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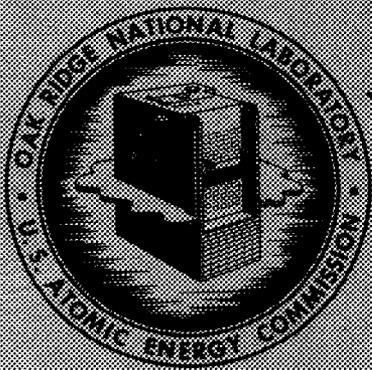
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CAPTURE OF ELECTRONS IN
MOLECULAR OXYGEN

G. S. Hurst
T. E. Bortner



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HEALTH PHYSICS DIVISION

CAPTURE OF ELECTRONS IN MOLECULAR OXYGEN

G. S. Hurst and T. E. Bortner

Date Issued

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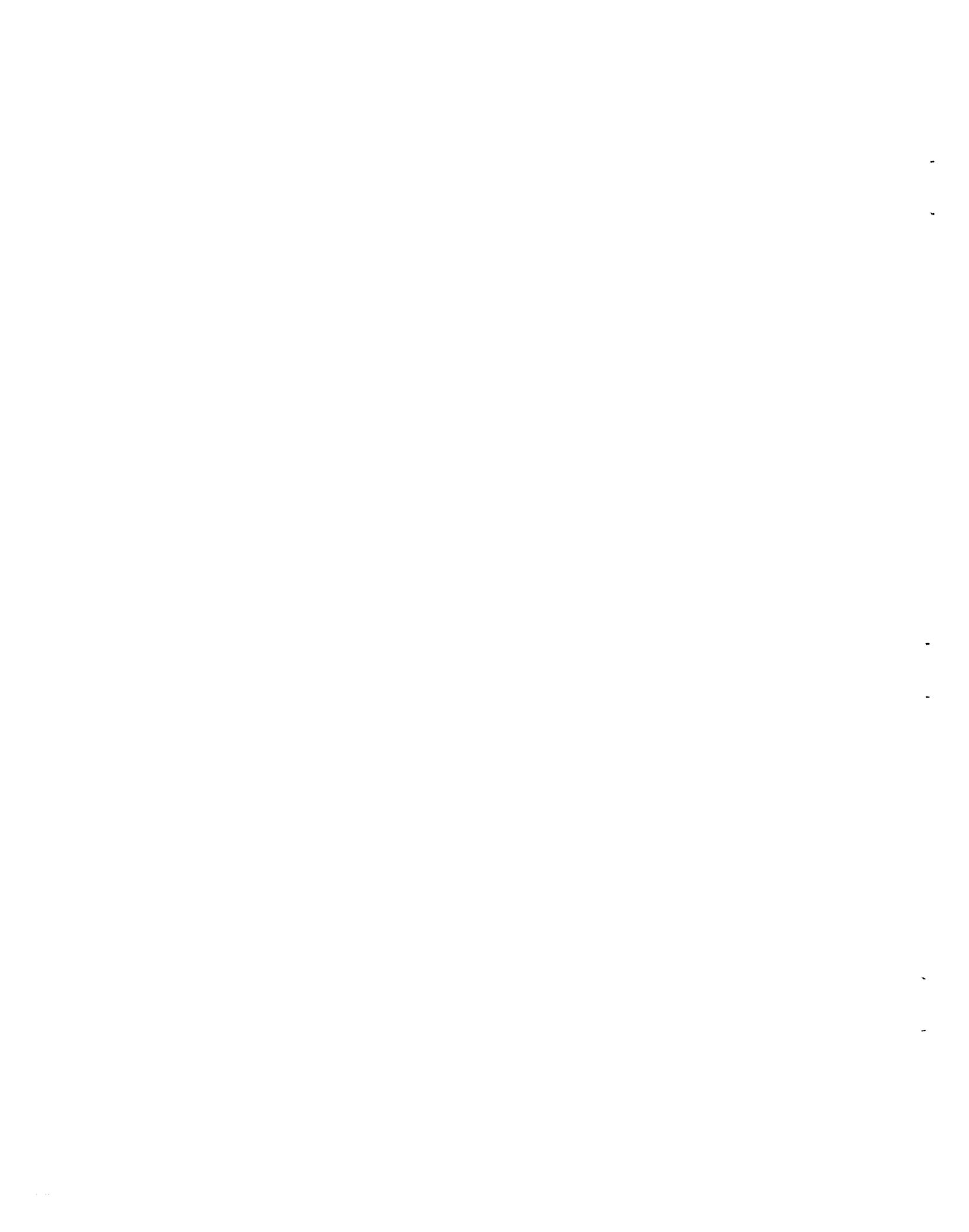
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CHAPTER I

INTRODUCTION AND THEORY

General Introduction

Formation of negative ions has important consequences in a number of fields including radiation chemistry, radiation biology, upper atmosphere physics, and physical instrumentation. For example, negative ions are important intermediates in the action of ionizing radiation on many chemical and biological systems, and reactions of negative and positive ions are important elementary processes. Excellent reviews of the general field have been made.¹⁻⁴

Only a few substances are known to capture (or attach) low energy electrons directly to form negative ions. Even in these cases the attachment process is relatively inefficient, e.g. in O_2 the average number of impacts per electron capture is approximately 10^4 . In the case of direct capture, energy must be removed from the system before a stable ion is formed. The details of ways in which energy may

¹H. S. W. Massey, Negative Ions (Cambridge University Press, Cambridge, 1950).

²J. L. Magee and M. Burton, *J. Am. Chem. Soc.* **73**, 523 (1951).

³L. B. Loeb, in Handbuch der Physik, S. Flügge, ed. (Springer-Verlag, Berlin, 1956), p. 445.

⁴L. M. Branscomb, in Advances in Electronics and Electron Physics, L. Marton, Ed. (Academic Press, New York, 1957), p. 43.

be transferred (often referred to as stabilization processes) are central problems in direct capture studies. Indeed this is the case in O_2 as will be seen later. Negative ions may also be formed by molecular dissociation in which case the removal of energy is not a necessary condition for the formation of a stable ion.

Two types of experimental methods have been applied to the study of the formation of negative ions of oxygen: (1) electron beam methods in which the electrons are nearly monoenergetic, and (2) electron swarm experiments in which the electrons have a considerable spread of energies. In general, electron beam studies are limited to the energy region above 2 ev; thus swarm methods provide valuable supplementary tools for the study of the low energy (less than 2 ev) region. Since the electron beam studies are somewhat easier to interpret we discuss this method first.

