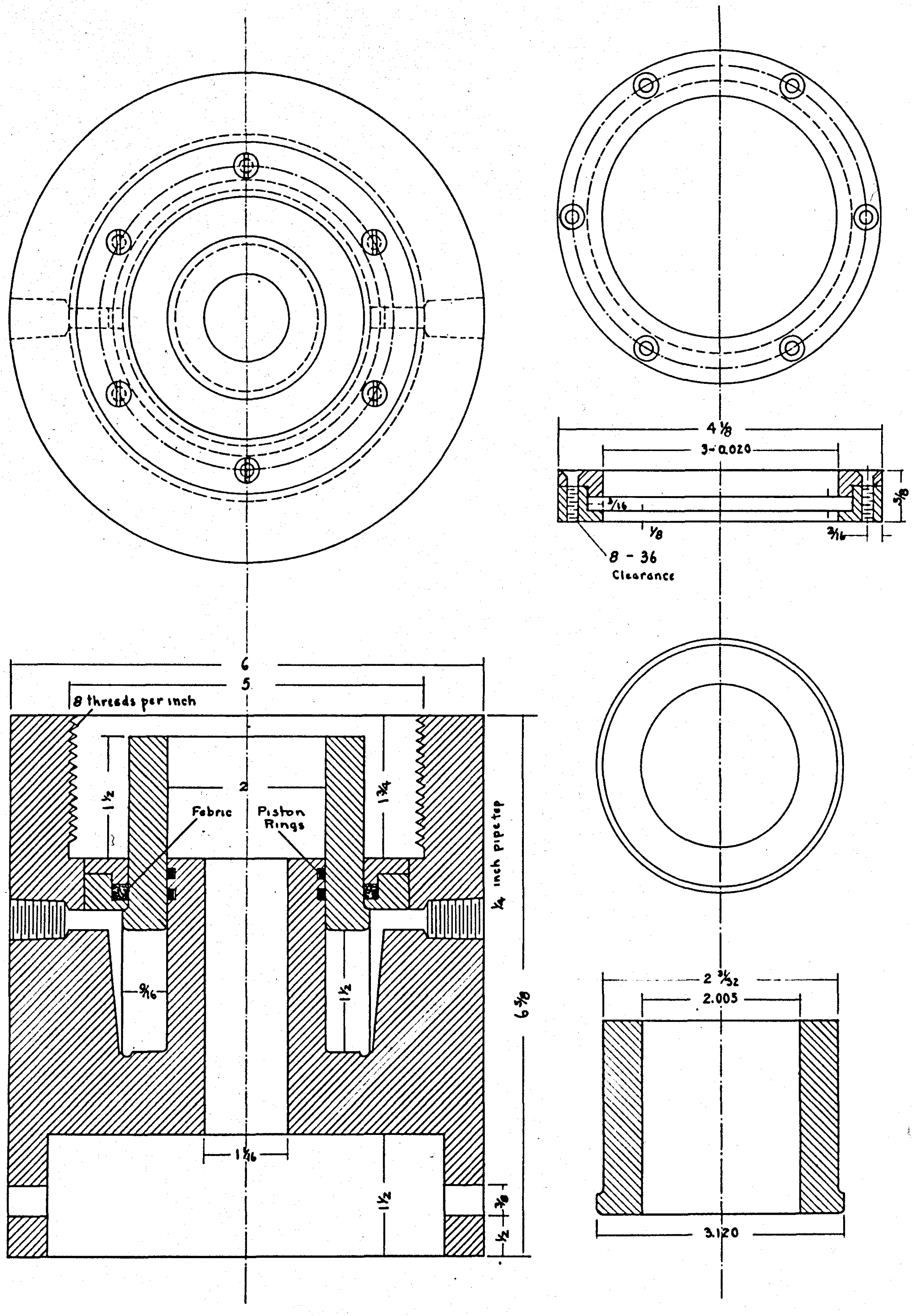
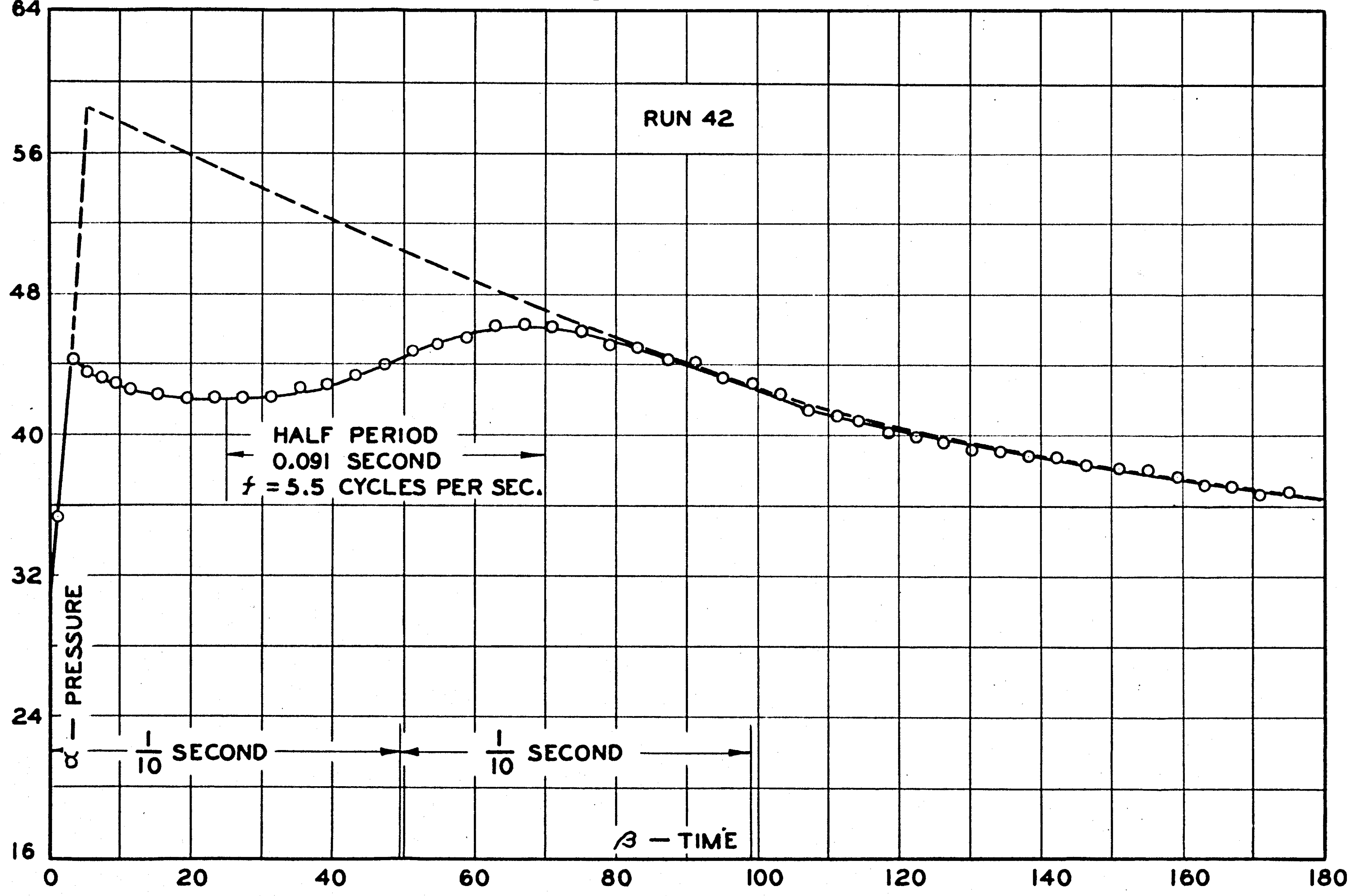


Figure 50 - A

Hydraulic Brake	M.I.T.
Machine Steel	Fuel + Gas Eng'rg.
	V.C.Smith- 4-4-29.

Figure 51


RUN 42
HALF PERIOD
0.091 SECOND
f = 5.5 CYCLES PER SEC.
α — PRESSURE
1/10 SECOND
1/10 SECOND
β — TIME
64
56
48
40
32
24
16
0
20
40
60
80
100
120
140
160
180

.2) Soft Metal Cone Absorber.

In the second type of absorber that has been used for this work the energy in the plunger is dissipated by deforming metal cones, the number, size, shape and material of which may be varied. The metals tested were lead, solder, and copper, but lead has been used chiefly. The scheme that was adopted for this absorber is shown in Fig. 52. A steel collar, A, which can be easily placed on the stopping collar, is drilled and counterbored. The metal cones, B, are placed in the holes as shown in the diagram so that the plunger head strikes them directly as it completes its stroke. Two schemes were tested: a) the volume of the counterbore is greater than the volume of the cone; b) the volume of the counterbore is less than the volume of the metal cone. Results that have been obtained with both types of collars will be given.

.3) The Effect of the Air Pressure and Volume.

It has been mentioned that an attempt was made to supplement the shock absorber action in eliminating rebound by reducing the velocity at impact without changing the time of compression, or by increasing the resisting pressure for the same velocity at impact, or by both. Several cylinder arrangements have been used for these tests. These arrangements were as follows:

