# EFFLUX OF GASES THROUGH SMALL ORIFICES

By Edgar Buckingham and Junius David Edwards

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## 1. INTRODUCTION

In Bunsen's effusion method for determining the relative densities of gases, two gases are successively allowed to flow under a small pressure head through a very small hole in a thin plate. The denser the gas the slower is the rate of efflux or effusion, and if the conditions of pressure and temperature are the same for both gases, the times required for the escape of a given volume are approximately proportional to the square roots of the densities. Accordingly, the densities may be set proportional to the squares of the times, and the subsistence of this relation permits

of a simple experimental comparison of the densities by means of time measurements.

In general, the relation just mentioned is only roughly approximate and except with special precautions the effusion method is not at all satisfactory, errors of 30 or 40 per cent being possible. It has been used to a considerable extent in the natural gas industry, and in consequence of difficulties encountered in practice this Bureau was requested, in 1915, to investigate the subject and, if possible, suggest means for making the method more reliable. The work was undertaken by one of the present authors and the results obtained, in so far as they are of immediate interest to gas engineers, have already been published[1] and need not be further discussed from the purely practical point of view. The present paper deals with the more strictly scientific aspect of the investigation.

At the beginning of the experiments it was impossible to foresee the length to which the work would need to be carried, and the experimental accuracy aimed at in designing the apparatus to be used, while ample for the commercial ends then in view, was not so high as we could have desired when the work had gone on for some time and the complexities of the subject were better appreciated. Some improvements and refinements were, however, introduced as opportunity offered and the later measurements are more satisfactory than the earlier ones.

The chief fault to be found with the experimental data is that there are not more of them. It would be interesting, with our accumulated experience, to resume and extend the work, which was interrupted in the summer of 1917. This, however, is impossible and we therefore publish a description of the results of the investigation in the hope that in spite of their obvious incompleteness they may be of interest.

## 2. GENERAL OUTLINE OF THE INVESTIGATION

Preliminary experiments with a number of orifices and with several gases, the densities of which had been determined gravimetrically, gave rather surprising discrepancies and irregularities in the rates of effusion, and showed that the difficulties encountered in the commercial determination of specific gravities by the effusion method could not all be ascribed to faulty procedure or unsatisfactory manipulation, but represented inherent characteristics of the method itself. It soon became evident

[1] J. D. Edwards, Tech. Paper No. 94, Bur. of Standards; Met. Chem. Eng., 16, pp. 518–524, 1917.

that a systematic investigation would be required and that the experimental work must be planned and the results as obtained analyzed and interpreted in the light of such theoretical considerations as could be brought to bear. The first task was, therefore, to devise some sort of theory, making it very simple at first and adding to or modifying it as might be found necessary in order to fit the observed facts as the experiments proceeded.

The orifices being rather small, it seemed at first sight that it might be necessary to have recourse to the kinetic theory of gases. But since even the smallest diameter used is about 300 times the mean free path for hydrogen, under the working conditions, it appeared upon consideration that it would probably be sufficient to regard each gas as a continuum and to treat the orifices merely as small steam-turbine nozzles, keeping in mind that disturbing causes which are of negligible importance for nozzles and orifices of diameters of the order of 1 cm might well have appreciable effects for diameters 100 times smaller. The theory was therefore developed on this basis.

The general method was first to compare the experimental results obtained with the equations for adiabatic flow of an ideal gas through a frictionless orifice. It at once appeared that there was no agreement and that the flow was certainly not of this character. An allowance for the effect of viscosity was then introduced and a qualitative agreement between theory and observation was obtained, but it was evident that at least one more disturbing factor must be taken into account. Transmission of heat from the walls of the orifice to the jet of gas was next considered and a correction for this was tentatively introduced into the theoretical equations. The theory as thus modified seems to be adequate to representing the observed facts quantitatively, for most of the orifices on which much work was done, within the rather wide limits of error of the experiments.

For orifices with a very sharp entrance, and presumably, therefore, for orifices in very thin plates, it appears that the occurrence of contraction of the jet enters as an additional complication; while the effect of this has been recognized, we have not succeeded in representing it quantitatively in the equations. To do so would require a long series of accurate experiments which can not now be undertaken. We have, therefore, to rest satisfied with having devised a rational physical interpretation of the major portion of the observed facts, which appears to be sound so far as it goes, thus giving us some understanding of the phenomena

and enabling us to make qualitative predictions with respect to the relative behavior of gases of known physical properties flowing through small orifices with rounded entrances.

A great deal of time had to be spent in devising and testing various modifications of the theory, but only the final form of

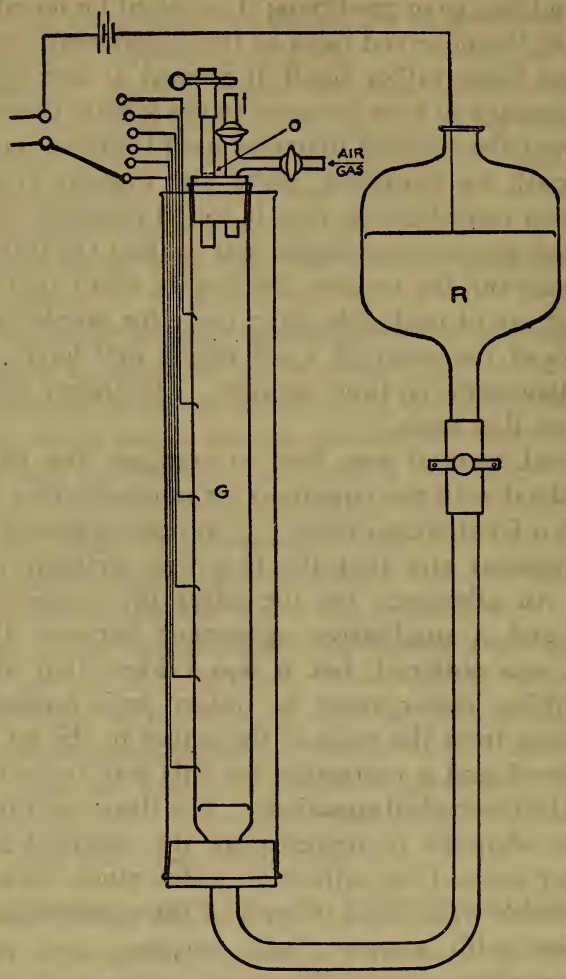



FIG. 1.—*Effusion apparatus with automatic timing system*

it need be discussed in any detail. The bare experimental results, if presented separately from the theory, would be difficult to grasp, and it seems that the best mode of exposition will be to develop the theory, comparing it step by step with the facts which it purports to represent. After describing the apparatus, the experimental procedure, and the materials, we shall pursue the plan just mentioned.

## 3. EFFUSION APPARATUS AND METHOD OF EXPERIMENTING

Apparatus No. I, which was used in most of the effusion experiments, is shown in outline in Fig. 1. It consisted of a vertical, cylindrical, glass gas chamber *G*, surrounded by a water jacket and connected through a glass tube to the mercury reservoir *R*. The rubber stopper which closed the upper end of the gas chamber carried, first, a glass tube in which the orifice was mounted and, second, an inlet tube through which the gas could be introduced under pressure.

During the course of a run, with the inlet tube closed and the orifice tube open, the gas in *G* was under an excess of pressure equal to the difference of level of the mercury in the two sides of the apparatus. As the gas escaped through the orifice, the mercury, falling in *R* and rising in *G*, swept the gas before it, and at the same time the excess pressure gradually decreased as the mercury surfaces in *R* and *G* approached the same level.

The internal diameter of *G* was about 22 mm and that of the tube connecting it with *R* was about 8.5 mm. A short length of heavy-walled rubber tubing was inserted at a break in this tube, so that the mercury reservoir could be cut off by a pinchcock when it was desired to evacuate the gas chamber. The connecting tube was not blown on to the lower end of *G*, as shown in the figure, but attached through a short rubber connector so that the connection could be broken at this point.

Six platinum contact points were sealed into the wall of *G* and insulated connecting wires were led from them up through the water jacket. When gas was escaping from the orifice during a run, the mercury rising and driving the gas before it made electrical contact with these points, one after the other, and the instants of contact were recorded automatically on a chronograph controlled by the master clock of the Bureau. The time interval between any two successive contacts could thus be determined to about 0.05 second.

The spacing of the six contact points determined five volume intervals. The volume of each was found by weighing the mercury required to fill it, the gas chamber *G* being disconnected for this purpose so that mercury could be run out at the bottom. The volumes of the intervals, counting from the bottom up, were found to have the values shown in Table 1.

**TABLE 1.—Volumes for Apparatus No. I**

| Interval | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Volume in cubic centimeters | 18.59 | 17.85 | 17.45 | 17.06 | 13.23 |

The difference of the chronograph readings for the beginning and end of any interval gives the time required for the escape of a mass of gas which occupied the volume of that interval under the conditions of pressure and temperature prevailing within the apparatus. When the volume of the interval is divided by this time, the result is the mean rate of decrease of volume of the confined gas, in cubic centimeters per second, a quantity required in the computations as a measure of the rate of effusion.

For a given gas and a given orifice the rate of effusion depends on the excess of pressure within the container $G$ over the barometric pressure of the outside atmosphere into which the gas escapes; in other words, on the difference of level of the mercury surfaces in $R$ and $G$. With a given apparatus and a given volume of gas, this head $\Delta p$ depends on the amount of mercury used. With apparatus No. I, as actually used, the heads of mercury at the instants of contact with the six points, counting from the bottom up, were as shown in Table 2:

**TABLE 2.—Values of $\Delta p$ for Apparatus No. I**

| Number of point | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $\Delta p$, millimeters | 251 | 201 | 154 | 108 | 59 | 17 |

The loss of head due to the resistance of the connecting tube to the flow of mercury was estimated and found to be negligible.

The total pressure $p_0$ within the gas chamber at any instant is the sum of the instantaneous values of the head $\Delta p$ and the outside barometric pressure $p$, which was read from a standard barometer.

The temperature of the water in the jacket was always nearly the same as that of the room and did not vary more than a few tenths of 1 degree C during any one experiment, comprising several runs on air and several on one of the test gases. It was assumed to be the same as the temperature of the gas within $G$. The slight error in this assumption, due to the fact that the gas is expanding slowly, was computed and found to be quite negligible.

In addition to the apparatus just described, a second which we shall designate as apparatus No. II, was used in a few of the later

experiments. In its general design it was much like No. I and in was used in the same way, but it was larger, so that the times of effusion were longer and the errors in timing, therefore, less important. The water jacket, which had given rise to some insulation difficulties, was replaced by an oil jacket in which circulation and uniformity of temperature were maintained by means of an air lift in a vertical side tube which was joined to the jacket at top and bottom.

Apparatus No. II had nine contact points defining eight volume intervals. The volumes, measured as before by weighing mercury, were found to have the values shown in Table 3.

TABLE 3.—Volumes for Apparatus No. II

| Number of interval.. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Volume in cubic centimeters..... | 54.69 | 48.38 | 50.71 | 50.56 | 41.56 | 35.06 | 27.47 | 22.60 |

The heads of mercury at the instants of contact with the points were found to be as shown in Table 4:

TABLE 4.—Values of $\Delta p$ for Apparatus No. II

| Number of point... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| $\Delta p$, millimeters.... | 266.9 | 223.1 | 184.2 | 143.6 | 103.1 | 69.9 | 42.2 | 19.8 | 1.5 |

A few experiments were also made with a third piece of apparatus. This was intended for use with very low heads and sulphuric acid of denisty 1.84 was used instead of mercury. There was only one interval and its volume was 189.4 cc. The heads at the beginning and end of this interval were 110 and 6 mm of $H_2SO_4$, equivalent to 14.9 and 0.81 mm of mercury.

## 4. ORIFICES

The orifice plates were made from a stiff platinum-iridium alloy and were about 5 or 6 mm in diameter. The hole was pierced with a fine needle and then reamed out as desired. Any burr could be removed and the plate ground down by rubbing on fine emery paper, the appearance of the orifice during the finishing operation being observed under the microscope. The thickness of the plate was measured by a micrometer caliper and the diameter of the hole was deduced from a number of measurements under a micrometer microscope. When the plate was finished it was sealed into the end of a glass tube and another piece of tube was then sealed on, so that when the job was complete the orifice

plate formed a diaphragm across the middle of a continuous glass tube 8 or 10 cm long.

The dimensions of the orifices to which reference will be made in this paper are given in Table 5:

TABLE 5.—Dimensions of the Orifices in Millimeters

| | | | | |
|---|---|---|---|---|
| Number of orifice | 23 | 28 | 29 | 31 |
| Diameter of hole | 0.070 | 0.069 | 0.055 | 0.087 |
| Thickness of plate | .04 | .10 | .05 | .10 |

Orifice No. 23 was used in two positions and will be referred to as 23A or 23B, depending on which face was uppermost.

It was not practicable to finish such small orifices with any great nicety, hence the holes were not quite round and their edges were more or less irregularly rounded off and neither perfectly smooth nor perfectly sharp.

## 5. GASES

Four samples of gas were used in addition to air which served as the standard. They were stored in steel cylinders at high pressure and drawn off as needed through pressure regulators which delivered them at a convenient rate for filling the apparatus. The gases were not pure, but to avoid circumlocution each gas will be designated by the name of its most important constituent and, when appropriate, denoted by the chemical symbol of that constituent. The gases may be described as follows:

*Hydrogen*, $H_2$.—This was a commercial electrolytic gas. Its specific gravity referred to air, when determined gravimetrically at the beginning of the investigation, was found to be 0.08854, the value for pure hydrogen being 0.06951. Assuming the impurity to consist of oxygen, the oxygen content was about 1.8 per cent by volume.

After an interval of about one year, during which the gas had been kept in a steel cylinder under pressure, new effusion experiments indicated that the gas had become lighter. A new determination of the specific gravity was therefore made and the result was 0.08587, corresponding to an oxygen content of 1.6 per cent by volume.

*Methane*, $CH_4$.—This was a sample of natural gas. It contained over 90 per cent of methane and its specific gravity was found to be 0.583, the value for pure methane being 0.554.

*Carbon Dioxide*, $CO_2$.—This was a commercial gas of specific gravity 1.528; since the specific gravity of pure carbon dioxide is 1.529, this sample appears to have been fairly pure.

*Argon, Ar.*—This was a mixture of argon, oxygen, and nitrogen, obtained from liquid air. Its specific gravity was 1.167, and this, together with a volumetric determination of the oxygen content, showed that the composition, in volume per cent, was approximately

$$Ar = 33 \quad O_2 = 46 \quad N_2 = 21$$

The details of the method of gravimetric determination of gas density are given in Techonologic Paper No. 94 of this Bureau.

In addition to the specific gravities of the gases, data on certain other physical properties were required for use in developing and testing the theory. The first of these was the specific heat ratio $C_p/C_v = k$. It was assumed that the value for air was $k = 1.400$ and that the value for hydrogen was the same. The values for the other three gases were measured in terms of the value for air by means of a Kundt's tube, using the measured specific gravities in the computations. The precision of the Kundt's tube measurements was ample, the accuracy of $k$ being limited by that of the gravimetric determinations of specific gravity. The values of $k$ are given in Table 6.