Survey of Electron Beam Experiments

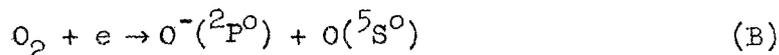
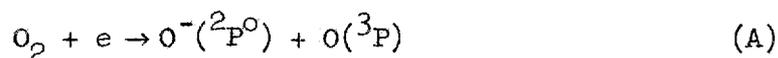
In the Lozier method⁵⁻⁷ nearly monoenergetic electrons are introduced into and are constrained to move in a cylindrical region by means of a magnetic field, while negative ions moving perpendicular to

⁵W. W. Lozier, Phys. Rev. 36, 1285 (1930).

⁶W. W. Lozier, Phys. Rev. 44, 575 (1933).

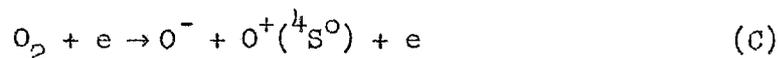
⁷J. T. Tate and W. W. Lozier, Phys. Rev. 39, 254 (1932).

the axis of the cylinder escape from the field. By means of retardation potentials the energy distribution of the ions may be determined. Lozier⁸ applied his method to the study of oxygen, and obtained the results shown in Figure 1. Since the groups peaking at 7 ev and 15 ev have a narrow energy spread, they were interpreted as processes of dissociative electron capture, i.e.



where $^2\text{P}^o$ is the ground state of O^- and the superscript o indicates

that $\sum_i l_i$ over all the electrons in the atom is odd. Both O^- and O^+ were found above 18.9 ev; therefore, this process was interpreted as



Lozier's experiment⁸ gives the ratio of the number of these negative ions formed to the number of direction ionizations in oxygen. Thus, using the cross sections for ionization of the molecule,⁹ Massey¹

⁸W. W. Lozier, Phys. Rev. 46, 268 (1934).

⁹J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).

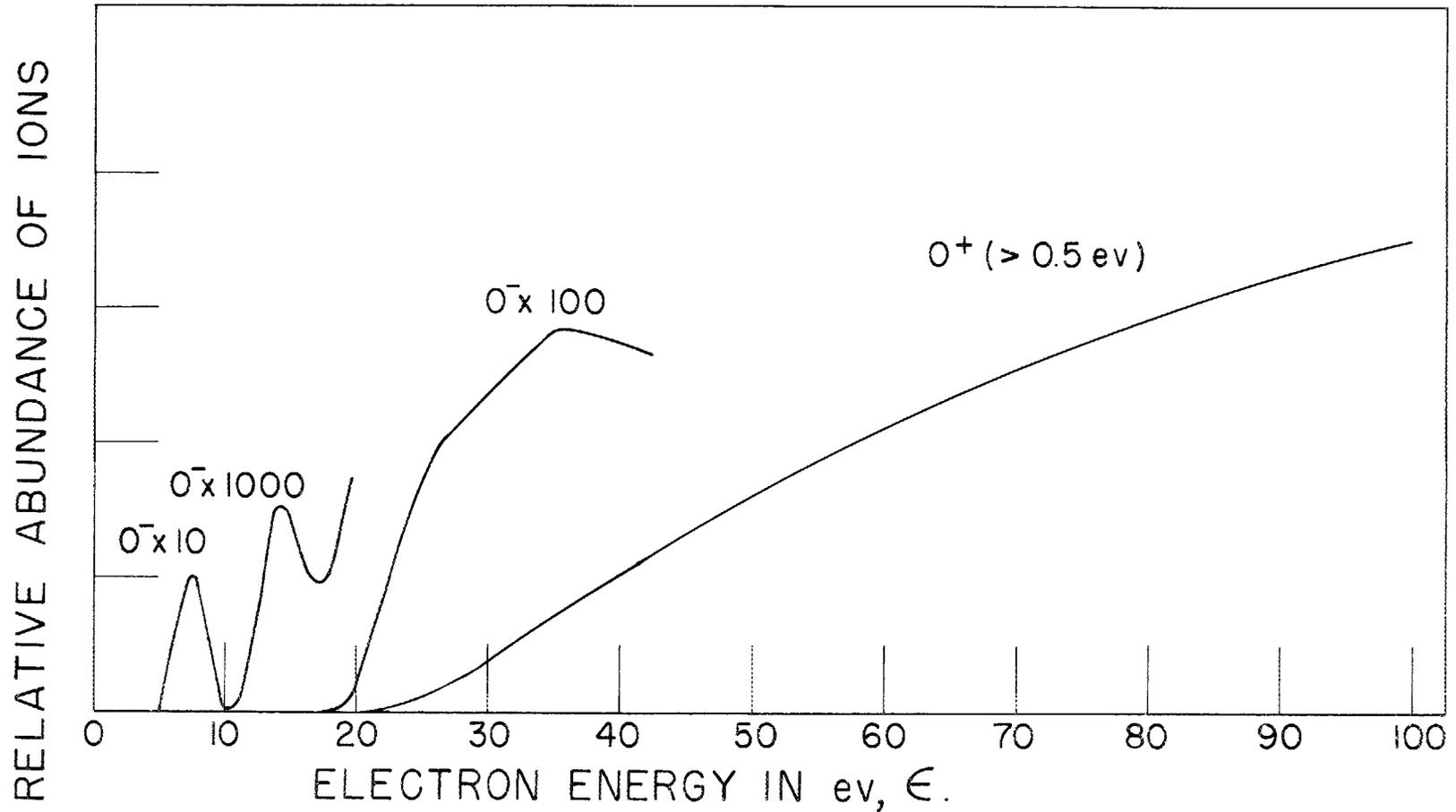


FIG. 1 LOZIER'S DATA FOR THE RELATIVE ABUNDANCE O^- O^+ AS A FUNCTION OF ELECTRON ENERGY

estimates maximum cross sections of $8 \times 10^{-19} \text{ cm}^2$, $1.3 \times 10^{-20} \text{ cm}^2$, and $2.2 \times 10^{-19} \text{ cm}^2$ for processes A, B, and C, respectively. Hagstrum and Tate,¹⁰ making use of a mass spectrometer, verified Lozier's groups A and C, but did not observe a group at 15 ev. Craggs et al.,¹¹ using essentially the Lozier method, observed groups A and C, but again not group B.

