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Physics and Mathematics

MEASUREMENT OF ELECTRON ATTACHMENT IN OXYGEN-METHANE AND OXYGEN-CARBON-DIOXIDE MIXTURES

L. B. O'Kelly
G. S. Hurst
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HEALTH PHYSICS DIVISION

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I. INTRODUCTION

When an electron passes through a gas it undergoes numerous collisions with the gas molecules. In some gases there is a certain probability that the electron will be captured by a molecule with which it collides, forming a heavy negative ion. The ions formed in this manner do not readily lose their excess electrons. Some of the gases in which this phenomenon occurs are oxygen, water vapor, nitric oxide, ammonia, the halogens, and others. Gases which will not form ions in this manner include nitrogen, carbon dioxide, ethylene, the noble gases, methane, and others; however this does not mean that they will not form negative ions by some method other than direct electron impact. For example, a positive ion can strike the wall of an ion chamber and by extracting two electrons from the wall becomes a negative ion.[1] Events of this kind would be of no consequence in the work to be described since the method used depends on a decrease in the number of electrons rather than an increase in the number of ions. Electron attachment in this paper will refer only to electron capture due to collision of an electron and a neutral gas molecule.

There are two basic processes by which attachment can occur: dissociative capture,

$$AB + e \rightarrow A^- + B \tag{1}$$

and non-dissociative capture,

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[1] F. L. Arnot and J. C. Milligan, Proc. Roy. Soc. 156A, 538 (1936).

$$AB + e \rightarrow AB^- \tag{2}$$

In the latter case the ion is left with an excess of internal energy equal to the binding energy, or electron affinity of the molecule, plus the relative kinetic energy of the two particles. If this excess energy is not disposed of in a short time, the electron may be re-emitted. If the electron affinity of one of the fragments formed by breaking a bond in the molecule plus the kinetic energy of the electron is greater than the strength of the bond in question, then process (1) may occur. In this case any excess energy is carried off as kinetic energy by the two fragments and no stabilization of the ion is necessary. If the sum of the electron affinity and the kinetic energy is less than the strength of the bond involved, then attachment can occur by process (2) only.

In process (2) some type of energy transfer is necessary if the ion is to be stable. This process of stabilization by energy transfer has been of interest to investigators since the study of electron attachment began. Several methods of stabilization have been proposed of which radiation was the first. This, at first glance, would seem a logical explanation since the energy released by changes in the electronic states of an atom or molecule normally appears as radiation. Calculations, however, showed that the cross section for this process was much too low to explain the observed attachment rates and at best could account for only a small fraction of the total cross section. Attempts to observe the spectrum that would result from this method of stabilization also gave negative results.[2]

A complicating factor in early attempts to explain the non-dissociative attachment process was the report by several investigators[3,4] that in oxygen the process was independent of pressure. This would seem to rule out stabilization by collision of the unstable ion with another gas molecule, resulting in energy transfer since the probability of this occurring in a given time interval would increase as pressure increased. Recent investigations with oxygen[5-7] reveal the process actually to be pressure dependent at low energies and thus stabilization by collision with a third body seems a plausible explanation.

Most gases which attach electrons do so by process (1). This type of attachment is characterized by a threshold energy below which little or no attachment takes place and above which the probability of attachment increases with increasing energy. Gases which attach electrons by process (2) are characterized by an attachment probability that decreases as energy increases.[8] Oxygen is somewhat unusual in that it attaches by either process, depending on the electron energy. If the attachment prob-

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[2] O. Oldenburg, Phys. Rev. <u>43</u>, 534 (1933).

[3] N. E. Bradbury, Phys. Rev. <u>44</u>, 833 (1933).

[4] V. A. Bailey, Phil. Mag. <u>50</u>, 825 (1925).

[5] G. S. Hurst and T. E. Bortner, Rad. Res. (Suppl. 1), 547 (1959).

[6] L. M. Chanin, A. V. Phelps, and M. A. Biondi, Westinghouse Research Laboratory Report 403FD317-R1 (1958).

[7] G. S. Hurst and T. E. Bortner, Phys. Rev. <u>114</u>, 116 (1959).

[8] F. Bloch and N. E. Bradbury, Phys. Rev. <u>48</u>, 689 (1935).

ability in oxygen is plotted against electron energy, a curve is obtained that has a minimum at about 1.4 electron volts (ev).

The methods that have been used to study attachment may be divided into two broad categories: beam methods and swarm methods. Beam methods employing monoenergetic electrons give results that are more easily interpreted, however they have the disadvantage of being restricted to above 2 ev. Swarm methods are capable of operating at practically any energy, however the energy distribution is generally not known. Some of the swarm methods that have been used include the diffusion method used by Bailey,[4] the electron filter method used by Cravath[9] and Bradbury,[3] and methods using time analysis of the ion and electron currents used by Doehring,[10] Chanin and Biondi,[6] and others. Our method[11] uses a pulsed ion chamber and separates the effects due to ions and electrons by a suitable selection of the amplifier time constant. Electron sources that have been used include the photoelectric effect, heated filaments, and, in our case, ionization by alpha particles.

Of the several factors which can affect the attachment rate for a given molecule, the electron energy is probably most important; however, other things such as total pressure, and in the case of mixtures, the other types of molecules present also have an effect. The energy an

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[9] A. M. Cravath, Phys. Rev. 33, 605 (1929).

[10] A. Doehring, Z. Naturforschung 7a, 253 (1952).

[11] T. E. Bortner and G. S. Hurst, Health Physics 1, 39 (1958).

electron attains in a gas is a function of E/P (the "reduced electric field" in volts per centimeter per millimeter of pressure); however, this function varies considerably with different gases. As a result, when a small amount of an attaching gas is mixed with a much larger amount of a non-attaching gas, the electron energy will be determined primarily by the non-attaching gas, and the attachment rate will be that of electrons at this energy. Thus it is easy to see that there can be considerable difference in the attachment rate when the attaching gas is present as an impurity rather than in the pure state. In addition to the change in energy, other effects due to differences in the stabilizing qualities of different molecules can cause further changes in the attachment rate in the case of non-dissociative capture.

Electron attachment, particularly in oxygen and water, is of importance in a number of fields including radiation detection, radiation chemistry and biology and more recently in studies of the upper atmosphere where the reaction of free electrons and atmospheric oxygen influences the propagation of radio signals.

The operation of ionization chambers and other radiation detectors whose operation depends on the collection of gaseous ions is greatly influenced by the presence of electronegative impurities. In G-M and proportional counters, where the passage of a gamma ray may initially be represented by a single electron, the event may be missed altogether if the electron is captured before producing secondaries. In pulse type ion chambers the output will be reduced, however integrating type ion chambers will not be greatly affected. Normally all attaching gases are carefully removed from these devices. An exception is the halogen quenched G-M tube, where small concentrations of the halogens are used in spite of their strongly attaching nature because of other desirable properties.

The study of chemical reactions induced by radiation reveals that the attachment of free electrons is of fundamental importance. This is especially true in the chemistry of biological systems which contain large quantities of water and oxygen.

II. METHOD

The method and apparatus have been described previously,[11] however a brief description of the method and a more complete description of the apparatus will be given here.

The apparatus consists of a plane electrode ionization chamber, the associated electronic equipment necessary for analysis of the chamber output, and a gas purification system. Alpha particles from Pu^{239} are collimated in a plane parallel to the collecting electrode and used as a source of electrons in the ion chamber. The electrons released by the passage of the alpha particles travel under the influence of an electric field to the collecting electrode. The signal from this electrode is examined with a linear amplifier and a pulse height analyzer. This system is useful for mixtures containing small amounts of the attaching gas since the chamber pressure must be 250 mm Hg or more in order to stop completely the alpha particles in the sensitive volume of the gas. If it were filled to this pressure with a pure attaching gas, nearly all of the limited number of electrons released by an alpha particle would be captured and the output pulse would be less than the amplifier noise. However, if a small amount of an attaching gas is mixed with a non-attaching gas, the attachment coefficient can be found. (The attachment coefficient, α, is the probability of capture per centimeter of travel in the field direction and per millimeter of pressure of the attaching gas).

As a first step in the determination of the attachment coefficient it is necessary to find the response of the chamber to the pure non-attaching member of the mixture. This response can be calculated from a knowledge of the amplifier time constant and the electron drift rate in the gas in question or it can be easily determined experimentally. A comparison of the calculated and experimental curves is useful as an indication of gas purity. The curves for pure carbon dioxide and pure methane are shown in Figs. 1 and 2, respectively.

If oxygen (or any other attaching gas) is mixed with the non-attaching gas, the pulse height will decrease by an amount that is dependent on E/P and the partial pressure of each gas. This occurs because a certain fraction of the electrons will be captured before they reach the collecting electrode and therefore will contribute less to the output pulse than electrons which travel the full distance. The negative ions formed will also move toward the collecting electrode, however their drift velocity will be on the order of 10^{-3} times that of the electrons and if the amplifier time constant is suitably short, their contribution to the output pulse will be negligible. Thus, that part of the pulse due to electrons only is observed. The coefficient of attachment can then be calculated from the decrease in pulse height.

A diagram of the apparatus is shown in Fig. 3. The chamber is a stainless steel cylinder twelve inches in diameter and has a volume of twelve liters. It is sealed with Teflon gaskets. The electrodes and field rings are made of brass and are gold plated. The field rings are spaced one centimeter apart on fluothene insulators and are held at the appropriate potentials by a voltage divider system using 22.4-megohm

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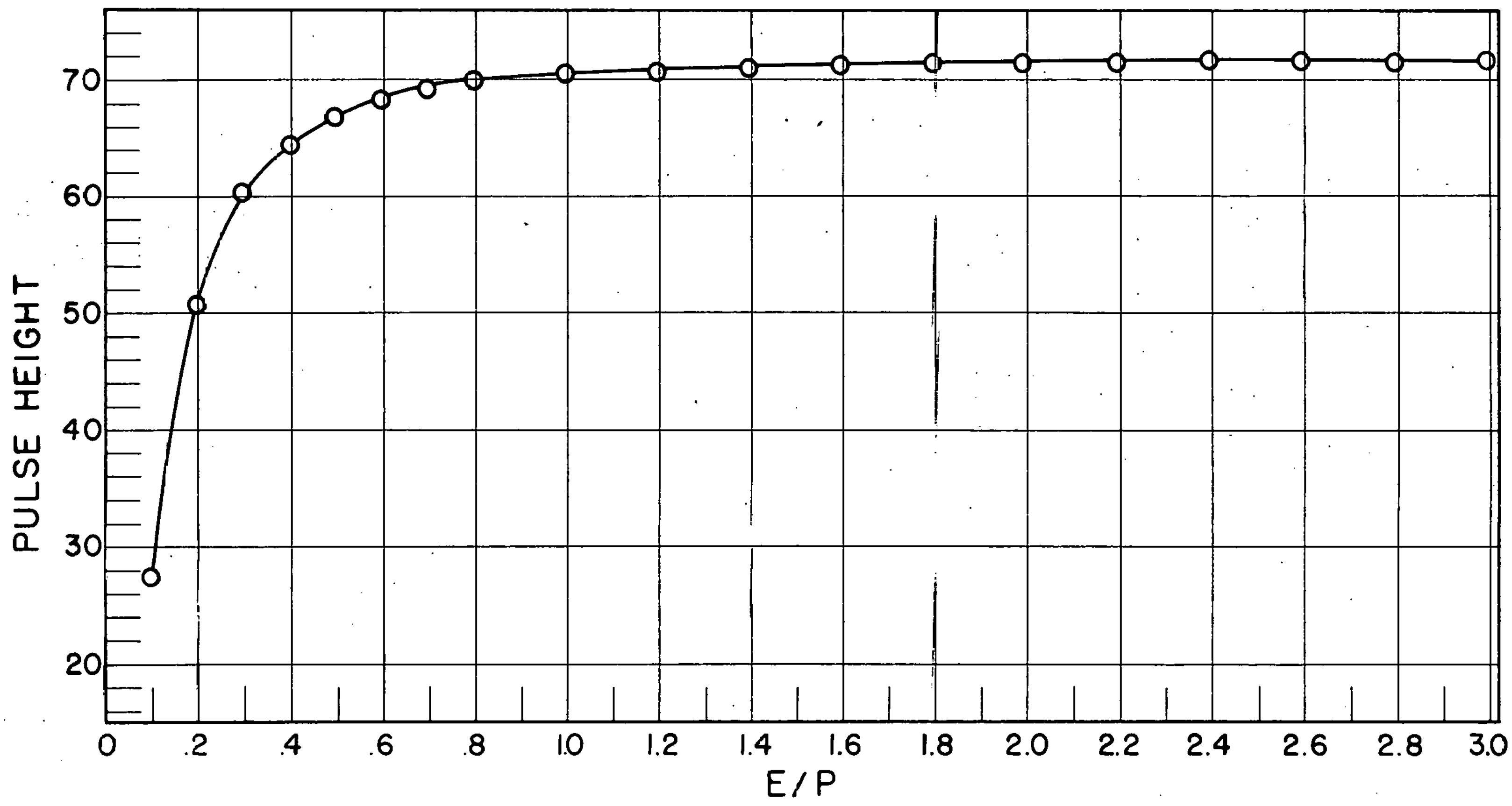

Fig. 1. E/P vs Pulse Height for Pure Carbon Dioxide.

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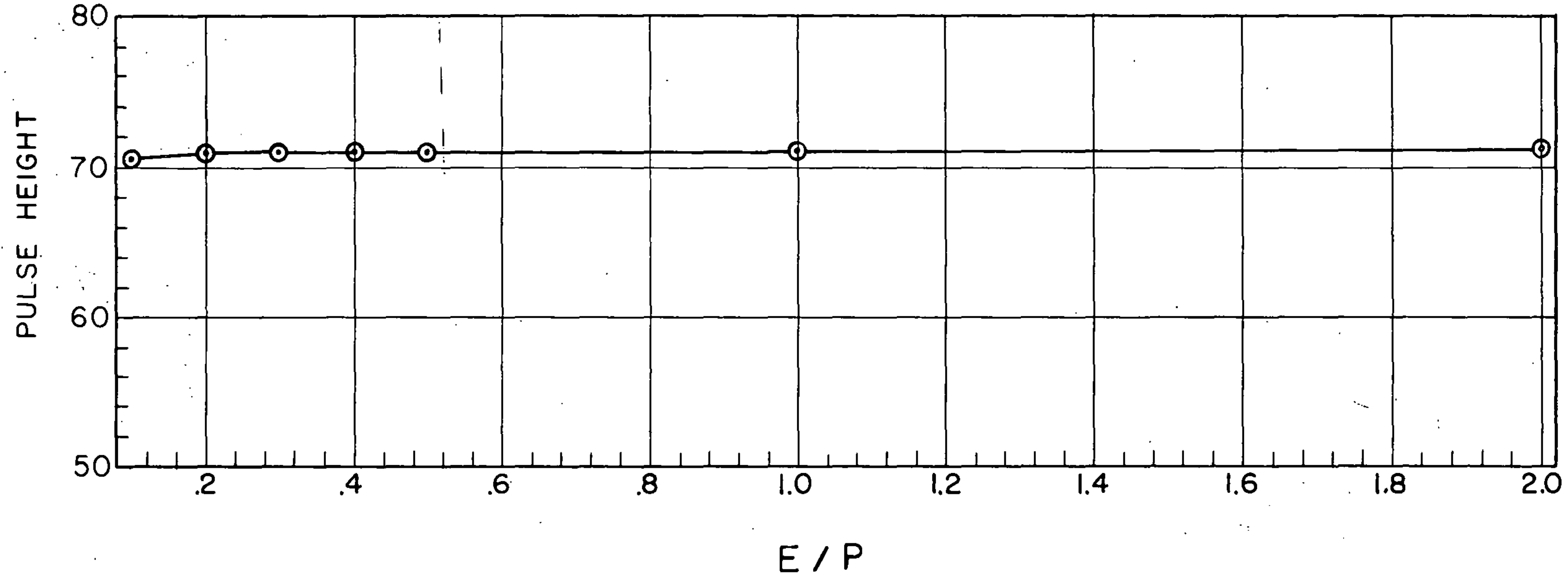

Fig. 2. E/P vs Pulse Height for Pure Methane.

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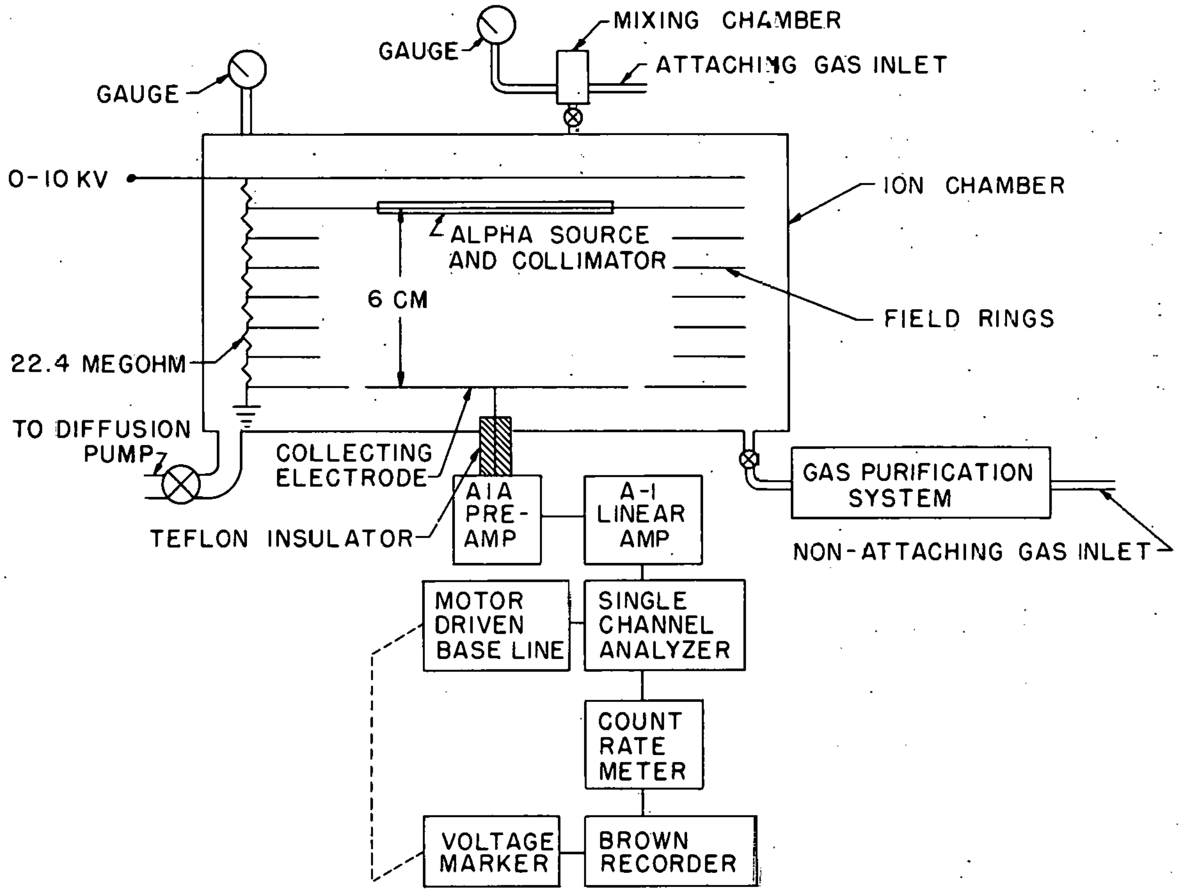

Fig. 3. Diagram of the Apparatus.

resistors between each ring. Each of these resistors consists of four 5.6-megohm, one-watt resistors connected in series and enclosed in a Teflon jacket sealed with ceresin wax. Electrical connections into the chamber are made through Teflon insulators.

The chamber is evacuated by a three-inch Consolidated Electrodynamics type MCF300 diffusion pump with a Welch Duo-Seal forepump. The gas purification system is evacuated by another Duo-Seal pump. The entire system can be evacuated to one micron of Hg or less. The pressure is measured with a Wallace and Tiernan differential pressure gauge except at very low pressures where a thermocouple gauge is used.

The high voltage is obtained from a New Jersey Electronics model H-30, ten-kilovolt power supply with an external voltage control system added. The control system is shown in Fig. 4. The potentiometer voltage is controlled by a ten-turn helipot and can be calibrated against an internal standard cell. The balance amplifier and motor are standard Brown recorder equipment and control an external variac which is connected to the primary of the high voltage transformer. The reset accuracy of the system is quite good. However, in actual use the voltage is set approximately with the potentiometer dial calibration and then the final setting made with an electrostatic voltmeter to insure a high degree of accuracy. The control system limits the maximum voltage to approximately 8500 volts.

The cable connecting the high voltage supply to the chamber is shielded to prevent noise from getting into the amplifier system. A number of cables with several types of insulation, including Teflon, have

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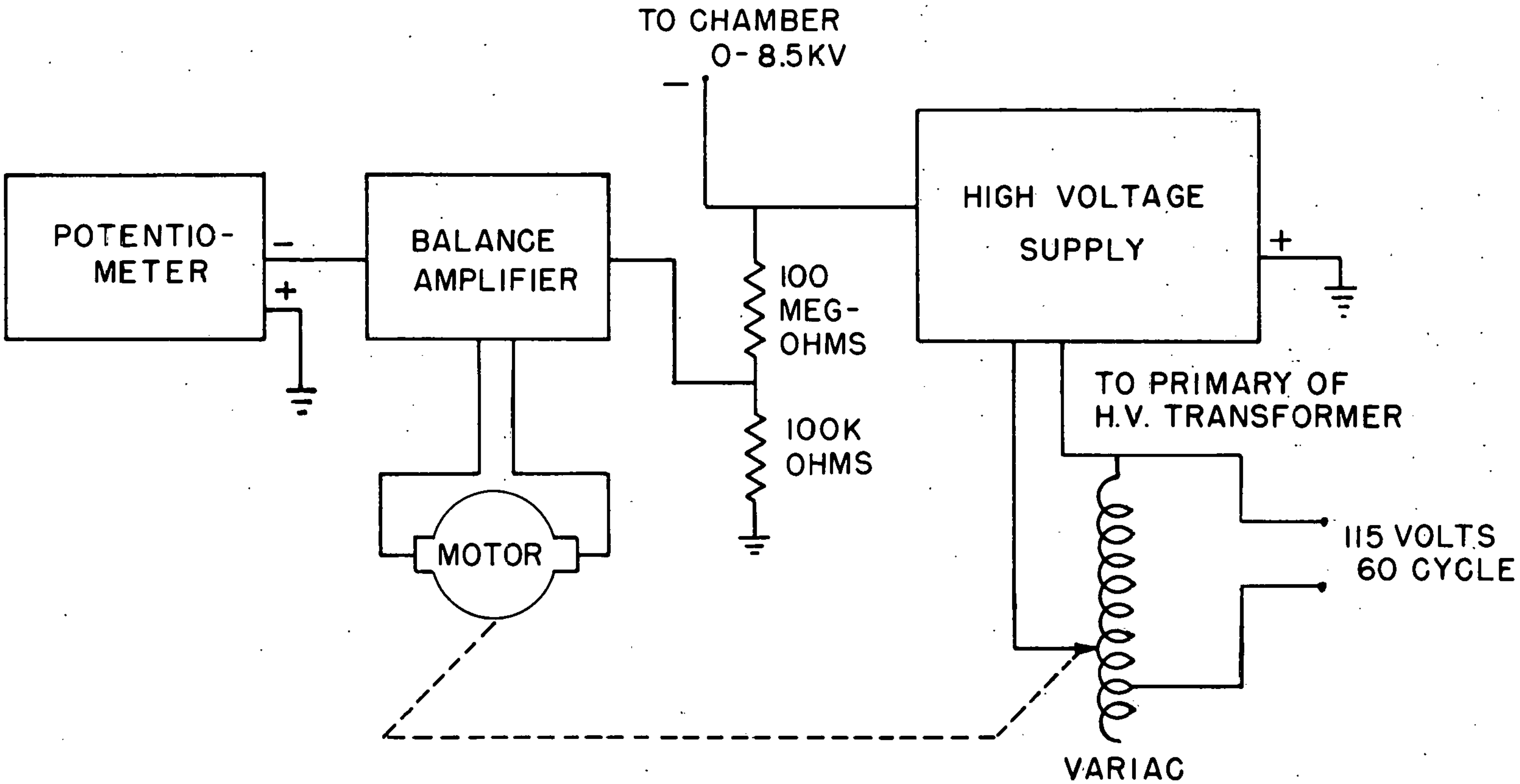

Fig. 4. Diagram of the Voltage Control System.

been tested. The best with respect to the absence of noise and the type presently in use is automobile ignition wire shielded with a wire braid, however there is still a noticeable loss in resolution at higher voltages due to cable leakage.