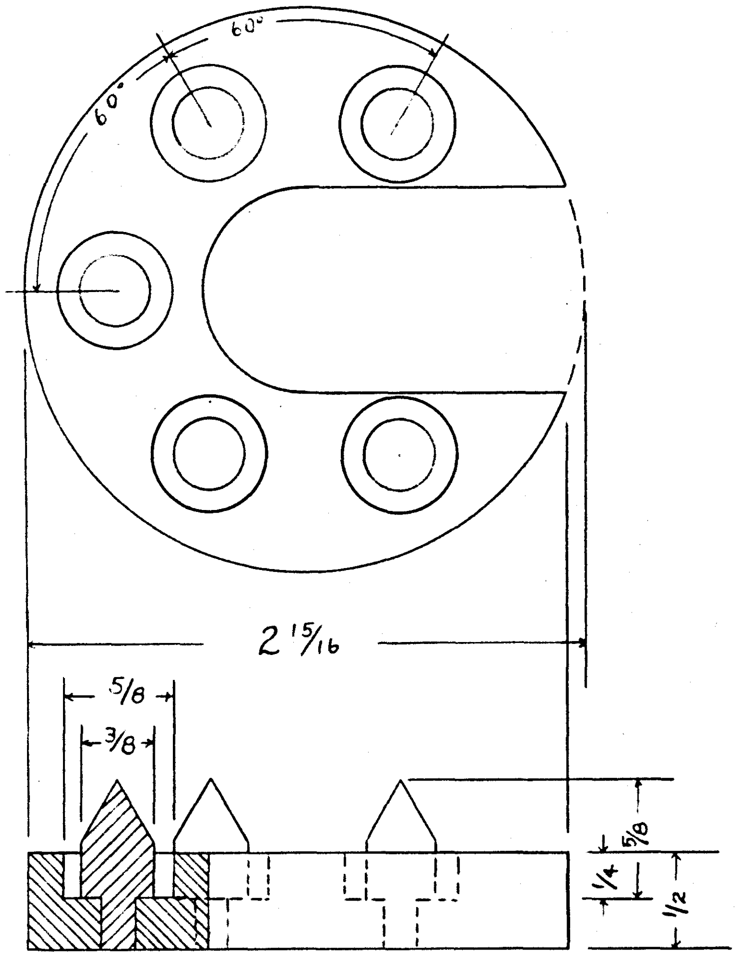
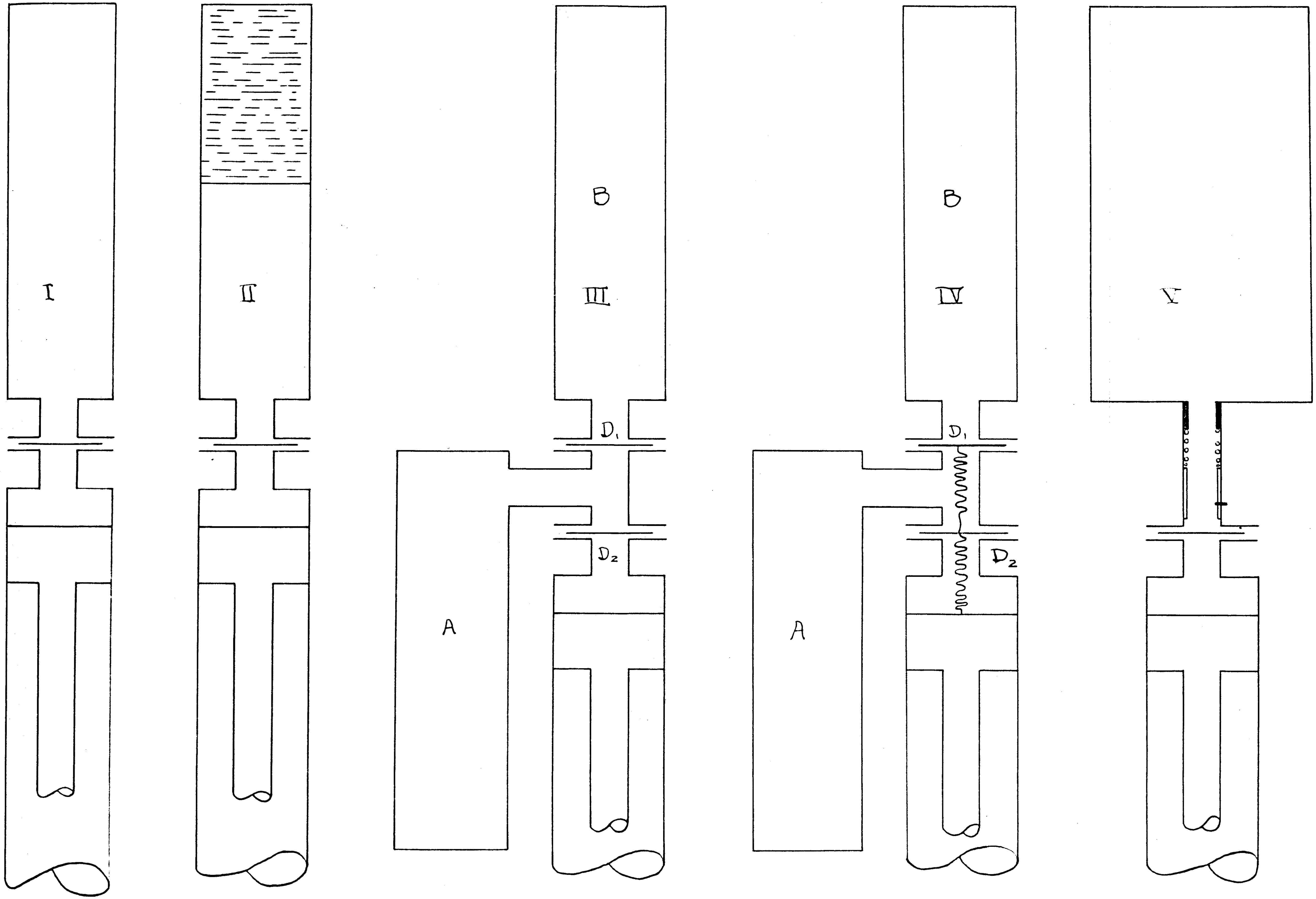


Fig. 52

Mass Inst. of Technology
Fuel and Gas Engineering
Collar and Cones for Shock
V.C Smith 2|25|30

The diagrammatic sketches shown in Fig. 53 represent the methods that have been used for the air cylinders. I and II represent conditions for large changes in initial volume and pressure in the air cylinders. For the same time of compression, the pressure must be higher in II than in I, consequently the velocity would be higher during the first part of the stroke and lower during the latter part. The energy to be dissipated at the end of the stroke varies as the square of the final velocity and it may be expected that the tendency to rebound would be less in II.

Schemes III and IV were adopted to apply a high pressure to the piston at the end of its stroke, the time of application being such that the force does not increase the piston velocity but merely resists rebound. In both cases air pressure is built up in cylinder, B, to some point not exceeding the bursting strength of diaphragm D_1; diaphragm D_2 is chosen to give the desired time of compression on bursting, and pressure is built up in cylinder, A, to any point exceeding its value after expansion but not exceeding its bursting strength. In Case III, pressure is then built up in B exactly to a point where the pressure difference between the air cylinders equals the bursting strength of D_1



Diagrammatic Sketches of Air Cylinders

Fig. [redacted] 53

after the expansion in the lower chamber.

The above method is difficult to carry out due to the close regulation necessary for successful operation. Satisfactory results could never be obtained and a more positive method such as IV is necessary. In this case close regulation is unnecessary except in the length of the chain connecting D_1 with the piston. A safe factor was allowed on the bursting strength of D_1 so that it broke only when subjected to the sudden tension placed upon it by the chain when the piston was about two inches from the end of its stroke. Fig. 54 shows a result obtained by this method and it is noted that there is little rebound. However, operation is difficult with this scheme and a final one shown as V was adopted. It was thought that scheme V would have permitted a relatively high final pressure differing but little from the initial. Actually the initial pressure required for times of compression equal to the other cases was so low that the final pressure was too low to be very effective in reducing rebound. This is apparent from the series of runs carried out as follows:

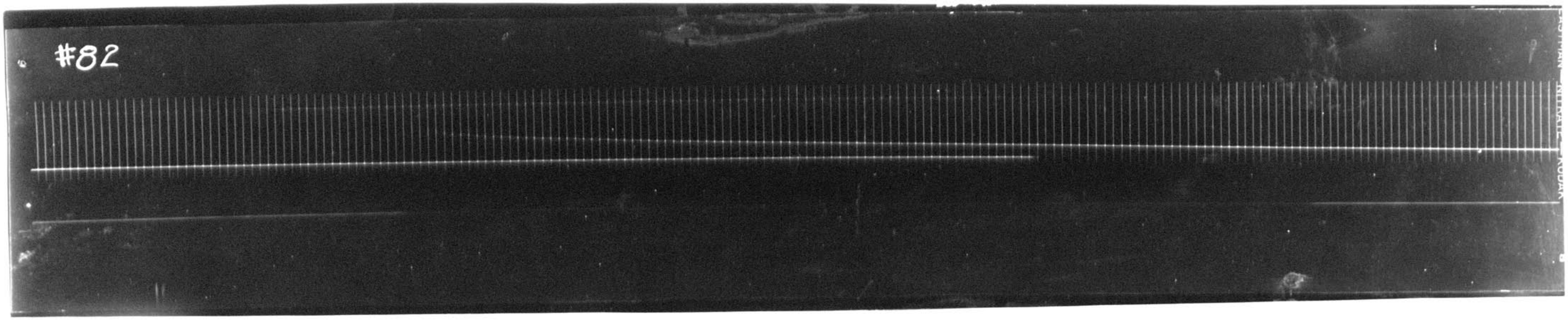


Figure 54

Run 82. P_A = 220 lb. per sq. in.
P_B = 480 " " " "
2 lead cones

$V_A = V_B$ = 1750 cc.
Pi = 6.7 cm. Hg;
Pf = 304 cm. Hg.
Indicator - 0.014 corrugated diaphragm

Run	Air Pressure Lb. per sq. in.	Lead Cones	Remarks
85	125	5	Complete deformation of cones
86	100	3	4 mm. from complete deformation
88	110	3	Complete deformation
89	105	3	Complete deformation
90	110	5	Complete deformation
91	105	5	Complete deformation

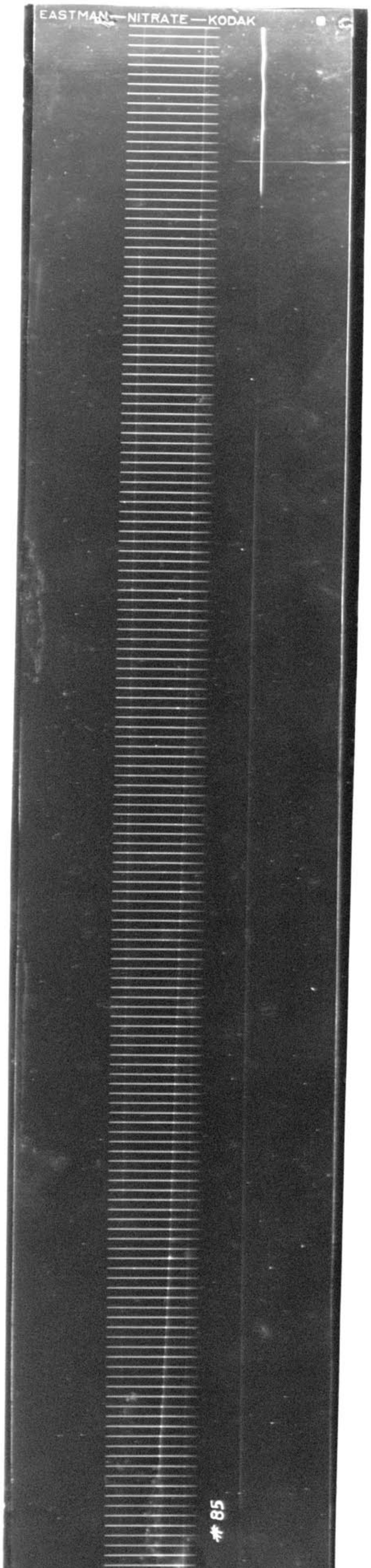
Initial pressure = 6.7 cm. Hg.