It was also necessary to know the relative viscosities of the gases, although no high accuracy was required because the values were to be used only in computing corrections. The determinations were made by substituting, in apparatus No. I, a long fine glass capillary for the orifice tube, and comparing the rates of escape of air and of the gas in question under identical conditions of pressure and temperature. The values of the relative viscosity $\mu'/\mu$ referred to air are given in Table 6. The quantities $P$ and $\beta'/\beta$ which are also included in Table 6 will be discussed later.

**TABLE 6.—Physical Properties of the Gases**

| Specific gravity | Air | $H_2$ | $CH_4$ | $CO_2$ | Ar |
|---|---|---|---|---|---|
| $\rho'/\rho = \delta$ | 1.000 | 0.08854 (1916)<br>.08587 (1917) | 0.583 | 1.528 | 1.167 |
| $C_p/C_v = k$ | 1.400 | 1.400 | 1.303 | 1.290 | 1.462 |
| $(k-1)/k = \alpha$ | $\frac{2}{7}$ | $\frac{2}{7}$ | .233 | .225 | .316 |
| $\mu'/\mu$ | 1.000 | .519 | .618 | .815 | 1.126 |
| $\alpha'\mu'/\alpha\mu\sqrt{\delta} = P$ | 1.000 | 1.745 | .660 | .519 | 1.153 |
| $\beta'/\beta$ (tentative) | 1.00 | 1.69 (1916)<br>1.62 (1917) | .47 | .46 | 1.10 |
| $\beta'/\beta$ (as finally used) | 1.00 | 1.50 | .75 | .40 | 1.04 |

The values for air are all given by definition or assumption.

## 6. METHOD OF REPRESENTING THE EXPERIMENTAL RESULTS

In order to compare the results obtained with different gases so as to get an insight into the relation of the errors of Bunsen's method to the physical properties of the gases, it seemed desirable to represent the results in such a way as to exhibit the fractional rather than the absolute errors and the following plan was adopted:

Let $p$ = the outside or barometric pressure

Let $p_0 = p + \Delta p$ = the pressure within the gas chamber, or the initial pressure as we shall call it.

Let $r = p/p_0$; it will be called the pressure ratio. At the start of a run, $\Delta p$ has its largest value and $r$ its smallest, and as the run proceeds, $\Delta p$ approaches zero and $r$ increases toward unity.

Let $\tau$ = the time in seconds required for the volume of gas within the apparatus to decrease by 1 cc, when the pressure ratio has a particular value $r$ and the gas under experiment is air.

Let $\tau'$ = the corresponding time for the test gas under identical conditions.

Let $\delta$ = the specific gravity of the test gas, referred to air.

Then the relation on which the effusion method of determining specific gravity is based is that $\delta = (\tau'/\tau)^2$, approximately.

Let

$$\left(\frac{\tau'}{\tau}\right)^2 \Big/ \delta = R$$

If the effusion method gave correct results, we should have $R = 1$, and in practice the observed value of $(R - 1)$ is the fractional error of a determination of specific gravity by this method.

In the experiments with apparatus No. I, which had five volume intervals, each experiment gave five mean values of $\tau'/\tau$ and therefore of $R$, each corresponding to a certain mean value of $r = p/p_0$. With apparatus No. II each experiment gave eight instead of five values of $R$. What we have done is to plot the observed mean values of $R$ as ordinates against the corresponding mean values of $r$ as abscissas.

When the results of any one experiment are plotted in this way, the points lie along a more or less smooth curve, and by plotting the results of a number of supposedly identical experiments an idea may be formed of the accidental errors of the observations.

If Bunsen's method were correct in principle, the points would always be grouped indiscriminately about the straight line $R=1$, and any grouping of points about a different curve indicates the presence of a systematic error in the method itself, upon which the accidental errors of experiment are superimposed. When all the results obtained with different gases but the same orifice are plotted together on one diagram, we have a convenient means of comparing the behavior of the gases.

If we can then build up a theory for predicting the behavior of the gases from a knowledge of their physical properties, and compute values of $R$ in terms of $r$, we may plot theoretical curves $R=f(r)$ for comparison with the observed values of $R$, and thus test the ability of the theory to represent the observed facts.

By examining plates 2 to 7, the reader may form an estimate of the accidental errors of the observations which are represented by the plotted points, all the points of any one series being denoted by the same symbol. The curves on these plates are drawn from the theory which will be discussed in detail later on.

The theory is based on the consideration of the steady flow of fluids, whereas in the experiments the rate of flow was not constant but continually decreasing. This change of rate was so slow that there is no doubt that at any instant it was sensibly the same as if the conditions had already been held constant for a long time; but the *observations* of the rates of efflux had to be made by means of a small number of contact points and gave, of course, only average rates over considerable ranges of variation of the pressure ratio $r$. Each value of $\tau$ or of $\tau'$ was obtained by dividing the observed time in seconds for the interval in question by the volume of the interval in cubic centimeters. The corresponding value of $r$ was taken to be the geometric mean of the values at the beginning and end of the interval; it did not in any case differ more than 0.2 per cent from the arithmetic mean.

## 7. REMARKS ON THE ACCIDENTAL ERRORS OF THE EFFUSION RATES

Each experiment or "series" consisted of several runs on the test gas, preceded or followed by several runs on air under nearly identical conditions of temperature and barometric pressure. A "run" was made by filling the gas chamber with dry gas under pressure until the mercury level was somewhat below the lowest contact point, opening the orifice tube, and recording on the chronograph the times at which the mercury surface reached the

contact points as it rose and swept the gas before it through the orifice. The number of runs in each series was usually from five to eight with each of the two gases, and the values of $\tau$ and $\tau'$ for the series were means of the values for the separate runs.

It sometimes happened that separate runs which should have differed only by accidental errors in reading the chronograph sheets differed considerably more than this. It seems probable that these irregularities are to be attributed mainly to dust or condensed mercury catching on the edges of the orifice; for they were most frequent in the case of orifice No. 23, which had rougher edges than the other orifices and so was more adapted to catching and retaining small particles. Occasionally two series, each of which gave values of $R=f(r)$ lying along a smooth curve, would differ considerably without there being, a priori, any evident reason for the difference. It seems likely that such differences were due to dust particles which may in one case have lodged in the orifice at the start and remained in the same position throughout the series.

Another sort of irregularity sometimes observed consisted in a delay of the time registered for one of the contacts, and resulted in too long a time for the preceding and too short a time for the following interval. This may have been due to a slight sticking of the rising mercury surface at the glass wall (the contact points being rather near the wall instead of in the middle of the gas chamber) or to irregularities in the action of the chronograph.

Any error in timing, whatever its source, would have more effect on the values of $R$ computed from the time intervals if the time intervals were short—that is, the effusion rapid—than if they were long. Accordingly it was to be expected that the results would be much more irregular and scattering for hydrogen than for the other gases and this is what actually happened as may be seen from the plates.

## 8. GENERAL EQUATION FOR EFFLUX OF ANY FLUID

Let a fluid be flowing steadily along a channel with impermeable walls; the walls may be material or the channel may be merely a stream tube within the fluid, its boundary being an imaginary surface across which no fluid passes either in or out. Let us consider a portion of the channel or tube extending from an entrance section $A_0$ to an exit section $A$, $A_0$ and $A$ being drawn so as to be, at each point, normal to the mean direction of flow at that point. Let the sections be at the same level so that no

gravitational work is done by or on the fluid in its passage from $A_0$ to $A$.

Let $p_0$ and $p$ be the pressures, and $\theta_0$ and $\theta$ the absolute temperatures in the fluid at the two sections. Let $v_0$, $\epsilon_0$, $T_0$ be, respectively, the volume, internal energy, and kinetic energy of each gram of the fluid as it enters at $A_0$; and let $v$, $\epsilon$, $T$ be the corresponding values at $A$. Let $Q$ be the quantity of heat added from outside the channel to each gram during its passage from $A_0$ to $A$; $Q$ includes only heat which actually passes through the boundary of the channel and does not include heat developed within the fluid by viscous or other resistances.

The work per gram done on the fluid as it enters at $A_0$ is $p_0v_0$; and the work done by it on the fluid ahead of it, as it issues at $A$ is $pv$. We therefore have, by the first law of thermodynamics, the equation

$$(T+\epsilon)-(T_0+\epsilon_0)=p_0v_0-pv+Q \tag{1}$$

We proceed to apply this equation to the case of a fluid escaping in a jet through a small orifice in the wall of a large container in which the fluid is at rest except for its slow general motion toward the orifice.

Let $A$ be the minimum section of the jet; if the entrance to the orifice is sufficiently rounded off there is no contraction, and $A$ is the minimum or throat area of the orifice. The symbols $p$, $\theta$, $v$, $\epsilon$, $T$ now refer to conditions in the jet. If the jet speed is less than that of sound in the fluid, $p$ is equal to the outside back pressure and this was the case in our experiments, the pressure ratio $r$ being always greater than the critical ratio, which for air is about 0.53.

Let $A_0$ be described within the container, normal to the direction of flow toward the orifice and far enough back along the stream that $A_0$ is very large compared with $A$ and the motion at $A_0$ very slow compared with the speed at the jet. The kinetic energy $T_0$ will then be negligible and $p_0$, $\theta_0$ will be the pressure and temperature of the nearly stationary fluid within the container.

By setting $T_0=0$ in (1) we now obtain the equation

$$T=(\epsilon_0+p_0v_0)-(\epsilon+pv)+Q \tag{2}$$

No restrictions have been imposed on the properties of the fluid or the nature of the motion so that equation (2) is general.

## 9. EFFLUX OF AN IDEAL GAS

Let the fluid be an ideal gas[2]—that is, one for which the equations

$$pv = m\theta \qquad C_v = const \tag{3}$$

are satisfied—$\theta$ being measured on the thermodynamic scale, and $C_v$ denoting the specific heat at constant volume. In our experiments the range of temperature was less than 30° C, and the pressures were between 1 and 1.4 atmospheres. And while the gases used are by no means strictly ideal, they are so nearly ideal that over this small range of pressure and temperature equations (3) may be applied to them without sensible error.

It is easily shown by elementary thermodynamics that for the ideal gas defined by equations (3), the further equations

$$\epsilon = \theta C_v + Const. \tag{4}$$

$$C_v + m = C_p \tag{5}$$

are always satisfied, $C_p$ denoting the specific heat at constant pressure. If we eliminate $\epsilon$, $\epsilon_0$, $pv$, and $p_0v_0$ from (2) by means of (4) and (3) and then apply (5), we obtain the equation

$$T = (\theta_0 - \theta)C_p + Q \tag{6}$$

which is sensibly exact as applied to our experiments on efflux.

Let $S$ be the mean speed of the jet at $A$, and let us set

$$T = \frac{1}{2}S^2 \tag{7}$$

This amounts to assuming, first, that the kinetic energy of turbulence is negligible in comparison with that of the axial motion, and second, that the arithmetical mean speed taken over the section $A$ is sensibly identical with the square-root-of-mean-square speed; that is, that the speed is nearly uniform all over the section. Both these assumptions are known to be legitimate for larger orifices and there is no reason to expect that they will lead us into any difficulties. We therefore adopt them and so, by means of (7), reduce equation (6) to the form

$$\frac{1}{2}S^2 = (\theta_0 - \theta)C_p + Q \tag{8}$$

Subject to the assumption of equation (7), equation (8) is entirely general as applied to the efflux of an ideal gas. Any sort

[2] See Bull., Bur. Standards, 6, No. 3, p. 409, 1910; Scientific Paper No. 136.

of passive resistance will, of course, decrease the jet speed $S$; but the dissipation of energy by the resistance heats the fluid and raises its final temperature $\theta$, so that $(\theta_0 - \theta)$ is also decreased and equation (8) remains satisfied.

It frequently happens that the transmission of heat from the orifice to the jet of gas is so small as not to produce any sensible effect on the phenomena. The efflux is then sensibly adiabatic, and by setting $Q = 0$ we have, for adiabatic efflux of an ideal gas,

$$^{I}S^2 = (\theta_0 - \theta)C_p \tag{9}$$

If we were dealing with such ranges of pressure and temperature as occur at the valve of an air liquefier, it would not be legitimate to treat the gases used in our investigation as ideal; in fact, the possibility of liquefying gases by the Hampson-Linde method is due to their not being ideal.[3] But for our present purposes it is safe to treat the gases as ideal, and for simplicity we may as well drop the adjective ideal and, for the future, speak merely of "gases."

## 10. ISENTROPIC EFFLUX OF A GAS

As a first attempt to formulate a theory, let us suppose that the efflux is adiabatic and that there are no passive resistances and therefore no development of heat within the fluid; that is, no dissipation. Then the gas expands isentropically from its initial pressure $p_0$ to the back pressure $p$, which exists at the minimum section of the jet so long as the jet speed is less than the speed of the sound in the gas at $p$, $\theta$. Hence, we may use the familiar equations for isentropic expansion of an ideal gas, namely:

$$p\, v^k = const \tag{10}$$

$$\theta\, v^{k-1} = const \tag{11}$$

$$\theta = const \times p^{\frac{k-1}{k}} \tag{12}$$

If, for convenience, we introduce the abbreviations

$$\frac{p}{p_0} = r \text{ and } \frac{k-1}{k} = a \tag{13}$$

we have by (12)

$$\frac{\theta}{\theta_0} = r^a \tag{14}$$

[3] See Bull., Bur. Standards, 6, No. 1, p. 125, 1909; Scientific Paper No. 123.

and equation (9) for adiabatic efflux of a gas may be written

$$\frac{1}{2} S^2 = \theta_0 C_p (1 - r^\alpha) \tag{15}$$

From equation (5) together with the definitions of $k$ and $\alpha$, we have the relation

$$C_p = \frac{m}{\alpha} \tag{16}$$

Substituting in (15) and setting $m\,\theta_0 = p_0\,v_0$ we now have

$$\frac{1}{2} S^2 = p_0\,v_0\,\frac{1 - r^\alpha}{\alpha} \tag{17}$$

which is one form of the familiar equation of St. Venant. Since we are interested in the density $\rho$ rather than its reciprocal, the specific volume $v$, we substitute $v_0 = 1/\rho_0$ and write equation (17) in the form

$$\frac{1}{2} S^2 = \frac{p_0}{\rho_0}\,\frac{1 - r^\alpha}{\alpha} \tag{18}$$

This is not yet in shape for immediate use, because in the experiments on efflux the quantity measured is not the speed of the jet but the time required for a certain volume of gas at $p_0$, $\theta_0$ to disappear from the container. We have, therefore, to eliminate $S$.

Let $\tau$ be the observed time rate of disappearance of the gas, in seconds per cubic centimeter, and let $V_0 = 1/\tau$, so that $V_0$ is the volume, measured in cubic centimeters at $p_0$, $\theta_0$, of the mass of gas which escapes from the orifice per second. Let $V$ be the volume of this same mass of gas measured at $p$, $v$, the conditions which prevail in the jet at $A$. Then since the expansion is isentropic we have, by equations (10) and (13)

$$V = \frac{V_0}{r^{1-\alpha}} \tag{19}$$

But we have also, obviously, the equation

$$V = AS \tag{20}$$

and therefore by (19)

$$S = \frac{V_0}{A r^{1-\alpha}} \tag{21}$$

If we substitute this value of $S$ in equation (18), replace $V_0$ by $1/\tau$, and solve for $\rho_0/\tau^2$, the result is

$$\frac{\rho_0}{\tau^2} = 2A^2 p_0 \frac{r^{2-2\alpha}}{a}(1 - r^\alpha) \tag{22}$$

a relation which would subsist between the observed value of $\tau$ and the other quantities involved, if the efflux were isentropic.