A Jordan-Bell type A-1 pulse amplifier[12] is used in conjunction with an A-1A preamplifier. The total gain from this system is approximately 100,000. The preamplifier is attached directly to the collector electrode terminal to prevent signal loss and noise pickup. The input tube is a Western Electric type 403B low-noise pentode. Whenever it is changed a number of new ones are tried, and the one giving satisfactory gain and the lowest noise is selected. The input resistance of the preamplifier is 100 megohms.

The output of the amplifier goes into an ORNL model Q-1192 single channel analyzer with a motor driven base line that scans uniformly in time. The output of the analyzer drives a count rate meter, the output of which is displayed on a Brown recorder. A second pen on the recorder marks one-volt intervals on the edge of the chart. It is driven by a solonoid connected to a microswitch which is actuated by pins spaced at one-volt intervals on the shaft of the analyzer base line potentiometer. This gives a scale from which the pulse height can be determined.

Although it is not necessary to know the exact gain of the amplifier system, it is necessary that it remain constant. For this reason it was set each morning with an ORNL model Q-1066 precision pulse generator and

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[12] W. H. Jordan and P. R. Bell, Rev. Sci. Instr. <u>18</u>, 703 (1947).

checked several times during the day. The Q-1066 uses a mercury relay to generate sixty pulses per second from a 1.3-volt mercury cell. The output is variable from zero to 10^5 microvolts and can be calibrated against a standard cell. The gain was set to give a 75-volt output pulse for an input of 600 microvolts with the carbon dioxide and a 70-volt output for an input of 675 microvolts with the methane. In each case this gave a maximum signal of about seventy volts from the amplifier with the pure gas in the chamber.

The laboratory in which the equipment is located has controlled temperature and humidity to reduce the error due to changes in environment. A noticeable change in amplifier gain occurs if the temperature changes, the gain decreasing as the temperature increases. A recording thermometer is kept near the equipment for a check on the temperature. Generally, several days are required for the gain to stabilize after the equipment is turned on, and for this reason it is turned off only for maintenance.

The gases used were the purest available in commercial cylinders, however further purification was required. It was necessary to develop a different technique of purification for each gas because of their different characteristics. Several procedures were tried and the one which gave the greatest pulse height and best reproducibility was selected. Another indication of purity was obtained by plotting E/P versus pulse height and comparing with the calculated curves. If the gas was pure, the curves matched rather closely, however electronegative impurities caused a sharp drop in pulse height at low E/P.

A diagram of the purification and filling system is shown in Fig. 5. The de-oxo trap is a Baker model D. It operates by catalytically combining hydrogen and oxygen to form water at room temperature. According to the manufacturer, it will reduce the oxygen concentration in a stream of gas from one per cent to less than 0.0001 per cent if supplied with two volumes of hydrogen for each volume of oxygen to be removed. The water formed is removed with a dehydrator. Our unit did not operate with this efficiency, however this was probably due to an insufficient quantity of hydrogen.

The drying traps are stainless steel cylinders 1.5 inches in diameter and eighteen inches long and are filled with anhydrone (magnesium perchlorate). After some experimentation it was found that the cold traps alone gave a better pulse height, and the drying traps were removed from the system.

The cold traps are made of two-inch brass tubing and are eight inches long. Those used with methane were filled with copper turnings for better thermal conductivity. It was feared that this might cause them to stop up when used with solidified carbon dioxide and thus the copper turnings were removed. The cold traps were cooled with liquid nitrogen or dry ice, depending on the temperature desired.

The carbon dioxide was purified by fractional distillation. It was first passed through the de-oxo unit and then the proper quantity measured out by filling the chamber to 1.5 times the pressure to be used. It was then withdrawn into a cold trap which was cooled with liquid nitrogen and distilled twice. The chamber was then flushed with pure gas and

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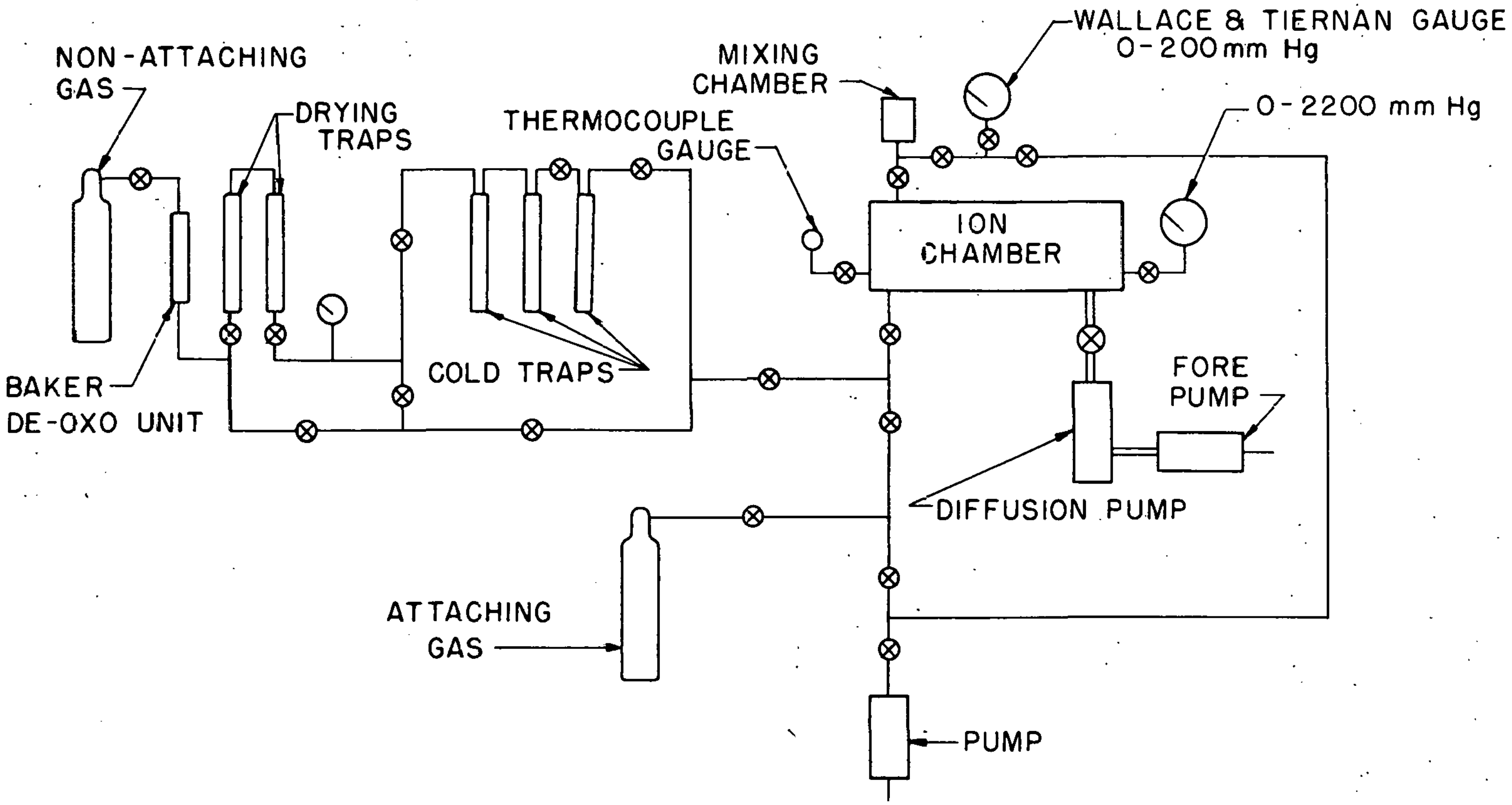

Fig. 5. Diagram of the Gas Purification System.

filled to the desired pressure. This gave a highly reproducible pulse height curve that matched the calculated curve quite well.

Because of the small amounts of oxygen used with the CO_2 it was necessary to measure the oxygen in a small auxiliary chamber of known volume and then mix it with the gas in the main chamber. Since the ratio of the two volumes was known, oxygen pressures of a fraction of a millimeter in the large chamber could be obtained with good accuracy. Mixing was accomplished by cooling the small chamber with liquid nitrogen and thereby condensing all the gas from both chambers in it. It was then warmed and the mixture allowed to flow back into the main chamber. Satisfactory mixing was obtained by repeating this procedure until there was no further change in pulse height.

The methane purification was somewhat simpler since it is much more tolerant of oxygen than is carbon dioxide and the same degree of purity was not required to give a good pulse height curve. The gas was passed through the de-oxo trap and the cold traps which were cooled with dry ice, and then into the chamber. At first the drying traps were used also, however it was found that a better pulse height was obtained using the cold traps alone. Distillation was also tried, however, it was difficult to control because of the low boiling point (- 161.5° C) of methane and satisfactory results could not be obtained.

The quantities of oxygen used with the methane were large enough that it could be added directly to the chamber and the pressure read directly from the main pressure gauge with sufficient accuracy to give reproducible results except for the lowest value where an auxiliary chamber was used.

One of the purposes of this research was to check the pressure dependence of electron attachment. For this reason data were taken at a number of different values of both total pressure and oxygen concentration. The values of total pressure went in 50-mm steps from 250 mm Hg to 600 mm Hg for carbon dioxide and in 100-mm steps from 400 mm Hg to 800 mm Hg for methane. In each case the lowest pressure that could be used was determined by the stopping power of the gas since the alpha particles had to be completely stopped in the sensitive volume of the gas in order to obtain uniform pulses.

The method of taking data was as follows: The chamber was filled to the maximum pressure (600 or 800 mm Hg) with the desired oxygen-carbon dioxide or oxygen-methane mixture and the voltage set to give the lowest value of E/P. The pulse height analyzer base line was then set slightly above the pulse height voltage appearing at the output of the amplifier and allowed to sweep downward. This caused a peak to appear on the recorder chart as the analyzer base line voltage swept through the amplifier output voltage. The center of this peak at half maximum was taken as the pulse height and the value was read from the voltage scale at the edge of the chart. The chamber voltage was then set to give the next E/P value and the procedure repeated. With carbon dioxide the range from E/P = 0.1 to E/P = 3.0 was covered while with methane E/P = 0.1 to E/P = 2.0 was covered. After a complete set of readings had been taken, the pressure was reduced to the next value and the procedure repeated. A complete run covering all pressures and including time for gas purification and mixing required from seven to nine hours.

III. RESULTS

The results for methane and oxygen are shown in the form of pulse height versus E/P curves in Figs. 6 through 10. These curves were drawn as the data were collected, each point being plotted as soon as it was read off the recorder chart. Any point not falling on a smooth curve was re-run along with points on each side to determine if an error had been made. Errors in setting the voltage or in reading the chart could be found in this way. Generally, any point was reproducible to ± 0.2 volts.

In all cases the pulse height increased (indicating a decrease in attachment) as E/P increased. This is to be expected with low energy electrons in oxygen and is a characteristic of non-dissociative capture. All other investigations in this energy range show a similar effect. Dissociative capture is not observed at the low values of E/P that were used except in mixtures with the rare gases, which have very large agitation energies.[7,13]

The equations relating pulse height and the attachment coefficient are quite complicated and their complete solution for each pulse height value would be extremely tedious. For this reason a set of curves have been plotted relating the normalized pulse height and the quantity $f = \alpha f_1 Pd$ for values of τ_0/t_1 from zero to five, where f_1P is the oxygen pressure; d is the source to collector distance; t_1 is the amplifier

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[13] G. S. Hurst and T. E. Bortner, Oak Ridge National Laboratory Report ORNL-2670 (1959).

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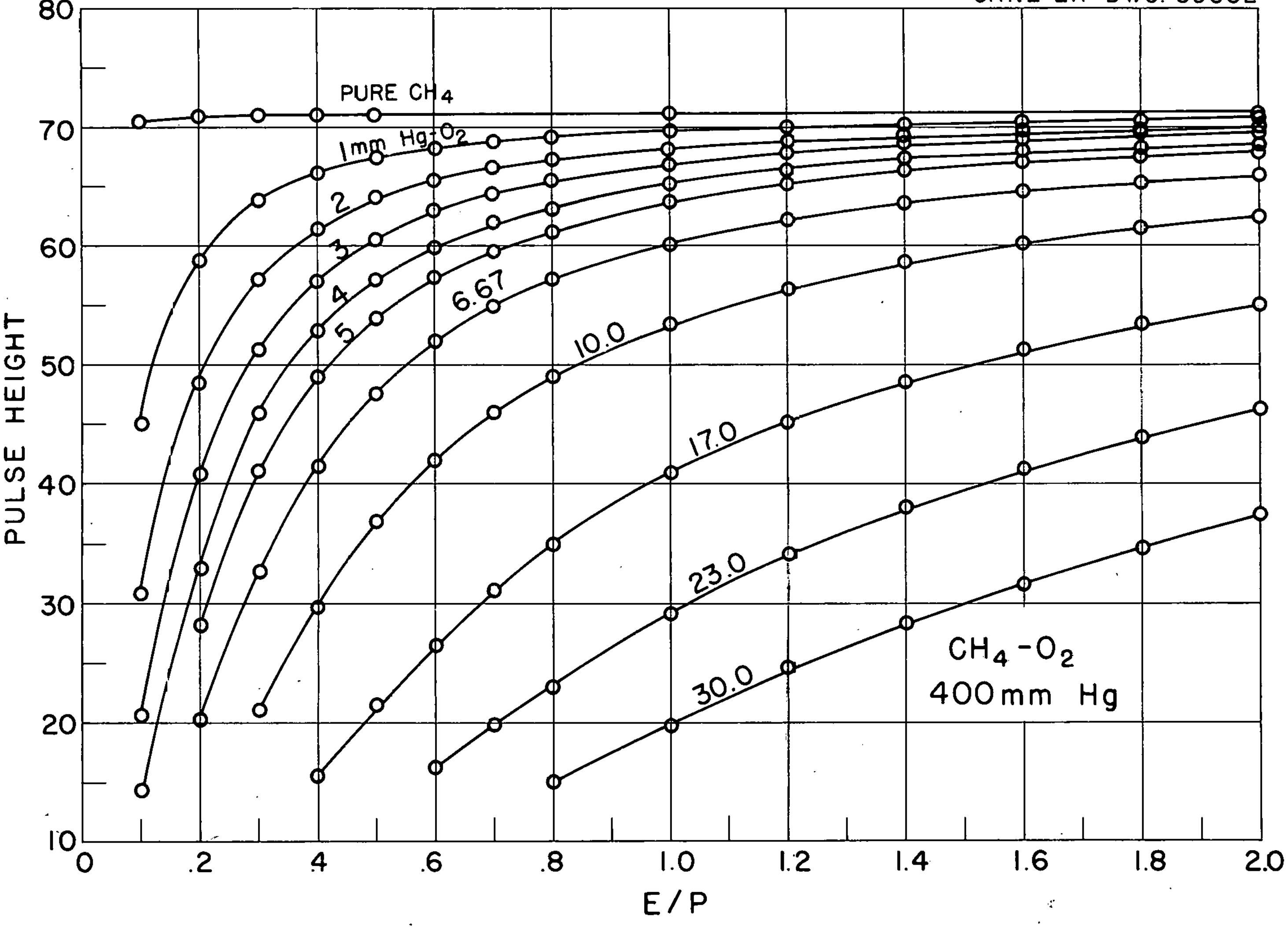

Fig. 6. E/P vs Pulse Height for Methane and Methane-Oxygen Mixtures at 400 mm Hg.

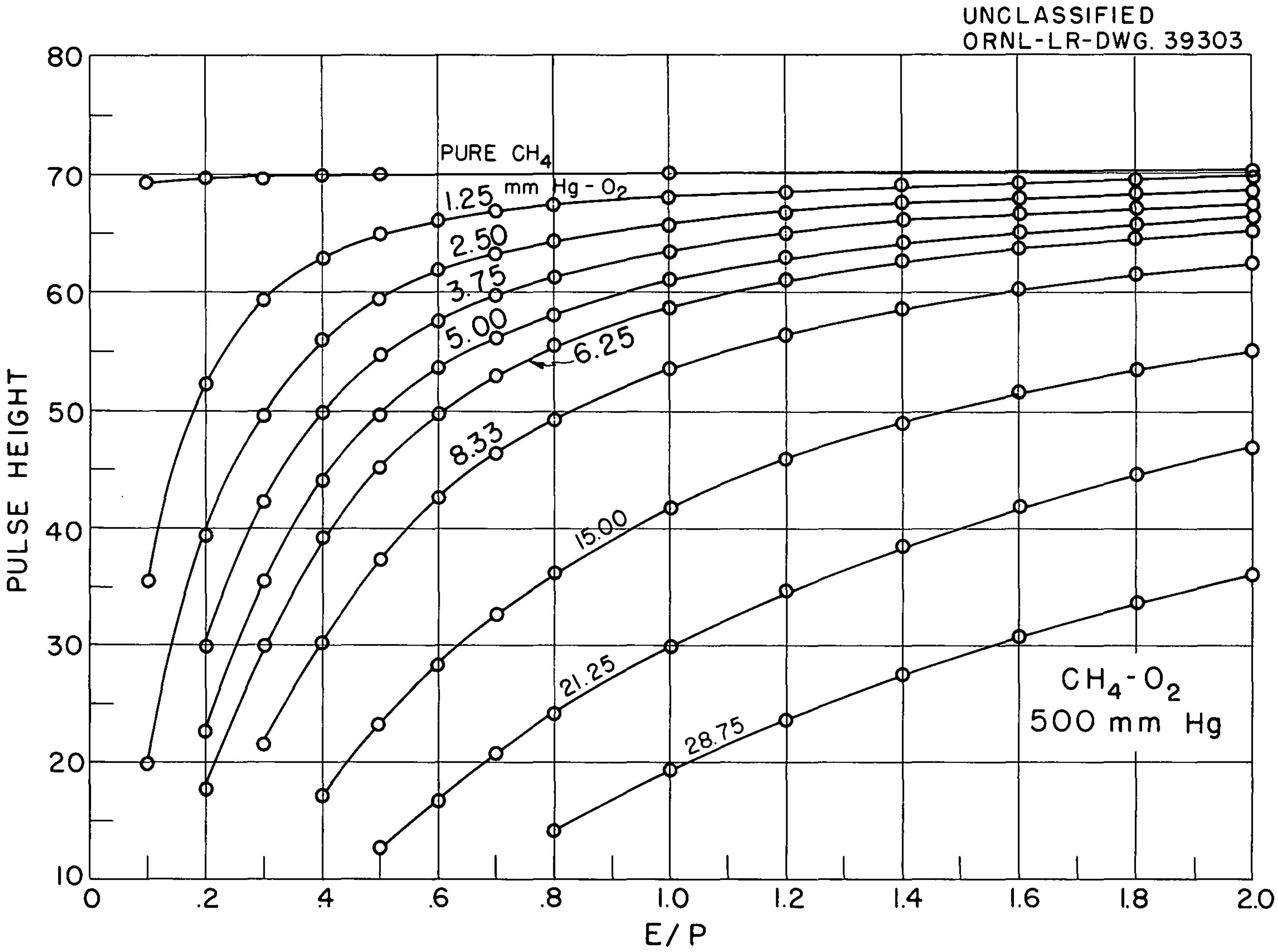

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Fig. 7. E/P vs Pulse Height for Methane and Methane-Oxygen Mixtures at 500 mm Hg.

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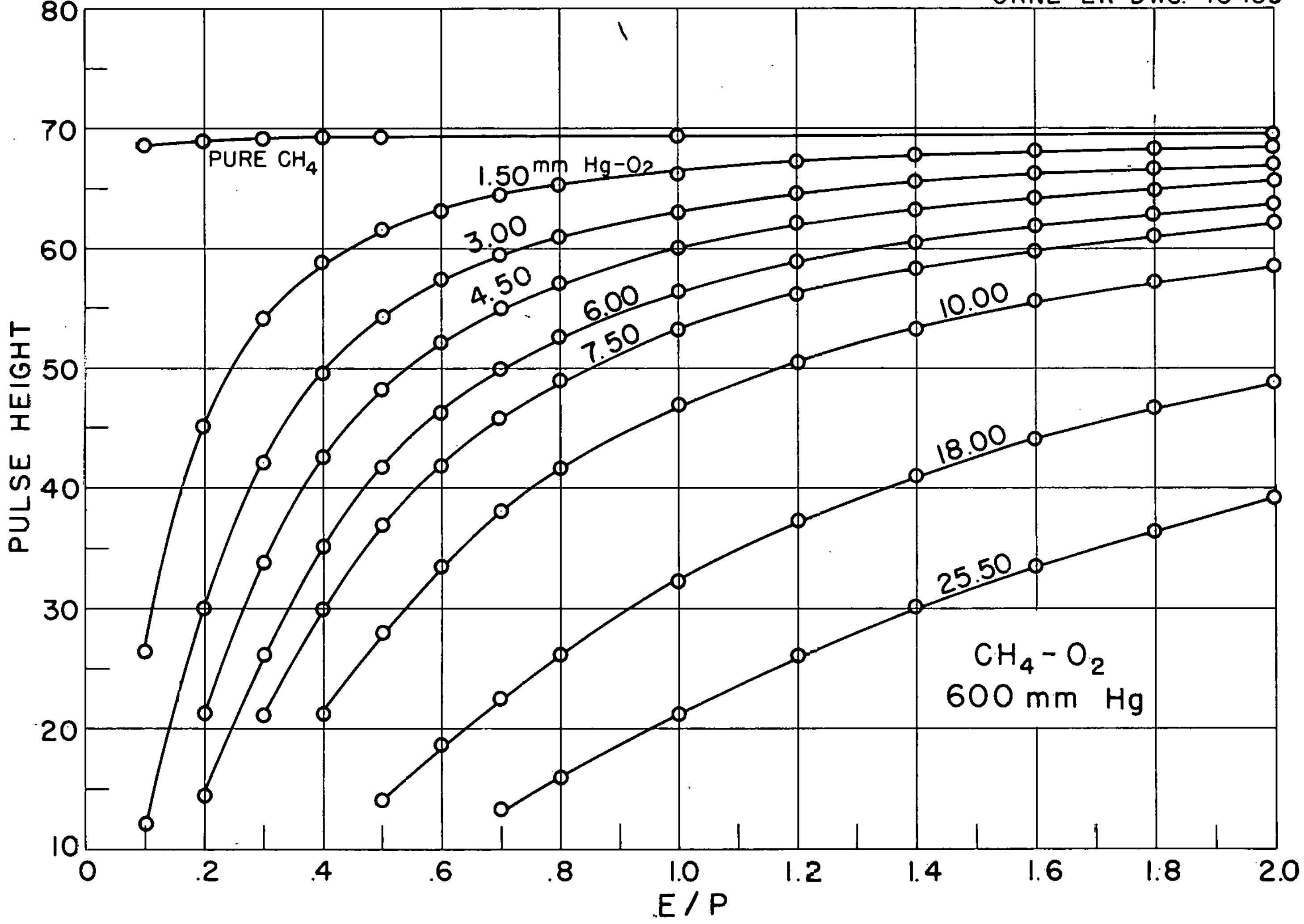

Fig. 8. E/P vs Pulse Height for Methane and Methane-Oxygen Mixtures at 600 mm Hg.