Survey of Electron Swarm Experiments

Interpretation of the results of electron swarm experiments is complicated by the fact that the detailed energy distribution of electrons is unknown. Loeb¹² gives a historical summary of the various distribution laws which have been used. A complete theoretical study is now available¹³ and has been applied to a few cases^{14,15} where adequate experimental data on electron impact cross sections are available.

¹⁰H. D. Hagstrum and J. T. Tate, Phys. Rev. 59, 354 (1941).

¹¹J. D. Craggs, R. Thorburn, and B. A. Tozer, Proc. Roy. Soc. (Lond.) A240, 473 (1957).

¹²L. B. Loeb, Basic Processes of Gaseous Electronics (University of California Press, Berkeley and Los Angeles, 1955).

¹³T. Holstein, Phys. Rev. 70, 367 (1946).

¹⁴D. Barbriere, Phys. Rev. 84, 653 (1951).

¹⁵J. C. Bowe, Argonne National Laboratory Report ANL 5829, 1958 (unpublished).

Most of the experimental data on electron capture have been compared by plotting the attachment coefficient against the mean energy of agitation of the electrons, as derived from electron diffusion experiments. Table I summarizes various studies of the mean energy of agitation of an electron as a function of E/P (volts cm^{-1} mm Hg $^{-1}$) for O_2 , N_2 , Air, C_2H_4 , and A. The table of values shows that at a fixed E/P the Townsend coefficient k_T , the ratio of the mean energy of agitation of an electron to the mean energy of agitation of a gas molecule, $3/2 k_T$, at 20 °C, strongly depends on the type of gas. This fact permits the swarm measurements of electron attachment to be performed over a considerable range of energies. Unfortunately, sets of data obtained by various observers are not in good agreement; thus the scale of mean energy may not be fixed with certainty.

Several variations of the swarm method have been applied to the study of oxygen and air. The details of the methods used by previous observers will not be discussed in the text. Table II shows some of the most important features of the methods and lists the range of pressure and E/P employed by the various observers.

Ideally, all measurements should be compared by plotting the cross section for electron attachment, σ_a , (in cm^2) against the mean electron energy, $\bar{\epsilon}$, in ev. In practice this is very difficult since necessary data are not consistent. For example, in Table I it is seen that if one wished to compare data for the cases of pure O_2 , air, and small amounts of O_2 in N_2 the scale of energy would be difficult to

TABLE I

RATIO OF MEAN ENERGY OF AGITATION OF AN ELECTRON TO THE MEAN ENERGY OF AGITATION OF A GAS MOLECULE (AT 20°C) FOR VARIOUS GASES AS A FUNCTION OF E/P {VOLTS cm^{-1} (mm Hg) $^{-1}$ }

Oxygen				Air				
E/P	Townsend and Bailey ¹⁶ K_H	Brose ¹⁷ K_H	Healey and Kirkpatrick ¹⁸ K_H	E/P	Townsend and Tizard ¹⁹ K_H	Townsend and Bailey ¹⁶ K_H	Bailey ²⁰ K_H	Huxley and Zaazou ²¹ K_H
0.25			5.5	0.25	3.0			
0.4		6		0.50	4.0			
0.5			9.5	1	10	11	8.3	18
0.6		8.4		2	22	22	27.0	32.9
0.8		10.8		3	29			45.5
1		13	19	4	34			54.5
2	22.5	24	32	5	37	38		
5		47	43	6	40			65.7

¹⁶J. S. Townsend and V. A. Bailey, *Phil. Mag.* 42, 873 (1921).

¹⁷H. L. Brose, *Phil. Mag.* 50, 536 (1925).

¹⁸R. H. Healey and C. B. Kirkpatrick in *The Behaviour of Slow Electrons in Gases* (Amalgamated Wireless Ltd., Australasia, 1941).

¹⁹J. S. Townsend and H. T. Tizard, *Proc. Roy. Soc. (London)* A88, 336 (1913).

²⁰V. A. Bailey, *Phil. Mag.* 50, 825 (1925).

²¹L. G. Huxley and A. A. Zaazou, *Proc. Roy. Soc. (London)* A196, 402 (1949).

TABLE I (continued)

RATIO OF MEAN ENERGY OF AGITATION OF AN ELECTRON TO THE MEAN ENERGY OF
AGITATION OF A GAS MOLECULE (AT 20°C) FOR VARIOUS GASES AS A
FUNCTION OF E/P {VOLTS cm^{-1} (mm Hg) $^{-1}$ }

Oxygen				Air				
E/P	K_{H} Townsend and Bailey ¹⁶	K_{H} Brose ¹⁷	K_{H} Healey and Kirkpatrick ¹⁸	E/P	K_{H} Townsend and Tizard ¹⁹	K_{H} Townsend and Bailey ¹⁶	K_{H} Bailey ²⁰	K_{H} Huxley and Zaazou ²¹
6	45			8	43			76.3
7		56		10	45	46		86.3
10	50	64	52	14	50			
12		69		20	56			128
14	55.5			50		57		
15		77	57.5	100		102		
20	70	90	62			160		
30		113	71					
40		133						
50	136	150	95					

TABLE I (continued)

RATIO OF MEAN ENERGY OF AGITATION OF AN ELECTRON TO THE MEAN ENERGY OF
 AGITATION OF A GAS MOLECULE (AT 20°C) FOR VARIOUS GASES AS A
 FUNCTION OF E/P {VOLTS cm⁻¹ (mm Hg)⁻¹}

Nitrogen		Ethylene		Argon	
E/P	Townsend and Bailey ¹⁶ k _T	E/P	Bannon and Brose ²² k _T	E/P	Townsend and Bailey ²³ k _T
0.25	7.5	1.26	2.07	0.125	100
0.5	13.0	2.5	5.3	0.195	120
1	21.5	4	11	0.275	140
2	30.5	5	15	0.355	160
3	35.5	6	19.3	0.525	200
5	41.3	10	31.3	0.71	240
10	48.5	20	45.3	0.95	280
20	59.5	40	64.4	1.25	320
30	72.5	60	80.2	5	310
40	89	80	95.0	10	324
50	108			15	324
60	126				
100	180				

²²J. Bannon and H. L. Brose, Phil. Mag. 6, 817 (1928).

²³J. S. Townsend and V. A. Bailey, Phil. Mag. 44, 1033 (1922).