## 11. APPLICATION TO THE COMPARISON OF DIFFERENT GASES

Having made a run with the standard gas and determined $\tau$ under the given conditions, $p_0$, $\theta_0$, $r$, let us repeat the experiment under the same conditions with a second gas and determine its time $\tau'$. The specific gravity of the second or test gas as indicated by the results of the efflux method is $(\tau'/\tau)^2$, while if $\rho_0$ and $\rho_0'$ are the densities of the gases at $p_0$, $\theta_0$, the true value of the specific gravity of the test gas in terms of the standard is $\delta = \rho_0'/\rho_0$.

Let
$$\left(\frac{\tau'}{\tau}\right)^2 / \delta = R \tag{23}$$

When Bunsen's method gives a correct value, $R = 1$; and $(R - 1)$ is the fractional error in the specific gravity of the test gas as determined by this method. The value of $R$ which would result from the observations if the efflux were isentropic for both gases shall be denoted by $R_i$.

Let equation (22) refer to isentropic efflux of the standard gas and let the corresponding equation for the test gas be

$$\frac{\rho'_0}{\tau'^2} = 2A'^2 p_0 \frac{r^{2-2\alpha'}}{a'}(1 - r^{\alpha'}) \tag{24}$$

The area $A'$ is that of the minimum section of the jet of the test gas; and if the orifice is sharp edged so that a vena contracta is formed, $A'$ may differ from $A$, even though the orifice be unchanged. For the present, however, we shall suppose the orifice to have a rounded entrance so as not to give rise to contraction, and we shall set $A' = A$

If we divide equation (22) member for member by (24), set $A' = A$, utilize (23), and replace $R$ by $R_i$, we have

$$R_i = \frac{a'}{a} r^{2(\alpha'-\alpha)} \frac{1 - r^\alpha}{1 - r^{\alpha'}} \tag{25}$$

For two gases, for example, air and hydrogen, which have the same specific heat ratio, $a'=a$ and $R_i=1$ for all values of the pressure ratio $r$. For two such gases Bunsen's method would give a correct value of the relative density if the efflux were isentropic. But if $a'\neq a$, $R_i$ will differ from unity and Bunsen's method would not give a correct value of the relative density, even under ideal isentropic conditions.

In plate 1 curves of $R_i=f(r)$ are plotted from equation (25) using the known values of $a$ and $a'$ for the gases investigated, $a$ referring to air, which was treated as the standard. The separate points plotted are values of $R=(\tau'/\tau)^2\div\delta$ computed from values of $\tau$ and $\tau'$ actually obtained in experiments on orifice No. 23A, series 2, 5, 9, and 21.

Upon comparing the observed values of $R$ with the computed curves of $R_i$ it appears that there are large systematic differences which increase as $r$ approaches unity, that is, as the pressure difference and the jet speed approach zero. The departure of the observed values of $R$ from the computed values of $R_i$ is of the same general nature for all four gases though it is positive for hydrogen and argon, and negative for methane and carbon dioxide. It is evident that equation (25) does not represent the facts accurately and that the efflux is not isentropic, hence we must reexamine the assumptions that have been made, the principal ones being that there are no viscous resistances to flow and that there is no heat leakage to the escaping gas.

Since the orifices are of more or less irregular shapes, which moreover are not accurately known, it would be quite useless to attempt to attack the problem of computing the resistance by the ordinary methods of hydrodynamics, even if we were sure that the motion were strictly in stream lines and quite free from turbulence. Similarly with the question of heat transmission from the walls of the orifice to the gas—to treat this in detail by reference to the temperature gradients would require a complete knowledge of the motion of the gas, so that such a treatment is out of the question. Accordingly we are forced to do the best we can with very elementary physical reasoning, and our aim will be merely to develop equations containing empirical orifice constants, one for the viscous resistances and one for the effect of heat leakage, which shall be correct or at least satisfactory in their forms, so that when the values of the two orifices constants are suitably

chosen, the theoretical equations may represent the observed facts within the limits of experimental error.

Hitherto we have assumed that the only resistance that limited the speed of efflux of the gas was the kinetic or inertia resistance, due to its density and proportional to the square of the linear speed. On the other hand, viscous resistances, if present, would be proportional to the first power of the speed, and the disturbing effect of such resistances should therefore become more pronounced as the linear speed diminished; that is, as the pressure ratio $r$ approached unity. This is just the character of the departures of the observed values of $R$ from the computed values of $R_i$, hence it seems advisable to proceed next to a consideration of the probable effect of viscosity, and attempt to make an addition to our theory which shall allow for it while still assuming that the flow is adiabatic.

## 12. ADIABATIC EFFLUX OF A VISCOUS GAS

In consequence of the passive resistance due to viscosity, heat is developed within the gas during its passage from $A_0$ to $A$ or, as we say, there is a certain amount of "dissipation." We shall denote this quantity of heat or amount of dissipation, per gram of gas, by the letter $D$.

The major part of the dissipation will evidently occur close to or in the orifice where the gas has almost attained its lowest pressure, both because the gas has there nearly reached its greatest speed and because the reduction in cross section of the stream increases the transverse velocity gradients and the rate of shear. The final net result of the dissipation must, therefore, be nearly the same as if the gas first expanded isentropically to the back pressure $p$ and the dissipation then all occurred at the constant pressure $p$, reducing the speed from the value attained in isentropic expansion and given by equation (18), and simultaneously raising the temperature from its lowest value by an amount $D/C_p$. Since we can do no better, we shall adopt this simplified view of the matter, which is certainly a fair approximation, and proceed as if the dissipation really did occur in this way.

The temperature after isentropic expansion being $\theta_0 r^\alpha$, by equation (14), the final temperature at $A$ is now

$$\theta = \theta_0 r^\alpha + \frac{D}{C_p} \tag{26}$$

Substituting this value in equation (9), which is satisfied for adiabatic efflux regardless of dissipation, we have

$$\frac{1}{2}S^2 = \theta_0 C_p(1 - r^\alpha) - D \tag{27}$$

or after eliminating $\theta_0 C_p$ as before

$$\frac{1}{2}S^2 = \frac{p_0}{\rho_0}\frac{1 - r^\alpha}{\alpha} - D \tag{28}$$

We must next express $D$ in terms of the other quantities, and to do this we first *assume* that for an orifice of given shape the value of $D$ depends on and is determined by the diameter of the orifice $a$, the jet speed $S$, the viscosity of the gas $\mu$, and its initial density $\rho_0$. The subsistence of such a relation may be symbolized by writing

$$D = f(a, S, \mu, \rho_0) \tag{29}$$

and dimensional conditions require [4] that any relation involving these five quantities and no others have the form

$$D = S^2\varphi\left(\frac{a\rho_0 S}{\mu}\right) \tag{30}$$

in which $\varphi\left(\frac{a\rho_0 S}{\mu}\right)$ is an unknown function of the single dimensionless quantity $(a\rho_0 S/\mu)$ and remains to be found by other than dimensional considerations.

The flow toward and into the orifice is convergent, and we know from observation that convergence tends to suppress turbulence and maintain stream line flow. We shall therefore *assume*, as a sufficient approximation to the true state of affairs, that there is no turbulence whatever. But in purely stream line motion the resistances and the dissipation are, other things being equal, directly proportional to the viscosity of the fluid; hence it follows from our assumption that $\varphi\left(\frac{a\rho_0 S}{\mu}\right)$ must be directly proportional to $\mu$, and that equation (30) must have the form

$$D = B\frac{\mu S}{a\rho_0} \tag{31}$$

in which $B$ is a dimensionless constant shape factor determined by the shape of the orifice and of the approach to it. By substitut-

[4] See Trans. Am. Soc. Mech. Engineers, 37, p. 263, 1915; or Phys. Rev., 4 p. 345, Oct. 1914.

ing this expression for $D$ in equation (28) we obtain the equation

$$\frac{1}{2}S^2=\frac{p_0}{\rho_0}\frac{1-r^\alpha}{\alpha}-B\frac{\mu S}{a\rho_0} \tag{32}$$

which serves as the starting point of our tentative theory of the effusion method of determining the relative densities of gases which are not free from viscosity.

To eliminate the jet speed $S$ and replace it by the observed quantity $\tau$ or its reciprocal $V_0$, we proceed as follows. If $V$ is the volume, measured at $p$, $\theta$, of the gas which escapes per second; and $V_0$ its volume at $p_0$, $\theta_0$, we have by (3)

$$\frac{V}{V_0}=\frac{p_0}{p}\frac{\theta}{\theta_0}=\frac{1}{r}\frac{\theta}{\theta_0} \tag{33}$$

whence by (26)

$$V=\frac{V_0}{r^{1-\alpha}}\left[1+\frac{D}{r^\alpha\theta_0 C_p}\right] \tag{34}$$

We next eliminate $\theta_0 C_p$ by means of (16) and (3), replace $D$ by its value from (31), and combine with the equation $V=AS$ which subsists as before. The result is

$$S=\frac{V_0}{Ar^{1-\alpha}}\left[1+\frac{B\mu\alpha S}{ar^\alpha p_0}\right] \tag{35}$$

an equation which may be used with (32) for eliminating $S$.

For convenience in the algebraic work we introduce the abbreviation

$$\frac{B}{Aa}=C \tag{36}$$

Since the orifices were so small that neither $A$ nor $a$ could be determined at all accurately, and since furthermore the value of $B$ is entirely unknown, $C$ is a purely empirical orifice constant.

We shall also use the further abbreviation

$$\frac{B}{Aa}\frac{\alpha\mu V_0}{rp_0}=\frac{C\alpha\mu}{p\tau}=X \tag{37}$$

For a given orifice and a given back pressure, $C/p$ is constant. In all our experiments $p$ was nearly constant, being simply the barometric pressure of the outside atmosphere. For a given gas and a given temperature, $\alpha\mu$ is also constant so that $X$ depends sensibly only on $\tau$, which varies with the pressure ratio $r$.

Upon eliminating $S$ between (32) and (35) we now have the equation

$$\left\{\frac{1}{Ar^{1-\alpha}\tau(1-X)}\right\}^2+\frac{2p_0r^\alpha X}{\alpha\rho_0(1-X)}=2\frac{p_0}{\rho_0}\frac{(1-r^\alpha)}{\alpha} \tag{38}$$

whence

$$\frac{\rho_0}{\tau^2}=2A^2p_0\frac{r^{2-2\alpha}}{\alpha}[(1-r^\alpha)-(2-r^\alpha)X+X^2] \tag{39}$$

By comparing (39) with (22) which was deduced for isentropic efflux we see that the result of our considerations on the effects of viscosity has been to modify the isentropic equation by the addition of two correction terms which involve the viscosity of the gas. It is to be presumed that these terms are small enough that the second, containing $X^2$, will be negligible. Trial computations with values of $C$ found from the experiments confirm this inference and show that for our purposes the $X^2$ term may be ignored and equation (39) used in the simpler form

$$\frac{\rho_0}{\tau^2}=2A^2p_0\frac{r^{2-2\alpha}}{\alpha}[(1-r^\alpha)-(2-r^\alpha)X] \tag{40}$$

## 13. EQUATIONS FOR THE COMPARISON OF VISCOUS GASES

Let the value of $R$ which would be obtained from the observations, if the efflux of each of two gases were adiabatic but affected by their viscosities in the manner assumed in the foregoing section, be denoted by $R_\mu$. Let equation (40) refer to the standard gas, and a similar equation with the appropriate letters primed refer to the test gas. Then upon comparing the two equations and assuming as before that $A'=A$, we have

$$R_\mu=\frac{\alpha'}{\alpha}r^{2(\alpha'-\alpha)}\frac{(1-r^\alpha)-(2-r^\alpha)X}{(1-r^{\alpha'})-(2-r^{\alpha'})X'} \tag{41}$$

and we now wish to find out whether this equation can be made to fit the observed facts by a suitable choice of the orifice constant $C$. The graphical comparison of theory with observation is the most enlightening and in order to use equation (41) for computing and drawing a curve $R_\mu=f(r)$ we must first undertake some further transformations.

By equation (37) which defines $X$ and $X'$, we have

$$X'=X\frac{\alpha'}{\alpha}\frac{\mu'}{\mu}\frac{\tau}{\tau'} \tag{42}$$

and by the definition of $R$ in equation (23) we have for the present case of adiabatic efflux under the influence of viscosity

$$\frac{\tau}{\tau'}=\sqrt{\frac{\rho_0}{\rho'_0 R_\mu}} \tag{43}$$

so that by (42)

$$X'=X\frac{a'}{a}\frac{\mu'}{\mu}\sqrt{\frac{\rho_0}{\rho'_0}}\cdot\frac{1}{\sqrt{R_\mu}} \tag{44}$$

Let

$$\frac{a'}{a}\frac{\mu'}{\mu}\sqrt{\frac{\rho_0}{\rho'_0}}=P \tag{45}$$

The quantity $P$ is a dimensionless constant which expresses the value of a certain property of the test gas in terms of the corresponding property of the standard. Its value is known because the values of $a'/a$, $\mu'/\mu$ and $\rho'_0/\rho_0$ have been measured for all the gases used, except that $\alpha'$ for hydrogen was assumed to be equal to $\alpha$ for air and was not measured. The value of $\mu'/\mu$ was, to be sure, measured only for a single temperature; but since the viscosity of gases does not vary rapidly with temperature nor very differently for different gases, and since the whole temperature range in our work was small, a single constant value of $\mu'/\mu$ may be used for each gas. The values used for $P$ have been given in Table 6.

By equations (44) and (45) we now have

$$X'=\frac{P}{\sqrt{R_\mu}}X \tag{46}$$

whence by substitution in (41) we have

$$(1-r^{\alpha'})R_\mu-(2-r^{\alpha'})PX\sqrt{R_\mu}=\frac{a'}{a}r^{2(\alpha'-\alpha)}[(1-r^{\alpha})-(2-r^{\alpha})X] \tag{47}$$

If we solve this for $R_\mu$, the result may be written in the form

$$R_\mu=L+2G^2[1+\sqrt{1+L/G^2}] \tag{48}$$

where

$$\left.\begin{aligned} L&=\frac{a'}{a}r^{2(\alpha'-\alpha)}\frac{(1-r^{\alpha})-(2-r^{\alpha})X}{1-r^{\alpha'}}\\ G&=\frac{2-r^{\alpha'}}{1-r^{\alpha'}}\frac{PX}{2}\\ X&=\frac{Ca\mu}{p}\cdot\frac{1}{\tau}\end{aligned}\right\} \tag{49}$$

Trial computations showed that the positive value of the radical in (48) was the proper one to use, so the negative sign in omitted.

## 14. METHOD OF COMPARING THE FOREGOING THEORY WITH THE OBSERVATIONS

The value of $R_\mu$ computed for any value of $r$ from equations (48) and (49) depends upon: (a) The values of $\alpha$, $\alpha'$, $\mu'/\mu$, and $\rho'_0/\rho_0$ which were determined experimentally; (b) the value selected for the orifice constant $C$; and (c) the value of $\tau$ observed for air at the given $r$.