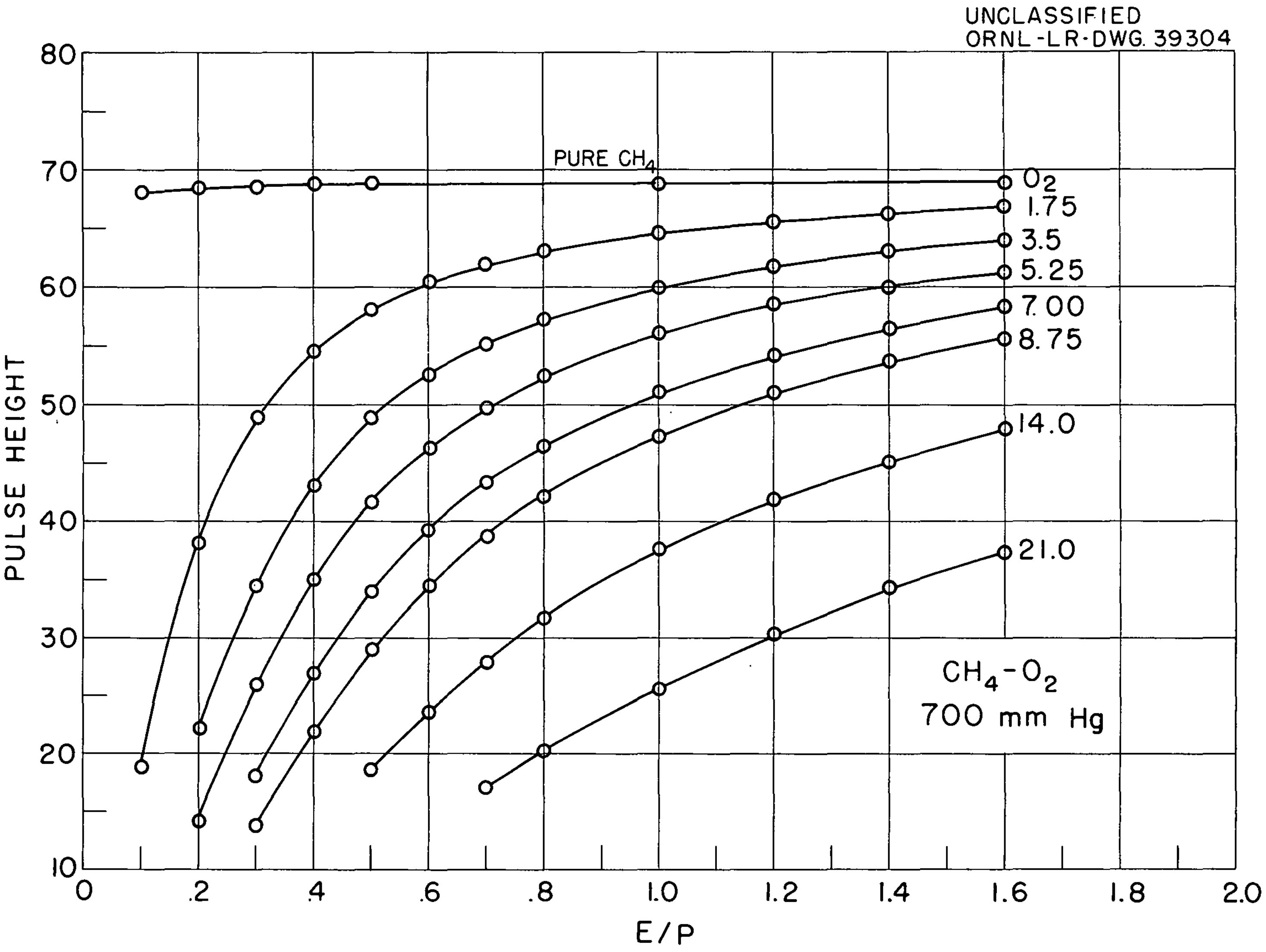

Fig. 9. E/P vs Pulse Height for Methane and Methane-Oxygen Mixtures at 700 mm Hg.

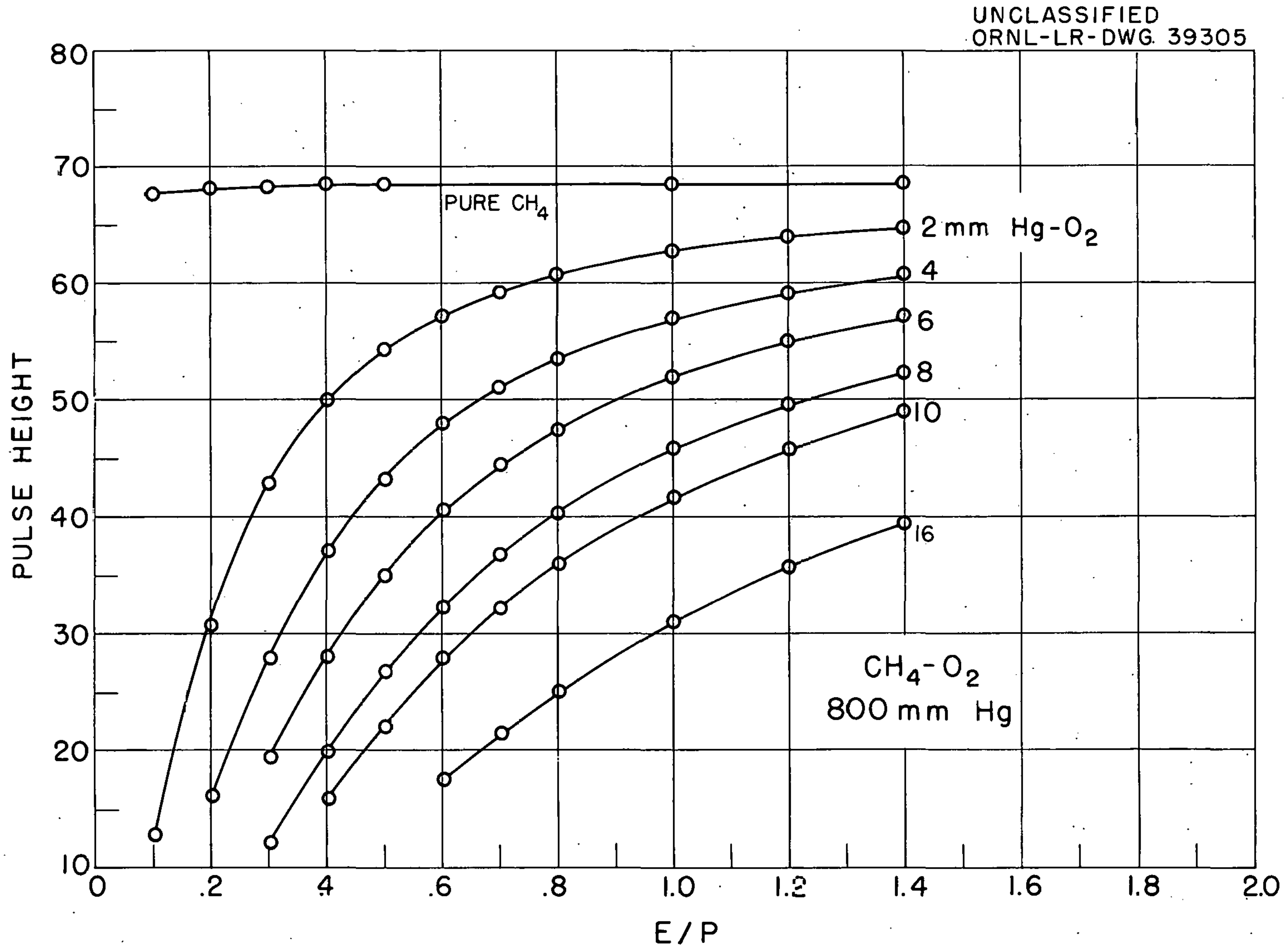

Fig. 10. E/P vs Pulse Height for Methane and Methane-Oxygen Mixtures at 800 mm Hg.

time constant; and τ_o is the electron collection time. These curves are shown in Fig. 11. The electron collection time is related to the drift velocity W by $\tau_o = d/W$. For our apparatus d is six centimeters and τ_o is sixteen microseconds. The only quantities now needed to evaluate α for any oxygen pressure are the drift velocity and the pulse height in the pure non-attaching gas and in the oxygen mixture.

The actual calculation of α is best illustrated by an example. Consider the point at E/P = 1.0 on the $f_1P = 10.0$ mm Hg curve in Fig. 6. First, the drift velocity must be known at this E/P. If it is known, the drift velocity in the mixture rather than in the pure gas should be used since small amounts of impurities can change the drift velocity in some gases. The drift velocities obtained by Bortner, Hurst, and Stone[14] were used for all calculations in this paper. In the case of methane, values are given for the pure gas and for mixtures with oxygen. There is some change when oxygen is added, however it is inconsequential for these calculations. For carbon dioxide, no values are given for oxygen mixtures, however the very small amounts of oxygen used would not be likely to cause any significant change in drift velocity.

The drift velocity given for methane at E/P = 1.0 is ten centimeters per microsecond. From this, τ_o / t_1 is found to be 0.04; therefore, the curve $\tau_o/t_1 = 0$ in Fig. 11 will be used for the calculation. This curve gives a pulse height of 0.368 for the pure non-attaching gas (f = 0). By interpolation the pulse height for pure methane in Fig. 6 at

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[14] T. E. Bortner, G. S. Hurst, and W. G. Stone, Rev. Sci. Instr. 28, 103 (1957).

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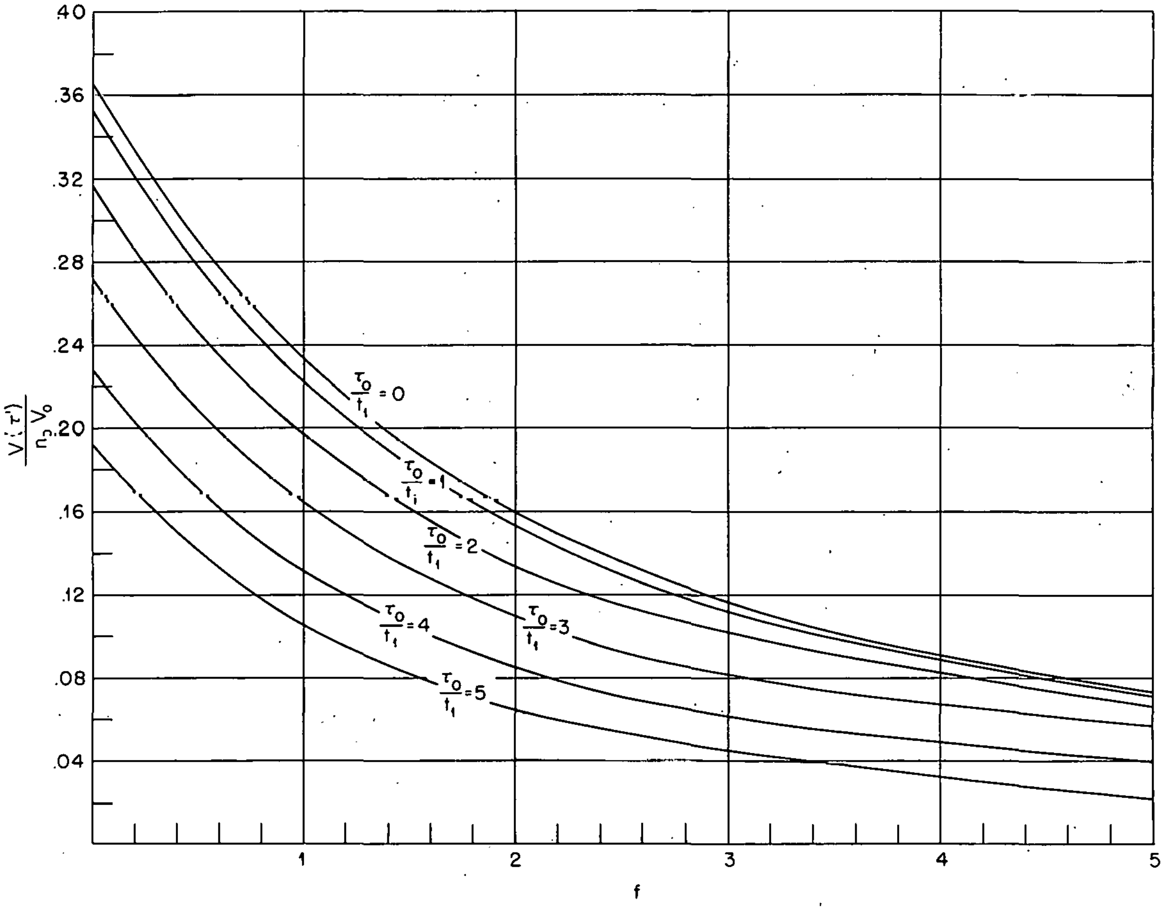

Fig. 11. Normalized Pulse Height vs f.

$E/P = 1.0$ is 71.1. The pulse height in Fig. 6 can be normalized to that in Fig. 11 by dividing it by $71.1/0.368 = 193.75$. The pulse height given by the $f_1P = 10$ mm Hg curve at $E/P = 1.0$ is 53.3. Dividing it by the same factor gives a normalized pulse height of 0.276. The value of f corresponding to this pulse height (on the $\tau_o/t_1 = 0$ curve) is 0.61. Substituting these values in the formula $\alpha = \frac{f}{(f_1P)d}$ gives

$$\alpha = \frac{0.61}{(10.0 \text{ mm Hg})(6.0 \text{ cm})} = 0.0102 \text{ (cm - mm Hg)}^{-1}.$$

Because of its high electron drift rate the only curve used when calculating α in methane is $\tau_o/t_1 = 0$. However, this is not generally the case with other gases which have slower drift rates.

Figures 12 through 23 show α for methane and oxygen mixtures plotted against oxygen pressure. It is apparent that α depends on both total pressure and oxygen pressure. This is in accord with other recent investigations[5-7] but contrary to some earlier work.[3,4]

The results for carbon dioxide and oxygen are shown in the form of pulse height versus E/P curves in Figs. 24 through 31. The calculation of α was done in the same manner as for methane. Figures 32 through 44 show α plotted against oxygen pressure as was done for methane. A dependence on both total pressure and oxygen pressure is also observed here.

The most striking difference between the two gases is their difference in sensitivity to oxygen contamination. The highest concentration used with carbon dioxide was 0.42 mm Hg of oxygen in 250 mm Hg of carbon dioxide while 30.0 mm Hg of oxygen in 400 mm Hg total pressure was the maximum with methane. In each case the pulse height was reduced

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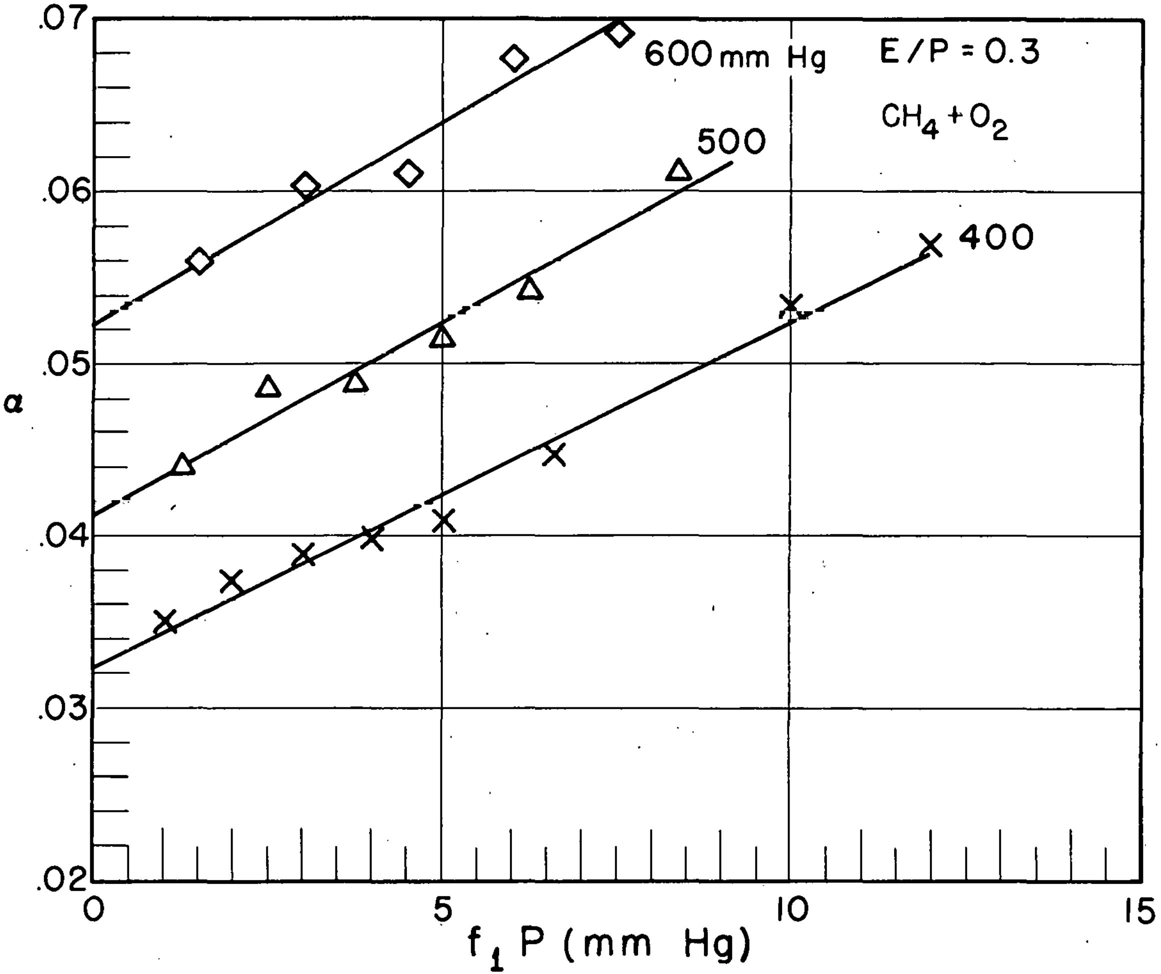

Fig. 12. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.3 in Methane-Oxygen Mixtures.

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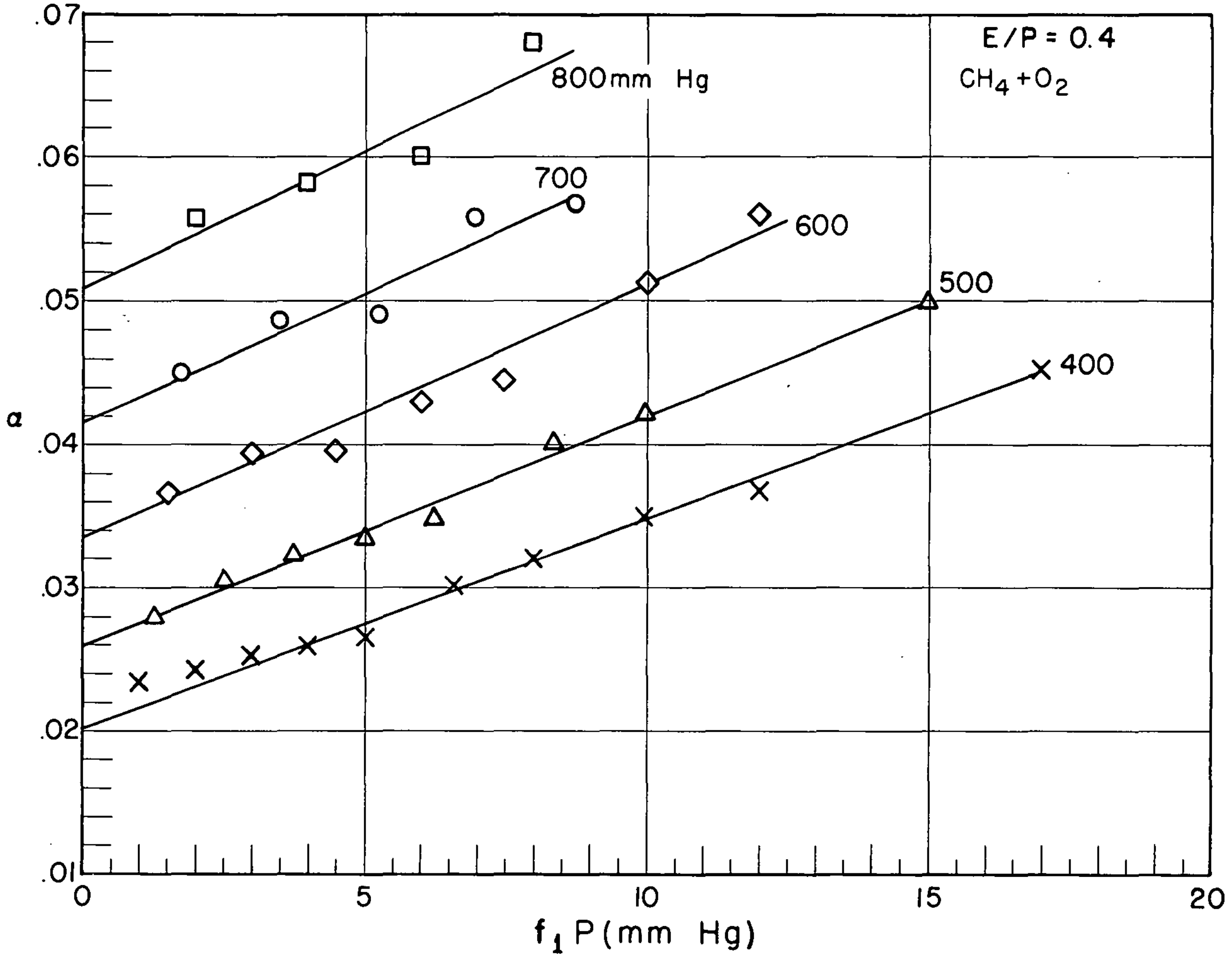

Fig. 13. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.4 in Methane-Oxygen Mixtures.

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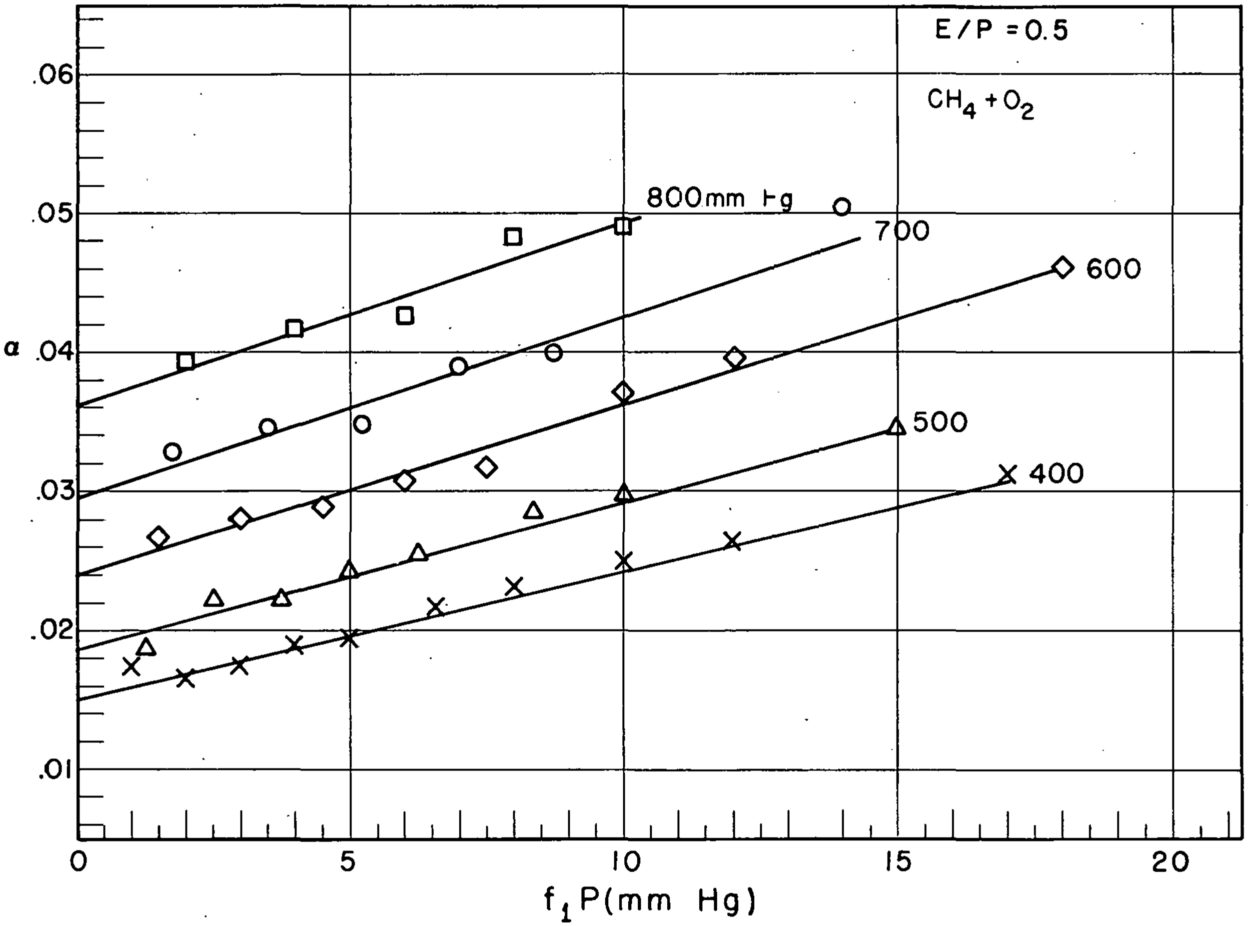

Fig. 14. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.5 in Methane-Oxygen Mixtures.