TABLE II

SUMMARY OF SOME EXPERIMENTAL INVESTIGATIONS OF
ELECTRON CAPTURE IN O_2 , USING SWARM METHODS

Investigators	Basis of Method	Electron Source	Gas	Pressure Range (mm Hg)	E/P Range volts $cm^{-1}(mm\ Hg)^{-1}$
Bailey, Ref. (20)	Electron Diffusion	Photoelectric	Air	(6 - 23)	(0.3 - 2.5)
Cravath (24)	Loeb Electron "Filter"	Hot Filament	Air	(15 - 120)	(0.1 - 3.0)
Bradbury (25)	Loeb Electron "Filter"	Photoelectric	O_2 Air	(4 - 60)	(0.5 - 5)
Healey and Kirk- patrick	Electron Diffusion	Photoelectric	O_2 O_2	Not Given	(0.25 - 50)
Geballe and Harri- son (26)	Measurements of Pre- breakdown Currents		O_2	(11 - 40)	(25 - 60)
Doehring (27)	Electron Time of Flight	Hot Filament	O_2	(15 - 50)	(0.5 - 10)

²⁴A. M. Cravath, Phys. Rev. 33, 605 (1929).

²⁵N. E. Bradbury, Phys. Rev. 44, 883 (1933).

²⁶R. Geballe and M. A. Harrison, Phys. Rev. 85, 372 (1952).

²⁷A. Doehring, Z. Naturforsch. 7a, 253 (1952).

TABLE II (continued)

SUMMARY OF SOME EXPERIMENTAL INVESTIGATIONS OF
ELECTRON CAPTURE IN O₂, USING SWARM METHODS

Investigators	Basis of Method	Electron Source	Gas	Pressure Range	E/P Range
				(mm Hg)	volts cm ⁻¹ (mm Hg) ⁻¹
Herreng (28)	Time Analysis of Electron Pulse in Parallel Plate Chamber	Ionization by X-Rays	O ₂ O ₂ + A	(10 - 50)	
Harrison and Geballe (29)	Measurements of Pre- breakdown Currents		O ₂	(11 - 40)	(25 - 70)
			Air	(40 - 80)	(25 - 60)
Chanin and Biondi (30)	Time Analysis of Negative Ion Current in Drift Tube	Photoelectric	O ₂	Not Given	(0.3 - 7)
Burch and Geballe (31)	Measurements of Pre- breakdown Currents		O ₂	(8 - 25)	(8 - 40)

²⁸P. Herreng, Cah. Phys. 38, 6 (1952).

²⁹M. A. Harrison and R. Geballe, Phys. Rev. 91, 1 (1953).

³⁰L. M. Chanin and M. A. Biondi, Westinghouse Research Laboratory Report 6-94439-7-R5, 1957 (unpublished).

³¹D. S. Burch and R. Geballe, Phys. Rev. 106, 183 (1957).

make. Harrison and Geballe,²⁹ however, have summarized some of the swarm data for O_2 in the desired form (Figure 2). To these we have added, as did Branscomb,⁴ a short curve indicating more recent data by Burch and Geballe³¹ and some points recently obtained by Chanin and Biondi.³⁰ In all cases σ_a is plotted against $\bar{\epsilon}$ as determined from the data of Brose,¹⁷ Table I.

The general behavior is that the cross section appears to increase as $\bar{\epsilon}$ increases in the 1- to 2-ev region and to decrease as $\bar{\epsilon}$ increases for $\bar{\epsilon} < 1$ ev. Bradbury²⁵ interpreted the mechanism of capture in the 2-ev region as a process in which electrons suffer inelastic collisions with oxygen molecules and are then captured in the very low energy region forming O_2^- . Bates and Massey³² have given another explanation to the 2-ev process. They point out that the experimental data are consistent with the idea that 2-ev electrons may be captured into either the ($^4\Sigma_u^-$), ($^2\Delta_u$), or ($^2\Pi_u$) state of O_2^- , (see Figure 3). Geballe and Harrison²⁶ and Craggs et al.¹¹ appear to have clarified the interpretation of the 2-ev process by showing that the magnitude of the capture cross section may be accounted for by assuming dissociation, i.e. Lozier's 7-ev group (Figure 1). Thus, the 2-ev process leads to the formation of O^- , not O_2^- as was originally postulated by Bradbury. This argument is supported by Harrison and Geballe's data which when corrected for ionization does not exhibit the sharp peak found in Bradbury's results.

³²D. R. Bates and H. S. W. Massey, Phil. Trans. A-239, 269 (1943).