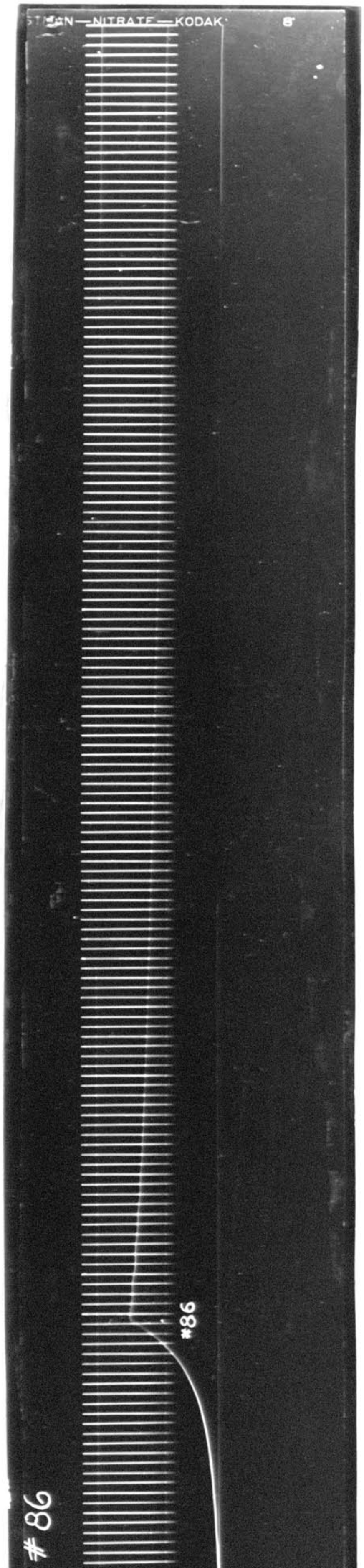
Final pressure = 304 " "

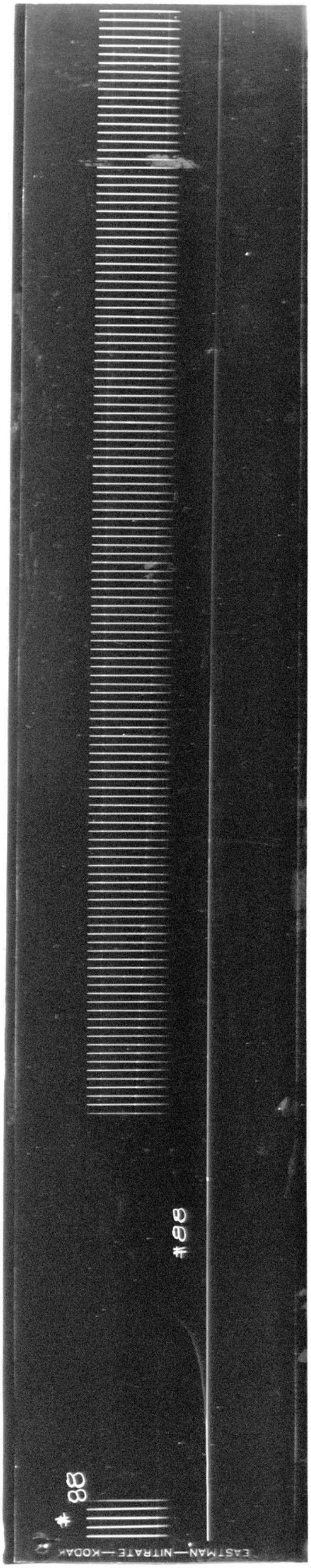
Indicator - 0.014 inch corrugated diaphragm.

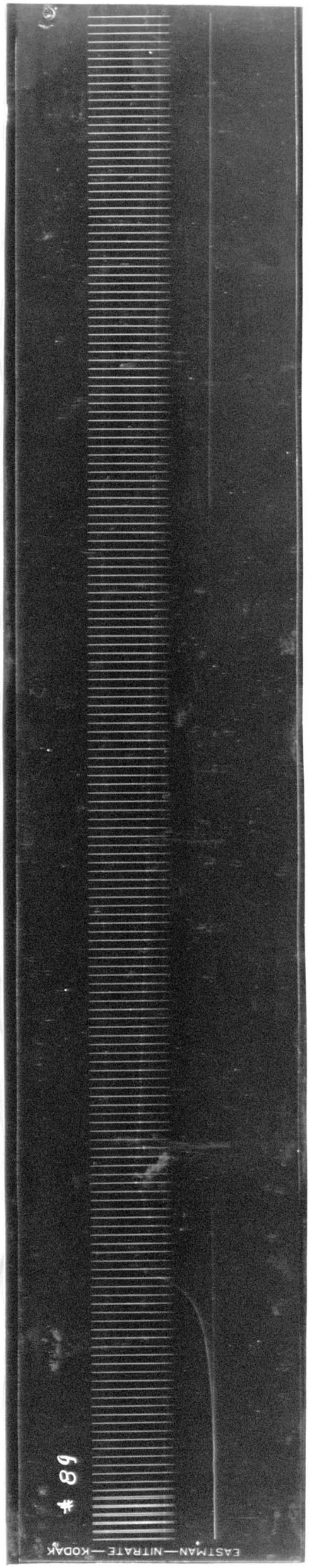
It is seen that except in Run 86 where deformation was incomplete, the rebound was of varying intensity depending on the pressure, and that an increase in the number of cones had little effect upon the results. In Run 86 the time of compression was 0.07 sec. and it was about 0.055 sec. for the others.

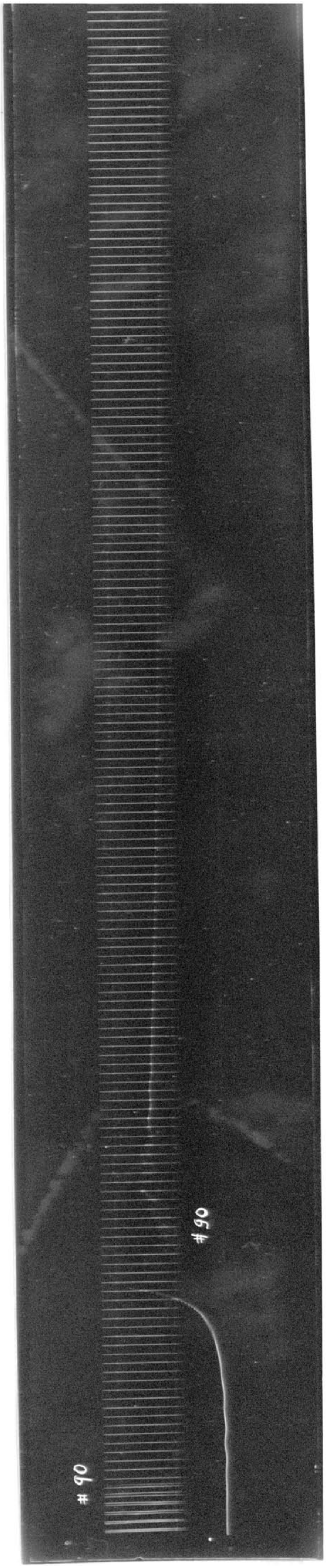
When the volume of the counterbore is less than the volume of the cone the steel head of the piston can never come in contact with the steel stopping collar. This means that the more elastic type of impact which gives rebound is avoided. However, there is introduced

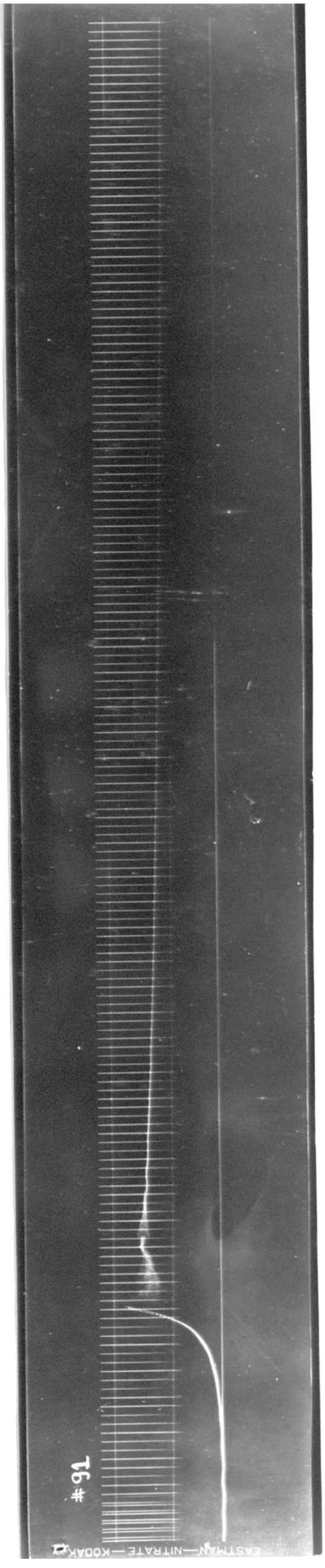

EASTMAN—NITRATE—KODAK
#85
#85


STMAN—NITRATE—KODAK
#86
#86


#88
#88
EASTMAN—NITRATE—KODAK


#89
EASTMAN—NITRATE—KODAK


#90
#90


#91
EASTMAN—NITRATE—KODAK

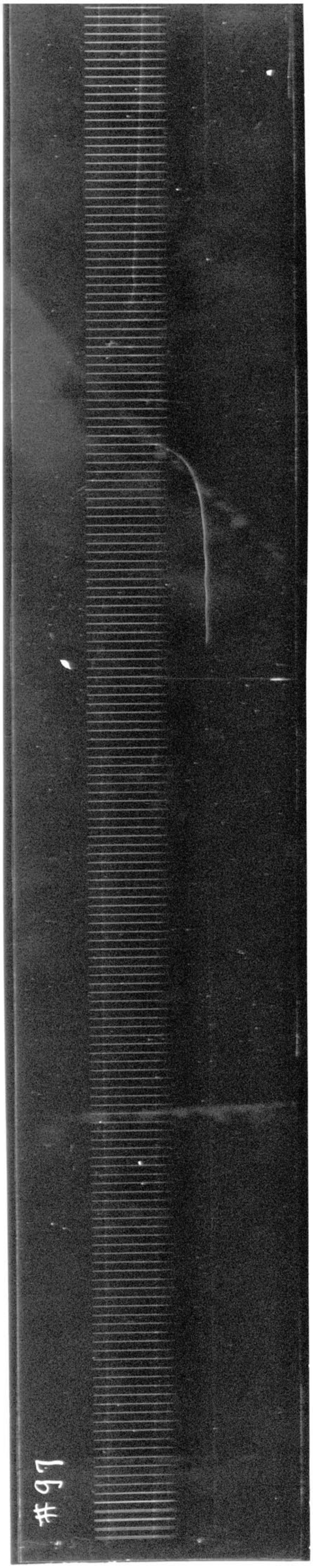
the uncertainty of a final definite piston position which prevents advance specification of the final temperature resulting from a compression. This may be a serious handicap if the ignition temperature is to be approached closely but not actually attained.