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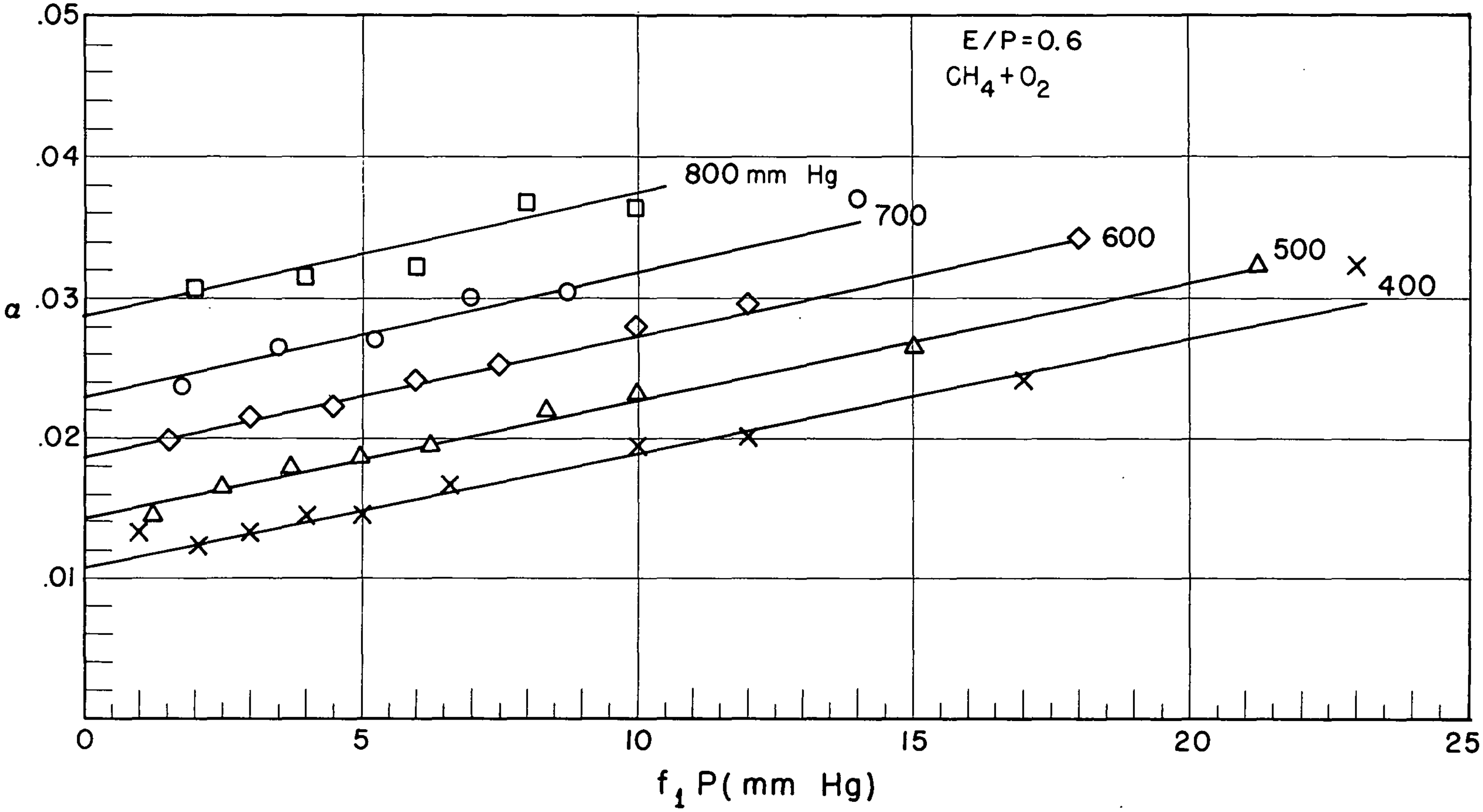

Fig. 15. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.6 in Methane-Oxygen Mixtures.

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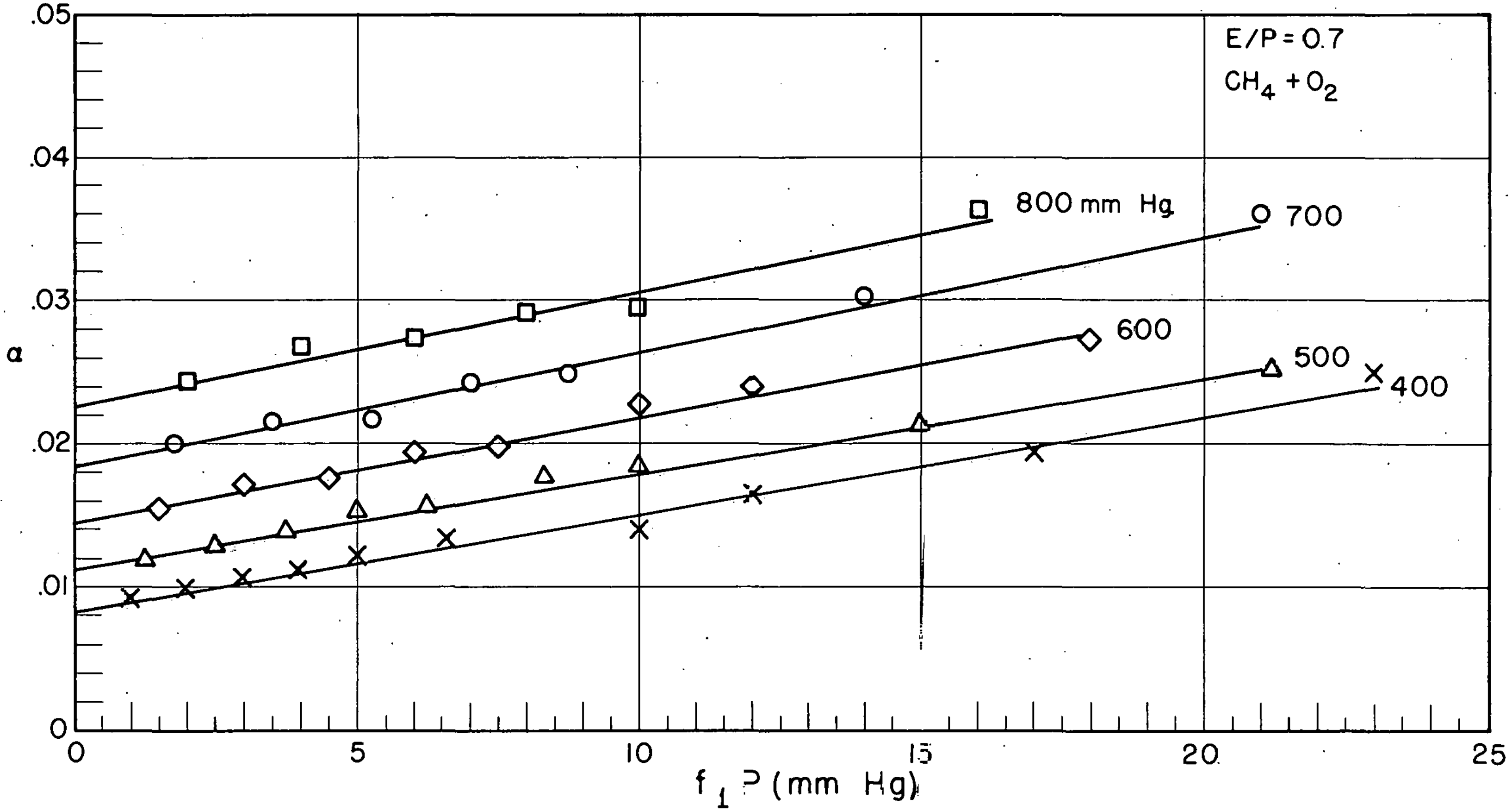

Fig. 16. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.7 in Methane-Oxygen Mixtures.

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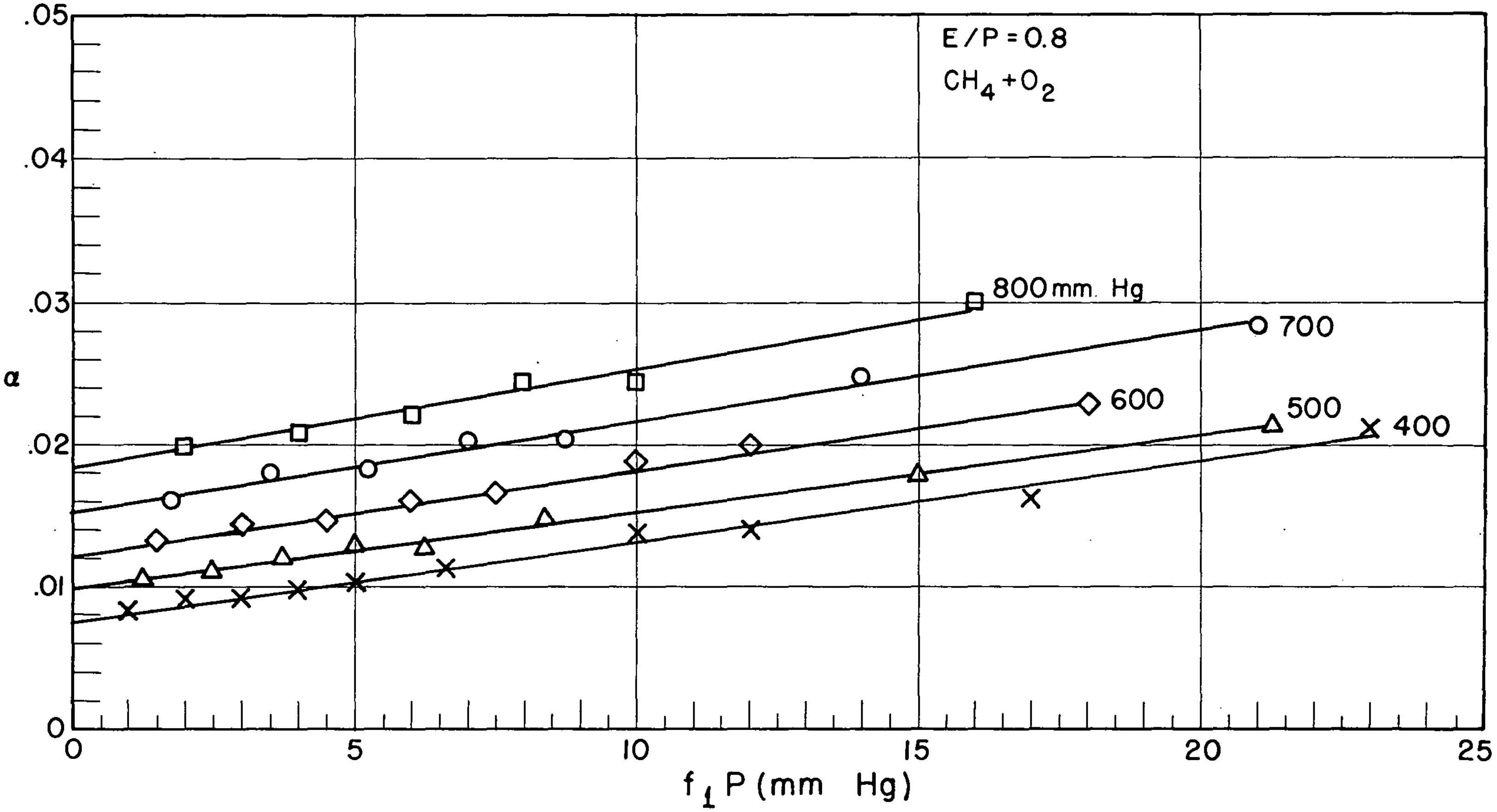

Fig. 17. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.8 in Methane-Oxygen Mixtures.

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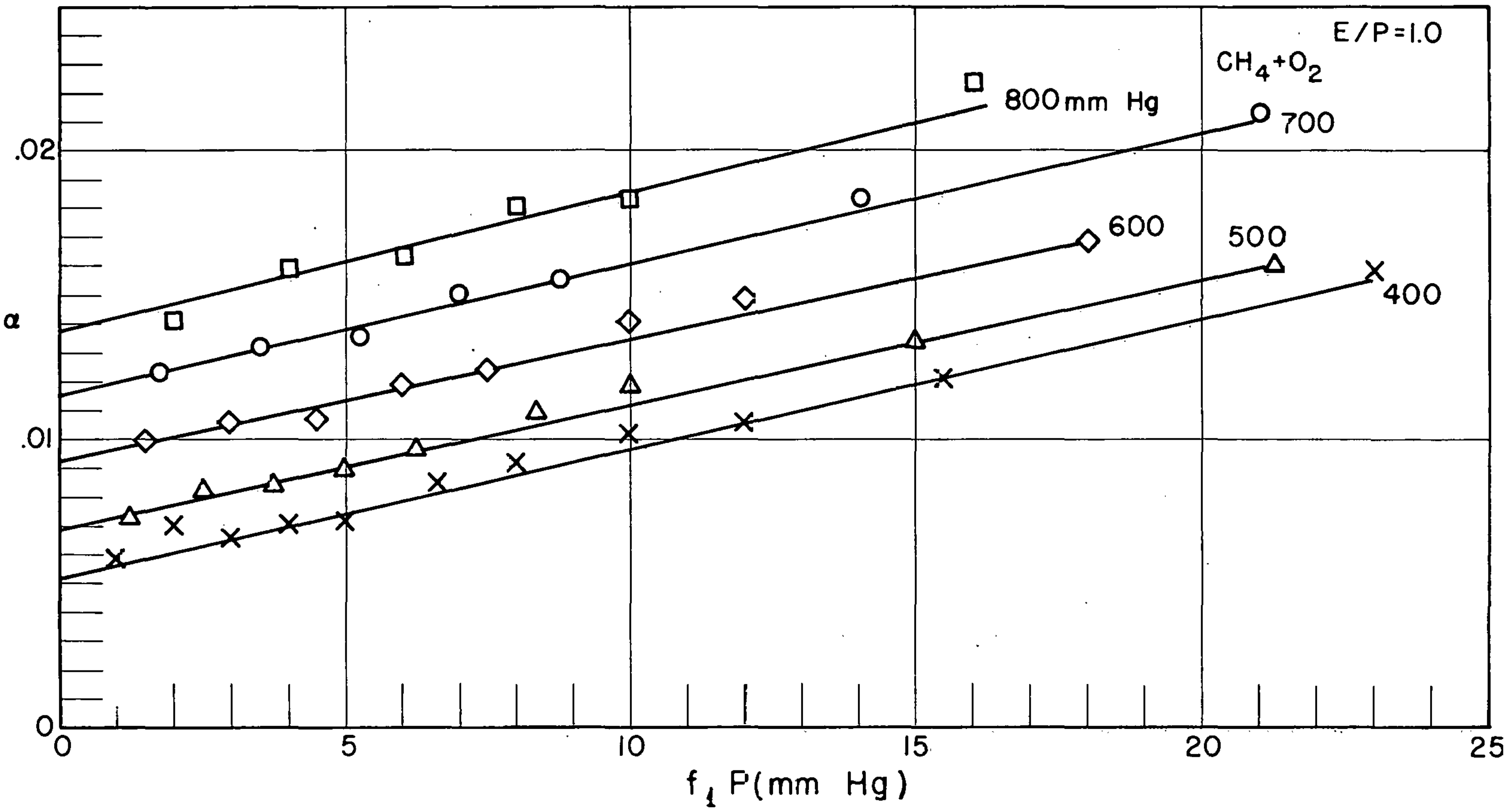

Fig. 18. The Attachment Coefficient vs Oxygen Pressure fo- E/P = 1.0 in Methane-Oxygen Mixtures.

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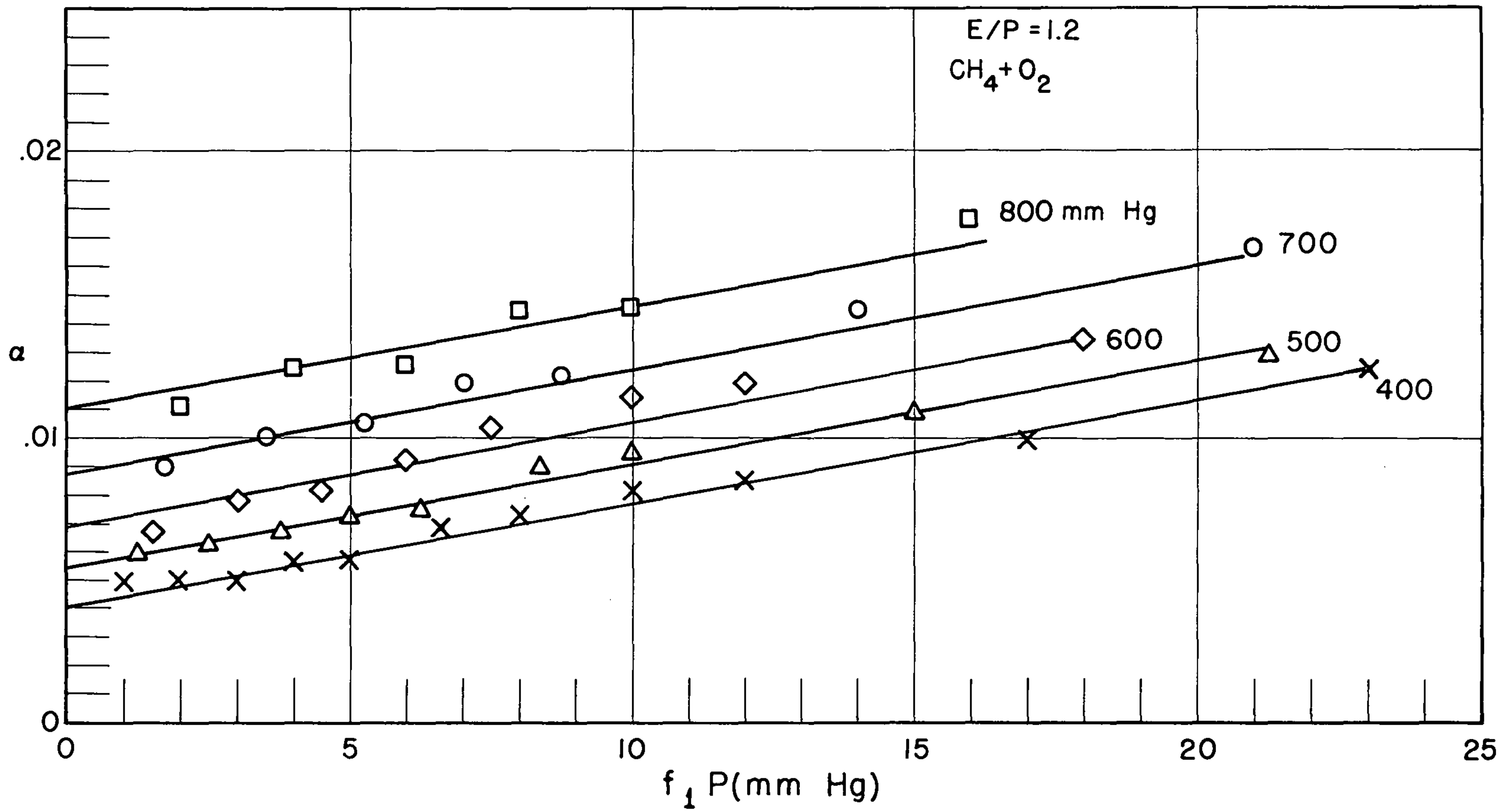

Fig. 19. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.2 in Methane-Oxygen Mixtures.

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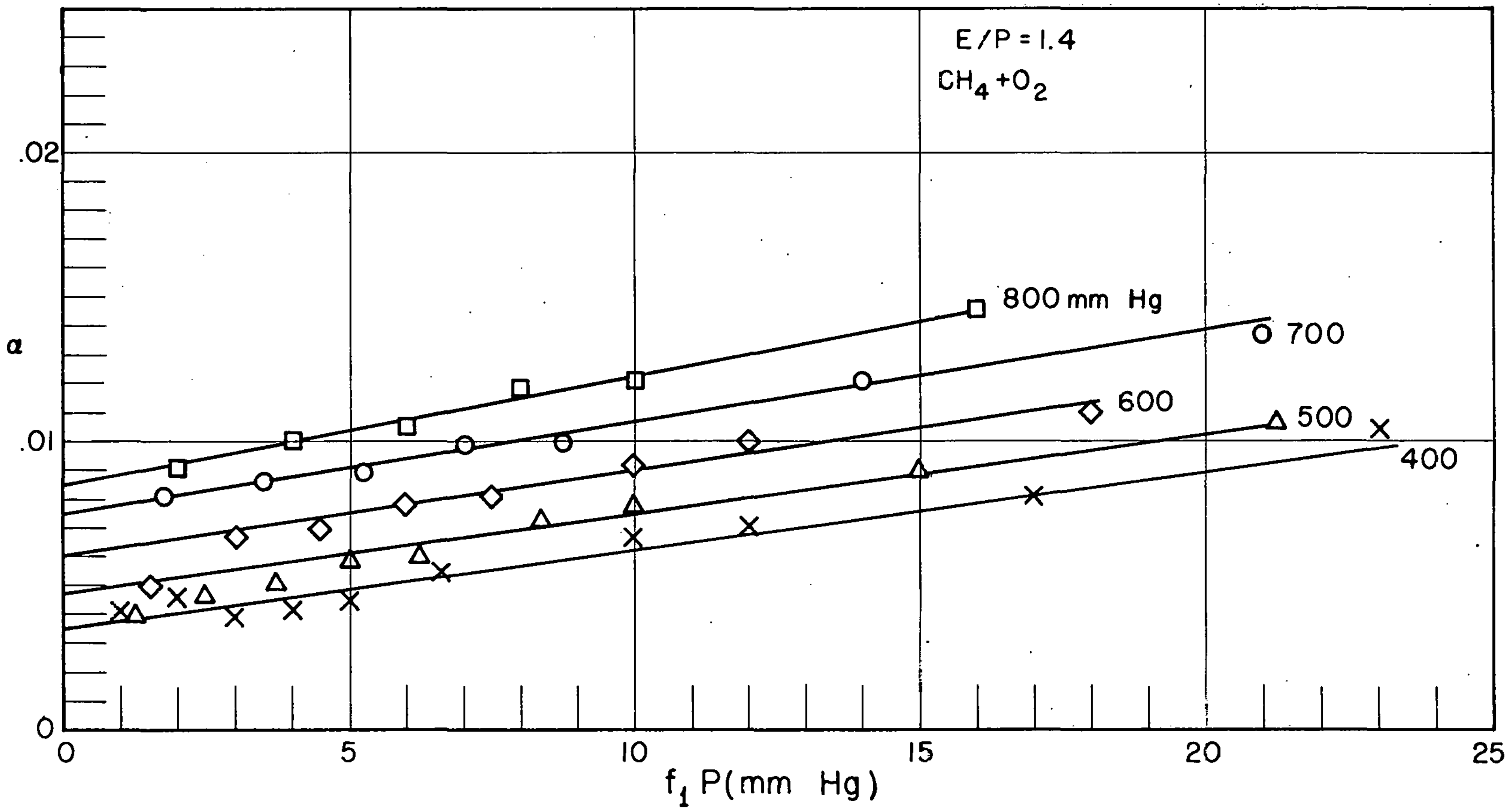

Fig. 20. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.4 in Methane-Oxygen Mixtures.