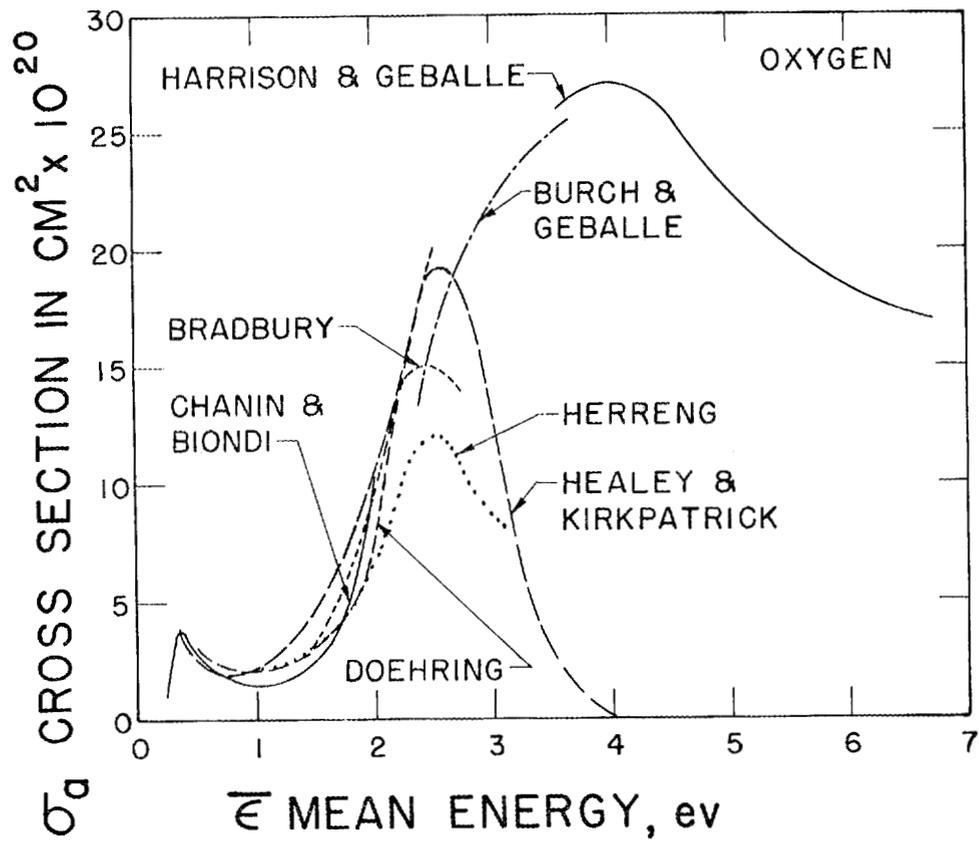
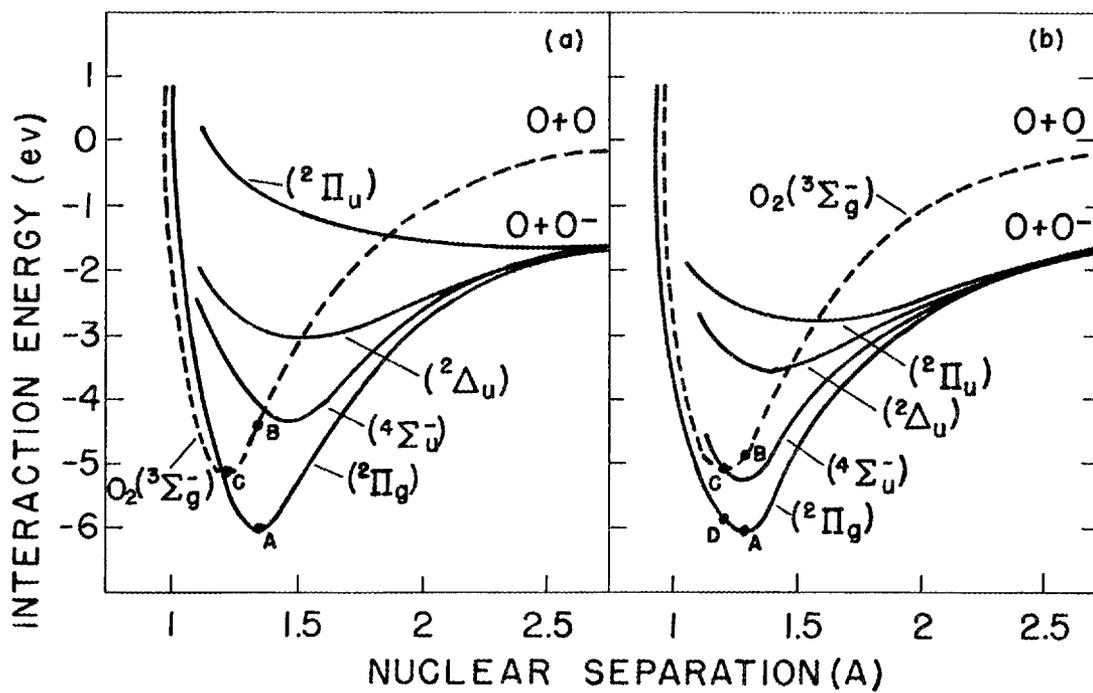
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FIG.2 SUMMARY OF SWARM EXPERIMENTS BY VARIOUS OBSERVERS

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PLAUSIBLE POTENTIAL CURVES FOR O_2^-
FIG. 3

For average energies less than 1 ev, the number of reliable experimental data is very limited. Figure 2 shows the experimental results of Bradbury,²⁵ Doehring,²⁷ and Chanin and Biondi.³⁰ With the exception of Chanin and Biondi very few data were reported. Bradbury and Doehring studied the process of electron capture over a limited range of pressure, but because of experimental difficulties their reported results for low energies were quite few. In the earlier work of Bailey²⁰ the author concludes that the attachment coefficient was pressure independent, although a careful examination of his results shows some increase of the values with pressure at low E/P. Cravath²⁴ found rather marked increases with pressure at low E/P in air, and gave some indication of the same type of behavior in the case of O₂. Since the data as regards pressure dependence are fragmentary at low energy, and since much of this can be questioned both on the basis of experimental difficulties and the disagreement of various sets of data, one should not conclude, as so often has been done, that the attachment cross section is pressure independent at low energies.

Interpretation of the Low Energy Process

There is considerable difficulty in interpreting the low energy process if pressure independence is assumed. According to the Bloch-Bradbury theory,³³ attachment in the low energy region is due to the

³³F. Bloch and N. Bradbury, Phys. Rev. 48, 689 (1935).

direct formation of $O_2^{-'}$ (the prime indicates vibration), which is unstable with respect to re-emission of the electron. The most effective means of stabilizing the $O_2^{-'}$ is by molecular collisions; hence the capture cross section must be pressure dependent at low pressure. Bates and Massey³² have shown that in order for the attachment cross sections to be pressure independent in O_2 for pressures as low as 3 mm Hg (Bradbury's experiment), the cross section for stabilization of $O_2^{-'}$ must be about 1000 times the gas kinetic value. This is very difficult to understand in view of calculations by Zener³⁴ and Rice³⁵ which show that even in the case of exact resonance the cross sections for vibrational transfer are less than gas kinetic by a large factor. For example, Zener shows that the cross section for transfer of vibrational energy from an N_2 molecule in its first excited state to a normal N_2 molecule at room temperature is 0.04 times the gas kinetic cross section. Vogt and Wannier³⁶ show, however, that the Coulomb attraction arising as a consequence of polarization of the neutral molecule can augment collision cross sections as much as 100 fold, but even this effect is too small to account for the large cross section for stabilization.

The large value for the stabilization cross sections led Bates

³⁴C. Zener, Phys. Rev. 37, 556 (1931).

³⁵O. K. Rice, Phys. Rev. 38, 1943 (1931).