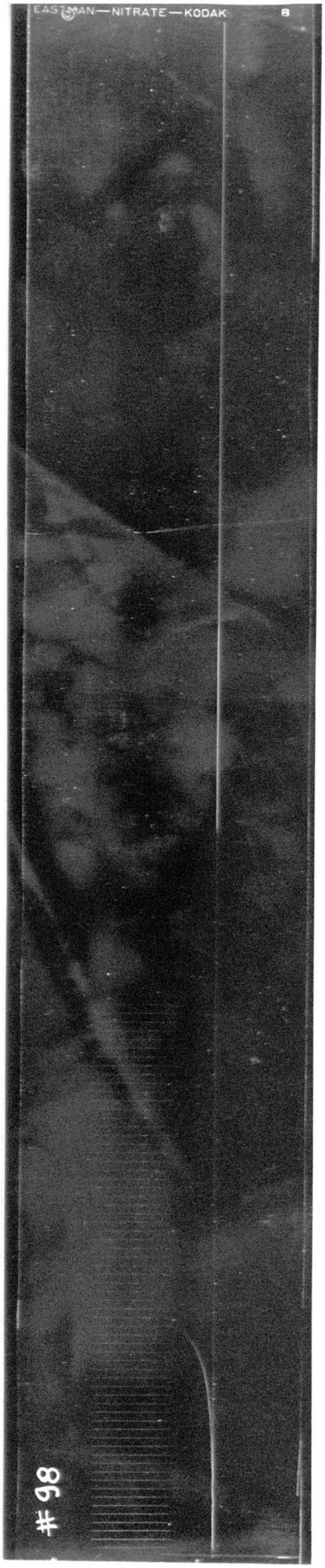
Many runs have been made with this absorber and there is, even in this type, a tendency for the piston to rebound. Runs 97-102, which illustrate this, were made under the following conditions:

Run	Air Pressure Lb. per sq. in.	Clearance between Piston and Stop	Time of Compression
97	100	0.4 mm.	0.055 sec.
98	92	1.2	0.058
99	87.3	1.0	0.065
100	81.7	1.0	0.067
101	70	4.2	0.075
102	75	1.7	0.065 + ?

Initial pressure = 6.7 cm. Hg.
Final " = 304 " "
Indicator - 0.014 corrugated diaphragm.

These runs show clearly that there is in any case a tendency for the plunger to rebound and that this tendency is less the longer the time of compression. This problem of piston rebound cannot be said to be completely solved and other work must be done.


#97



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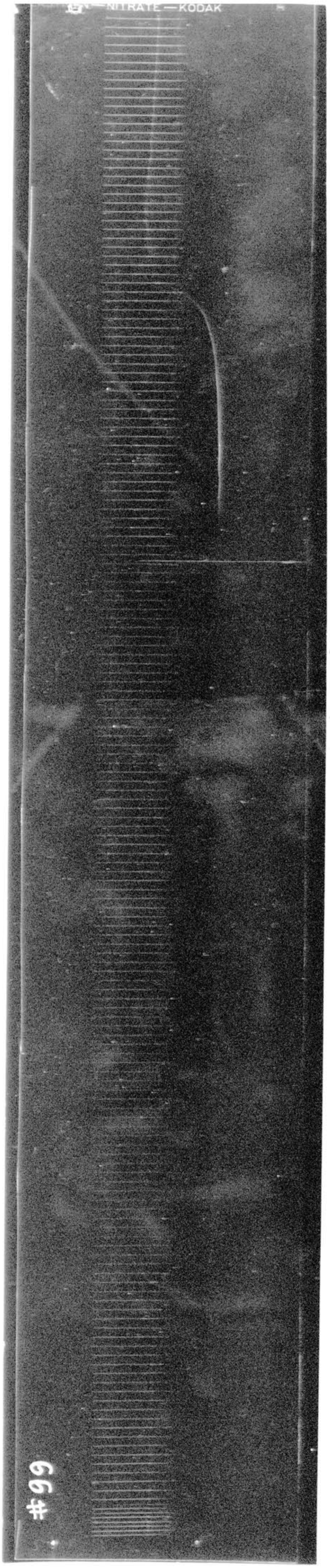
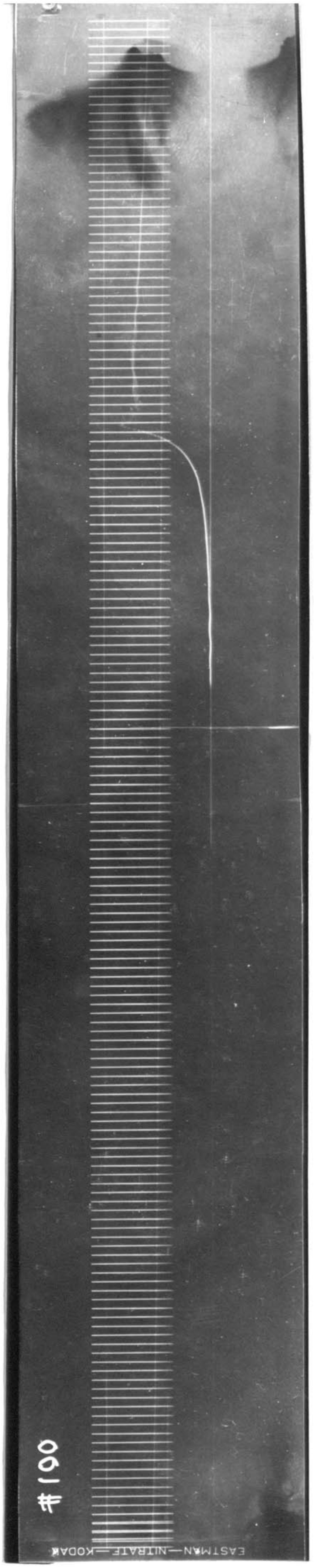

NITRATE—KODAK
#99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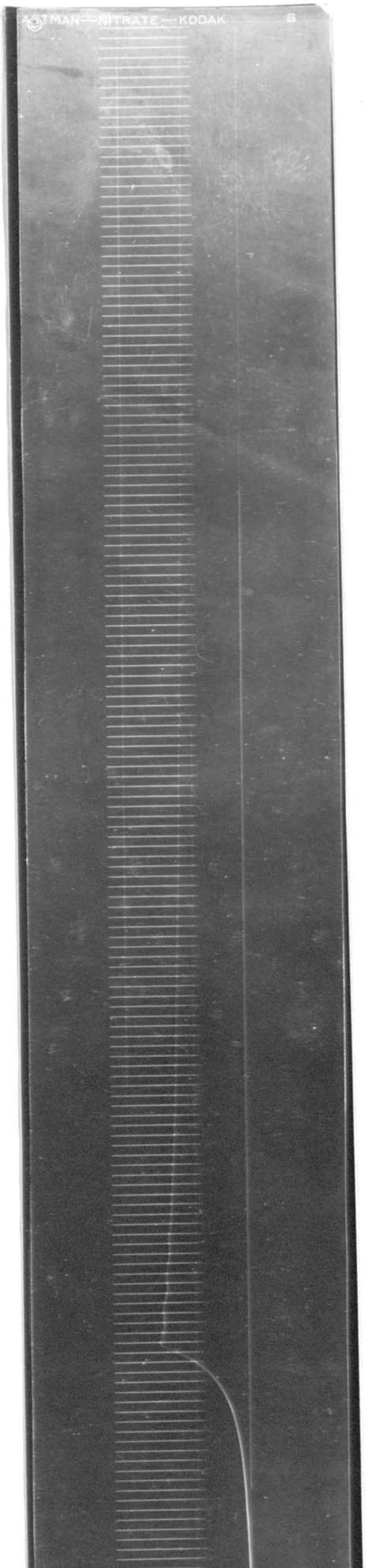
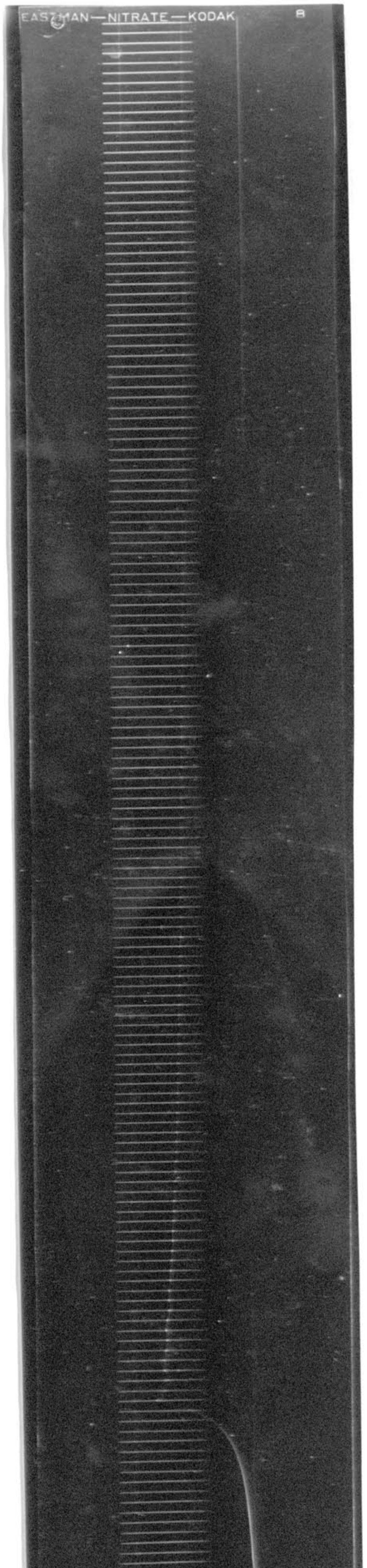
EASTMAN—NITRATE—KODAK


EASTMAN—NITRATE—KODAK 8
#101


EASTMAN—NITRATE—KODAK 8
#102

b) Other Sources of Vibration.

Piston rebound is not the only effect of the sudden release of the energy in the plunger when it is brought to a sudden stop. Some of the other possible effects will now be considered.

It may be expected that the high energy in a piston traveling at the speed at which the one travels in this work is capable of introducing vibrations many of which are difficult to discover and eliminate. This has been the case in this work. It has been stated already that it was believed beforehand that an optical indicator is not the most suitable kind for this work. The results indicate that this is true, but not so much for the reason that would normally be given, namely, that the indicator element is sensitive to shock. This latter could very well be serious but there are other shock effects that have been found to supersede it. Two of these effects are: a) vibration of the light source; b) relative motion between the indicator and light and between the indicator and camera.

The method of eliminating vibration in the light source depends upon whether the vibration is in the filament only or in the body of the lamp. Flashing the lamp at the time of shock tends to accentuate the vibration of the filament and vibration from this cause can be eliminated by using a lens and slit in conjunction with the filament. Elimination of vibration in the body of the lamp because of motion in the housing can be effected by mounting the housing in a shock-proof base. The latter course has been followed to determine the source of the vibrations. The method consisted of placing the lamp first of all in a socket which allowed no vibration; the socket was in turn rigidly fastened in a 150-pound broad-base casting which was separated from the base of the compression apparatus, being placed on the floor but resting on four wads of felt. This method is effective in removing some of the vibrations as may be seen by comparing Run 114 shown in Fig. 55 with the series of runs that have just been presented. It is seen that a low frequency vibration which begins at the start of the compression and persists long after the maximum pressure is reached is absent from Run 114. There remain, however, vibrations of high frequency in the portion of the record just after the completion of the stroke.