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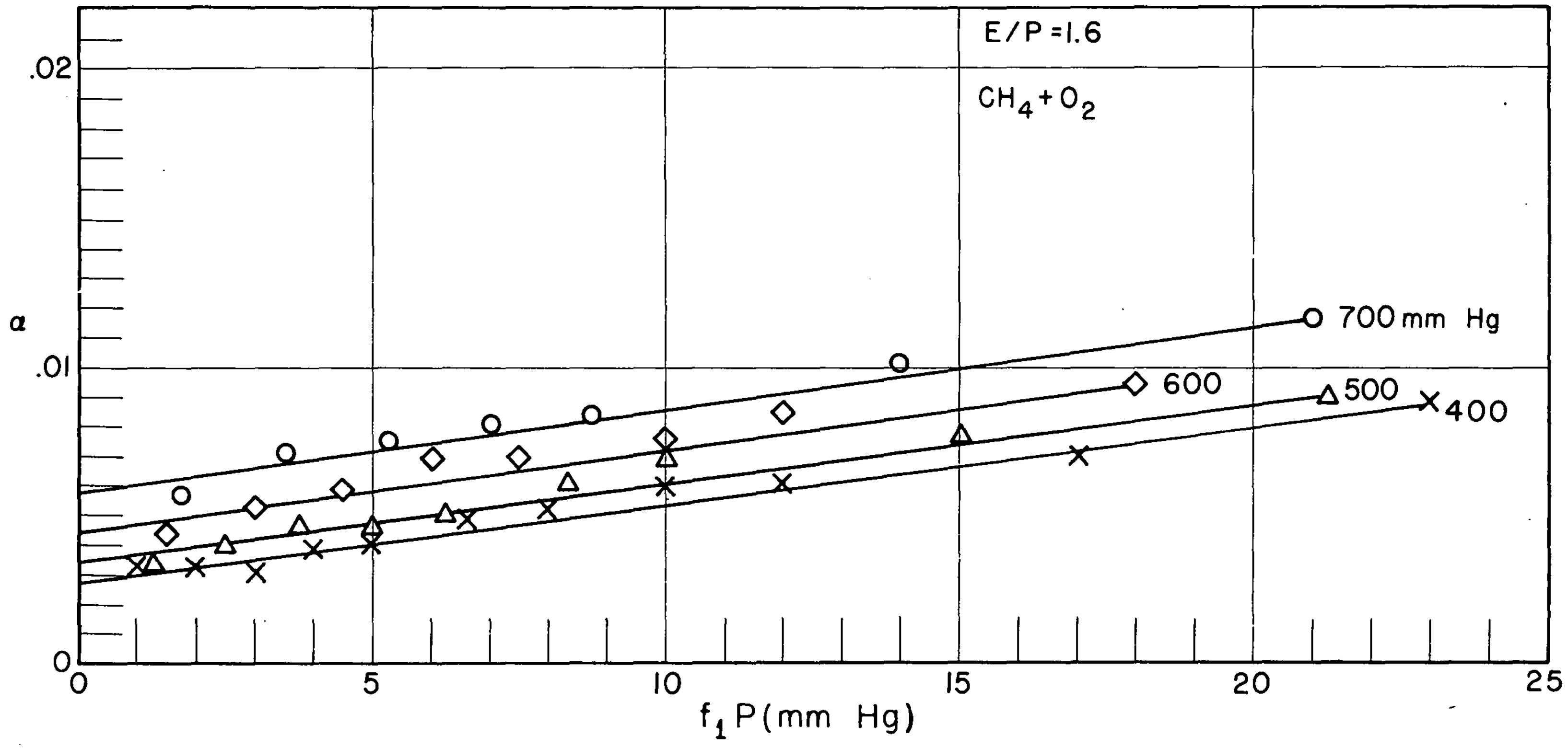

Fig. 21. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.6 in Methane-Oxygen Mixtures.

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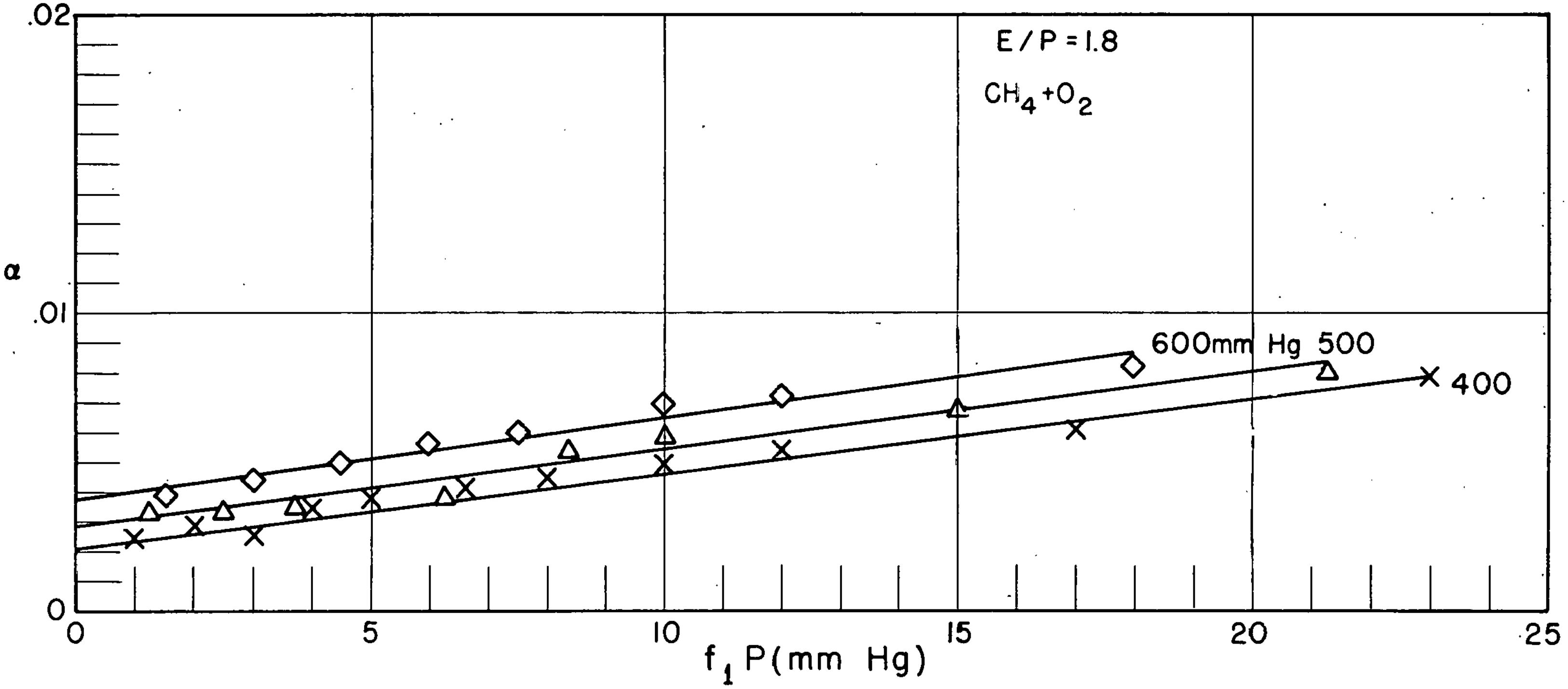

Fig. 22. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.8 in Methane-Oxygen Mixtures.

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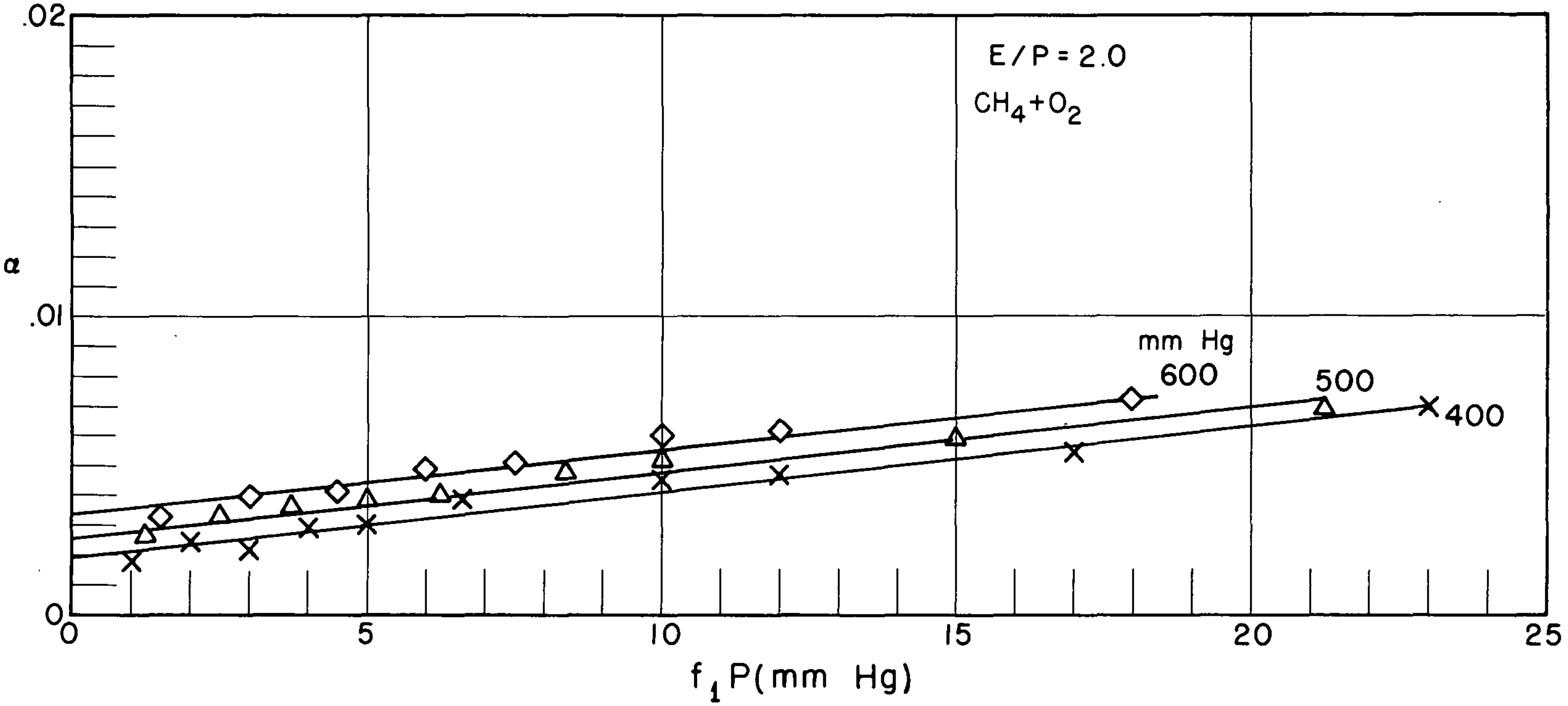

Fig. 23. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.0 in Methane-Oxygen Mixtures.

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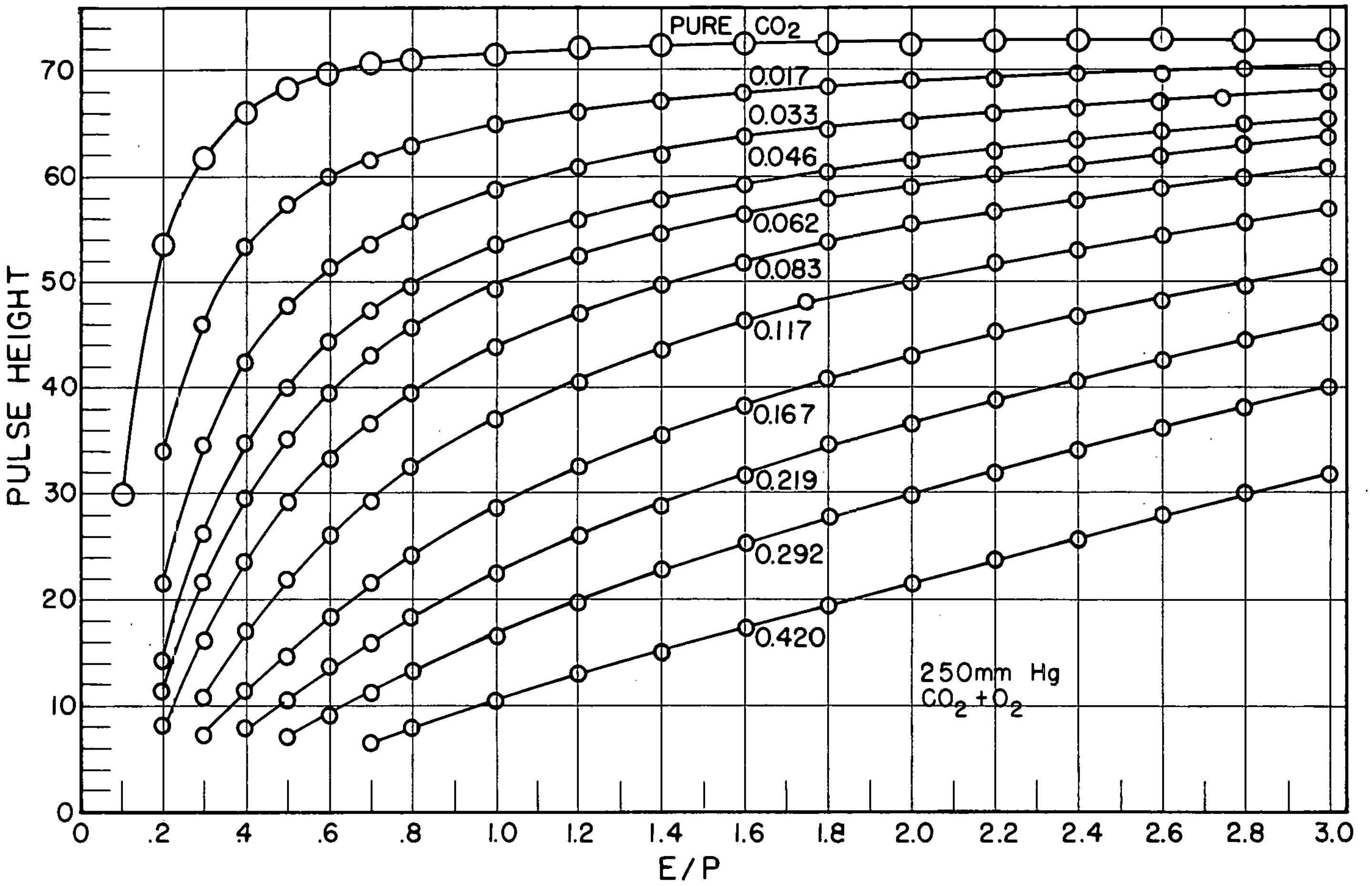

Fig. 24. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 250 mm Hg.

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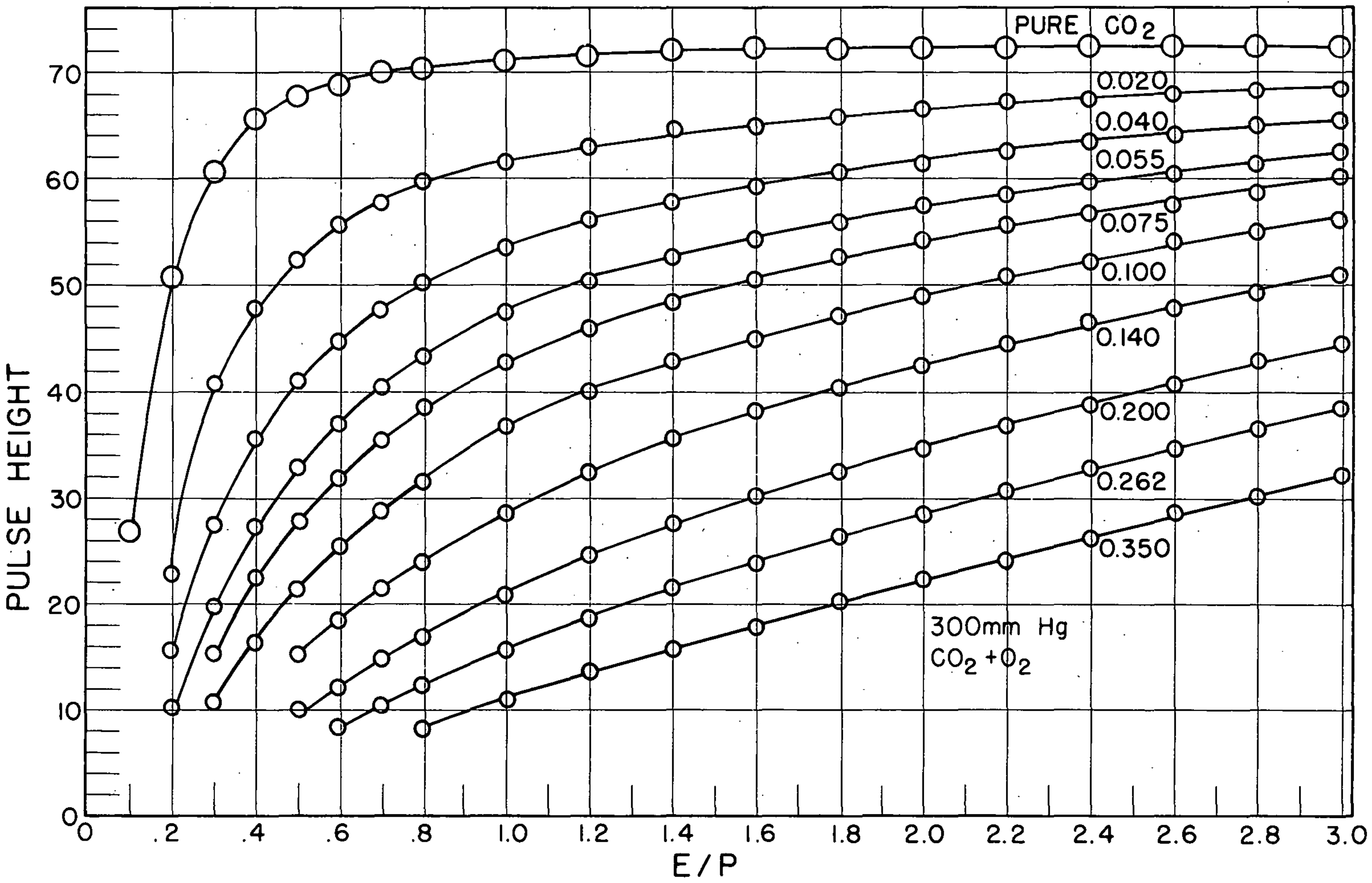

Fig. 25. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 300 mm Hg.

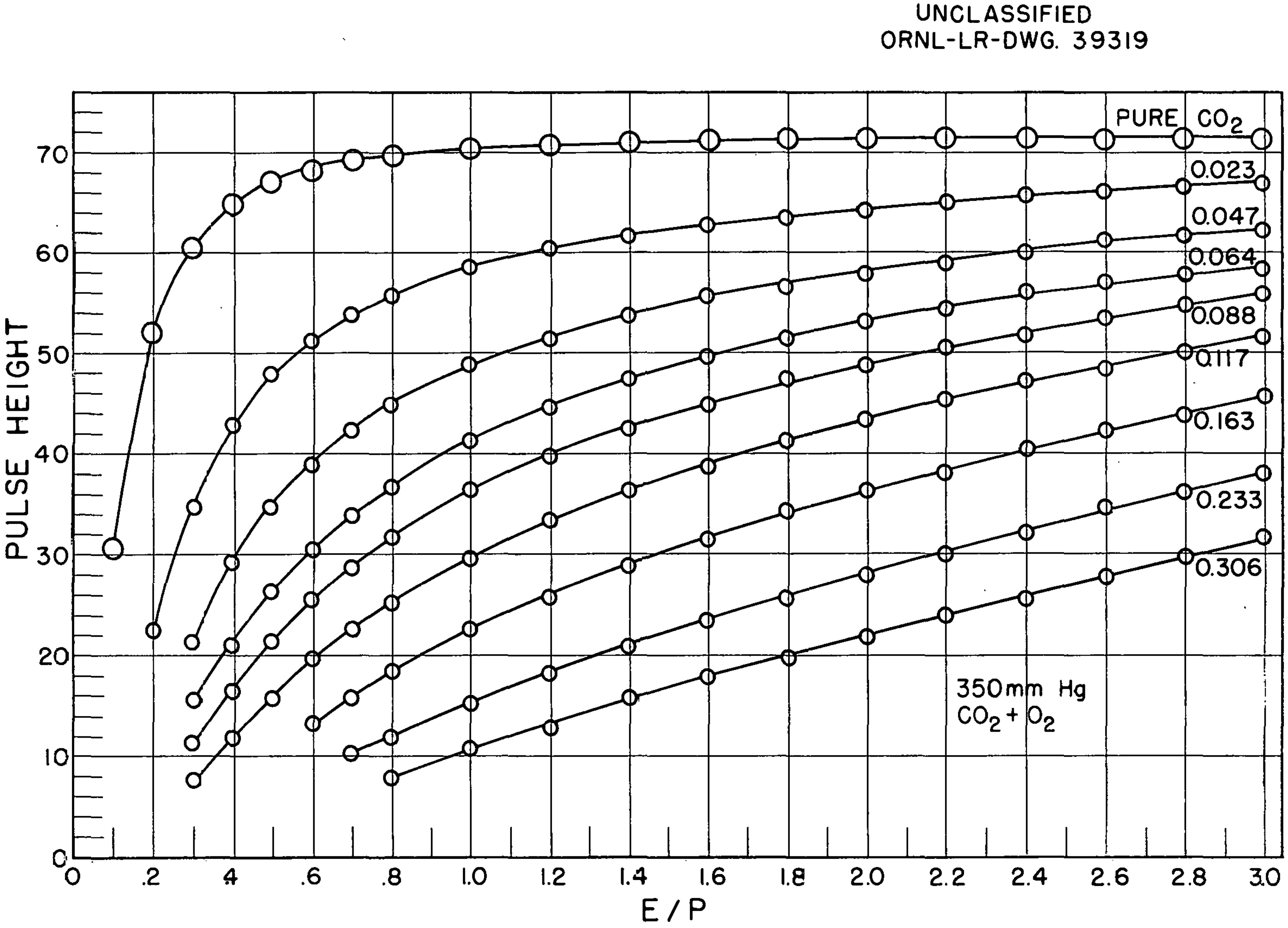

Fig. 26. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 350 mm Hg.

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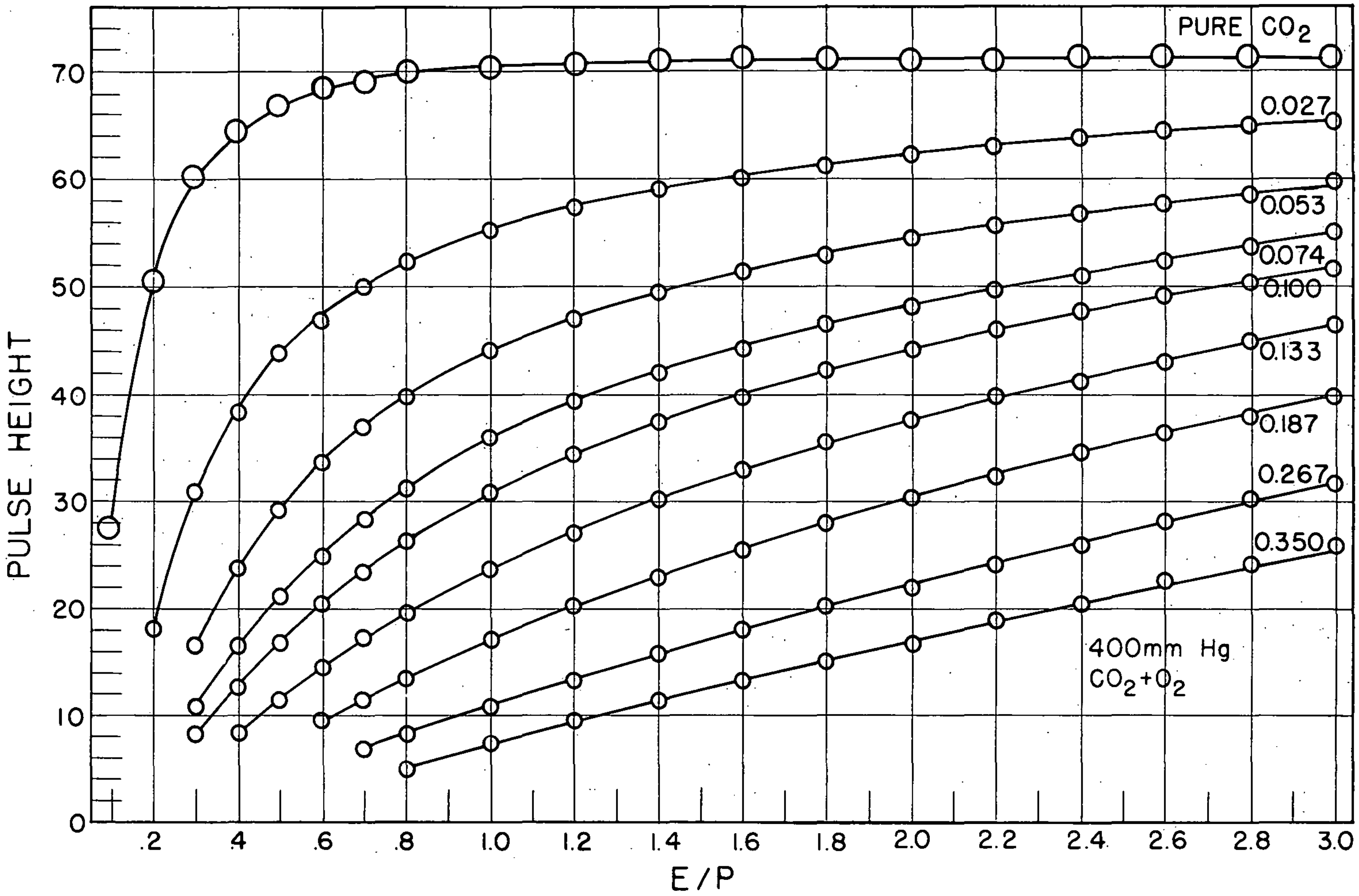

Fig. 27. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 400 mm Hg.