³⁶E. Vogt and G. H. Wannier, Phys. Rev. 95, 1190 (1954).

and Massey³² to consider alternative explanations of the process of electron capture at low energy. Figure 3 shows their version of two possible sets of potential energy curves for O_2^- , as modified by Branscomb⁴ to reflect an electron affinity of 1.48 ev for atomic oxygen. In both cases (a and b) the electron affinity of molecular oxygen is assumed to be nearly 1 ev as determined from thermochemistry. In case (a) electrons are captured to form $O_2^-(^2\Pi_g)$ which, because of the 1-ev electron affinity, is left with a high degree of vibrational excitation. In case (b), $O_2^-(^4\Sigma_u^-)$ is formed with low order vibrational excitation since part of the energy now appears as electronic excitation. According to Bloch and Bradbury,³³ the order of magnitude of the absolute value of the attachment cross section can be accounted for only if the vibrational excitation is low in order, hence alternative (b) brings this fact into harmony with the 1-ev value for the electron affinity of O_2 . Unfortunately, these two sets of potential energy curves are only two of a large number of possibilities; hence the mechanism of low energy capture cannot be set down in detail.

Objectives of the Present Study

The main uncertainties associated with the process of electron capture to form O_2^- are: (1) the electronic state in which O_2^- is left immediately after electron capture, and (2) regardless of the state of excitation of O_2^- , it is difficult to understand stabilization cross sections whose magnitude are 1000 times gas kinetic values. The object

of the present work is to investigate the low energy process and, in particular, to examine the pressure dependence of the capture cross section at very low energies. This can be achieved by performing swarm experiments with small quantities of O_2 mixed with various gases, providing a considerable range of electron energies (see Table I). If pressure dependence is found, then the stabilization process in several gas mixtures can be examined.

CHAPTER II

EXPERIMENTAL METHOD

Basic Concepts

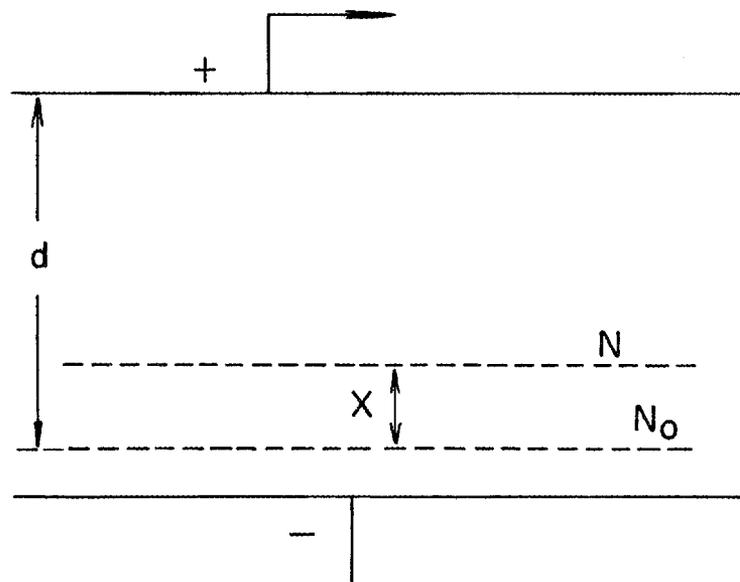
The effect of electron attachment on the pulse height in a plane geometry ionization chamber was chosen as the basis of a method of measuring attachment coefficients.¹ Suppose N_0 electrons are formed at a distance d (Figure 4) from a positively charged electrode. Because of attachment, at a distance x from the point of formation only N of the electrons are free (i.e., not attached). The number dN attached in a distance dx is given by

$$dN = -\alpha N f_1 P dx \quad (1)$$

which defines α the probability of attachment per cm of travel in the field direction and per mm of partial pressure ($f_1 P$) of the attaching gas. Let $P = f_1 P + f_2 P$, where $f_2 P$ is the partial pressure of a non-attaching gas. In this work, $f_1 P \ll f_2 P$; thus E/P refers approximately to the "reduced electric field" -- volts per cm and per mm Hg of the non-attaching gas.

¹The method has already been published in T. E. Bortner and G. S. Hurst, *Health Physics* 1, 39 (1958).

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SCHEMATIC OF ELECTRON ATTACHMENT IN A UNIFORM
ELECTRIC FIELD

FIG-4

Integration of Eq. (1) yields

$$N(x) = N_0 e^{-\alpha f_1 P x} \quad (2)$$

for the number of free electrons at distance x . The change in electrode potential dV due to the work done by the field in moving $N(x)$ electrons a distance dx is

$$dV = N(x) \frac{V_0}{d} dx \quad (3)$$

where V_0 is the change in potential due to a single electron moving the entire distance d . Integration of Eq. (3) using Eq. (2) for $N(x)$ shows that the change of potential $v(x')$ after the electrons have moved a distance x' is

$$V(x') = \frac{N_0 V_0}{\alpha f_1 P d} \left(1 - e^{-\alpha f_1 P x'} \right) \quad (4)$$

The time variation of the electrode potential is found by replacing x' by td/τ_0 , where τ_0 is the "collection time" and is related to the electron drift velocity W by $\tau_0 = d/W$. Thus, after replacing $N_0 V_0$ by A and $\alpha f_1 P d$ by f , Eq. (4) gives

$$V(t) = \frac{A}{f} \left(1 - e^{-f t/\tau_0} \right) \quad (5)$$

When α (hence f) approaches zero, Eq. (5) reduces to the familiar expression $V(t) = At/\tau_0$ for $0 \leq t \leq \tau_0$, which represents the pulse profile in a plane ionization chamber for the non-attachment case.

Let us now assume that the pulse represented by Eq. (5) is observed with a linear pulse amplifier having a response to a function having a step at $t = 0$.

$$V'(t) = \frac{t}{t_1} e^{-t/t_1} \quad (6)$$

where t_1 is the amplifier differentiating and integrating time constant (assumed equal). The output of the pulse amplifier will then be given by

$$V(\tau) = \int_0^{\tau_0} \frac{dV(t)}{dt} V'(\tau - t) dt \quad (7)$$

for $\tau > \tau_0$.