These vibrations are attributed to the relative motion between the indicator and camera and lamp. Their

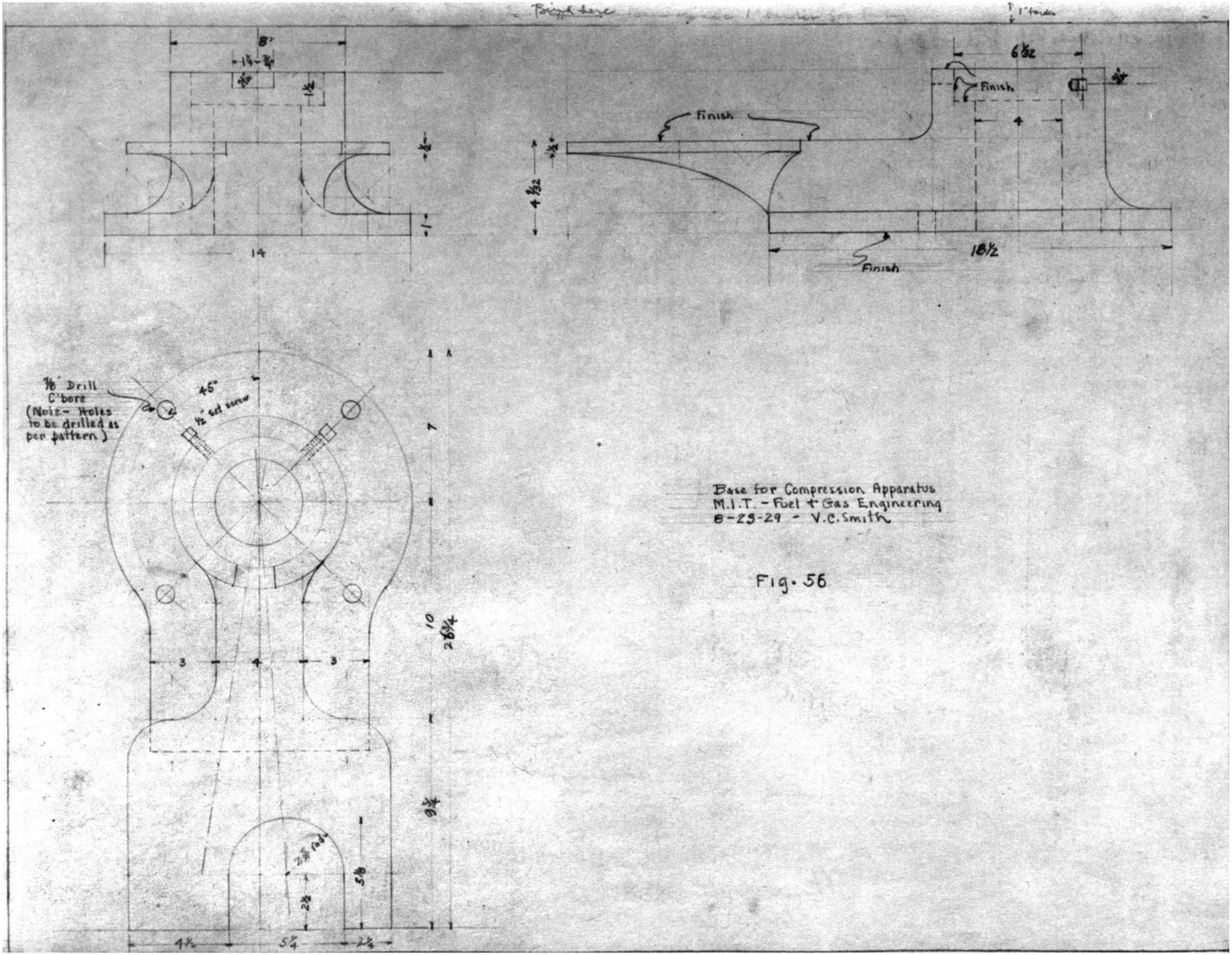
Figure 55

Run 114

Air Pressure = 90 lb. gage
Pi = 6.7 cm. Hg;
Pf = 304 cm. Hg.

5 lead cones; 1.75 mm clearance

Indicator - 0.018 corrugated diaphragm



Base for Compression Apparatus
M.I.T. - Fuel + Gas Engineering
8-29-29 - V.C. Smith

Fig. 56

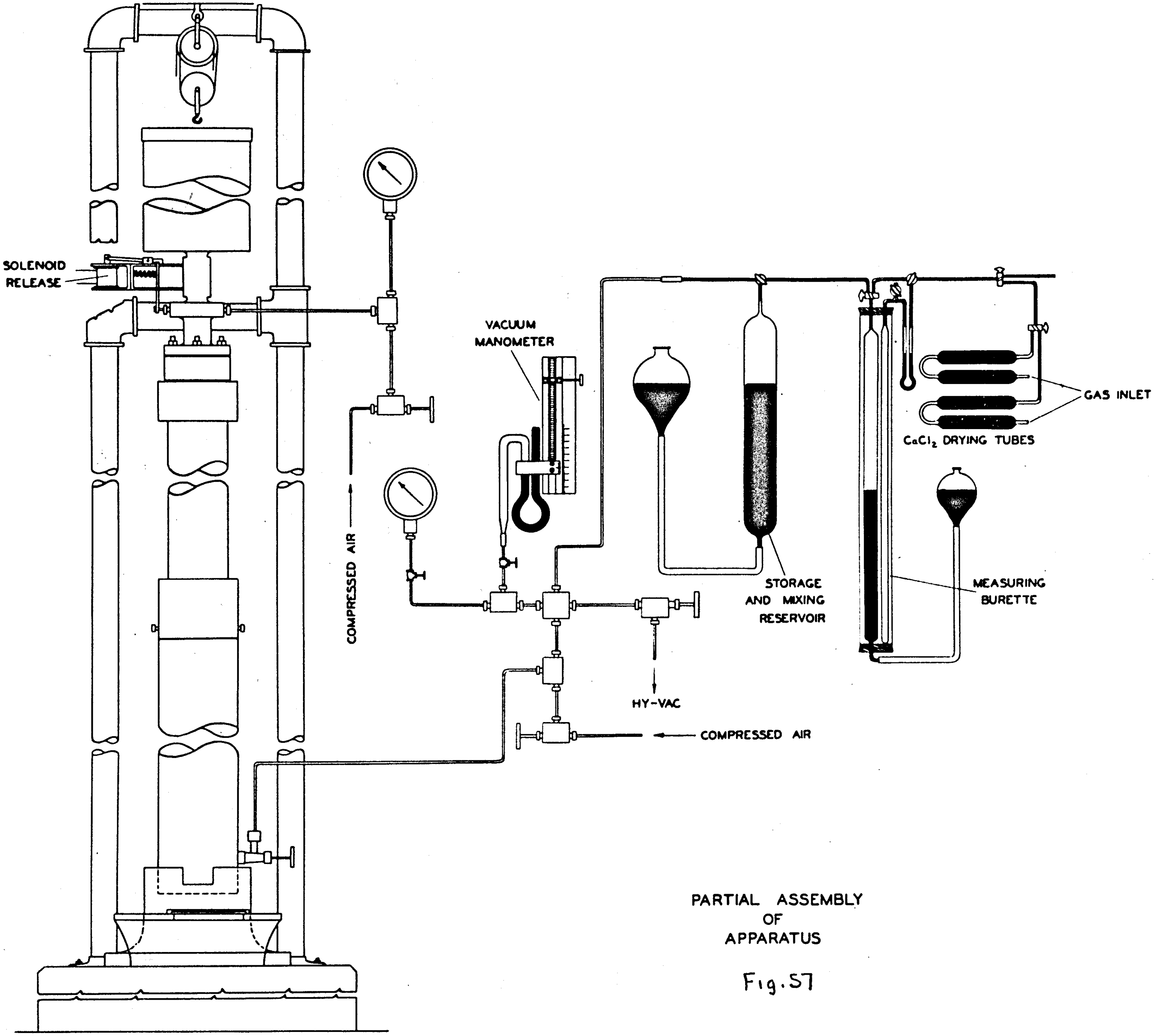
elimination can be effected only by mounting the camera and light source on the base of the compression apparatus in such a manner that there can be no relative motion. This was attempted when the type of base shown in Fig. 56 was constructed. Although this base has been in use during all of the later runs its effectiveness was not complete either because of failure of the camera to execute motions similar to the base or because of the ineffectiveness of the lamp mount.

6) Some Auxiliary Parts of the Apparatus.

In order to assure quantitative results, care has been taken to provide apparatus for accurate measurement of: a) gas quantity and composition; b) photographic records. These are discussed in the following paragraphs.

a) Gas Measuring Apparatus.

The uncertain effect of water vapor in many reactions requires that its amount in all reactions be accurately known. To assure complete drying, a long drying tube is used when the gas is passed into the measuring burette. Also, to have a completely homogeneous and similar mixture for initial and duplicate experimentation, the measuring apparatus contains an auxiliary mixing and storing chamber. Moreover,



PARTIAL ASSEMBLY
OF
APPARATUS

Fig. 57

the exact determination of the initial pressure and volume in the reaction cylinder is an absolute necessity for accurate work. A special monometer has been developed for this purpose with which the initial pressure is readily determined to one-tenth millimeter. The volume of the reaction cylinder is determined by evacuation and filling from a calibrated gas burette. These parts are shown in the partial assembly of the apparatus given in Fig. 57.

b) Film Reading Device.

The method adopted for reading the films accurately is shown in the photograph as Fig. 58. The films are placed on the light box and viewed with diffuse transmitted light. The measurements are made with a microscope mechanical stage, the vertical scale of which permits reading to 1/50 mm.

7) Complete Assembly.

The complete assembly of the apparatus is presented by a photograph shown in Fig. 59.

The wiring diagram for the whole assembly is shown in Fig. 60. The arrangement of the latter is such that the motion of the camera is synchronized with the motion of the piston through a synchronizing switch.