The most obvious procedure for testing the agreement of the theory with the observations is as follows: For each of the volume intervals of the apparatus we may find the mean pressure ratio from the barometric pressure $p$, and the pressure differences $(p_0-p)$ at the beginning and end of the interval, which have been measured once for all. We may next find the value of $\tau$ corresponding to each of these values of $r$ by dividing the air time for the interval by the known volume of the interval. We may then assume a value of $C$ and compute from (48) the value of $R_\mu$ which corresponds to each of the values of $r$. These computed values of $R_\mu$ may then be compared with the observed values of $R$, the clearest way of doing this being to draw a curve $R_\mu=f(r)$ from the computed values and plot the observed values of $R$ as separate points. A similar process may be carried out for each of the other experiments on the orifice in question, with the same value of the orifice constant $C$. Finally, the whole may be repeated with various values of $C$ until no further improvement can be obtained in the agreement between theory and observation.

Upon consideration of the cumbersome nature of the equations it is quite evident that the foregoing method would, in practice, be intolerably laborious and that a simpler one must be used. The procedure was therefore modified, the idea being, first, to work only at a few fixed values of $r$ for which values of the various functions such as $(1-r^\alpha)$ could be tabulated once for all; and second, to treat all the experiments on a single gas together and draw a single average curve $R_\mu=f(r)$ for that gas instead of a separate curve for each experiment.

The separate experiments differed, first, in that the initial temperature $\theta_0$ varied somewhat so that the air times $\tau$ for any one interval could not be expected to be quite the same even

if $r$ were the same; and second, in that the barometric back pressure also varied from one experiment to another with consequent small variations of $r$. Thus, for each of the volume intervals of the apparatus, the experiments on any one orifice gave a number of slightly differing values of $\tau$ corresponding to slightly differing values of $\theta_0$ and of $r$. The first step was to average these values and it was done as follows.

Considering one interval only, the values of $V_0 = 1/\tau$ were found for all the runs with air made through the orifice in question. From each of these the value of $V_0^2(295/\theta_0)$ was computed; this amounts to reducing the value of $V_0^2$ observed at $\theta_0$ to what would have been observed at 22° C on the assumption that the rate of efflux of air is proportional to the square root of the absolute temperature. The initial temperatures all fell between 19° and 28° with a mean of about 22°, and the reduction just mentioned was a short one. The reduction by setting $V_0 \propto \sqrt{\theta_0}$ was adopted because equation (22), which is a first approximation to the truth gives $V_0^2 \propto \theta_0$, and equation (39) would not give a very different relation since it differs from (22) only by correction terms.

These values of $V_0^2(295/\theta_0)$ were averaged and the corresponding values of $r$ also averaged. The mean values of $V_0^2(295/\theta_0)$ were plotted against the mean values of $r$ and a curve drawn through the points; this curve was used for interpolation and was of a satisfactory shape for the purpose. Readings were now made at the round values of $r$ which it had been decided to use in the computations, namely $r = 0.75$, 0.79, 0.82, 0.86, 0.90, 0.93, 0.96, 0.986. These were selected because while fairly evenly spaced they were not far from the means, so that in interpolating by means of the curve no great error could be introduced by the arbitrary shaping of the curve between the plotted points. The square root of the reciprocal of each interpolated value of $V_0^2(295/\theta_0)$ was now extracted and used in the computation of $R_\mu$ as if it were a value of the air time $\tau$ actually observed at the standard pressure ratio $r$.

It remained to select a mean value of $C' = C\alpha\mu/p$, $\alpha$ and $\mu$ being constant, and $p$ nearly so. This value, together with the values of $\tau$ obtained as described above, and the known values of $\alpha$, $\alpha'$ etc., was used to compute values of $R_\mu$ by means of equation (48). On the supposition that our theory is correct and that $C'$ has been properly chosen, these computed values of $R_\mu$ are

equal, as nearly as we can tell, to the values of $R$ which would have been found from observations at $r=0.75$, 0.79 etc., if: (a) the efflux had been strictly adiabatic; (b) the initial temperature had always been 22° C; and (c) the barometric pressure had been the same during all the runs.

A curve $R_\mu=f(r)$ was drawn through these computed points and the observed points were plotted separately. The effect of correcting the positions of the observed points to reduce them to 22° and a common mean value of $p$ would have been small compared with the experimental uncertainties of their positions and no such reduction was undertaken. The graphical comparison is therefore finally between a curve computed for 22° and constant $p$, and observations made under various conditions differing a little from these but not more than would be covered by the observational errors.

## 15. RESULTS OF THE COMPARISON

The method of making the computations with a particular value of $C'$ having now been described, the question remains whether, by repeating the computations and adjusting the value of $C'$ by trial, a satisfactory agreement with the observed facts can be achieved. If it can, our theory may be regarded as satisfactory, for in any event the constant $C'$ is purely empirical and can be found only by fitting the equations to the observations.

This question has to be answered in the negative: after all the laborious computations it was found that no possible value of $C'$ would make equation (48) fit the observations within their experimental uncertainties, and the theory as so far developed could not be regarded as satisfactory. But on the other hand, it was found that while the theory was not entirely satisfactory, it was not very bad. For a suitably chosen value of $C'$ would give computed curves which were fairly near to the observed points, so that the differences $(R_{\text{obs}}-R_\mu)$ were numerically very much smaller than the differences $(R_{\text{obs}}-1)$. In other words, our allowance or correction for the effects of viscosity did account for the major part of the observed errors of the effusion method; and moreover, the residual errors which could not be accounted for in this way appeared to have a regular systematic run which was of the same nature for all the gases. It therefore seemed probable that the theory was correct in its main outlines and in attributing to viscosity an important part in causing the errors of

Bunsen's method, but that either the treatment of viscosity required to be somewhat modified or some further disturbing cause remained to be allowed for.

Several modifications of the above-described theory of the effect of viscosity were developed by modifying the assumptions, and trial computations were undertaken with the resulting equations. None of these slightly different forms of the theory seemed any better founded in physical common sense than the original one already described; none of them gave any better agreement with observations; and none of them was so easy to use. We therefore abandoned further attempts in this direction and proceeded to search for an additional correction, due to some other cause than viscosity, which if added to the correction already made should lead to a better agreement between the theory and the observed facts.

The most obvious possibility is that in addition to the retardation of efflux by viscosity, heat transmission from the orifice to the jet may also have a sensible effect on the rate of efflux, the phenomenon being appreciably different from an adiabatic expansion; so we turned our attention to this subject. Since it seemed quite hopeless to attempt to treat viscosity and heat transmission simultaneously and with due allowance for their interaction, a more rudimentary plan was followed. In view of the fact that the effects of both viscosity and the second disturbing cause, now assumed to be heat transmission, are of the nature of corrections—that is, relatively small, at least until $r$ approaches unity—it was assumed that they might properly be treated separately as if each acted alone; and we therefore proceeded to develop a theory of the efflux of a nonviscous but thermally conducting gas, and to deduce an expression for the effect of heat transmission on the value of $R$.

This expression, like the one for $R_\mu$, contains an empirical orifice constant. After obtaining the expression, we make up a combined equation which purports to take account of the effects of both viscosity and heat transmission and contains therefore two empirical orifice constants. The theory must then be tested by adjusting the constants; if a pair of values can be found such that the computed values of $R$ are in satisfactory agreement with the observed, the theory in this final shape may be regarded as satisfactory and as probably correct in its main outlines if not in all details.

We may now go on to consider effusion which is affected by heat transmission but is not retarded to any sensible extent by viscous resistances.

## 16. EFFLUX WITH ADDITION OF HEAT BUT WITHOUT DISSIPATION

Since the rate of heat flow into the gas from the metal increases with the difference of temperature and with the intimacy of contact, it is evident that most of the heat transmission will occur in the orifice, after the gas has almost attained its lowest pressure. We shall therefore, assume as an approximation, that the effect of heat transmission on efflux is the same as if the gas expanded isentropically to the back pressure $p$ and a quantity of heat $Q$ per gram were then added to it at the constant pressure $p$, raising its temperature from the lowest point by the amount $Q/C_p$. This assumption is similar to one made in section 10 and it is unquestionably a fairly approximate representation of what actually occurs.

If $\theta$ denotes the final temperature of the gas and $\theta_1 = r^\alpha \theta_0$ its temperature after isentropic expansion, we have by the foregoing assumption.

$$\theta = r^\alpha \theta_0 + \frac{Q}{C_p} \tag{50}$$

Substituting this value of $\theta$ in equation (8) and reducing, we have

$$\frac{1}{2} S^2 = \theta_0 C_p (1 - r^\alpha) \tag{51}$$

$Q$ having disappeared. But (51) is identical with (15) which applies to isentropic efflux; whence it follows that addition of heat in the manner postulated above has no effect at all on the linear exit speed of the jet.

But though the speed of the gas at the section $A$ is not affected, the temperature is raised, and the specific volume is increased in the same ratio, viz,

$$\frac{\theta}{\theta_1} = 1 + \frac{Q}{r^\alpha \theta_0 C_p}.$$

The time required for a given mass to escape will be increased in this ratio; hence if $\tau_\lambda$ is the time observed under the present conditions, and $\tau_i$ the time that would be observed if the efflux were isentropic, we have

$$\frac{\tau_\lambda}{\tau_i} = 1 + \frac{Q}{r^\alpha \theta_0 C_p}. \tag{52}$$

We have next to find an expression for $Q$, and we again have recourse to the principle of dimensional homogeneity in the convenient form of the $\Pi$ theorem.[5] We assume that for an orifice of given shape, $Q$ is determined by the diameter of the orifice, the speed of the jet, the difference of temperature between the jet and the orifice, and the properties of the gas. The most obviously important of these properties are the density $\rho$, specific heat $C_p$, and thermal conductivity $\lambda$. But we shall also, at the start, include the viscosity $\mu$ as possibly affecting $Q$ through its influence on the nature of the flow, although it seems likely that $\mu$ will be of small importance, and we have already agreed to disregard dissipation. If we let $\Delta$ represent the temperature difference, our assumption regarding $Q$ is now symbolized by the equation

$$Q = f\,(a, S, \Delta, \rho, C_p, \lambda, \mu) \tag{53}$$

All the quantities except $Q$ and $a$ are to be regarded as mean values averaged over the time during which $Q$ is being transmitted to the gas, but as an approximation we shall indentify them with their values at the end of the isentropic expansion.

By applying the $\Pi$ theorem, equation (53) may be thrown into the form

$$Q = \Delta C_p \varphi\left\{\frac{\Delta C_p}{S^2}, \frac{\mu C_p}{\lambda}, \frac{\lambda}{aS\rho C_p}\right\} \tag{54}$$

and the next question is whether we have any information that will help us to make a rational guess at the form of the operator $\varphi$.

The greatest temperature drop in any of our experiments was less than 26° C; hence it seems safe to assume that $Q$ was sensibly proportional to $\Delta$. This assumption gives us a first simplification of (54) to the form

$$Q = \Delta C_p \varphi_1\left\{\frac{\mu C_p}{\lambda}, \frac{\lambda}{aS\rho C_p}\right\}. \tag{55}$$

For the gases used in our work the relative values of $\mu C_p/\lambda$ are approximately as follows:

| | Air | $H_2$ | $CH_4$ | $CO_2$ | Ar |
|---|---|---|---|---|---|
| $\mu C_p/\lambda =$ | (1.00) | 0.93 | 1.28 | 1.10 | 1.01 |

In view of the great uncertainty in the values of $C_p$ and $\lambda$, even for pure gases, and of the fact that we were obliged to rely upon

[5] See Trans. Am. Soc. Mech. Engineers, 37, p. 289; 1915.

a mixture rule for computing the foregoing values of $\mu C_p/\lambda$, it can not be said with certainty that the differences in the values are not illusory. Hence in the intercomparison of these gases we may as well treat $\mu C_p/\lambda$ as a constant and so reduce equation (55) to the simpler form

$$Q = \Delta C_p \varphi_2 \left\{ \frac{\lambda}{aS\rho C_p} \right\}. \tag{56}$$

The next point to be considered is whether or not we may regard the flow as stream line. If we may, $Q$ will be proportional to the conductivity of the gas and (56) will be still further simplified to the form

$$Q = N \frac{\Delta\lambda}{aS\rho} \tag{57}$$

in which $N$ is a dimensionless shape factor. We nave already made this assumption in treating the effects of viscous resistance, and we shall also make it here, although the point will be touched upon again in section 19.

Substituting from (57) into (52), we now have

$$\frac{\tau_\lambda}{\tau_i} = 1 + \frac{N\Delta\lambda}{aS\rho r^\alpha \theta_0 C_p}. \tag{58}$$

The comparisons already made between our equations for adiabatic efflux of a viscous gas and the observed facts, showed that the remaining discrepancy which we are now attempting to account for by heat transmission is small, though greater than the uncertainties of the experiments. Hence the correction term in (58) is small and we may write

$$\left(\frac{\tau_\lambda}{\tau_i}\right)^2 = 1 + \frac{2N\Delta\lambda}{aS\rho r^\alpha \theta_0 C_p}. \tag{59}$$

Let $\rho_n$ be the density at a normal state $p_n$, $\theta_n$, so that

$$\rho = \rho_n \frac{p}{p_n} \frac{\theta_n}{r^\alpha \theta_0}. \tag{60}$$

Let $\lambda_n$ be the value of $\lambda$ at this same normal state, and let us assume that $\lambda \propto \sqrt{\theta}$, a rough approximation but better than entirely disregarding the variation of thermal conductivity with temperature. Then we have

$$\lambda = \lambda_n \sqrt{\frac{r^\alpha \theta_0}{\theta_n}} \tag{61}$$

Substitute into (59) the values of $\rho$ and $\lambda$ from (60) and (61); also the values

$$\Delta = \theta_0(1 - r^\alpha) \tag{62}$$

and

$$S = \sqrt{2\theta_0 C_p(1 - r^\alpha)} \tag{63}$$

Let

$$\frac{\sqrt{2}Np_n\theta_0}{a\theta_n^{3/2}p} = W \tag{64}$$

and

$$\frac{\lambda_n}{\rho_n C_p^{3/2}} = \beta \tag{65}$$

Then after the substitutions and reduction we have

$$\left(\frac{\tau_\lambda}{\tau_i}\right)^2 = 1 + W\beta\sqrt{r^\alpha(1 - r^\alpha)} \tag{66}$$

In the quantity $W$ defined by equation (64) all the factors except $\theta_0$ and $p$ are constants, and $\theta_0$ and $p$ vary only slightly from one experiment to another. Under the circumstances it would be a waste of time to take any account of these relatively small variations, and we may therefore treat the quantity $W$ as an orifice constant.

The quantity $\beta$ defined by equation (65) measures a property of the gas in question, but its value is a priori, very uncertain indeed; for while the densities of our gases were measured, the values of the thermal conductivities and specific heats had to be obtained from Landolt and Börnstein's tables. The values of $\lambda$ are only very roughly known even for the pure gases, so that the values of $\beta$ which we could compute a priori had to be regarded as only tentative and subject to correction. The manner in which they were corrected will be described later.

Assuming for the instant that the orifice constant $W$, and the gas constant $\beta$ are known, equation (66) shows us how the rate of efflux of a nonviscous but thermally conducting gas will be affected by heat transmission from the orifice, if the simplifying assumptions used in developing the theory have been reasonably good approximations to reality.