On integration, Eq. (7) becomes

$$V(\tau) = \frac{A}{(\tau_0 - t_1 f)} \left[\left(e^{(\tau_0 - t_1 f)/t_1} - 1 \right) \tau - e^{(\tau_0 - t_1 f)/t_1} \left(\tau_0 - \frac{t_1 \tau_0}{\tau_0 - t_1 f} \right) - \frac{t_1 \tau_0}{\tau_0 - t_1 f} \right] e^{-\tau/t_1} \quad (8)$$

This expression has a maximum when $\tau = \tau' \geq \tau_0$ where

$$\tau' = \frac{e^{(\tau_0 - t_1 f)/t_1} \left[t_1 + \tau_0 - \frac{t_1 \tau_0}{\tau_0 - t_1 f} \right] + t_1 \left[\frac{\tau_0}{\tau_0 - t_1 f} - 1 \right]}{\left[e^{(\tau_0 - t_1 f)/t_1} - 1 \right]} \quad (9)$$

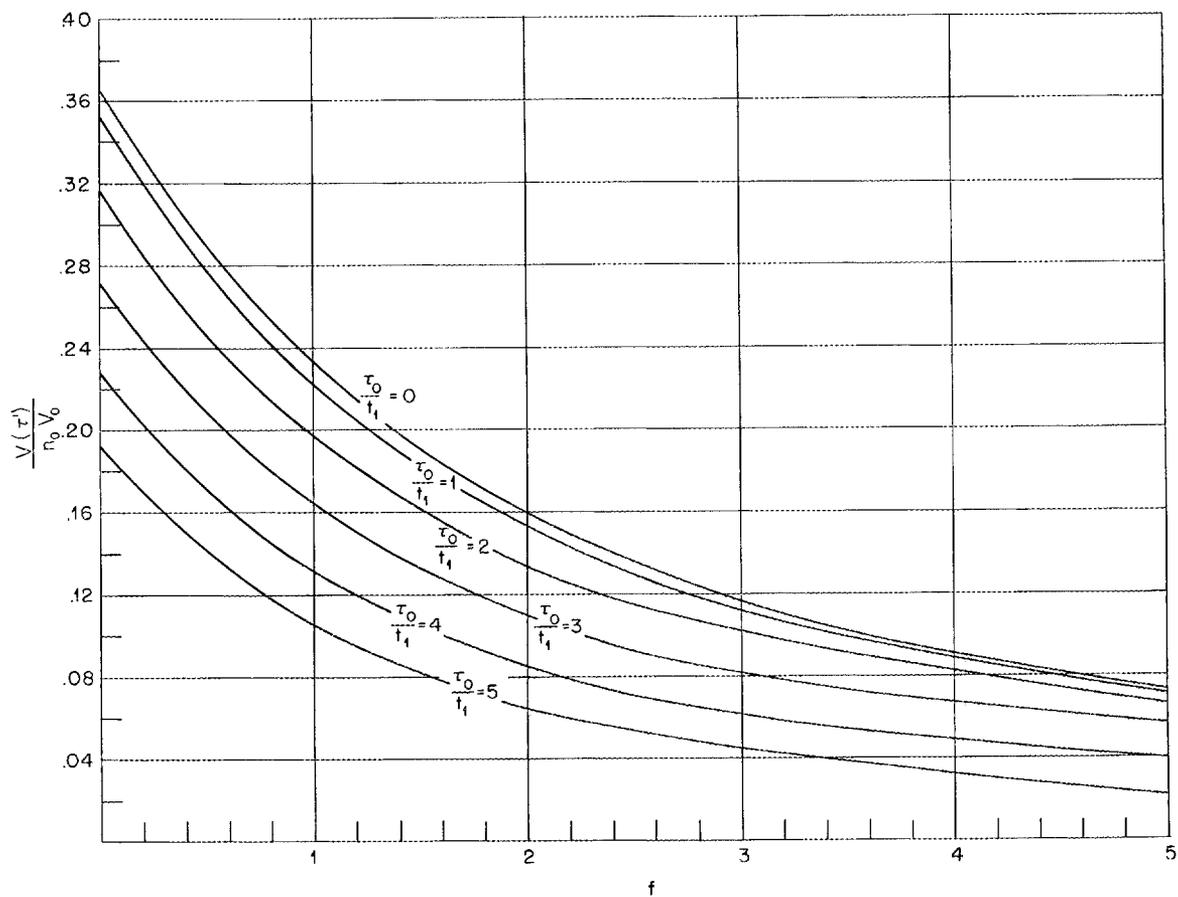
The pulse height $V(\tau')$ is determined by insertion of τ' for τ into Eq. (8).

The pulse height is plotted in Figure 5 as a function of f for various values of τ_0/t_1 . In Figure 6 the pulse height is plotted as a function of τ_0/t_1 for various values of f . These curves may then be used to calculate the attachment coefficient from the experimentally measured quantities $V(\tau')$ and τ_0 .

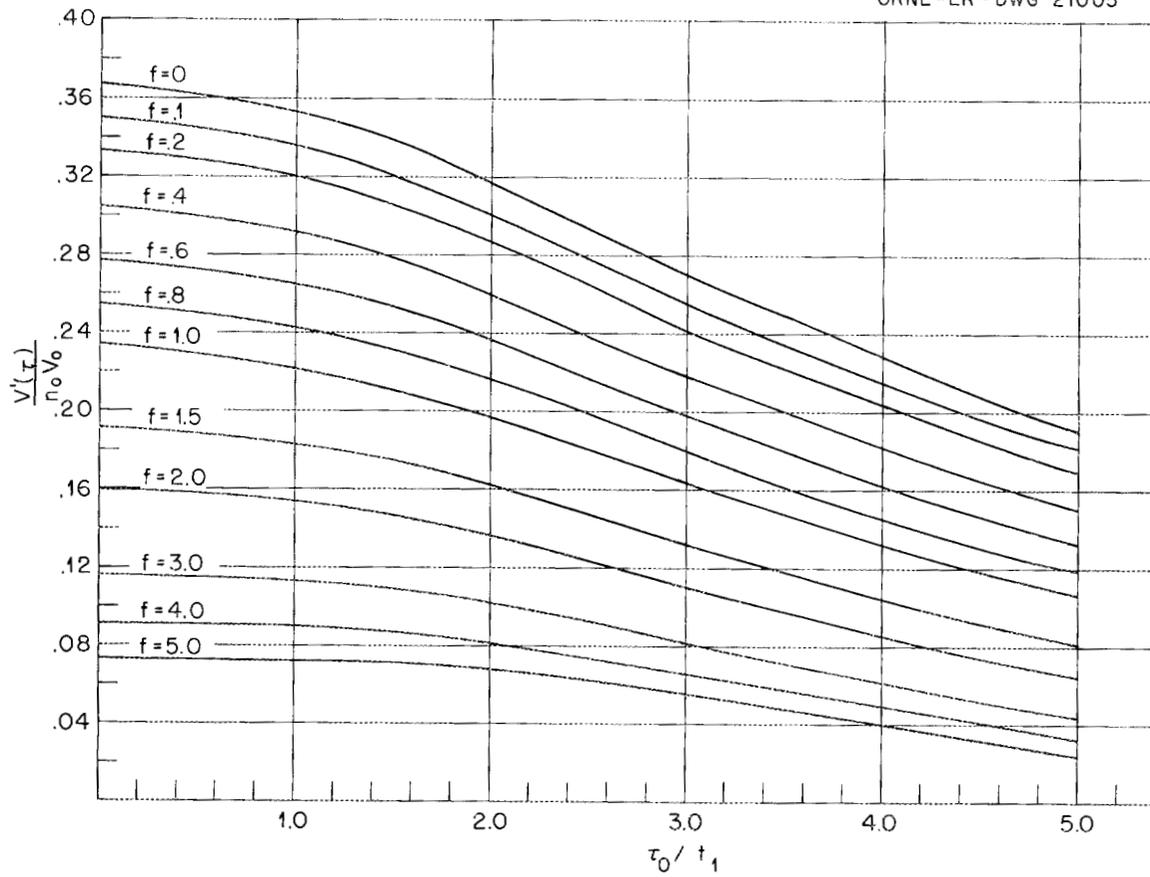
We have tacitly assumed that the amplifier constant t_1 is such that the response to the slowly moving negative ions can be neglected. This is the case when t_1 is of the order of τ_0 since, in general, the drift velocity of heavy ions is about 1/1000 that of the drift velocity of electrons.