Fig. 58

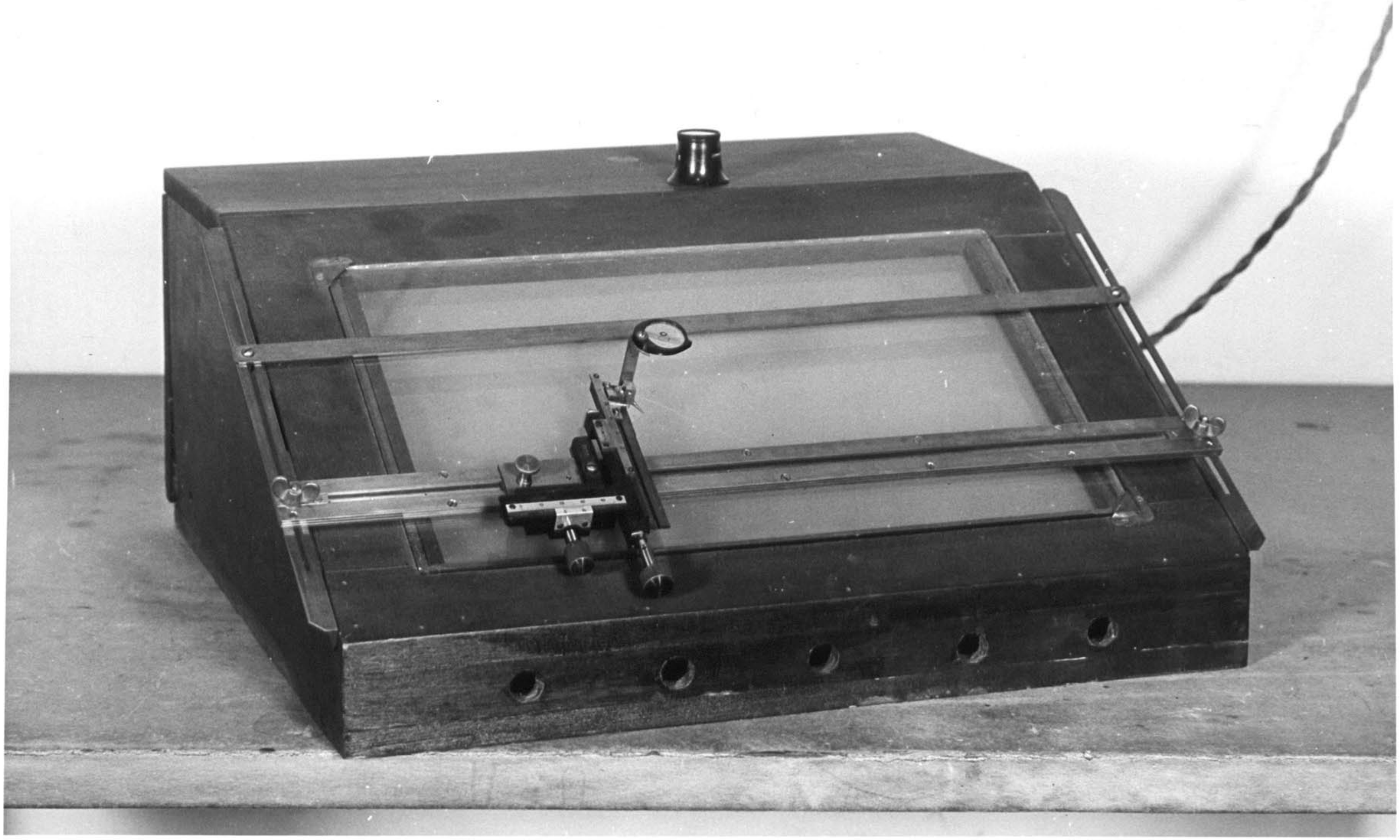
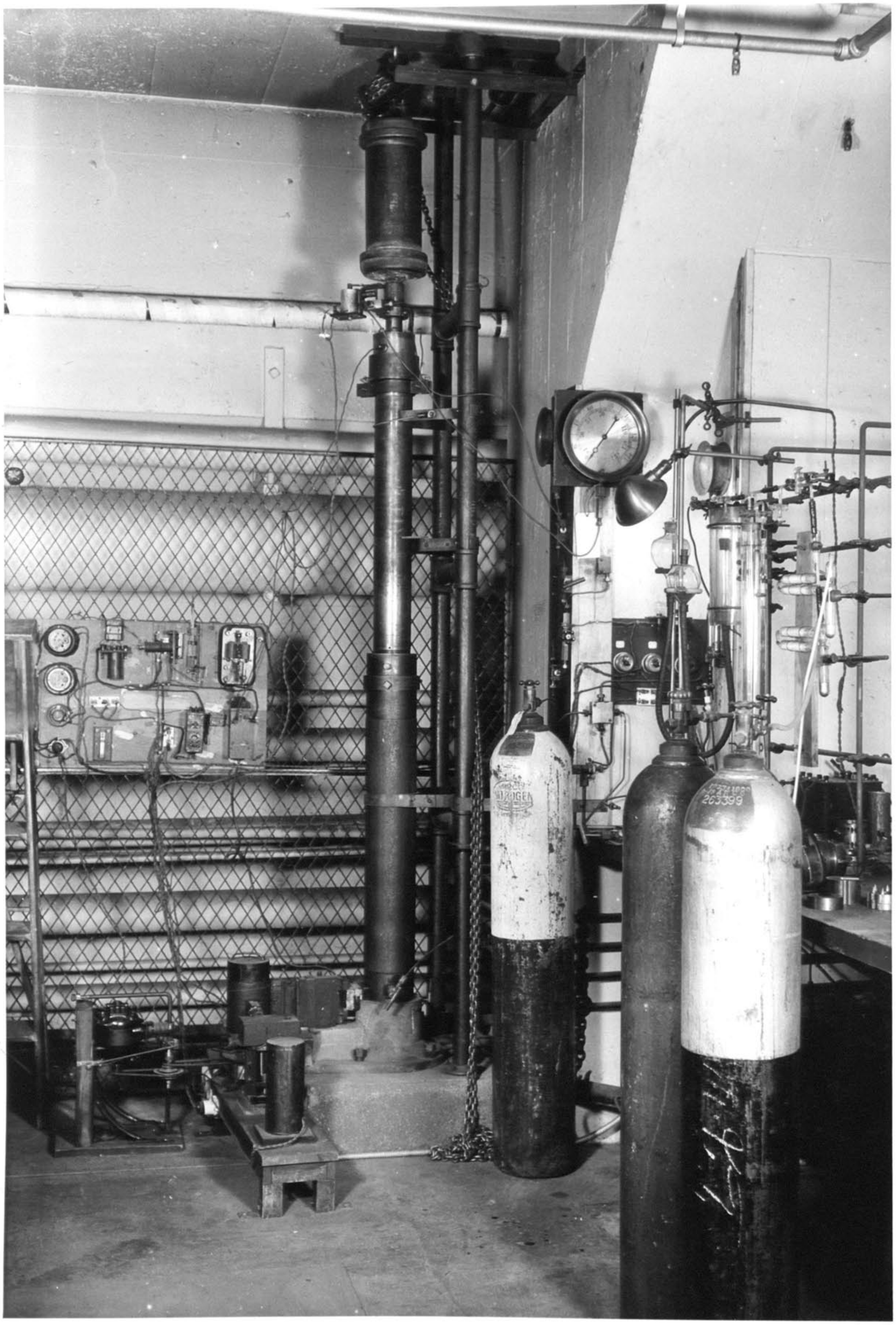
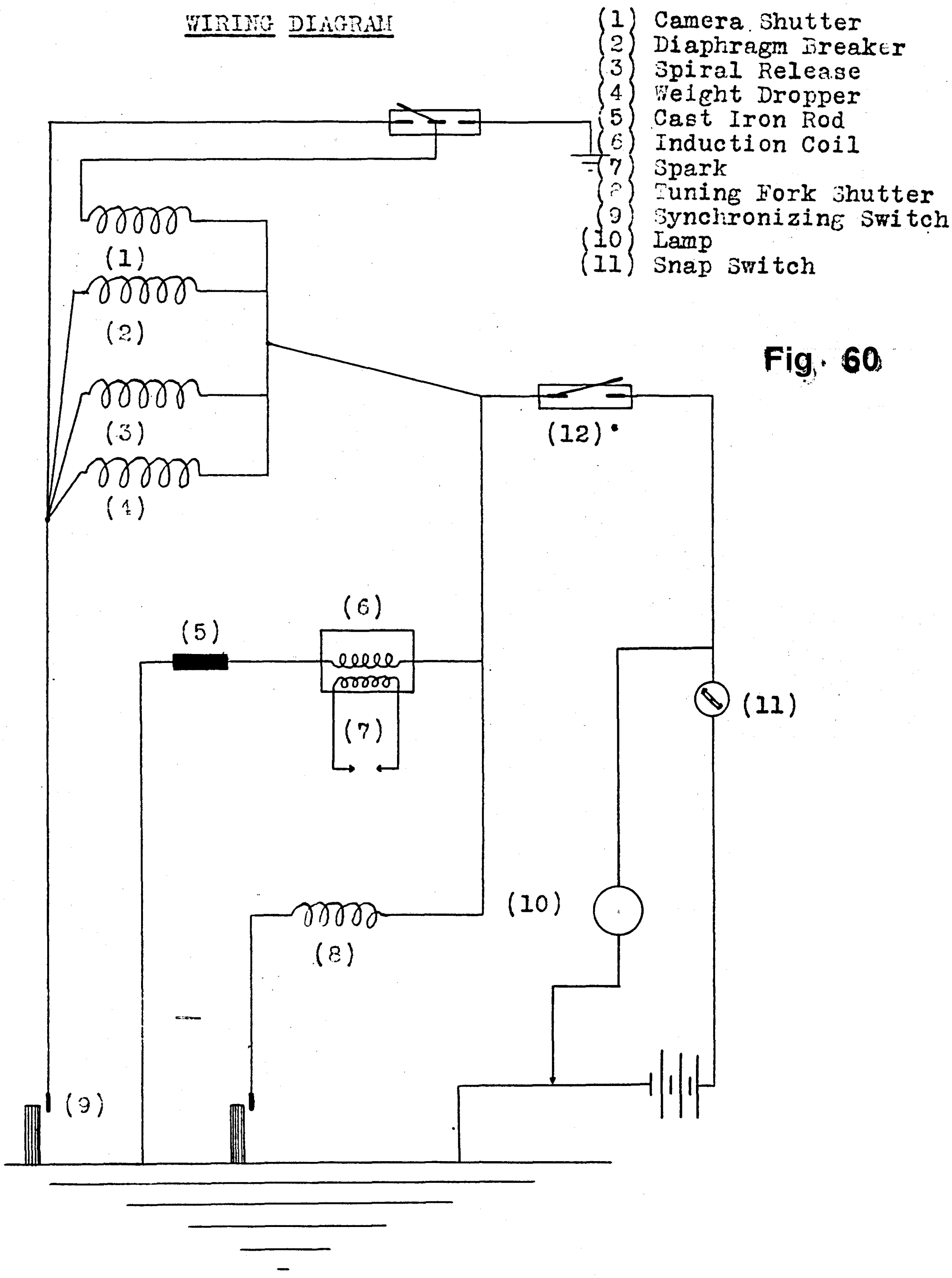


Fig. 59





WIRING DIAGRAM

(1) Camera Shutter
(2) Diaphragm Breaker
(3) Spiral Release
(4) Weight Dropper
(5) Cast Iron Rod
(6) Induction Coil
(7) Spark
(8) Tuning Fork Shutter
(9) Synchronizing Switch
(10) Lamp
(11) Snap Switch

Fig. 60

PART IV.

CONCLUSIONS.

Conclusions.

The conclusions that have been reached as a result of this research have been stated not only in the abstract but at appropriate places in the body of the discussion. Nevertheless, the general conclusions may be restated.

A method has been developed for determining the rate of reaction in reacting gas mixtures under homogeneous conditions.

The principle of the method is simple and consists merely of rapidly compressing the gas mixture in a cold cylinder to a point where the temperature is sufficiently elevated to produce measurable reaction.

If the volume is held constant after the temperature is thus raised, the fall in pressure of the gas mixture will be less than the fall in pressure of a non-reacting mixture otherwise similar.

The difference in this rate of fall in pressure has been shown to be a quantitative index of the rate of reaction in the system.

The simple principle of the method is not readily realized in an experimental apparatus because of the rigid requirements of the quantitative method.

The chief difficulty lies in the dissipation of the energy of the plunger when it is driven into the cylinder. The difficulty has been reduced to an undisturbing point but has not been entirely eliminated.