## 17. APPLICATION TO THE COMPARISON OF NONVISCOUS BUT THERMALLY CONDUCTING GASES

Let $R_\lambda$ be the value which would be found in a comparison of two gases by the effusion method if the flow were affected by heat transmission but not by viscous resistances; and as before let $R_i$ be the value for isentropic efflux. Then we have

$$\frac{R_\lambda}{R_i}=\left(\frac{\tau'_\lambda}{\tau_\lambda}\div\frac{\tau_i'}{\tau_i}\right)^2=\left(\frac{\tau'_\lambda}{\tau_i'}\right)^2\div\left(\frac{\tau_\lambda}{\tau_i}\right)^2 \tag{67}$$

Let equation (66) refer to the standard gas, and let us divide it, member for member, into the corresponding equation for the test gas. Then by equation (67) we shall have

$$\frac{R_\lambda}{R_i}=\frac{1+W\beta'\sqrt{r^{\alpha'}(1-r^{\alpha'})}}{1+W\beta\sqrt{r^{\alpha}(1-r^{\alpha})}} \tag{68}$$

or very nearly

$$\frac{R_\lambda}{R_i}=1+W[\beta'\sqrt{r^{\alpha'}(1-r^{\alpha'})}-\beta\sqrt{r^{\alpha}(1-r^{\alpha})}] \tag{69}$$

whence

$$R_\lambda-R_i=R_iW\beta\left[\frac{\beta'}{\beta}\sqrt{r^{\alpha'}(1-r^{\alpha'})}-\sqrt{r^{\alpha}(1-r^{\alpha})}\right] \tag{70}$$

Now in our experiments the value of $R_i$ always remained within the limits 0.986 to 1.027. Hence it will be legitimate to set $R_i=1$ in the second member of (70) because we know already that the correction we are trying to compute is small—in fact, not very much greater than the observational errors. Since $\beta$ is a constant for the standard gas, if we let

$$W\beta=M \tag{71}$$

$M$ is an empirical orifice constant. And if we let

$$R_\lambda-R_i=\Delta_\lambda \tag{72}$$

equation (70) may now be written

$$\Delta_\lambda=M\left[\frac{\beta'}{\beta}\sqrt{r^{\alpha'}(1-r^{\alpha'})}-\sqrt{r^{\alpha}(1-r^{\alpha})}\right] \tag{73}$$

Supposing all our hypotheses and approximations to be satisfactory and the values of $M$ and of $\beta'/\beta$ to be known, equation (73) would enable us to compute the amount $\Delta_\lambda$ by which the

value of $R$ found with conducting gases would exceed the value found if there were no conduction, viscous resistances being negligible in both cases.

## 18. ALLOWANCE FOR THE SIMULTANEOUS ACTION OF VISCOSITY AND CONDUCTIVITY

We have now devised a theory of the effect of viscosity alone on the results of Bunsen's method of determining relative density; and we have found it not adequate to representing the observed facts, though nearly so. We have then developed an equation for computing the effect of heat transmission acting alone. We shall now *assume* that when the gases are both viscous and conducting, as they all are in reality, the effects of viscosity and conduction are additive and may be computed by the equation

$$R = R_\mu + \Delta_\lambda \tag{74}$$

where by equations (48) and (49)

$$R_\mu = L + 2\,G^2\left[1 + \sqrt{1 + L/G^2}\right] \tag{75}$$

$$\left.\begin{aligned} L &= \frac{\alpha'}{\alpha}\, r^{2(\alpha'-\alpha)} \frac{(1 - r^\alpha) - (2 - r^\alpha)\,X}{1 - r^{\alpha'}} \\ G &= \frac{2 - r^{\alpha'}}{1 - r^{\alpha'}}\,\frac{PX}{2} \\ X &= \frac{C\alpha\mu}{p\tau} = \frac{C'}{\tau}; \end{aligned}\right\} \tag{76}$$

by equation (73)

$$\Delta_\lambda = M\left[\frac{\beta'}{\beta}\sqrt{r^{\alpha'}\,(1 - r^{\alpha'})} - \sqrt{r^\alpha\,(1 - r^\alpha)}\right]; \tag{77}$$

and $C'$ and $M$ are empirical orifice constants. It remains to be seen whether these equations are, in fact, capable of representing the observations, and this must be investigated by means of trial computations.

The values of $\alpha$, $\alpha'$ and $P$ have been discussed in sections 5 and 13, and the values of the air time $\tau$ in section 12. The values of $\beta'/\beta$ are known only very roughly and those of $C'$ and $M$ are altogether unknown. We therefore have set before us a rather complicated task of adjusting empirical constants, with no a priori certainty that a satisfactory adjustment is possible. The manner

in which the problem was attacked and the degree of success achieved will be be treated in sections 19 to 22.

## 19. ATTEMPTS TO ALLOW FOR TURBULENCE

A number of preliminary computations appeared to show that the results of experiments on orifices 23A, 23B, 28, and 29 could not be represented by equations (74) to (77), if the values of $\beta'/\beta$ given tentatively in Table 6 were used; but that if the values were arbitrarily changed to about the following

| | $H_2$ | $CH_4$ | $CO_2$ | Ar |
|---|---|---|---|---|
| $\beta'/\beta =$ | 1.5 | 0.75 | 0.37 | 1.13 |

values of $C'$ and $M$ could be found for each orifice which would make the theory agree pretty well with the facts. It was not clear from the results whether the theory of the conduction effect required modification or whether the tentative values of $\beta'/\beta$ required correction.

Attempts were made to modify the theory of the heat transmission effect by allowing for the possibility of turbulence in the orifice. One such attempt was made in connection with equation (56). Instead of assuming that there was no turbulence and so passing directly from (56) to (57), it was assumed that

$$\varphi_2\left\{\frac{\lambda}{aS\rho C_p}\right\} = N\left\{\frac{\lambda}{aS\rho C_p}\right\}^{\epsilon} \tag{78}$$

where $\epsilon$ is a new constant dependent on the degree of turbulence of the motion. If there were no turbulence at all, we should set $\epsilon = 1$ and get equation (57) as before. But if turbulence were present, the effect of the conductivity $\lambda$ would be decreased while that of the specific heat $C_p$ would be increased because of convection due to turbulence. Hence for turbulent motion we should have $\epsilon < 1$, and the greater the turbulence the more nearly $\epsilon$ would approach zero, the physical meaning of this being that if the motion were very turbulent virtually the whole of the transfer of heat would occur by convection and not by conduction.

The result of adopting equation (78) was to give the equation

$$Q = N\Delta C_p^{1-\epsilon}\left\{\frac{\lambda}{aS\rho}\right\}^{\epsilon} \tag{79}$$

instead of the simpler equation (57) to which it reduces when

$\epsilon = 1$. The same process of reasoning as already described then led to an equation of the form

$$\frac{R_\lambda}{R_1} = 1 + W\left\{\beta'^{\epsilon} r^{\alpha'\left[\frac{3\epsilon}{2}-1\right]}(1-r^{\alpha'})^{\left[1-\frac{\epsilon}{2}\right]} - \beta^{\epsilon} r^{\alpha\left[\frac{3\epsilon}{2}-1\right]}(1-r^{\alpha})^{\left[1-\frac{\epsilon}{2}\right]}\right\} \quad (80)$$

in place of equation (69) to which it reduces when $\epsilon = 1$. Equation (80) then permitted of our obtaining an expression for $\Delta_\lambda$, analogous to but far more complicated than that given by equations (73), and computations could then be made by equation (74).

Computations by this method with several values of $\epsilon$ and with the tentative values of $\beta'/\beta$ given in Table 6, left it doubtful whether any improvement had been attained to offset the increased difficulty of the computations.

## 20. RESULTS OF THE OBSERVATIONS ON ORIFICE NO. 31; VALUES OF $\beta'/\beta$ FOR HYDROGEN AND CARBON DIOXIDE

At this stage of the investigation the experiments were resumed. Improved apparatus (No. II) was constructed and calibrated, and greater accuracy of measurement ensured. A new orifice, No. 31, was also made, great care being taken to have its entrance smooth and trumpet-shaped on one side (31A) and sharp on the other (31B). With 31A, the entrance being smooth and rounded, it seemed safe to assume, first, that there would be little or no contraction, and, second, that the motion would be sensibly free from turbulence, so that if the rudimentary theory embodied in equations (74) to (77) were ever to be applicable, it would be to experiments made on this orifice.

For lack of time only two experiments were made with orifice 31A, one with hydrogen and one with carbon dioxide, but they appeared satisfactory as to experimental accuracy. Upon applying the theoretical equations to the experimental data the results were as follows.

(*a*) If the motion was assumed to be somewhat turbulent and the form of theory consequent on the assumption of equation (78) with $\epsilon$ considerably less than unity was adopted, no satisfactory agreement between the theory and the observations could be obtained with any possible values of the orifice constants $C'$ and $M$ or any values of $\beta'/\beta$ for hydrogen and carbon dioxide. It was clearly apparent that if $\epsilon$ were sensibly different from unity the *form* of the heat transmission term $\Delta_\lambda = f(r)$ was unsuitable. In other words, for this orifice, where we have every reason to

suppose that turbulence was absent, the equation developed on the assumption that turbulence was absent fits the facts better than the modification of it, which supposes that turbulence is present.

(*b*) By setting $\epsilon = 1$—that is, by assuming turbulence to be absent and using the theory as embodied in equations (74) to (77) and as first given—values of $C'$ and $M$ could be found which brought about an excellent agreement of the theory with the observations, if, but only if, at least one of the values of $\beta'/\beta$ (for hydrogen and carbon dioxide) was arbitrarily changed from its original tentative value.

On the strength of these results, obtained from new and improved apparatus but consistent with all the previous observations, we decided to accept the theory as developed and to correct the values of $\beta'/\beta$ arbitrarily by reference to the experiments, choosing such values, not greatly differing from the original tentative values computed a priori, as should if possible result in a satisfactory agreement between theory and observation.

After consideration of the above-mentioned experiments on orifice 31A the values

| | $H_2$ | $CO_2$ |
|---|---|---|
| $\beta'/\beta =$ | 1.5 | 0.4 |

instead of the original tentative values 1.69 or 1.62 and 0.46 were definitively adopted for use in all future computations on these two gases.

The constants $C'$ and $M$ of equations (76) and (77) were then adjusted by trial and the values

$$C' = 0.0075 \qquad M = 0.23$$

adopted. The values of $R = f\ (r)$ computed with these values from equation (74) are represented by the curves in plate 2, while the observed points are plotted separately.

## 21. OBSERVATIONS ON ORIFICE NO. 28; VALUES OF $\beta'/\beta$ FOR METHANE AND ARGON

It now remained to adopt values of $\beta'/\beta$ for methane and argon which had not been used with orifice 31A. For this purpose reference was made to the experiments on orifice 28, because the experiments on this orifice appeared to be more consistent and therefore probably more accurate than those on 23A, 23B, and 29. They were also more numerous and had been made with three

separate pieces of apparatus, so that the average results were less likely to be subject to systematic errors due to peculiarities of the apparatus or errors in calibration.

We proceeded as follows. With the values of $\beta'/\beta$ already adopted for hydrogen and carbon dioxide as suited to the experiments on orifice 31A, computations were undertaken by equations (74) to (77) and values of $C'$ and $M$ were determined as as to give as satisfactory an agreement as possible between the observations on hydrogen and carbon dioxide and the computed curves $R=f(r)$. These values were

$$C'=0.012 \qquad M=0.24$$

and the agreement between the computed curves and the observed points is to be seen by examining plate 3.

The values of $C'$ and $M$ having thus been determined without any attention to the observations on methane and argon, the computations were next made for the latter two gases with these same values of $C'$ and $M$ and with such values of $\beta'/\beta$ for methane and argon as to make the computed curves of $R=f(r)$ fit the observations as well as possible. The values finally adopted for all four gases were as follows:

| Gas | $H_2$ | $CH_4$ | $CO_2$ | $Ar$ |
|---|---|---|---|---|
| $\beta'/\beta=$ | 1.50 | 0.75 | 0.40 | 1.04 |

and these were used without further change in all the remaining computations. They differ considerably from the tentative values given in Table 6 but not by more than the uncertainties of those values.

The curves for methane and argon, computed with the foregoing values of $\beta'/\beta$, but with the values of $C'$ and $M$ determined by reference only to hydrogen and carbon dioxide, agree excellently with the observed points, the fit being on the whole decidedly better than for carbon dioxide and very much better than for hydrogen.

## 22. RESULTS OF APPLYING THE THEORY TO ORIFICES NOS. 29 AND 23A

The result so far is to show that if the values given above for $\beta'/\beta$ are adopted, the theory embodied in equations (74) to (77) is capable of representing the observed facts for orifices 31A and 28, nearly or quite within the limits of the experimental errors, except at the largest values of $r$, where the values of $(R-1)$ can no longer be regarded as small corrections, as demanded by the theory.

Satisfactory values of $\beta'/\beta$ having thus been obtained, the theory was applied to the observations on the other orifices, without further attempt to improve the values of $\beta'/\beta$. The work consisted merely in finding by trial for each orifice, a suitable pair of values for the orifice constants $C'$ and $M$.

*Orifice 29.*—The trial computations were all made with reference to hydrogen and carbon dioxide, no attention being paid to the observations on methane and argon. The values adopted were

$$C' = 0.013 \qquad M = 0.12$$

These were then used in computing the curves for methane and argon. The curves, together with the separate observed points, are shown on plate 4. As was found to be the case with orifice 28, the theory seems to fit the observations on methane and argon somewhat better than those on carbon dioxide and much better than it fits the observations on hydrogen.

*Orifice 23A.*—As before, the trial computations were all made with reference to hydrogen and carbon dioxide. One of the three series for carbon dioxide differed considerably from the other two and it was disregarded. This series had been ignored in our earlier computations as if under suspicion, but we have no note as to why this was done. The values found for the orifice constants were

$$C' = 0.01 \qquad M = 0.19$$

and these values, determined by reference to hydrogen and carbon dioxide, were used in the computations for methane and argon. The computed curves and the observed points are shown on plate 5.

In all the computations for orifices 31, 28, and 29 the values used for $\tau$ were means found from all the air runs on each orifice as described in section 14. But during the experiments on orifice 23A, some change in the orifice occurred about April, 1916, after all the experiments except those on argon had been completed. This change manifested itself by a change in the values of the air time $\tau$, which decreased a little as if the orifice had been enlarged or a slight obstruction removed from it. We therefore used the means of the earlier values of $\tau$ in the computations on hydrogen, methane, and carbon dioxide, but for argon we used the values of $\tau$ obtained from the argon series only.

A change in the air time means a change in the orifice, and after this change the orifice might be expected to behave as a different orifice with other values of $C'$ and $M$. In this instance, however, the change was slight and no attempt was made to determine a separate pair of values for the observations on argon. A more striking example of such a change occured with orifice 23B, which was merely 23A turned the other side up so that the direction of flow through the orifice was reversed.

## 23. BEHAVIOR OF ORIFICE NO. 23B

A study of the air times for orifice 23B showed that during the period of the experiments, January 26 to May 24, 1916, this orifice underwent three changes—two rather small, but the third quite marked. The orifice was therefore treated as four separate orifices with different constants, the computations being carried out with values of $\tau$ obtained from four separate mean curves of $V_0^2(295/\theta_0)=f(r)$.

I. Before February 27, 1916, two series were run with hydrogen, one with methane, and one with carbon dioxide. The results for hydrogen and carbon dioxide are not consistent; that is, no values of $C'$ and $M$ can be found which will make the theory agree well with the observations. On the other hand, by using the observations on hydrogen and methane a good agreement can be had by adopting the values

$$C'=0.0087 \qquad M=0.05$$

The observations for carbon dioxide are then very far from the carbon-dioxide curve found from these constants, and they show a systematic divergence from the *shape* of the curve, which we suspect to be due to the formation of a vena contracta.