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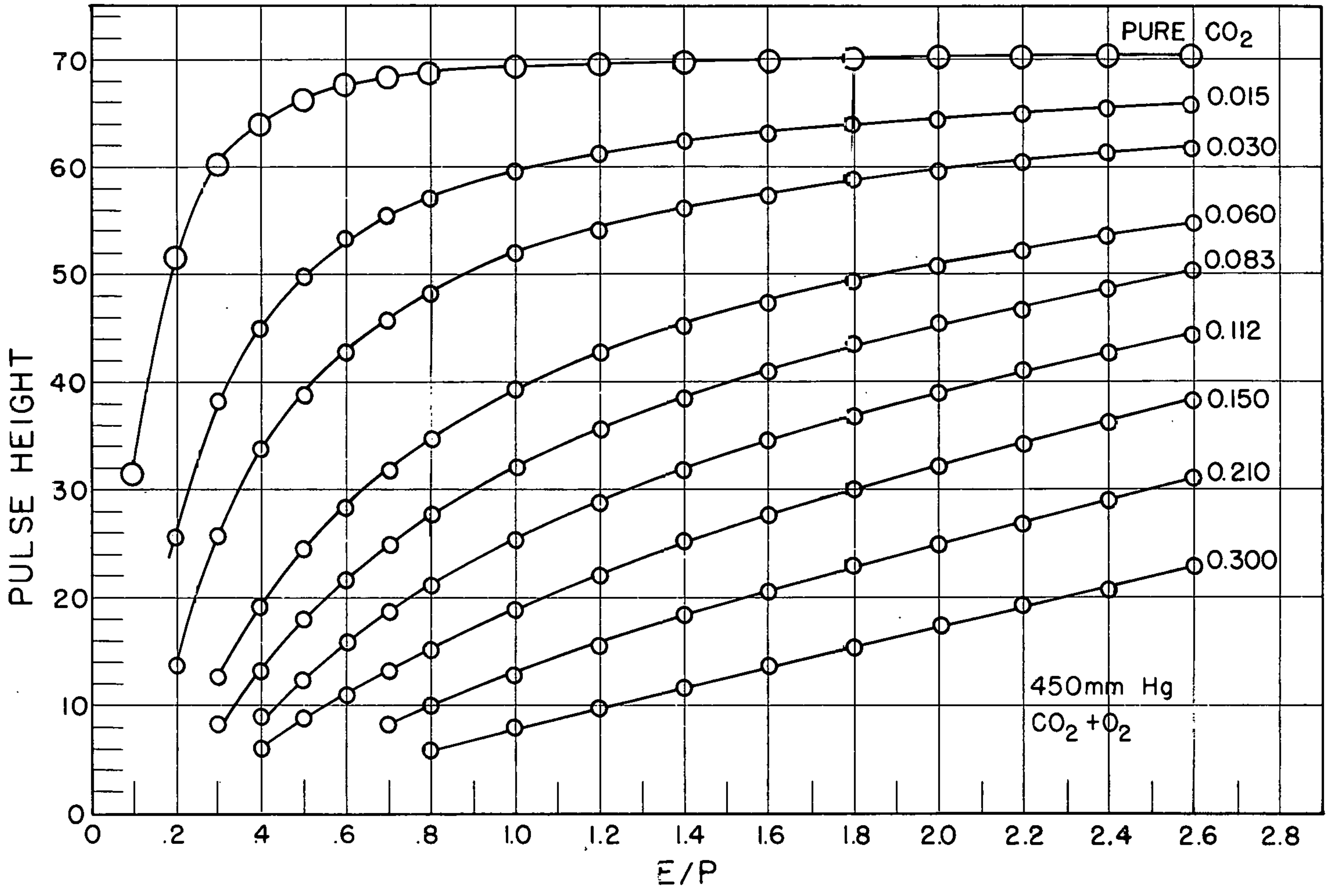

Fig. 28. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 450 mm Hg.

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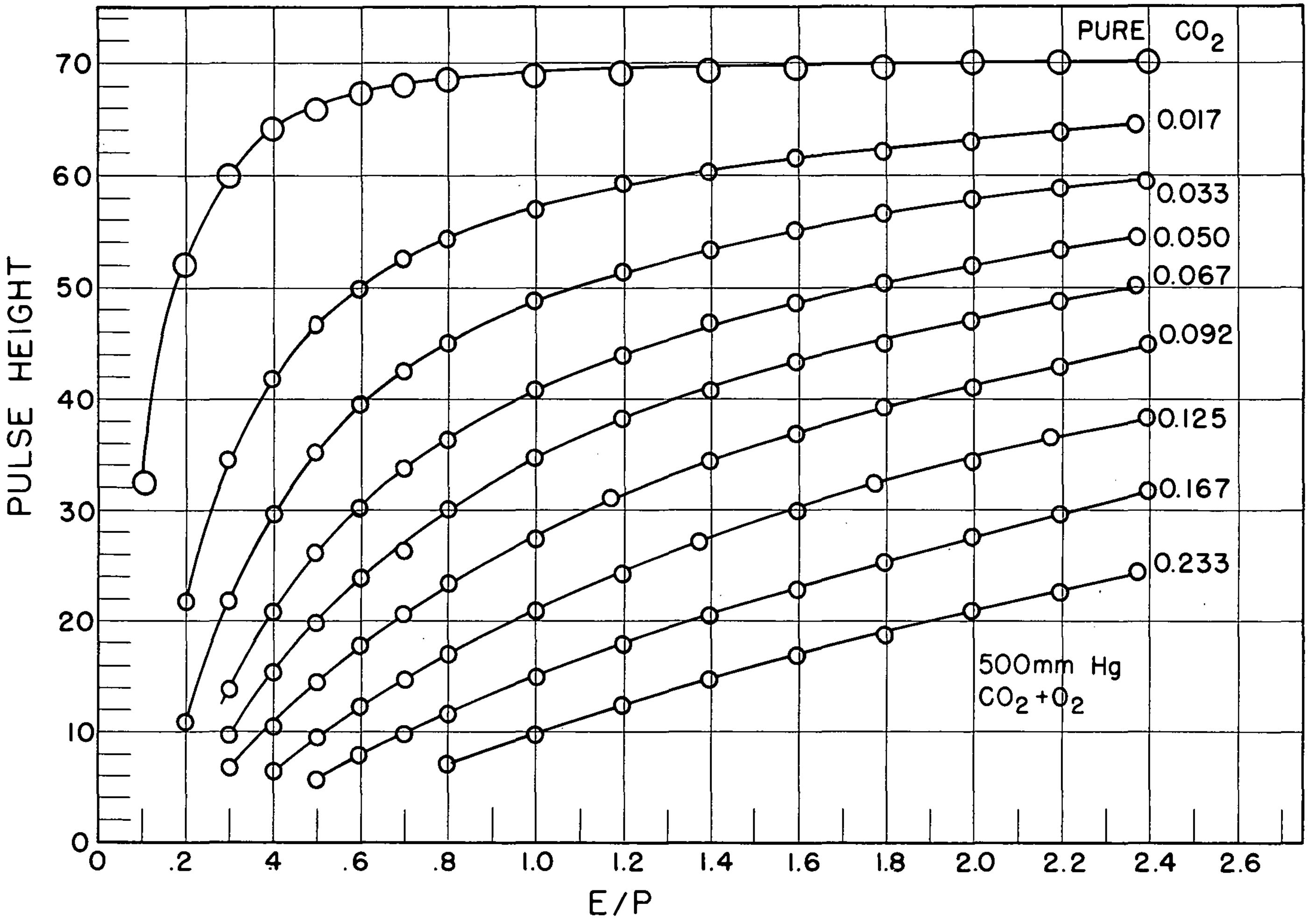

Fig. 29. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen-Mixtures at 500 mm Hg.

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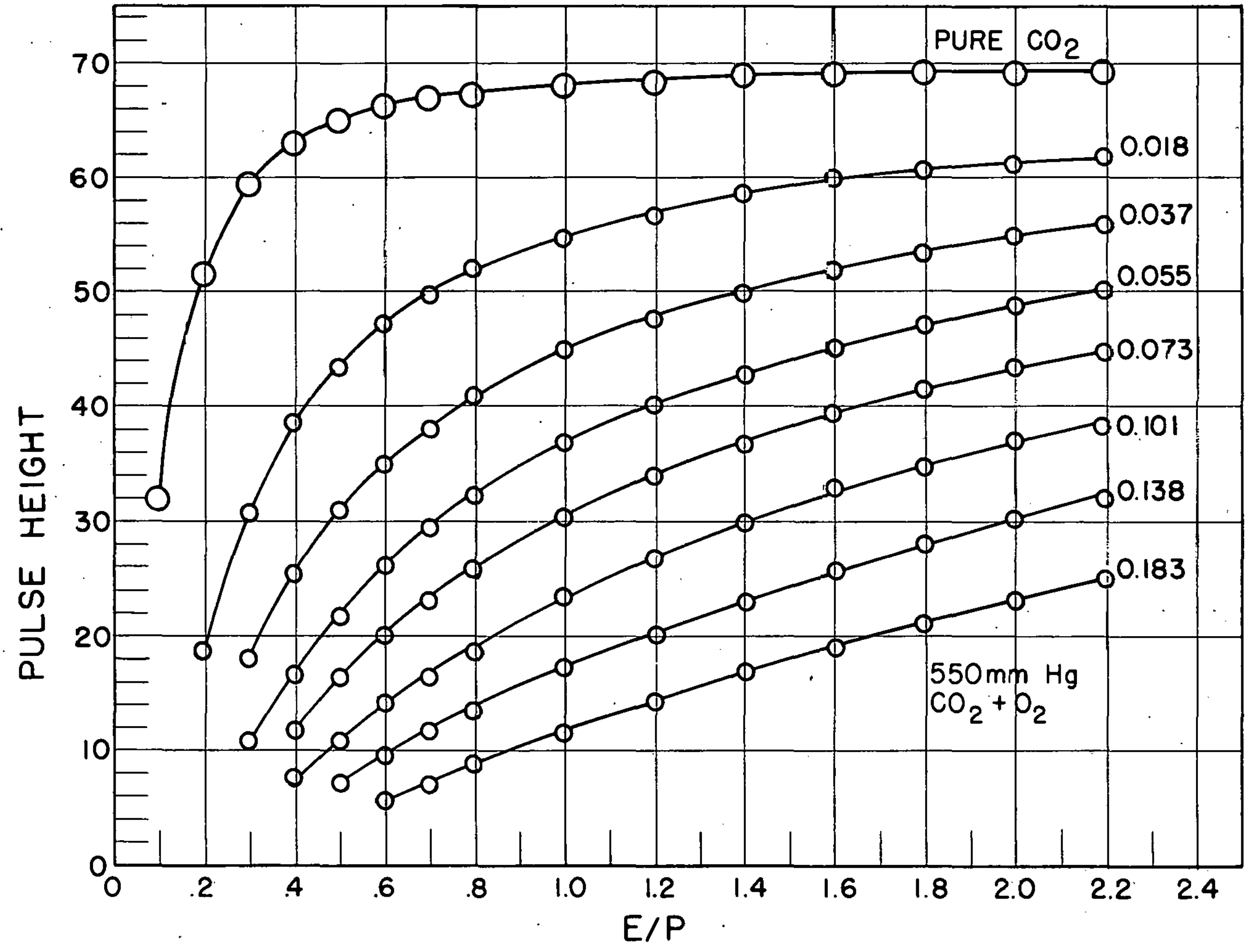

Fig. 30. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 550 mm Hg.

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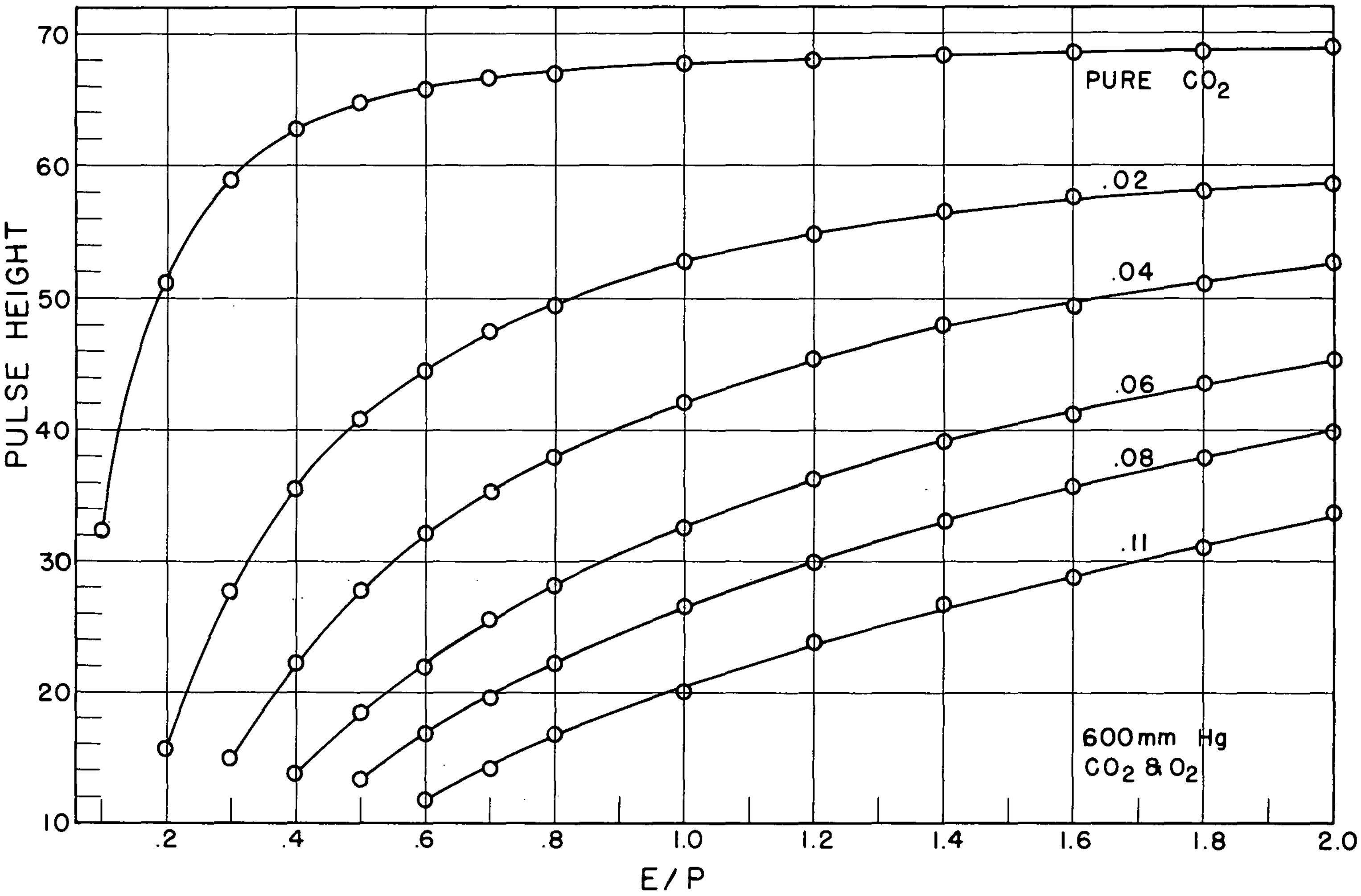

Fig. 31. E/P vs Pulse Height for Carbon Dioxide and Carbon-Dioxide-Oxygen Mixtures at 600 mm Hg.

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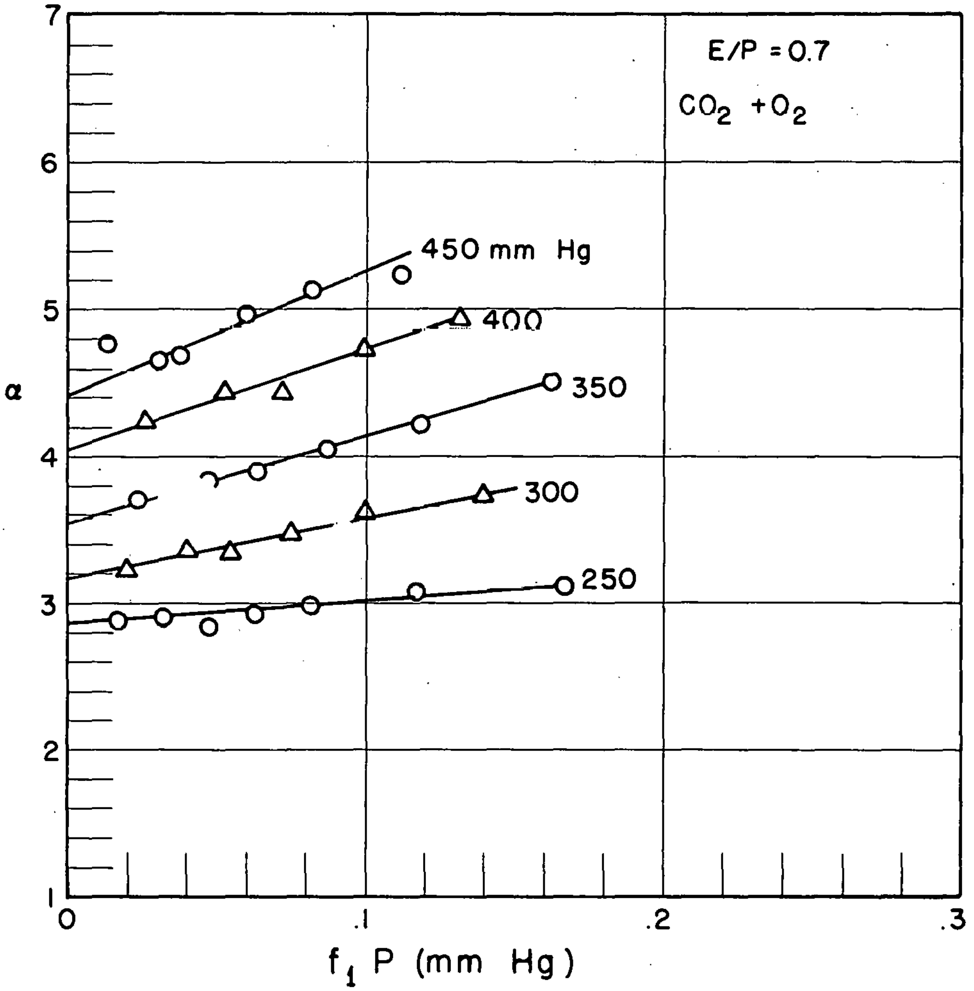

Fig. 32. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.7 in Carbon Dioxide-Oxygen Mixtures.

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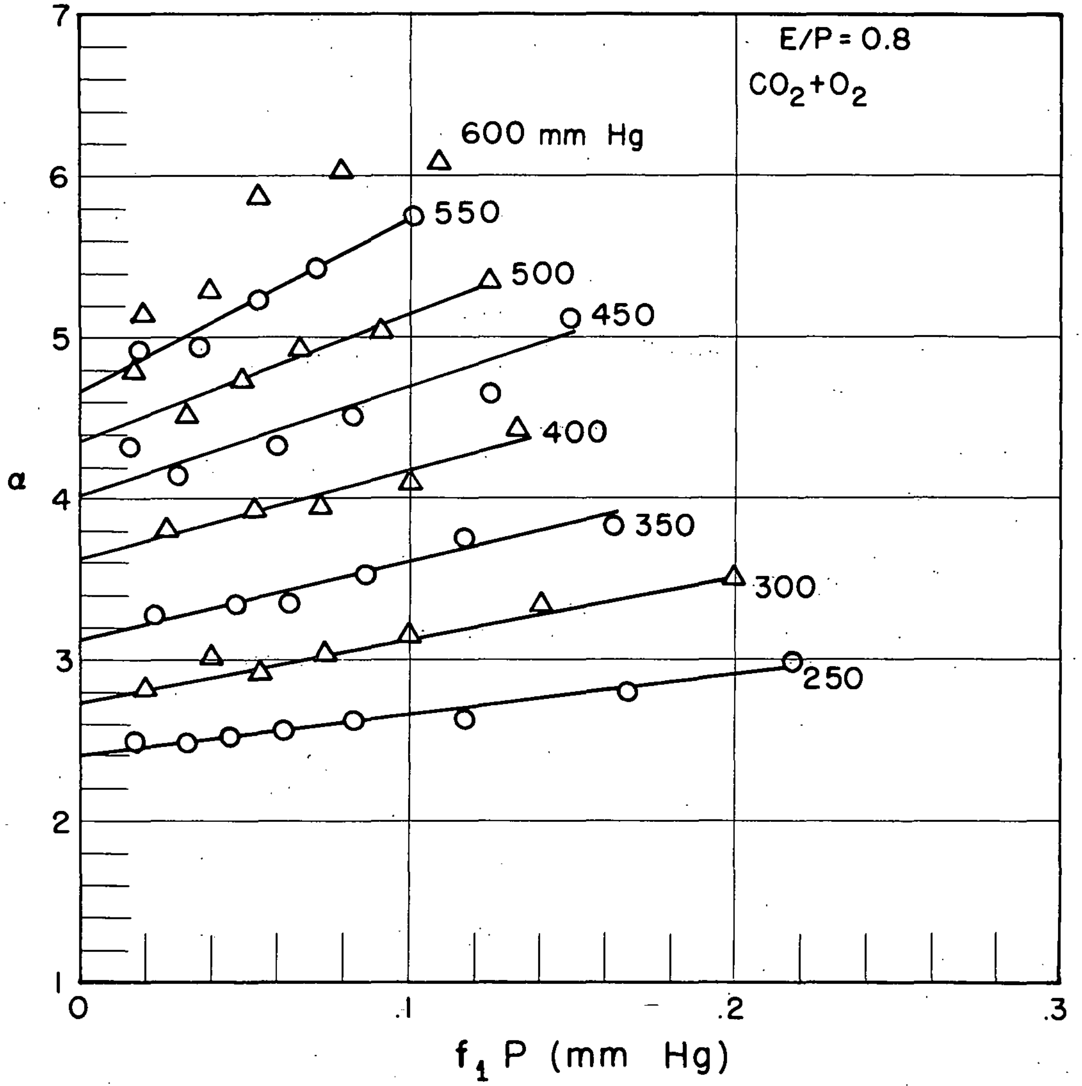

Fig. 33. The Attachment Coefficient vs Oxygen Pressure for E/P = 0.8 in Carbon Dioxide-Oxygen Mixtures.