In all other respects the method is satisfactory and with auxiliary parts that have been developed in its perfection, it is capable of application to the quantitative study of reaction velocity under the only conditions that have yet been found to be homogeneous.

PART V.

APPENDICES.

APPENDIX I

The Homogeneous Reaction Between Hydrogen and Oxygen

The advantages of beginning the study of combustion mechanism with the simplest gaseous mixtures are obvious. Hydrogen and oxygen are not only simple, but their reaction is of great theoretical and practical importance.

Although there are few gaseous reactions of more fundamental importance than that between hydrogen and oxygen, it can hardly be said that the kinetics of this combination are well understood. Many investigations have been made on the catalytic reaction which occurs when these gases are in contact with various surfaces, and of the phenomena accompanying the production of flame or explosion in the gas. Comparatively little is known about the homogeneous reaction and the conditions governing its rate, because while flames and explosions are in a sense homogeneous, there are other factors which enter to influence the change.

Bodenstein[76] following up some work begun by Victor Meyer made a series of experiments by streaming the two gases through thermostatically heated porcelain bulbs and on analyzing the products was able to conclude that the reaction was of the third order following the equation

$$\frac{d[H_2O]}{d\theta} = k[H_2]^2[O_2]$$

The rate was found to differ with different vessels, however, and he concluded that reaction was confined entirely to the surface of the bulb.

Bone and Wheeler[77] circulated mixtures of these gases at relatively low temperatures for long periods, measured the rate of slow surface combination in contact with various materials, including porcelain, and found that under these conditions the reaction was of the first order.

Comparing these results with those of Bodenstein it was concluded that the porcelain surface is covered with absorbed molecules, so that pressure has comparatively small effect on the reaction, hence the apparent first order. With increased temperature and diminished adsorption there would be increased chance for two molecules of hydrogen and one of oxygen to be so arranged at the surface to be proportional to the concentration product $[H_2]^2[O_2]$ in the gas phase.

Rowe[78] suggested, however, that Bodenstein's third order reaction really took place more in the gas phase than Bodenstein had supposed. He carried out experiments of a similar kind, but diluted the gases with steam and worked over a wider range of temperatures. His results showed variable, - but approaching third order - as the temperature increased.

Neither Bodenstein nor Rowe refer to the influence of concentration of steam on the course of reaction.

Falk[79] attempted to determine the mechanism and rate of reaction from ignition temperatures with sudden compression but his procedure was faulty.

Fiezel[80] studied the ignition temperatures of H_2 - O_2 mixtures at different temperatures and attempted to determine the velocity constant at different temperatures for knall-gas mixtures but his method was so crude that these were meaningless.

Hinselwood and Thompson[81] have examined the complete course of the combination of H_2 and O_2, at constant volume and temperature, over the range extending from the purely catalytic surface reaction up as nearly as possible to the point where the reaction ceased to be isothermal and became explosive. In the last 50° C of this range a reaction comes into prominence which is different from the low order, heterogeneous reaction. It is of high but variable order, the influence of pressure being on the average approximately of the fourth order; it is strongly catalyzed by steam, and has a high temperature coefficient. At high temperatures the normal positive catalytic effect of the walls of the reaction bulb gives way to a negative effect, which may be due to the catalytic destruction of an autocatalyst for the principal reaction, or the interruption of "reaction chains," or to both causes.

Gibson and Hinselwood[82] have continued the previous investigation between 500° and 600° C in porcelain instead of a quartz vessel. It was again found that above 500° a homogeneous reaction of high but variable order, and high temperature coefficient, comes into play. The reaction of high temperature is retarded by increasing the surface exposed to the gases. The rate is approximately proportional to the cube of the hydrogen concentration and to a power of the oxygen concentration greater than unity.

The reaction is very markedly accelerated by steam, but also by gases such as belium, nitrogen and drgan. Thus the steam is not autocatalytic in the ordinary sense.

The results are interpreted by assuming reaction chains to be propagated through the gas. These chains are broken by deactivation of molecules in a heterogeneous reaction at the walls of the vessel, and lengthened by the presence of the inert gases, which increase the time during which the molecules escape contact with the walls. The order of effectiveness of the gases correlated with their respective diffusion coefficients. Oxygen and hydrogen were also capable of exerting an"inert gas effect" in addition to their mass-action effect as participants in the reaction.

Pease and Chesebro[83] confirm the effect of increased surface on the rate of reaction, and likewise attribute it to the interruption of reaction "chains."

Thompson and Hinselwood[84] have examined the rate of reaction of H_2 - O_2 mixtures in the region 500 - 600° C, and found that at low pressures the reaction chains became "non-stationary," and the reaction explosive, between certain definite upper and lower critical pressures. An examination of the effect of temperature, nature and size of vessel, and other factors, on the pressure limits, and a comparison of the conditions governing the propagation of the stable reaction chains at higher pressures with those that determined the unstable chains between the two critical pressure limits, led to the theory that at low concentrations initiation of the explosion is due to hydrogen peroxide. This theory is in agreement with the observations of Gibson and Hinselwood[85] that at 400° C below the ordinary explosion temperatures, hydrogen and oxygen combine very slowly and on the surface of the vessel only.

If, however, small traces of nitrogen peroxide are added, the first additions produce no effect on the rate, but, on continuing, a sharply defined limit is reached beyond which immediate explosion of the gases occurs, on further additions a sharply defined upper limit is reached, beyond which no explosion occurs, but only the very slow reaction already referred to.*

---

*H. B. Dixon had found that nitrogen peroxide lowered the ignition temperature of H_2 in air by about 200° C.

APPENDIX II

Derivation of equation of adiabatic compression of a gas when specific heat is a second degree function of temperature.

$$C_V = \alpha + \beta T + \gamma T^2 \qquad (1)$$

$$C_V \cdot dT = - PdV \qquad (2) \qquad \text{Given}$$

$$PV = RT \qquad (3)$$

$$\frac{(\alpha + \beta T + \gamma T^2)}{\cdot T} dT = - \frac{R}{V} dV \qquad (4)$$

Integrating and setting in the limits T_1 and T_2, and V_1 and V_2,

$$\alpha \ln \frac{T_1}{T_2} + \beta(T_1 - T_2) + \gamma\frac{(T_1^2 - T_2^2)}{2} = R \ln \frac{V_2}{V_1} \qquad (5)$$

$$\alpha + \beta \frac{T_1 - T_2}{\ln \frac{T_1}{T_2}} + \gamma \frac{T_1 - T_2}{\ln \frac{T_1}{T_2}} \cdot \frac{T_1 + T_2}{2} = R \frac{\ln (V_2/V_1)}{\ln (T_1/T_2)} \qquad (6)$$

If we let T_L and T_A represent the logarithimic mean and arithmetic mean, respectively, of T_1 and T_2, we see that the left side of (6) is

$$\alpha + \beta T_L + \gamma \cdot T_L \cdot T_A , \qquad (7)$$

which we may call $C_{V_{ave}}$ if we define the special average by relation (7)

Equation (6) then becomes

$$C_{V_{ave}} = R \frac{\ln(V_2/V_1)}{\ln(T_1/T_2)} \text{ , or}$$

the familiar

$$\frac{V_2}{V_1} \qquad \left(\frac{T_1}{T_2}\right)^{\frac{C_{V_{ave}}}{R}}$$

APPENDIX III

Derivation of Equations for Compression with Cooling by Cylinder Walls.

The following relations are assumed to apply:

$$dQ = N\,Cv\,dT + P\,dV \qquad (1)$$

$$PV = NRT$$

$$PdV + VdP = NR\,dT$$

$$Cv = \alpha + \beta T$$

$$C_p = \lambda + \beta T$$

$$C_p - Cv = \lambda - \alpha = R$$

$$\gamma = C_p/Cv = \frac{\lambda + \beta T}{\alpha + \beta T} = 1 + \frac{R}{Cv}$$

$$R = Cv\,(\gamma - 1)$$

Substituting:

$$NR\,dT = N\,Cv\,(\gamma - 1)\,dT = PdV + VdP$$

$$NCv\,dT = \frac{1}{\gamma - 1}\,(PdV + VdP)$$

$$dQ = \frac{1}{\gamma - 1}\,(PdV + VdP) + PdV$$

$$= \frac{1}{\gamma - 1}\,(VdP + PdV + P\gamma\,dV - PdV)$$

$$dQ = \frac{1}{\gamma - 1}\,(VdP + P\gamma\,dV) \qquad (2)$$

It is assumed also that -

$$dQ = h\,A\,(T - T_w)\,d\theta \qquad (3)$$

where

T_w = Constant wall temperature

V = Cylinder volume at time θ

A = Area of cylinder wall at time θ

D = Diameter of Cylinder

H = Height of piston at time θ

Then, $V = \frac{\pi D^2 H}{4}$

$$A = \left(\pi DH + \frac{2\pi D^2}{4}\right)$$

$$= \frac{4}{D}\left(\frac{\pi D^2 H}{4} + \frac{\pi D^3}{8}\right) = \frac{4}{D}\left(V + \frac{\pi}{8} D^3\right) \qquad (4)$$

Substituting:

$$dQ = h\, k_1\, (V+K_2)(T-T_W)\, d\theta \qquad (5)$$

where

$$k_1 = \frac{4}{D}\,; \quad k_2 = \frac{\pi D^3}{8}$$

Equating (2) and (5)

$$\frac{1}{\gamma - 1}\,(VdP + P\gamma dV) = h\, k_1\, (V+k_2)(T-T_W)\, d\theta$$

$$\frac{1}{\gamma - 1}\, VdP + \frac{\gamma}{\gamma - 1}\, PdV = h\, k_1\, (V+k_2)(T-T_W)\, d\theta$$

$$\frac{\gamma}{\gamma - 1}\; \frac{PdV}{d\theta} = h\, K_1\, (V+K_2)(T-T_W) - \frac{1}{\gamma - 1}\; \frac{VdP}{d\theta}$$

$$\frac{dV}{d\theta} = \frac{h\, k_1\, (\gamma - 1)}{\gamma P}\,(V+k_2)(T-T_W) - \frac{1}{\gamma}\, \frac{V}{P}\, \frac{dP}{d\theta} \qquad (6)$$

In this work P and θ are obtained from the photographic record, and all other quantities except h and V are known. In addition, V_1 and V_2 are known. Therefore Fig. (6) must be solved by the point-to-point method in which a value of h is assumed and V is calculated from point-to-point, the assumed value of h being considered correct when the V-θ curve which starts at V_1 passes through V_2.

We may attack the problem from a different standpoint. If the pressure-volume curve assumes the form PV^n = constant, we may immediately determine the value of n from the known initial and final states. Obtaining n thus, we may then readily construct the V vs. θ diagram from the P-θ curve and the known P-V relation, and compare the form of the V-θ curve so obtained with that obtained by the preceding analysis.

APPENDIX IV.

EXPERIMENTAL AND CALCULATED DATA.