The computed curves and the observed points are shown on plate 6.

The first change in the orifice occurred between the foregoing and the next-mentioned experiments.

II. On May 3 and 4 two series were run with argon. The best values for representing these series are about

$$C'=0.0079 \qquad M=0.07$$

and the resulting fit is only fair as may be seen from plate 7.

Between these and the next series a second change occurred, and

III. On May 17 one series was run with hydrogen. The constants

$$C' = 0.0079 \qquad M = 0.03$$

give a computed curve which fits the observed points better than could have been expected. The curve and the points are shown on plate 7.

Between May 17 and May 24 a third and larger change occurred, and

IV. On May 24 one series was run with carbon dioxide. If the constants

$$C' = 0.075 \qquad M = 0.07$$

are used, the agreement of the computed curve with the observed points is excellent. The curve and observed points are shown on plate 7 along with those for cases II and III.

## 24. REMARKS ON ORIFICES NOS. 23A AND 23B, I, II, III, AND IV

A study of the behavior of orifice 23 is instructive in throwing light on some of the difficulties and sources of error in the effusion method of determining gas densities, and also in giving a probable qualitative interpretation of some of the divergences between theory and observation.

In the first place, examination under the microscope showed that this orifice was rather rough and irregular on both sides, and it appeared to have a burr on one side. In the second place, difficulties were encountered from the start, especially with position 23B, in getting consistent and reproducible results, whether with air or with one of the test gases. It seems highly probable that these difficulties and irregularities of behavior were due to the roughness of the edges of the orifice which would have a tendency to catch and hold, for a longer or shorter time, minute particles of dust which might be suspended in the gas. Large irregularities were observed on one occasion when there was reason to suspect that the gas had not been thoroughly dried, so that water droplets might have been formed. And although care was taken to have the gases dry and dust free, there was always the chance that mercury droplets might cling to the sides of the orifice. For the gas within the apparatus is presumably saturated with mercury vapor; and although the density of mercury vapor at room temperature is small, it nevertheless seems possible that the cool-

ing in the jet may have caused some condensation. At all events, the indications are that particles of some sort did catch on the edges of the orifice.

If the orifice were rougher on one side than on the other and especially if it had a burr on one side, it might be expected that these difficulties would be more pronounced when that was the entrance side. Furthermore, the presence of a rough or burred entrance would render the orifice more susceptible to mechanical changes than it would otherwise be. This describes the behavior of 23B as compared with 23A. The observations were more irregular, and more difficulty was found in getting reproducible results with 23B than with 23A; and while both showed the effect of mechanical changes, probably due in some way to handling, these changes were much more pronounced for 23B than for 23A. It looks therefore as if on the side B the entrance had been rough, possibly with a burr, while on the side A it had been smoother.

Now let us consider what further differences of behavior would probably be observed between two orifices of the same diameter and length, one of which had a burred or sharp-cornered entrance while the entrance of the other was smooth and well rounded.

In the first place, the sharp entrance might give rise to the formation of a vena contracta. If it did, the jet area A would be reduced and the discharge coefficient would be less than for the orifice with rounded entrance. This describes the behavior of 23B as compared with 23A: The discharge coefficient was smaller for 23B, that is, the air times were longer than for 23A.

In the second place, if the entrance is sharp, the high speed jet is in contact with the metal for a much shorter distance than if the entrance is rounded and there is no contraction. Hence, sharpness of entrance, while it reduces the discharge by causing contraction, will tend to decrease the effect of viscosity but more especially that of heat transmission. If 23B has, in fact, a sharper entrance than 23A, we should expect its values of $C'$ and $M$ to be lower than those for 23A. The values actually found were

for 23A.....$C'=0.010$ .....$M=0.19$
for 23B (mean).....$C'=0.0080$.....$M=0.054$

which agrees with the above-mentioned suppositions.

It therefore appears, although it could not have been predicted with certainty from the appearance of the orifice under the microscope, that this orifice behaved as though it had a rounded entrance when used in the position 23A and a sharp or burred entrance when used in the position 23B.

## 25. CONCLUDING REMARKS

In developing the equations used for representing the experimental results, we assumed that at any given value of $r$ the minimum section of the jet was the same for air as for the test gas, and the ratio $A'/A$ of the two sections therefore disappeared from the equations for $R$.

This condition would be satisfied if there were no contraction at all, for then $A'$ and $A$ would be simply the smallest section of the orifice. But it would also be satisfied if there were contraction, provided the amount of contraction were the same for the different gases at any given $r$, even though the contraction might vary with $r$. If the efflux could be made dynamically similar during the comparison of two gases, we could ensure that the forms of the jets should be the same and the contraction coefficients equal; but in the sort of comparison made in using Bunsen's method the conditions of dynamical similarity are not fulfilled.

An investigation of the values of the discharge and contraction coefficients for these small orifices would be interesting, and some attempts in this direction were made; but the experimental data are not sufficient in either number or accuracy to justify a description of these attempts. All that can be said definitely is that the variations of the discharge coefficient with the diameter of the orifice are qualitatively in agreement with what is known about the flow of water and air through larger orifices up to 4.5 inches diameter.

Upon considering the general nature of the agreement of the computed curves with the observed points, it appears that for hydrogen there is a systematic divergence; and it seems quite possible that this is due to a difference in the form of the jets for hydrogen and air, a difference which itself changes with $r$. For at a given value of $r$ jets of hydrogen and air are farther from dynamical similarity than, for instance, jets of methane and air which have more nearly the same density.

Certain early experiments with other somewhat larger orifices, which have not been discussed in this paper because the data were too few, gave points for carbon dioxide which seemed to diverge systematically from the computed curves in the same way as the carbon-dioxide points on plate 6 diverge from the curve there given, but to a more marked degree. Whether these divergences are really to be attributed to contraction and changed form of the jets can not be definitely stated, but if we were to pursue the

research farther, this is the direction in which we should first attempt to extend it.

It may be noted that the observations at $r = 0.986$ and 0.990 (pls. 2, 3, 4) are a good way off from the curves, the observed value of $(R - 1)$ being numerically greater than the computed value as shown by the position of the curve. Upon remembering that to manage the problem at all we were obliged to treat the errors—that is, the values of $(R - 1)$ as small quantities—it does not appear surprising that the approximation ceases to be satisfactory when $(R - 1)$ is so large as it is for these points, where the pressure ratio $r$ is approaching unity.

On the whole, it appears that the theory as given does represent the major part of the facts reasonably well, and that the physical ideas on which it was based are probably sound, so far as they go.

WASHINGTON, May 8, 1919.

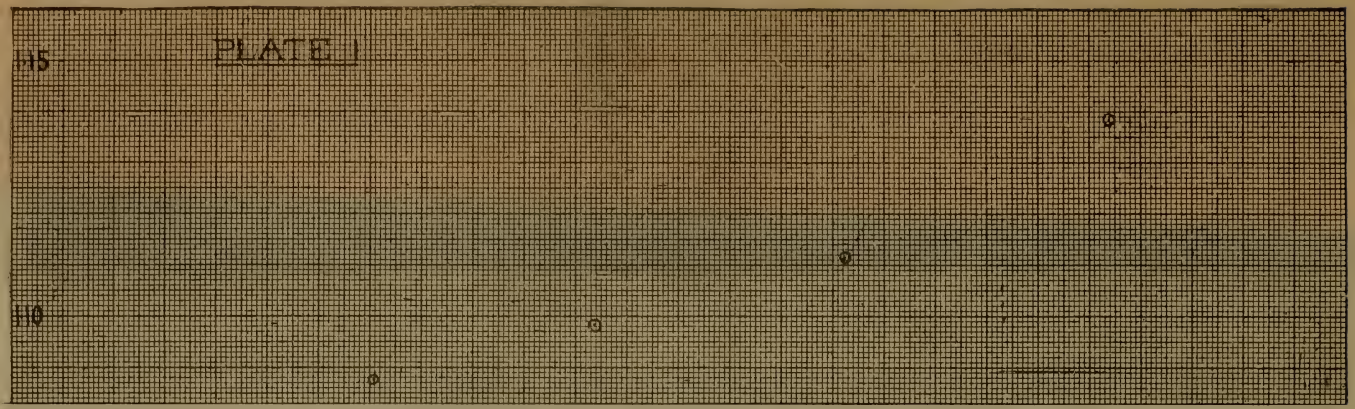


PLATE I
115
110

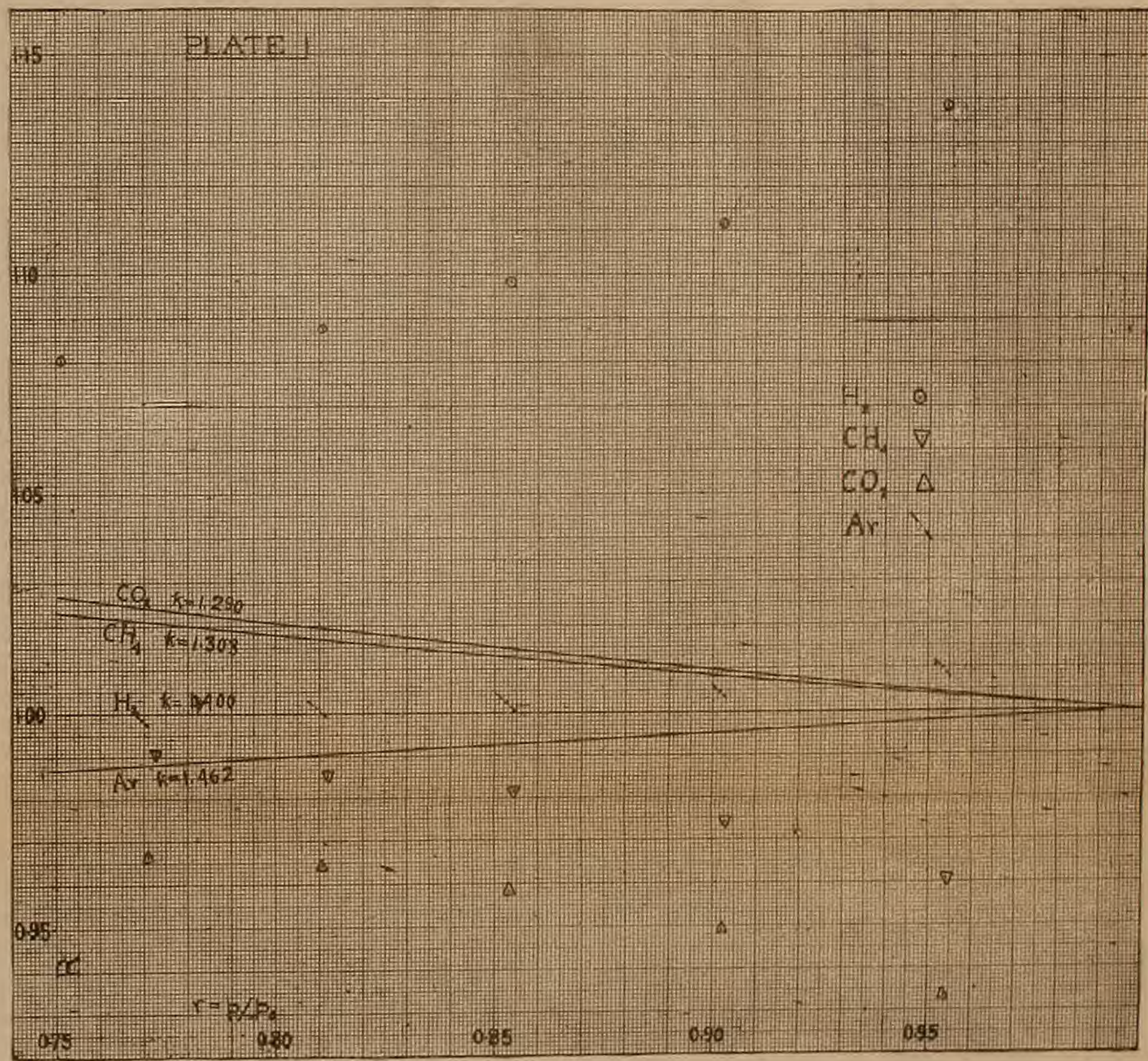


PLATE I
1.15
1.10
1.05
1.00
0.95
0.75
0.80
0.85
0.90
0.95
$H_2$ ○
$CH_4$ ▽
$CO_2$ △
Ar
$CO_2$ k=1.290
$CH_4$ k=1.303
$H_2$ k=1.400
Ar k=1.462
$r = p/p_s$