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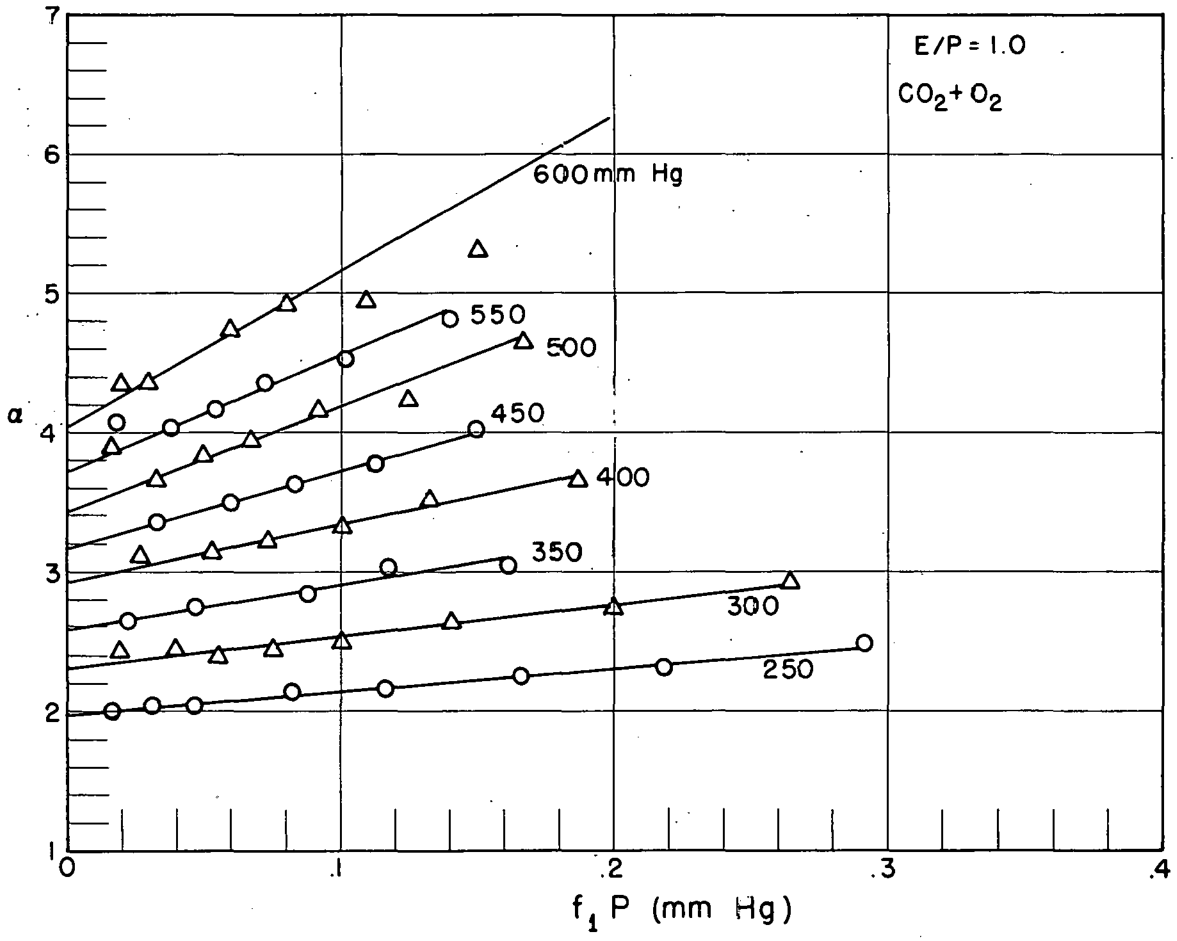

Fig. 34. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.0 in Carbon Dioxide-Oxygen Mixtures.

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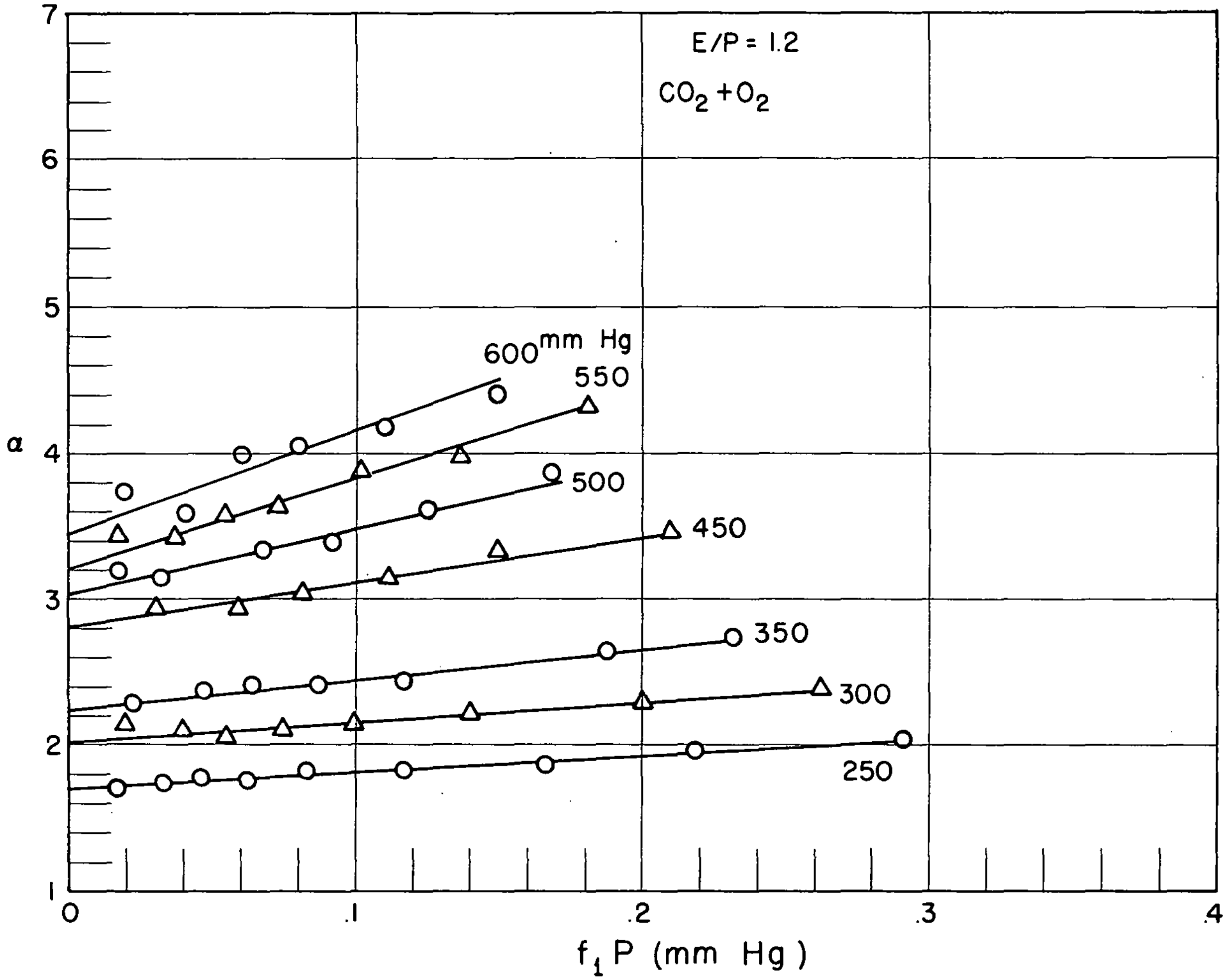

Fig. 35. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.2 in Carbon Dioxide-Oxygen Mixtures.

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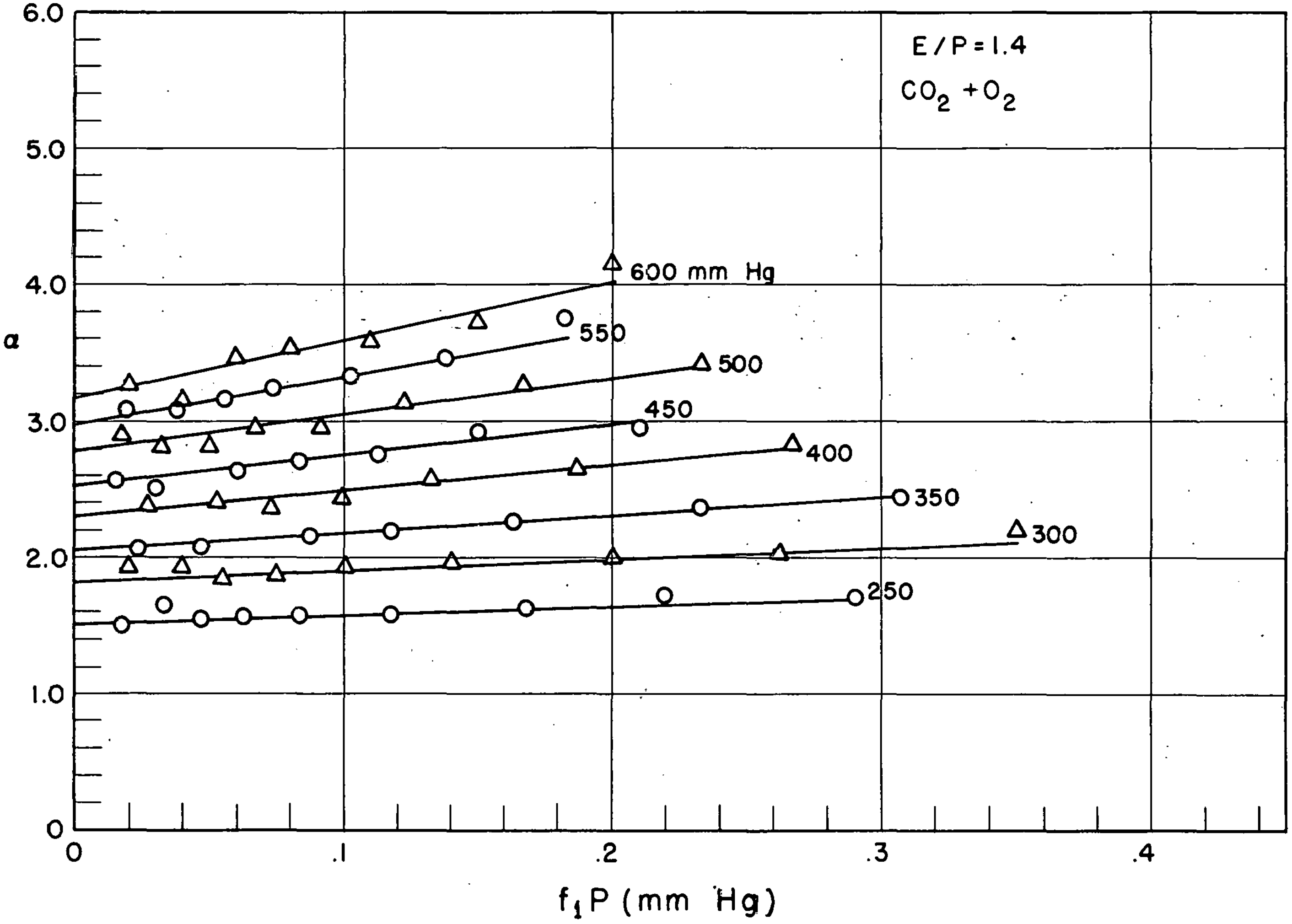

Fig. 36. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.4 in Carbon Dioxide–Oxygen Mixtures.

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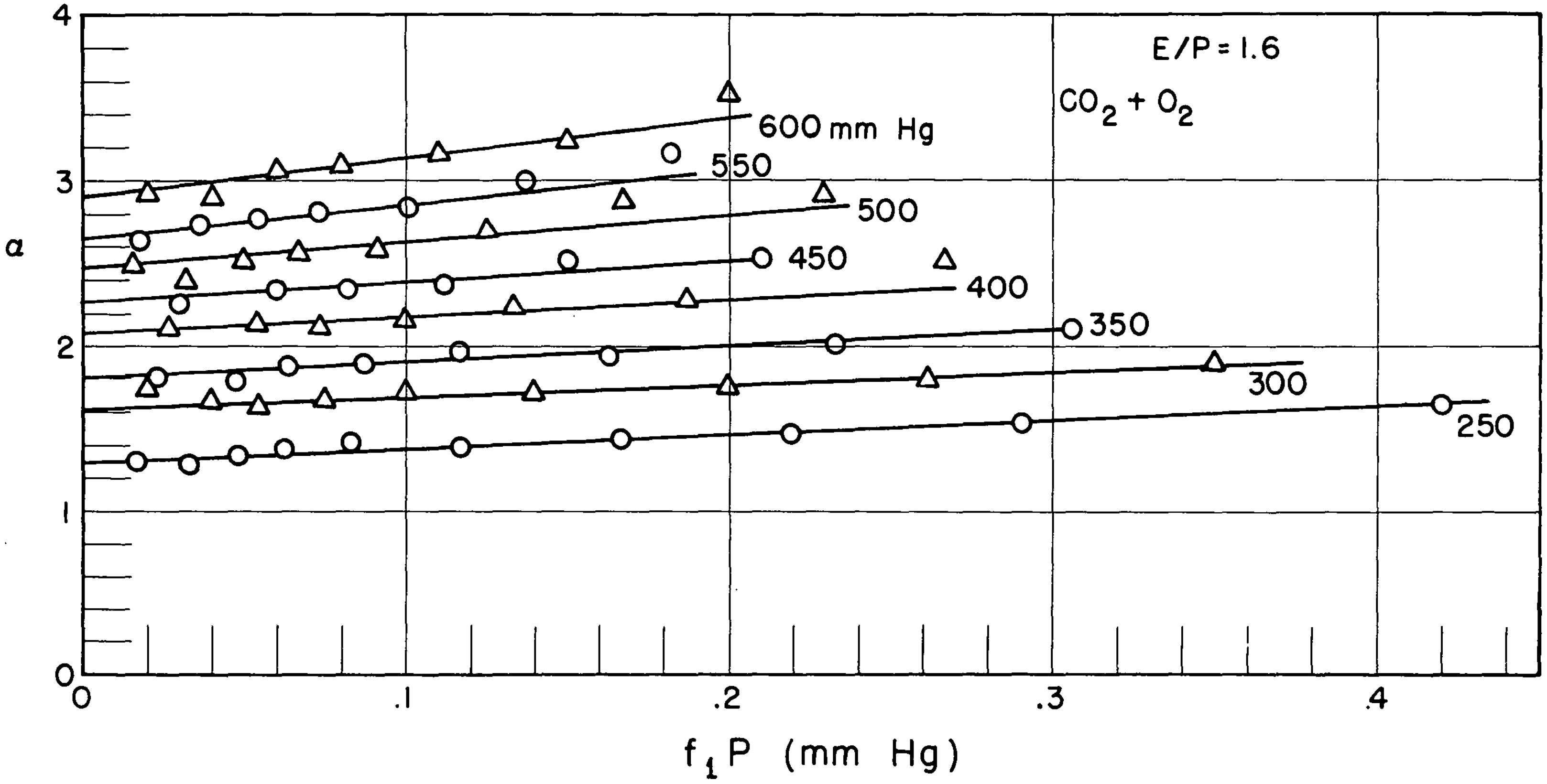

Fig. 37. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.6 in Carbon Dioxide-Oxygen Mixtures.

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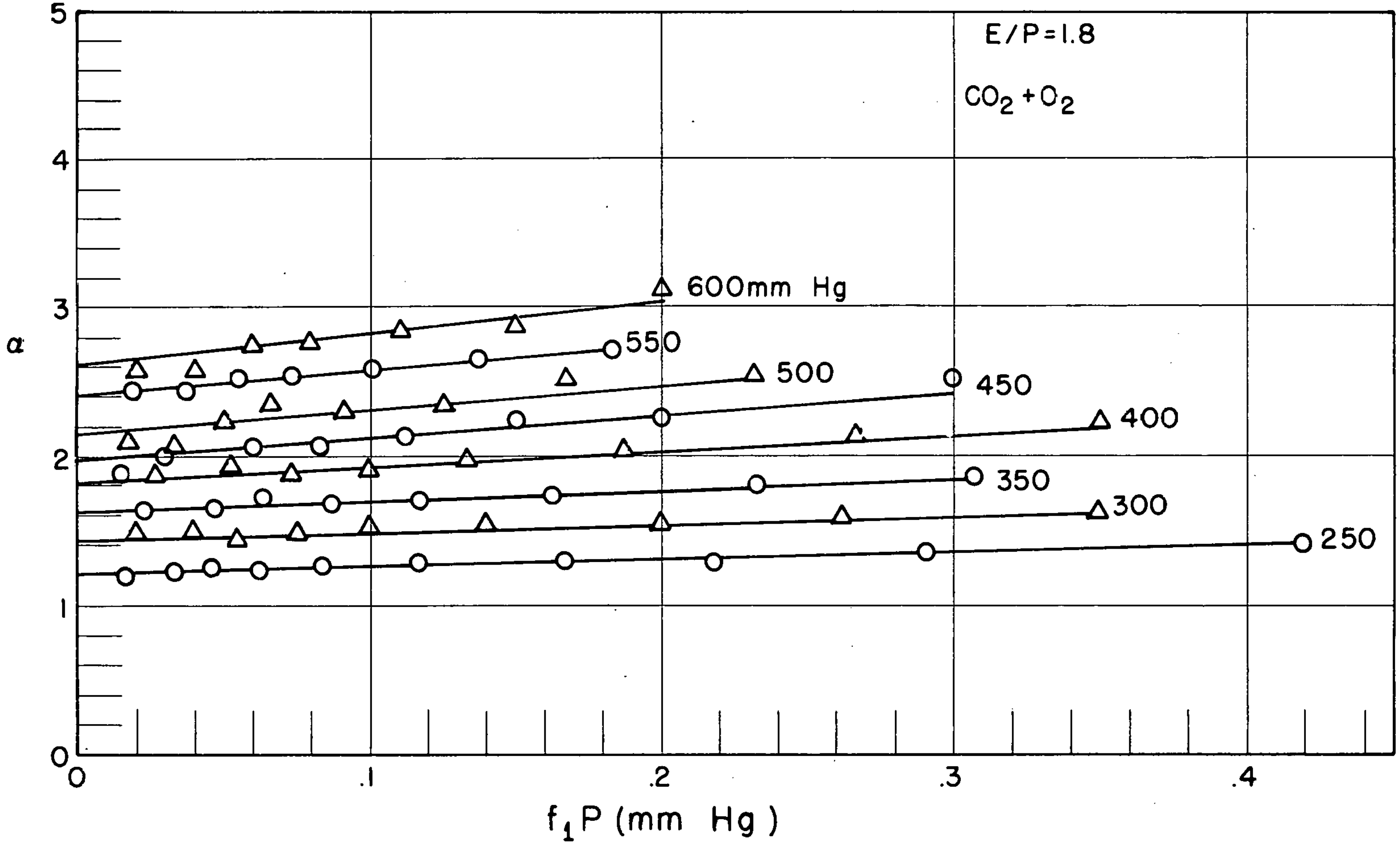

Fig. 38. The Attachment Coefficient vs Oxygen Pressure for E/P = 1.8 in Carbon Dioxide-Oxygen Mixtures.

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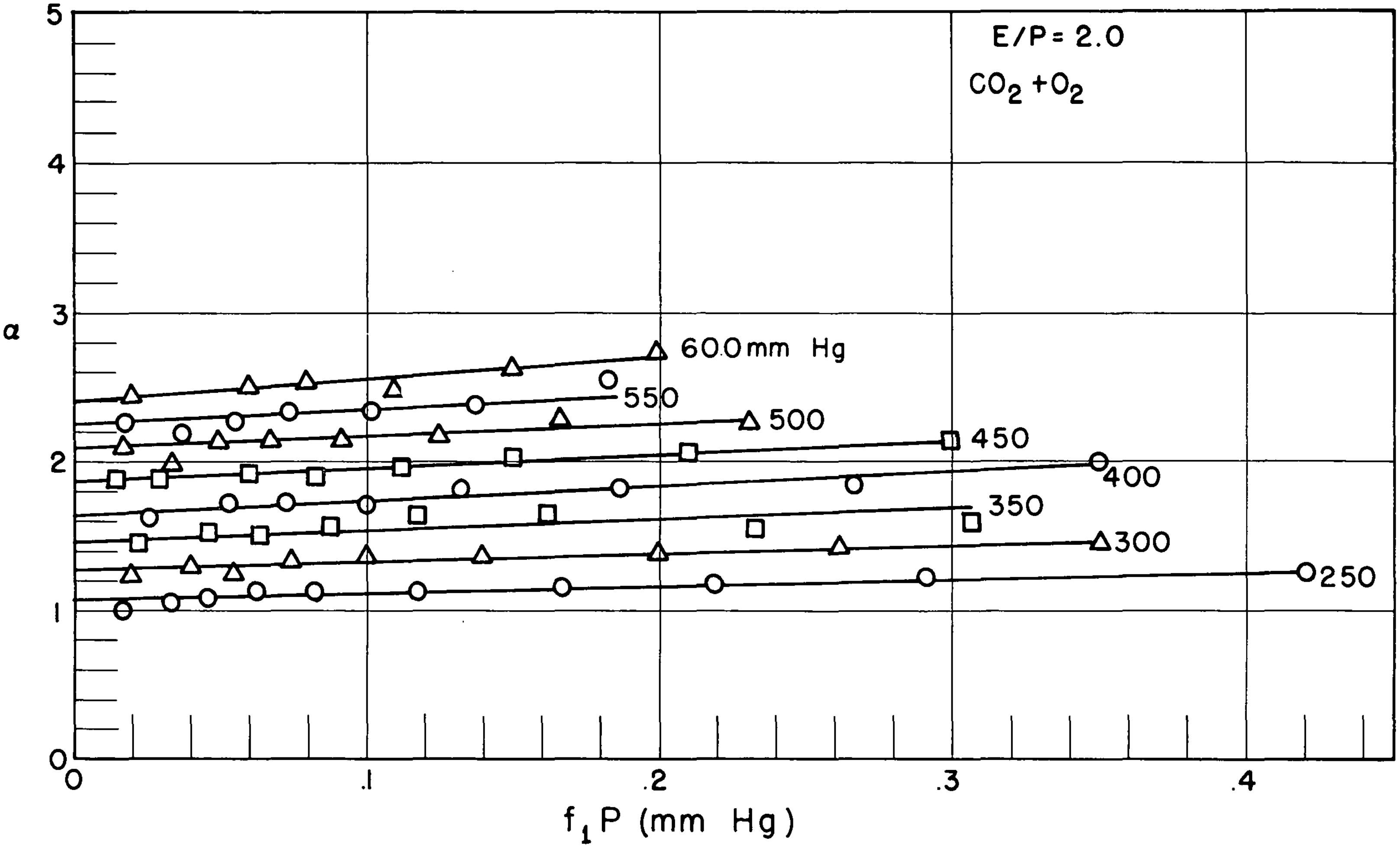

Fig. 39. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.0 in Carbon Dioxide-Oxygen Mixtures.