BURSTING STRENGTH OF ALUMINUM DISCS

(Aluminum Co. of America 2 SO)

Thickness	Bursting Strength - Lb./sq. in.	
inches	Lot 1	Lot 2
0.002	80	80
0.003		102
0.004	140	148
0.005		185
0.006	215	208
0.007		215
0.008	285	275
0.009		300
0.010	350	345
0.012	410	370

Case I for Springs

$l_2 = 4l_3$; a = 2.5 cm.

t = 2h inches	h cm	N cycle/sec	D cm./dyne/sq.cm.	$N_{f.d.}$ cycle/sec.	D_A 1/1000's in./atm.	N/D	$\frac{N_{f.d.}}{D_A}$
	0	15,900		o			
3.93×10^{-3}	0.005	10,050	312×10^{-8}	417	1248	8.40	0.334
7.87"	0.010	7,930	39"	833	156	50.8	5.34
11.8"	0.015	6,780	11.6"	1250	46.4	146	26.9
15.75"	0.020	6,040	4.9"	1666	19.6	308	85
19.7"	0.025	5,520	2.5"	2082	10.0	552	208
23.6"	0.030	5,230	1.44"	2500	5.26	910	434
31.5"	0.040	4,650	0.61	3333	2.44	1910	1365
47.2	0.060	4,300	0.181	5000	.724	5940	6900
63.0	0.080	4,410	0.076	6666	.304	14500	21900

Case I for Springs

$l_2 = 4l_3$; a = 1.25 cm.

t = 2h inches	h cm	N cycle/sec.	D cm/dyne/ sq.in.	$N_{f.d.}$ cycle/sec.	D_A 1/1000's in./atm.	N/D_A	$\frac{N_{f.d.}}{D_A}$
0	0	15,900		0			
3.93×10^{-3}	0.005	13,500	19.4×10^{-8}	1666	77.5	175	21.5
7.87 "	.010	12,030	2.43 "	3333	9.72	1240	342
11.8	.015	11,100	.72 "	5000	2.88	3870	1,740
15.75	.020	10,350	.304 "	6666	1.22	8500	5,460
19.7	.025	9,870	.156 "	8333	.645	15300	12900
23.6	.030	9,630	.09 "	10000	.36	26800	27800

Case I for Springs

$l_2 = 2\ l_3$; a = 2.5 cm

t= 2h inches	h cm	H cycle/ sec	D cm/dyne/ cm	$N_{f.d.}$ cycle/sec	D_A- 1/1000's inch/atm.	N/D_a	$\frac{N_{f.d}}{D_A}$
	0	15,900		0	0		
3.93×10^{-3}	.005	6,000	312×10^{-8}	417	1248	0.48	0.334
7.87 "	.010	4,400	39 "	833	156	28.2	5.34
11.8 "	.015	3,670	11.6 "	1250	46.4	79.1	26.9
15.75"	0.02	3,260	4.9 "	1666	19.6	166	85
19.7 "	0.025	3,000	2.5 "	2082	10.0	300	208.2
23.6 "	0.03	2,850	1.44 "	2500	5.26	542	475
31.5 "	0.04	2,750	.61 "	3333	2.44	1227	1365
47.2 "	0.06	2,950	.181 "	5000	.724	4070	6900
63.0 "	0.08			6666	.304	9700	21900

Case I for Springs

$l_2 = 2\ l_3$; $a = 1.25$ cm.

$t = 2h$ inches	h cm.	N cycles/sec	D cm/dyne/sq. cm.	$N_{f.d.}$ cycles/sec.	D_A 1/100's in per atm	N/D_A	$\frac{N_{f.d.}}{D_A}$
	0	15,900					
$3.93\text{x}10^{-3}$	0.005	10,050	$19.4\text{x}10^{-8}$	1666	77.5	135.5	21.5
7.87 "	.01	8,040	2.43 "	3333	9.72	827	342
11.8 "	.015	7,120	0.72 "	5000	2.88	2470	1740
15.75"	.02	6,660	0.304"	6666	1.22	5460	5460
19.7 "	.025	6,570	0.156"	8333	0.645	10200	12900
23.6 "	.03	6,700	0.09	10000	0.36	18600	27800

MAXIMUM ALLOWABLE PRESSURE FOR 1 INCH DIAPHRAGMS

$$P_{max} = 5.33\ t^2\ S_{max}\ \text{lb./sq.in.}$$

Thickness	P_{max} for diff. assumed S_{max}					
inches	S_{max} . - lb./sq.in.					
	25,000 lb/sq. in.	50,000 lb./sq.in.	75,000 lb/sq.in.	100,000 lb/sq.in .	125,000 lb/sq.in	150,000 lb/sq.in.
0.005	3.33	6.66	10	13.35	16.65	20
0.010	13.35	26.7	40	53.3	66.7	80
0.015	30	60	90	120	150	180
0.020	53.3	107	160	213	267	320
0.030	120	240	360	480	600	720
0.040	213.5	427	640	853	1067	1280

Maximum Allowable Pressures for $1\frac{1}{2}$ Inch Diaphragms Rigidly Clamped at the Edge.

P max. = $2.37t^2$ S max. #/sq. in.

Thickness Inches	P max. for Different S max. S max. lbs. per sq. in. 75,000	100,000	125,000	150,000	175,000
.008	11.4-	15.2	18.9	22.7	26.5
.010	17.5	23.7	29.6	35.5	41.5
.012	25.6	34.1	42.6	51.1	59.6
.014	34.9	46.5	58.1	69.7	81.3
.018	57.6	76.8	96	115.3	134.5
.022	86	114.8	143.5	172	201
.026	120	160	200	240	280
.030	160-	213	266-	320-	373

MAXIMUM ALLOWABLE PRESSURE FOR 2 INCH DIAPHRAGMS

$P_{max} = 4/3\ t^2\ S_{max}$ lb./sq. inch

Thickness inches	P_{max} for diff. assumed S_{max}					
	25,000	50,000	75,000	100,000	125,000	150,000
0.005	.831	1.66+	2.5	3.32	4.15	4.98
0.010	3.33	6.66	10	13.3	16.65	20
0.020	13.35	26.7	40	53.3	66.7	80
0.030	30	60	90	120	150	180
0.040	53.3	107-	160	213	267	320
0.050	83.2	167-	250	333	416	500-
01060	120	240	360	480	600	720

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.010 inch.

Pressure #/sq.in.	Deflection - Inch f_1	f_2	f_3
	*	**	*
0	0	.0090	.0090
10	.0034	.0137	
20	.0090	.0198	.0190
30	.0142	.0242	
40	.0188	.0285	.0275
50	.0232	.0323	
60	.0283	.0363	.0355
70	.0340	.0399	
80	.0434	.0434	.0439

* Increasing Pressure.

** Decreasing Pressure.

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.012 inch.

Pressure #/sq.in.	Deflection - Inch f_1 *	 f_2 **	 f_3 *
0	0	.0042	.0042
10	.0022	.0068	
20	.0051	.0105	.0096
30	.0093	.0148	
40	.0137	.0182	.0178
50	.0171	.0208	
60	.0204	.0234	.0234
70	.0233	.0256	
80	.0261	.0283	.0282
90	.0291	.0305	
100	.0327	.0327	.0328

* Increasing Pressure.

** Decreasing Pressure.

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.014 inch.

Pressure #/sq.in.	Deflection - Inch		
	f_1	f_2	f_3
	*	**	*
0	0	.0031	.0030
10	.0017	.0049	
20	.0037	.0069	.0064
30	.0058	.0090	
40	.0077	.0108	.0103
50	.0095	.0128	
60	.0114	.0147	.0143
70	.0135	.0163	
80	.0157	.0182	.0180
90	.0182	.0200	
100	.0217	.0217	.0216

* Increasing Pressure.

** Decreasing Pressure.

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.018 inch.

Pressure #/sq.in.	Deflection - Inch		
	f_1	f_2	f_3
	*	*	*
0	0	.0082	.0086
25	0.0052	.0128	
50	.0090	.0163	
75	.0122	.0195	
100	.0154	.0225	
125	.0188	.0259	
150	.0225	.0292	
175	.0264	.0322	
200	.0314	.0352	
225	.0380	.0383	.0384

* Increasing Pressure.

Load-Deflection Data for Corrugated Circular

Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch. Thickness, t = 0.022 inch.

Pressure #/sq.in.	Deflection-Inch f_1	f_2	f_3	$t^3f_1x10^8$
	*	**	*	
0	0	.0040	.0040	0
25	.0032	.0073		3.39
50	.0066	.0103	.0100	7.00
75	.0091	.0125		9.65
100	.0112	.0144	.0142	11.88
125	.0131	.0164		13.9
150	.0148	.0183	.0181	15.7
175	.0169	.0202		17.9
200	.0189	.0219	.0217	20.03
225	.0207	.0236		21.9
250	.0230	.0252	.0252	24.4
275	.0257	.0272		27.2
300	.0288	.0288	.0288	30.5

* Increasing Pressure.

** Decreasing Pressure.

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.026 inch.

Pressure	Deflection - Inch				
#/sq.in.	f_1	f_2	f_3	f_4	$t^3 f_1 x 10^8$
	*	**	*	*	
0	0	0	0	.0015	0
25	.0026				4.55
50	.0046	.0043			8.05
75	.0065				11.38
100	.0084	.0081		.0097	14.7
125	.0102				17.85
150	.0122	.0118			21.4
175	.0139				24.3
200	.0156	.0152	.0156	.0170	27.3
225			.0174		30.4
250			.0194		34.0-
275			.0215		37.6
300			.0238	.0238	41.6

* Increasing Pressure.

** Decreasing Pressure.

Load-Deflection Data for Corrugated Circular Steel Diaphragm Rigidly Clamped at the Edge.

Free diameter = $1\frac{1}{2}$ inch.

Thickness, t = 0.030 inch.

Pressure #/sq.in.	Deflection - Inch			$t^3 f_1 x 10^8$
	f_1	f_2	f_3	
	*	**	*	
0	0	0	0	0
25	.0019	.0020	.0020	5.13
50	.0034	.0034	.0035	9.18
75	.0048	.0048	.0051	12.97
100	.0062	.0063	.0068	16.75
125	.0076	.0077	.0082	20.53
150	.0091	.0092	.0096	24.6
175	.0105	.0105	.0110	28.4
200	.0119	.0118	.0122	32.1
225	.0131	.0131	.0136	35.35
250	.0144	.0144	.0150	38.85

* Increasing Pressure.

** Decreasing Pressure.

Pressure at the Proportional Limit for $1\frac{1}{2}$ Inch Rigidly Clamped Steel Diaphragms.

Thickness Inches	Observed P max. # / sq. in.
0.008	40
0.010	60
0.012	80
0.014	70
0.018	120
0.022	210
0.026	240
0.030	300

Data from Run 42 - Fixed Fulcrum Indicator.

Time Line*	Distance to Base-Inches**	Time Line	Distance to Base
1	.352	111	.410
5	.434	119	.400
11	.424	127	.397
15	.423	135	.390
19	.420	143	.387
23	.425	151	.381
27	.420	159	.375
31	.420	167	.370
35	.426	175	.366
39	.427	186	.357
43	.438	198	.351
55	.450	210	.345
63	.460	222	.341
71	.461	230	.338
79	.450	242	.335
87	.441	250	.332
95	.431		
103	.422		

* 494 time lines = 1 second.

** Height of pressure line above base line.

Appendix V - Bibliography.

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