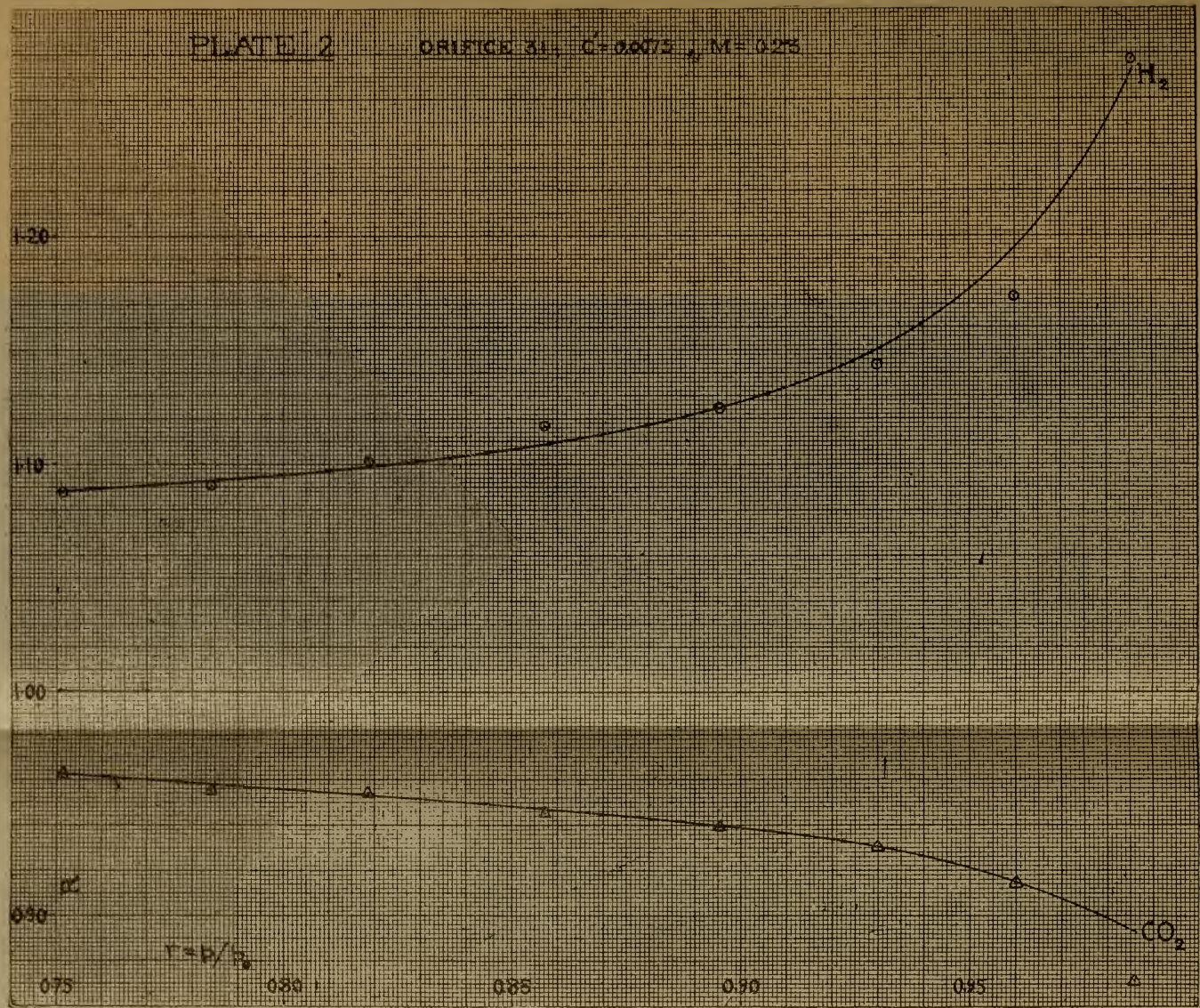
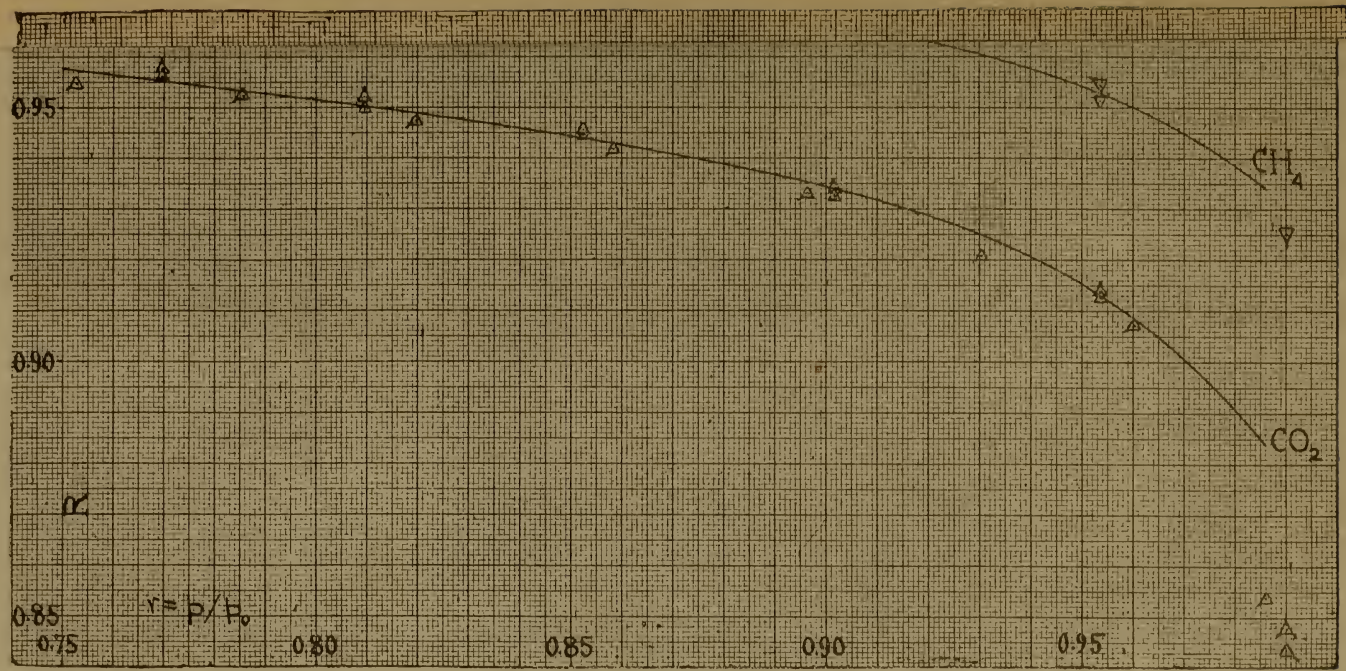


PLATE 2
ORIFICE 31, C'=0.0072, M=0.25
$H_2$
1.20
1.10
1.00
0.90
$CO_2$
r=p/p₀
0.75
0.80
0.85
0.90
0.95



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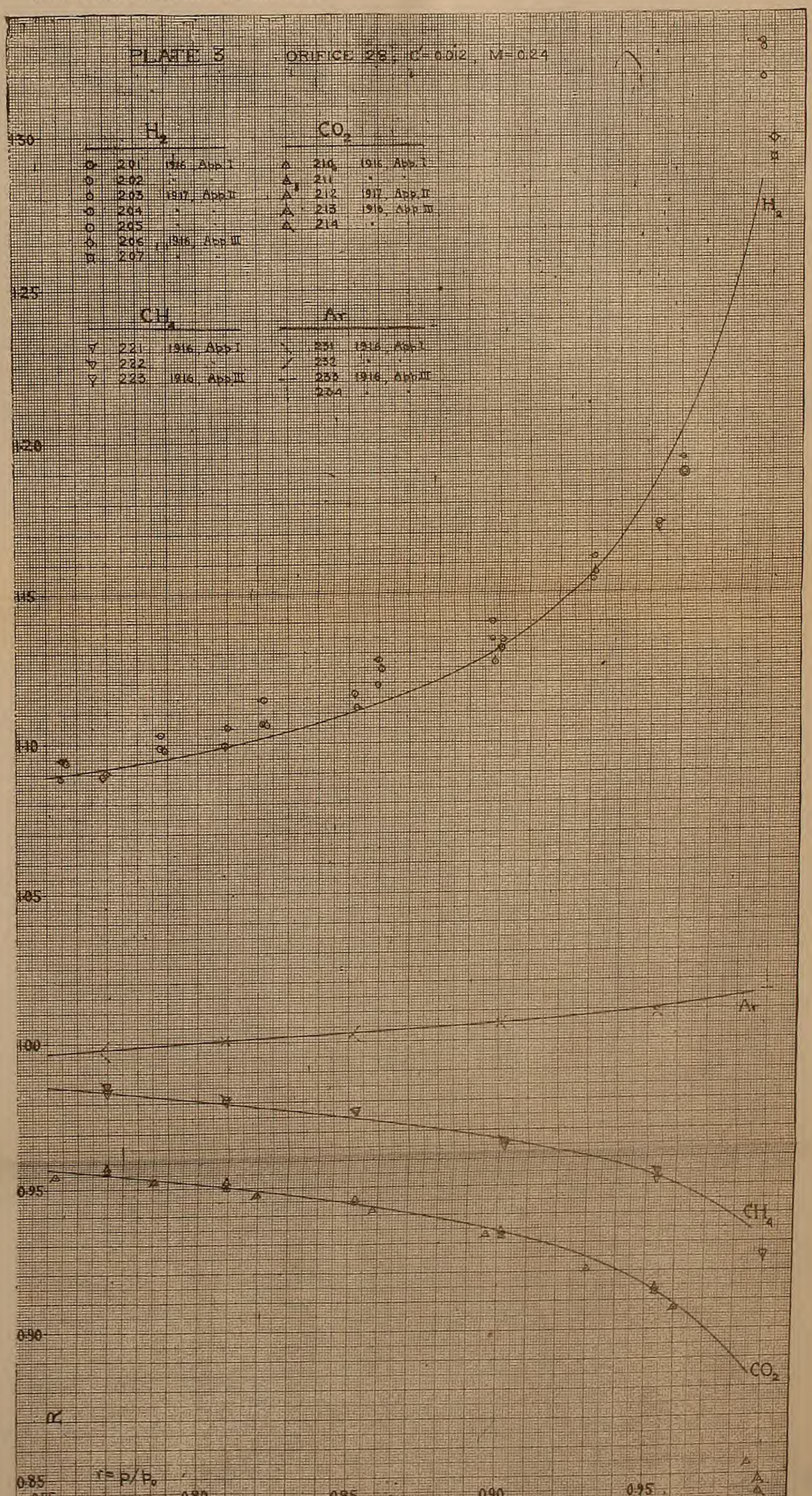
PLATE 3
ORIFICE 28; C'=0.012 M=0.24
H2
201 1916 App. I
202 "
203 1917 App. II
204 "
205 "
206 1916 App. III
207 "
CO2
210 1916 App. I
211 "
212 1917 App. II
213 1916 App. III
214 "
CH4
221 1916 App. I
222 "
223 1916 App. III
Ar
231 1916 App. I
232 "
233 1916 App. III
234 "
1.30
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
α
r = p/p₀
0.75
0.80
0.85
0.90
0.95
H2
Ar
CH4
CO2

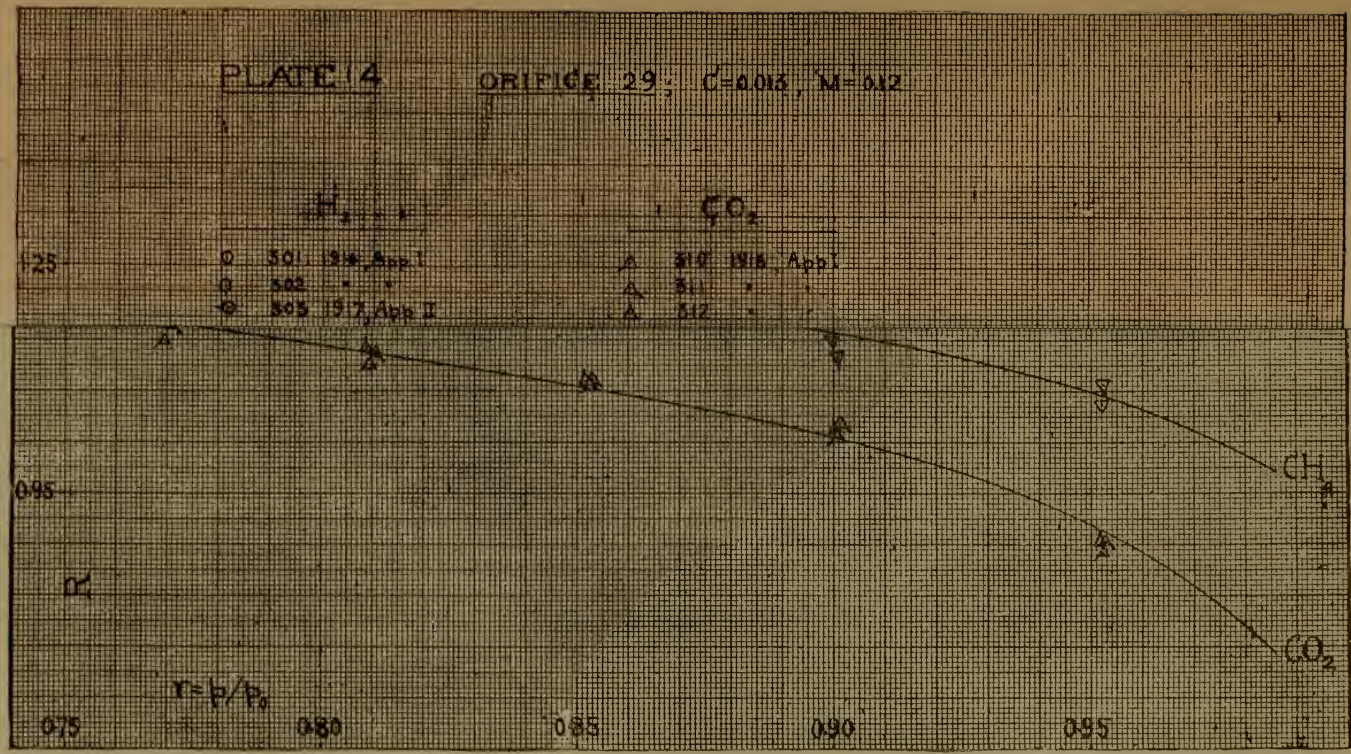
PLATE 14
ORIFICE 29; C=0.013, M=0.12
H2
CO2
1.25
0.95
CH4
CO2
r=p/p0
0.75
0.80
0.85
0.90
0.95



137547°—20

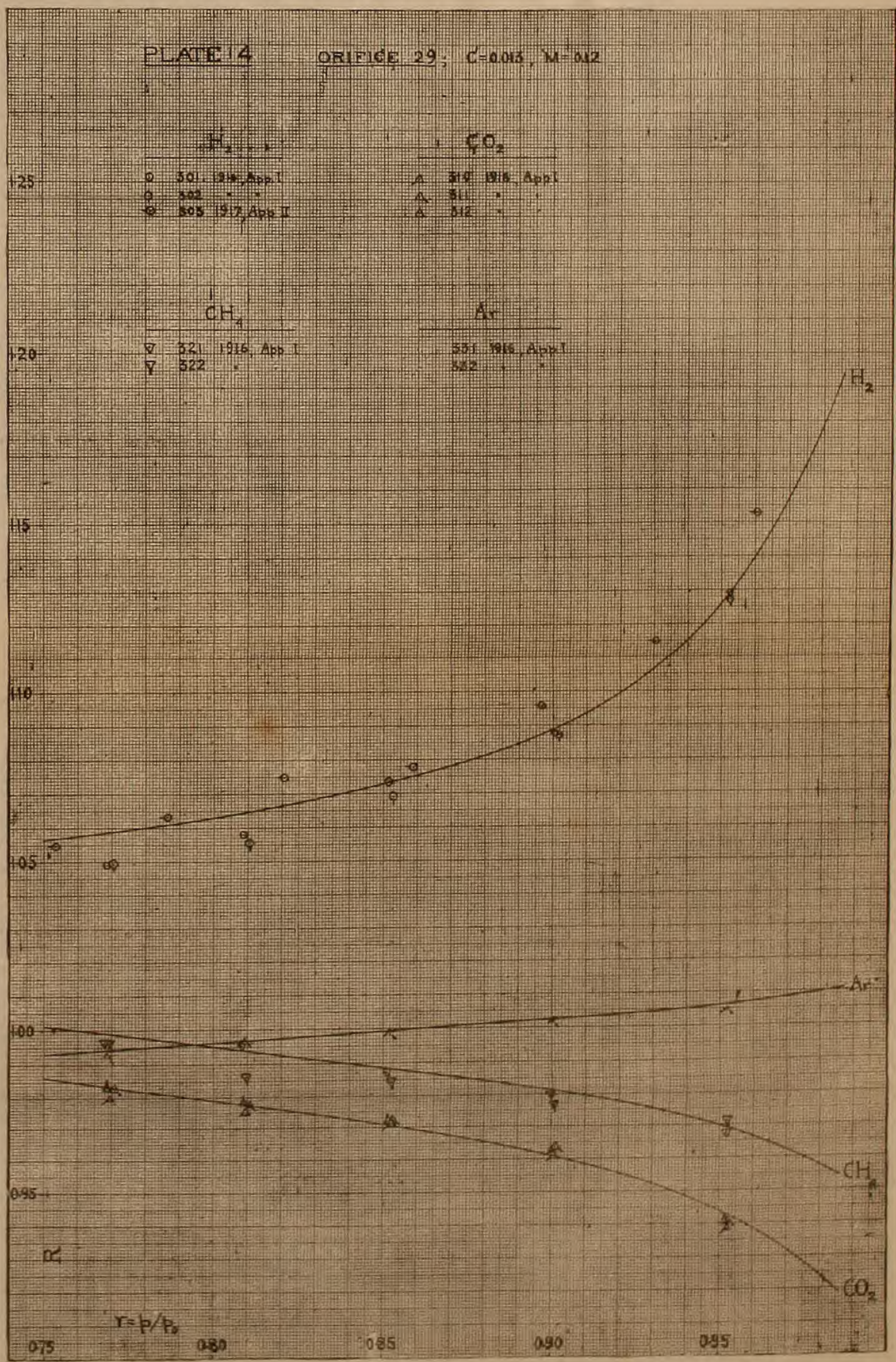
PLATE 14
ORIFICE 29; C=0.015, M=0.12
H2
501, 1916, App. I
502 " "
503 1917, App. II
CO2
511 1916, App. I
511 "
512 "
CH4
521 1916, App. I
522 "
Ar
531 1916, App. I
532 " "
1.25
1.20
1.15
1.10
1.05
1.00
0.95
α
r=p/p0
0.75
0.80
0.85
0.90
0.95
H2
Ar
CH4
CO2