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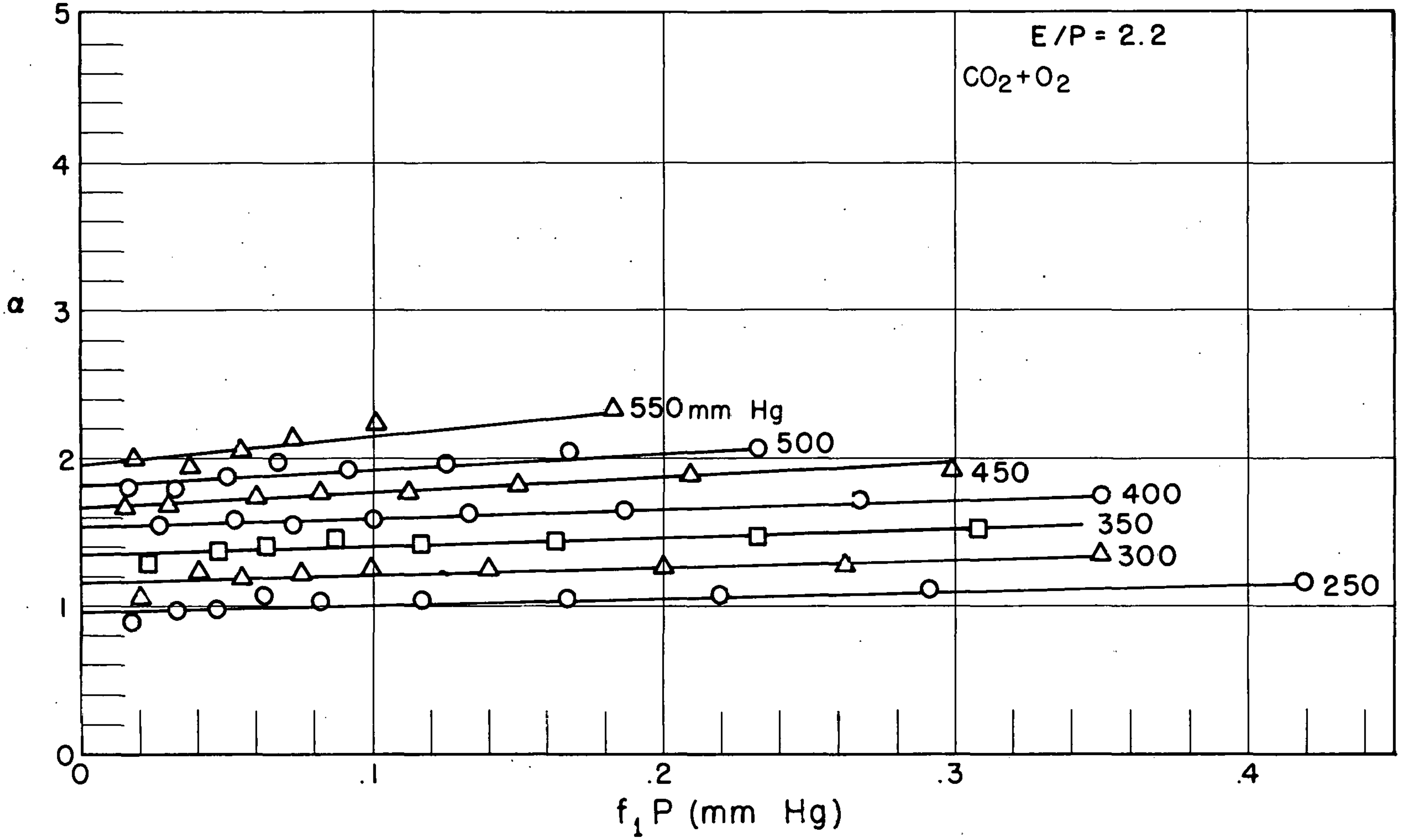

Fig. 40. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.2 in Carbon Dioxide-Oxygen Mixtures.

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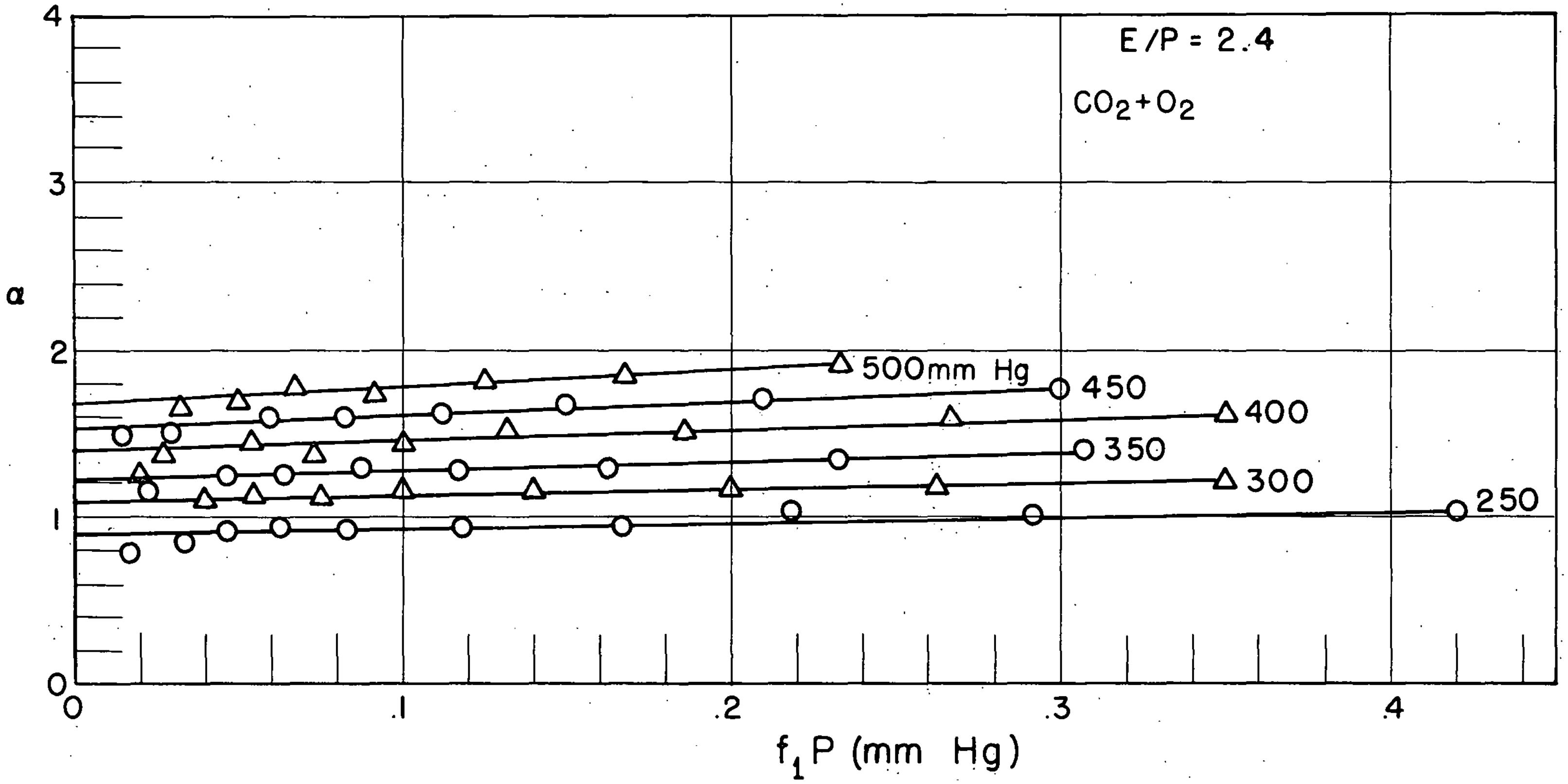

Fig. 41. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.4 in Carbon Dioxide-Oxygen Mixtures.

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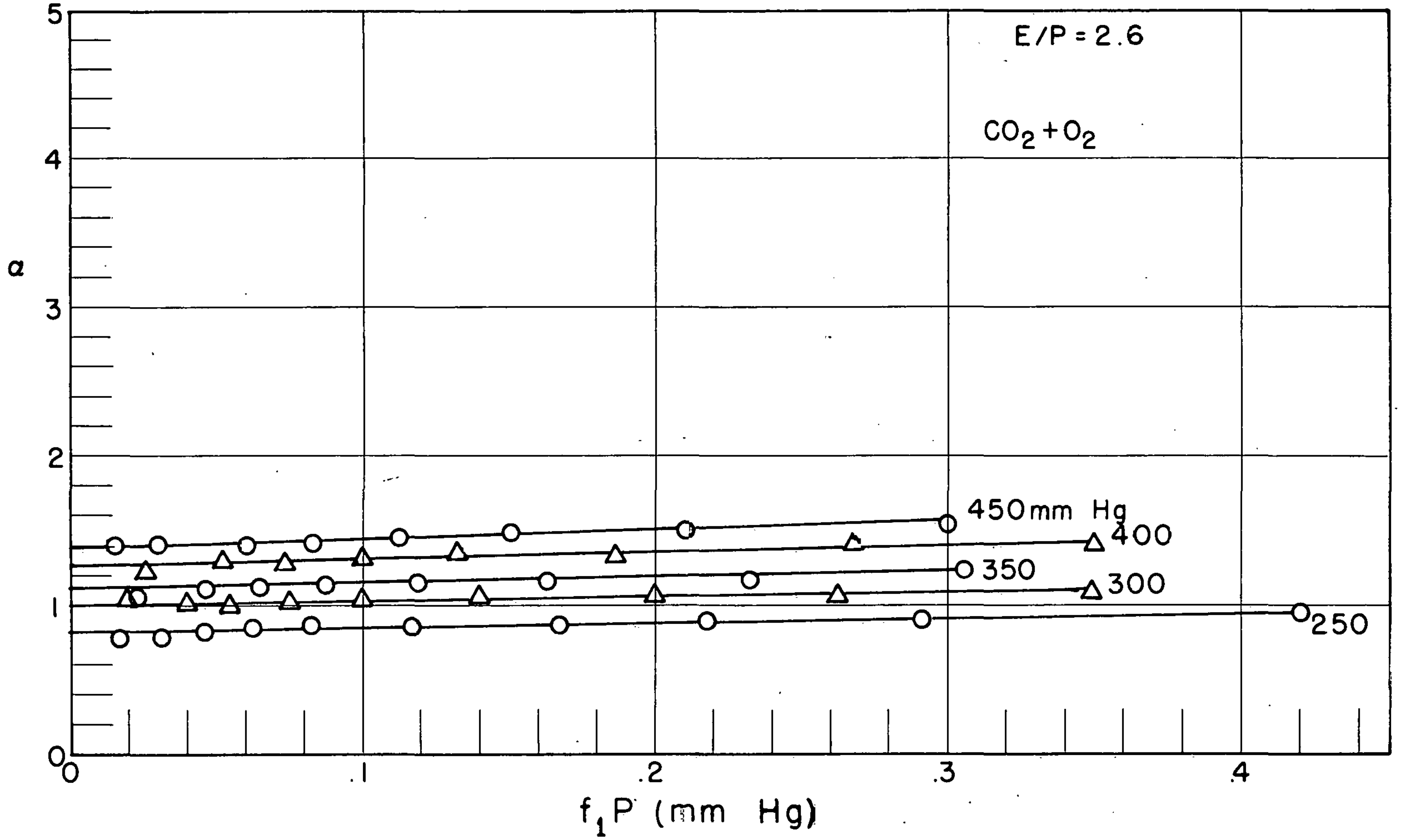

Fig. 42. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.6 in Carbon Dioxide-Oxygen Mixtures.

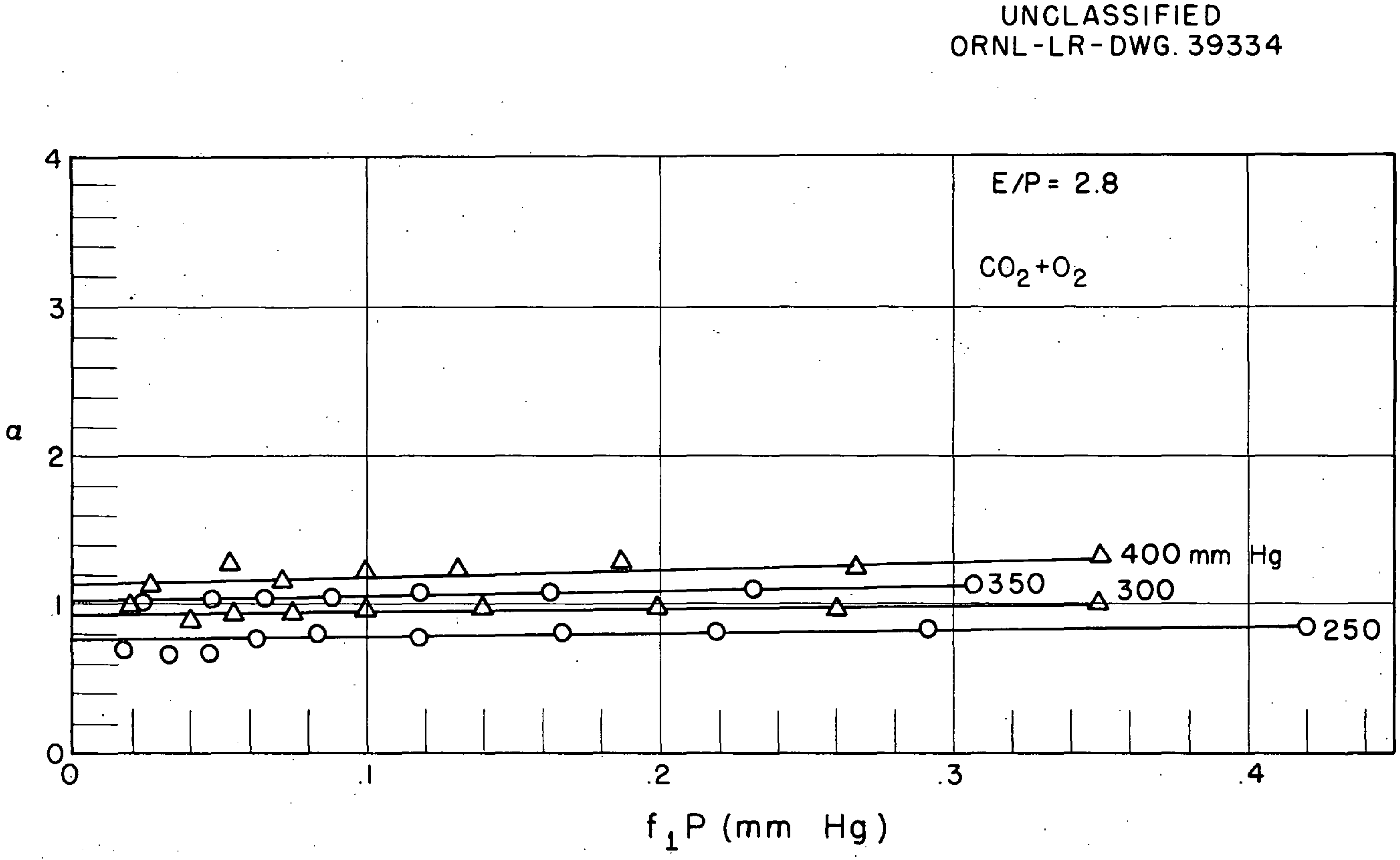

Fig. 43. The Attachment Coefficient vs Oxygen Pressure for E/P = 2.8 in Carbon Dioxide-Oxygen Mixtures.

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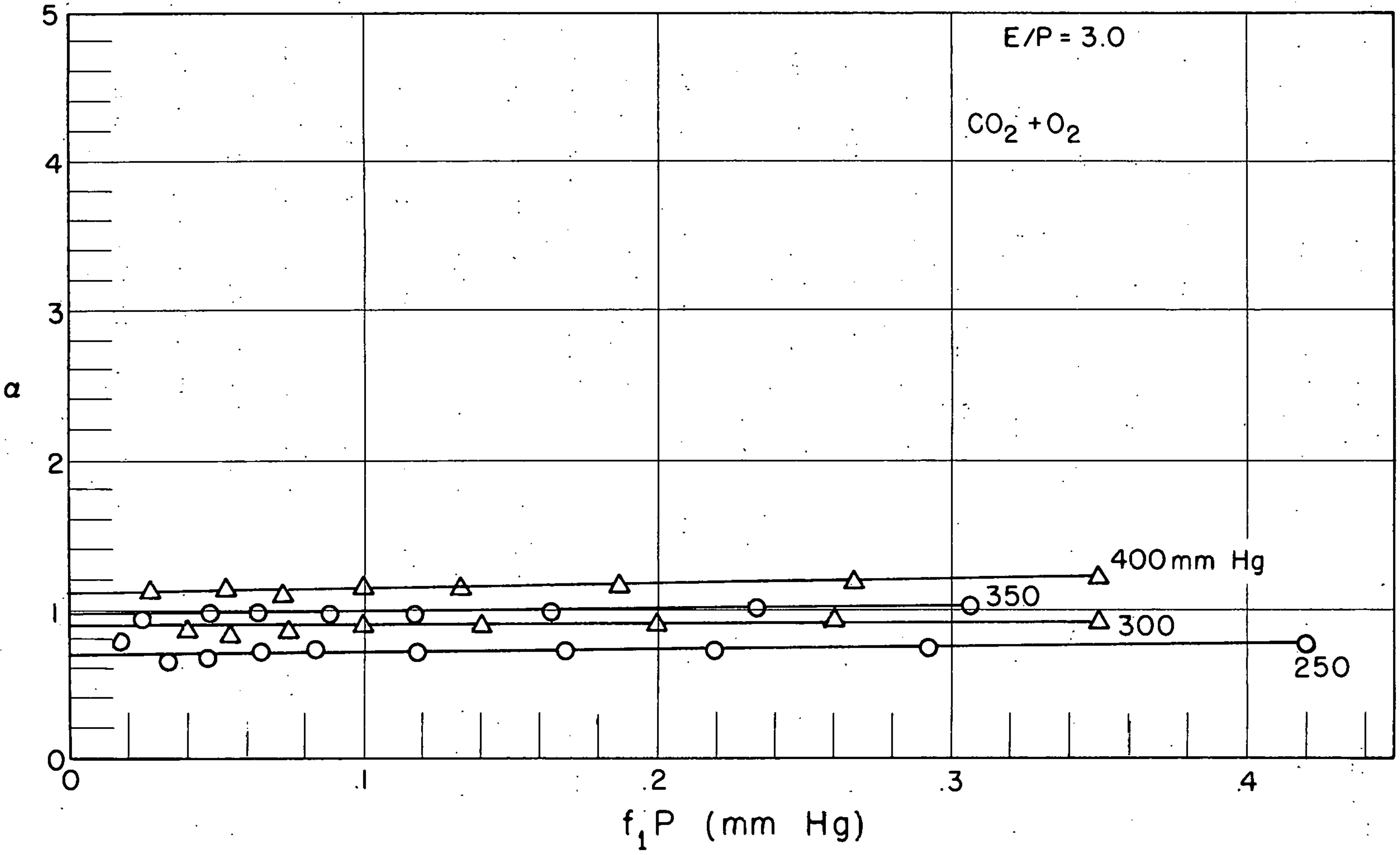

Fig. 44. The Attachment Coefficient vs Oxygen Pressure for E/P = 3.0 in Carbon Dioxide-Oxygen Mixtures.

to approximately one-third of its value in the pure gas.

The value of the attachment coefficient for the carbon dioxide mixtures is much greater than for the methane mixture at the same E/P. One reason for this can be found by examining the energy dependence of low energy electron capture in oxygen. As electron energy decreases, the probability of attachment in oxygen increases rapidly. In carbon dioxide the average electron energy is extremely low at the E/P values that were used for this work, and the amounts of oxygen that were added were too small to cause any significant change in the average energy. Thus, it is apparent that the attachment observed is that of very low energy electrons. This is probably not the only reason for the high attachment rates in carbon dioxide, but it is undoubtedly a contributing factor. Another factor affecting the attachment rates would be the stabilizing qualities of the carbon dioxide and methane atoms. With the carbon dioxide mixtures, the slope of the α versus f_1P lines increases while with the methane mixtures the lines are all parallel except possibly at very low values of E/P. This would seem to indicate that different stabilization processes are occurring in the two gases.

The attachment of electrons in oxygen-nitrogen mixtures has been shown to be a complex process that occurs in two stages.[11] The first stage involves the formation of the unstable 0_2^{-*} ion. (The asterisk indicates vibrational and electronic excitation). The second stage involves the removal of the excess energy by molecular collisions resulting in the formation of an 0_2^- ion which while not necessarily in its ground state is nevertheless stable with respect to re-emission of the electron. If a stabilizing collision does not occur during the lifetime of the unstable ion, the electron will be re-emitted. Since the probability of occurrence of such a collision in a given time interval increases as the pressure increases it would be expected that the attachment coefficient would depend on the total pressure. Since the probability of energy transfer depends on the kind of molecules involved, it is reasonable to expect the attachment coefficient to depend on the type of non-attaching gas present also.

It is hoped that by extending the pressure range and, if possible, increasing the accuracy of the experiment, suitable models can be derived that will explain the attachment process in methane and carbon dioxide in much the same manner as has been done for nitrogen.

IV. CONCLUSION

The formation of heavy negative ions by the attachment of low energy electrons to oxygen molecules was studies for small amounts of oxygen mixed with methane or carbon dioxide. The rate of attachment in both cases was found to depend on the electron energy, the pressure of the oxygen and the non-attaching gas, and on the kind of non-attaching gas. In general, the attachment increases as electron energy decreases or as either oxygen or total pressure increases.

The value of the attachment coefficient in oxygen-carbon dioxide mixtures is about 100 times its value in oxygen-methane mixtures. This large difference is probably due in part to differences in electron energy and partly to differences in the stabilizing qualities of the two molecules. Dissociative attachment, which should be pressure independent, does not occur at the low energies that were used in this work.

Both methane and carbon dioxide are sometimes used as filling gases for Geiger and proportional counters. The high sensitivity of carbon dioxide to oxygen contamination indicates that very pure gas should be used if the best operation is to be obtained. The low sensitivity of methane recommends it for counters where careful purification of the gas is difficult and particularly for flow counters where the possibility of contamination by atmospheric oxygen exists.

APPENDIX

Relationship Between α, h, and σ_c

There are three quantities that are presently in use for describing electron capture in electronegative gases. These are α, the probability of capture per centimeter of drift in the field direction and per millimeter of partial pressure of the attaching gas; h, the probability of capture per collision with a molecule of the attaching gas; and σ_c, the capture cross section.

The relationship between α and h can be derived as follows:

Let

h_m = the probability of attachment per collision with any molecule in the mixture;

α_m = the probability of attachment per centimeter of travel in the field direction;

N_m = the total number of collisions per centimeter of travel in the field direction.

It is apparent that

$$\alpha_m = N_m h_m .$$

However,

$$N_m = \left(\frac{\mu}{W}\right) \frac{1}{\lambda_m}$$

where

μ = mean agitation velocity of electrons in the gas mixture;

W = drift velocity of electrons in the gas mixture;

λ_m = mean free path for electrons in the gas mixture.

Therefore,

$$\alpha_m = \frac{\mu}{W}\,\frac{h_m}{\lambda_m} = \frac{\mu}{\lambda_m}\,\frac{h_m}{W}\,.$$

Since

$$\frac{\mu}{\lambda_m} = \frac{C}{W}\,\frac{e}{m}\,E, \quad \text{(Ref. 15)}$$

where

$\frac{e}{m}$ = the charge to mass ratio of the electron;

E = the electric field;

C = a constant dependent on the electron energy distribution;

then

$$\alpha_m = \frac{CE}{W^2}\,\frac{e}{m}\,h_m$$

which can be rewritten as

$$h_m = \alpha_m\,\frac{m\,W^2}{C\,e\,E} = \left(\frac{\alpha_m}{P}\right)\frac{m\,W^2}{C\,e\,(E/P)},$$

where P = the total pressure.

It can be easily shown that

$$\frac{h}{h_m} = 1 + \frac{\lambda_1}{\lambda_2}\,\frac{f_2}{f_1},$$

---

[15] R. H. Healey and J. W. Reed, THE BEHAVIOUR OF SLOW ELECTRONS IN GASES, The Wireless Press for Amalgamated Wireless Ltd., Sydney, Australia, 1941, p 16.

where λ_1 and λ_2 are the mean free paths in the attaching and non-attaching gas at 1 mm Hg, respectively; f_1 and f_2 are the male fractions of the attaching and non-attaching gas, respectively. Therefore,

$$h = \frac{\alpha_m}{P} \frac{m W^2}{C e (E/P)} \left(1 + \frac{\lambda_1 f_2}{\lambda_2 f_1}\right) .$$

Since

$$\alpha_m = \alpha f_1 P ,$$

then

$$h = \alpha f_1 \frac{m W^2}{C e (E/P)} \left(1 + \frac{\lambda_1 f_2}{\lambda_2 f_1}\right) = \frac{\alpha m W^2}{C e (E/P)} \left(f_1 + f_2 \frac{\lambda_1}{\lambda_2}\right) .$$

Since mean free path is a function of agitation energy, it must be taken at the agitation energy that exists in the mixture at the E/P in question. This will be determined by the non-attaching gas since generally f_2 is much greater than f_1 and will be different from the agitation energy that would exist in the pure attaching gas at this E/P.

The relationship between α and σ_c is

$$\alpha = \sigma_c N_1 \frac{\mu}{W} ,$$

where N_1 is the number of molecules of the attaching gas per unit volume (at a pressure of 1 mm Hg) and the other quantities are the same as used previously. The usual definition of cross section is given by

$$\alpha = \sigma N .$$

However, since α is defined for a distance of travel of one centimeter, the term $\frac{\mu}{W}$ is necessary to correct for the total distance traveled by the electron while moving one centimeter in the field direction.

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