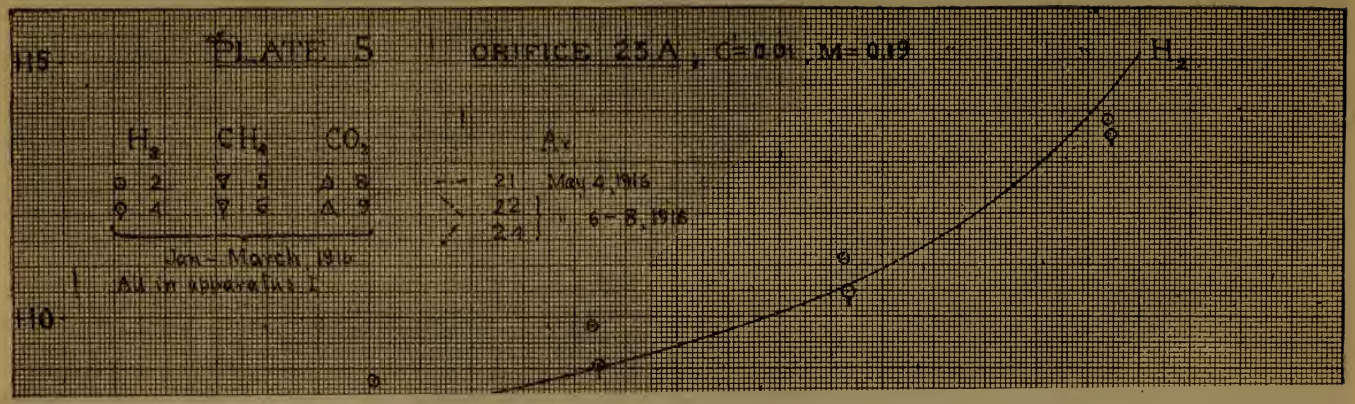
PLATE 5
ORIFICE 23A, C=0.01, M=0.019
115
110
H2
CH4
CO2
Av
21 May 4, 1916
22
24
6-8, 1916
Jan.-March 1916
All in appendix 2
H2

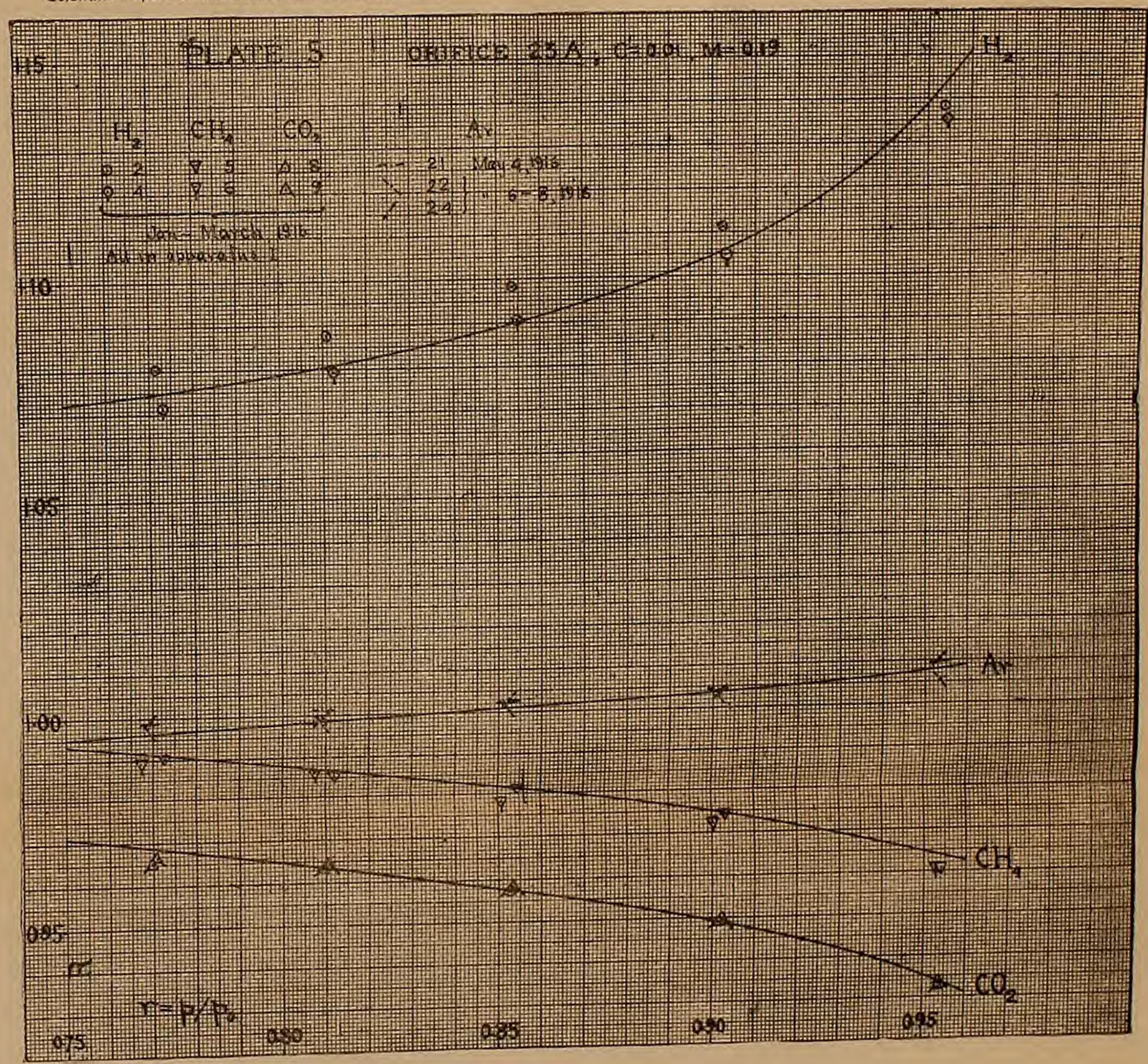
PLATE 5
ORIFICE 25A, C=0.08, M=0.19
H2
CH4
CO2
Ar
21 May 4, 1916
22
24
5–8, 1916
Jan.–March, 1916
All in apparatus I
1.15
1.10
1.05
1.00
0.95
α
r = p/p0
0.75
0.80
0.85
0.90
0.95
H2
Ar
CH4
CO2

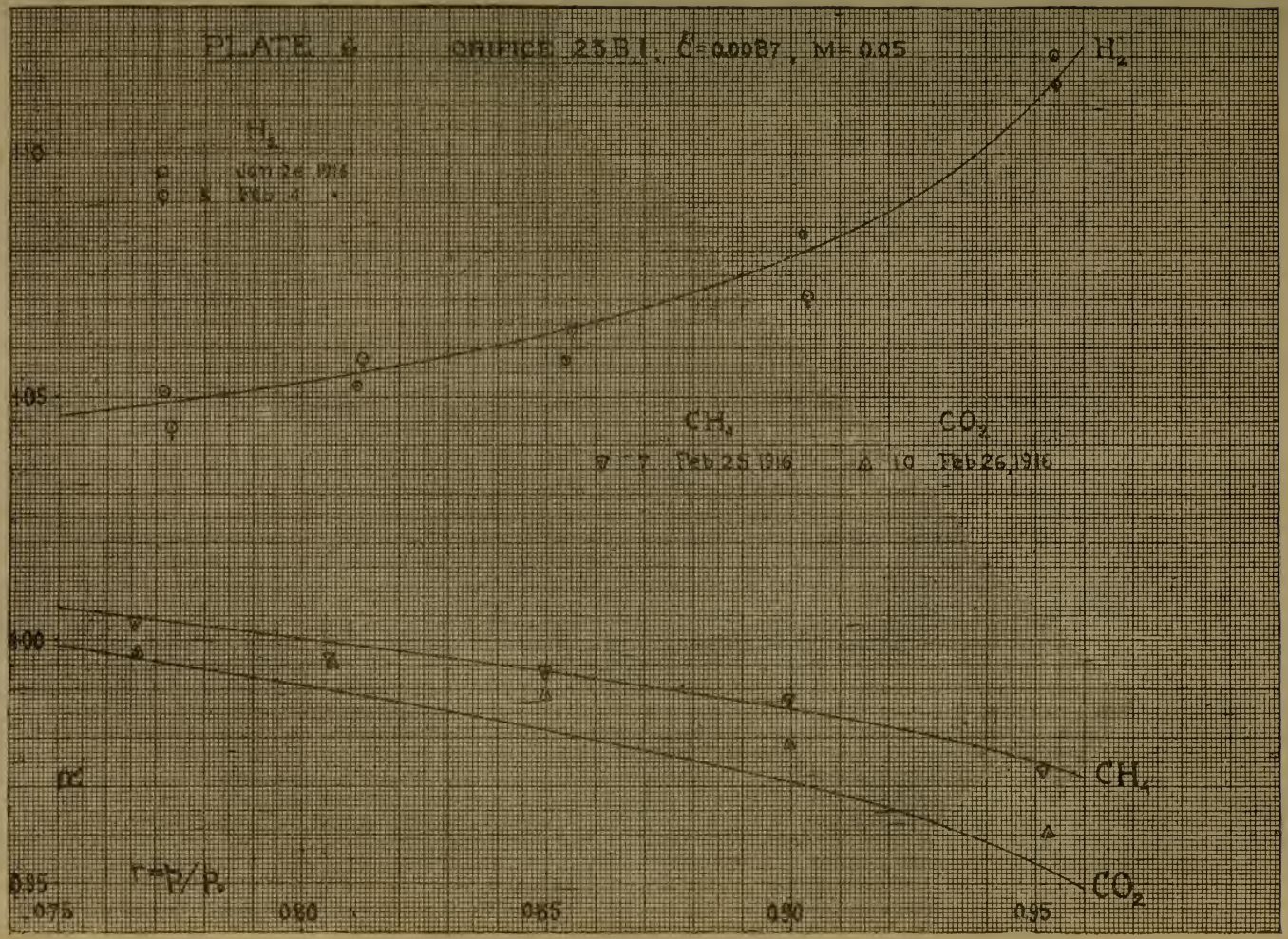
PLATE 8
ORIFICE 23B1, C=0.00187, M=0.05
H2
Jan 26, 1916
Feb 4
CH4
Feb 25 1916
CO2
Feb 26, 1916
CH4
CO2
r=P/P1
0.75
0.80
0.85
0.90
0.95

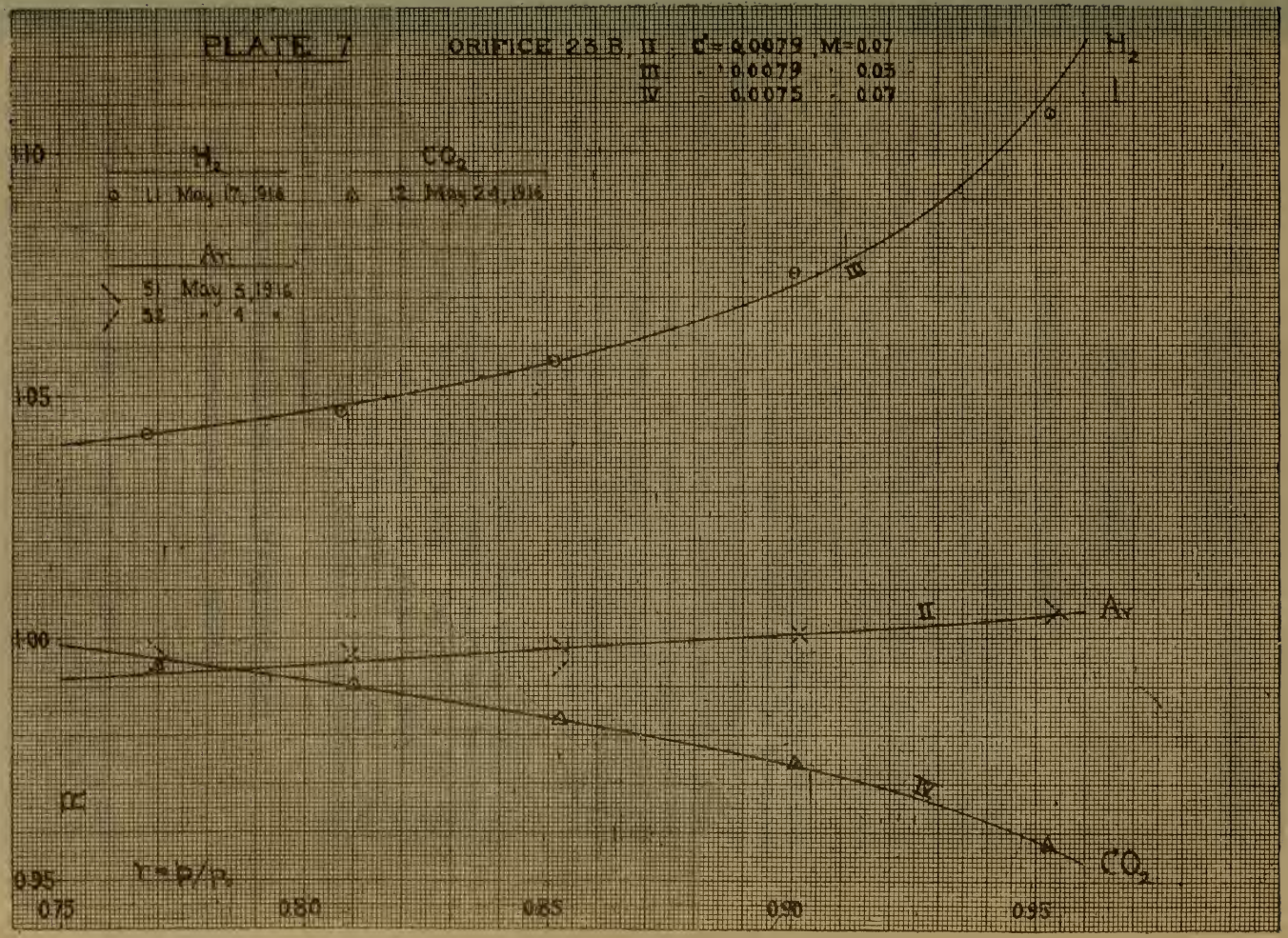
PLATE 7
ORIFICE 23 B, II C'=0.0079 M=0.07
III 0.0079 0.05
IV 0.0075 0.07
H2
CO2
Ar
1.10
1.05
1.00
0.95
C'
r=p/p0
0.75
0.80
0.85
0.90
0.95
I
II
III
IV