Apparatus

Since data on electron drift velocity are inadequate, especially for mixtures of gases, it is important to measure the drift velocity as well as pulse height. Furthermore, it is known that in many cases the drift velocity is extremely sensitive to contamination. The apparatus

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CALCULATED DEPENDENCE OF PULSE HEIGHT ON f FOR VARIOUS
VALUES OF τ_0/t_1
FIG-5

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CALCULATED DEPENDENCE OF PULSE HEIGHT ON τ_0 / t_1 , FOR VARIOUS
VALUES OF f
FIG-6

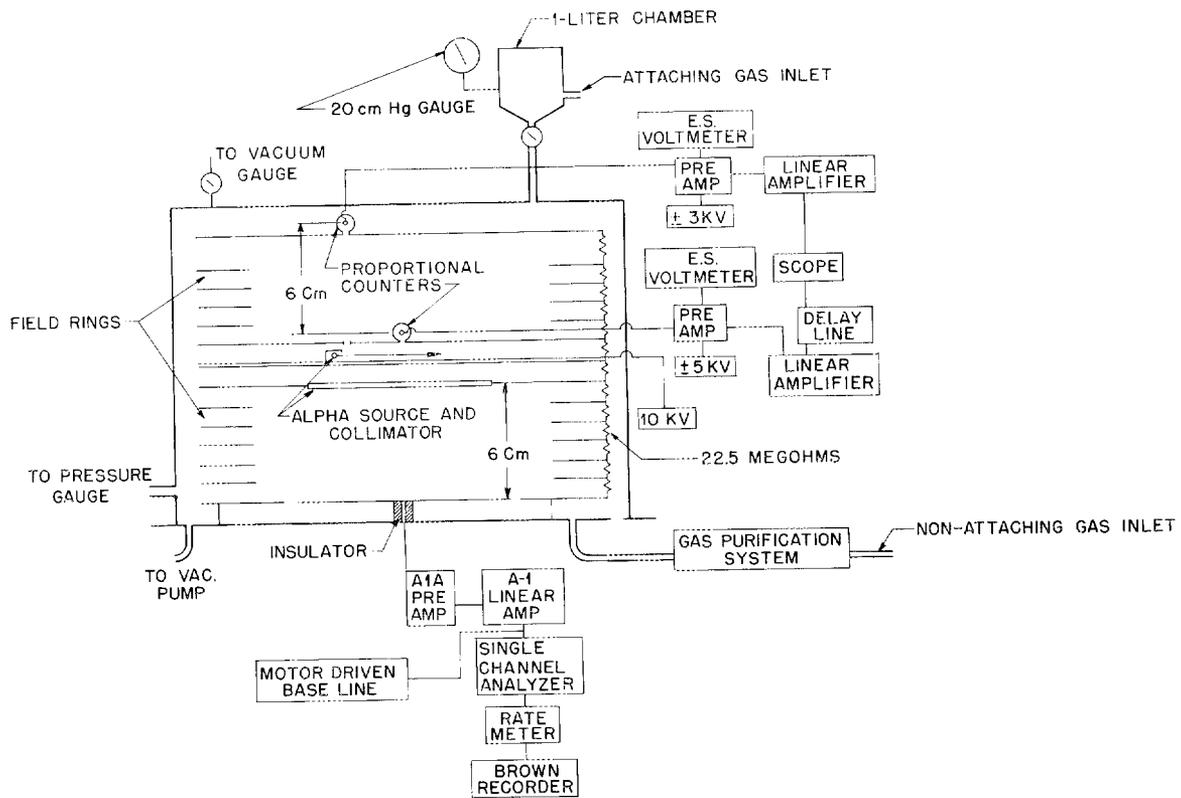
shown in Figure 7 permits measurement of both quantities in the same enclosure; thus even if a non-attaching contamination should affect the drift velocity in the gas mixture under study, the calculated attachment coefficient would be unaffected. The main vessel is made of stainless steel, and is sealed by teflon "O" rings. To improve uniformity of the electric field, rings are spaced 1 cm apart with fluorothene insulators. These are held at appropriate potentials with a voltage divider system using four 5.6-meg (1 watt Allen Bradley) resistors per stage. In the upper part of the chamber the drift velocity of electrons is measured with two proportional counters, as already described by Bortner, Hurst, and Stone.² The pulse height resulting from the electrons produced by collimated (in a plane parallel to the collecting electrode) Pu^{239} alpha particles is measured in the lower chamber. The collector to source distance d is normally 6.0 cm, although the apparatus is designed to permit various separations.

A linear pulse amplifier of the Jordan-Bell³ type was modified so that the long time constant position would give a pulse shape like that described in Eq. (6) with $t_1 = 15$ microseconds. The response of the particular amplifier used in this experiment to a step function pulse is shown in Figure 8. With $t_1 = 15$ microseconds, the agreement with the idealized response (Eq. 6) is good up to times of 50 microseconds.

²T. E. Bortner, G. S. Hurst, and W. G. Stone, Rev. Sci. Instr. 28, 103 (1957).

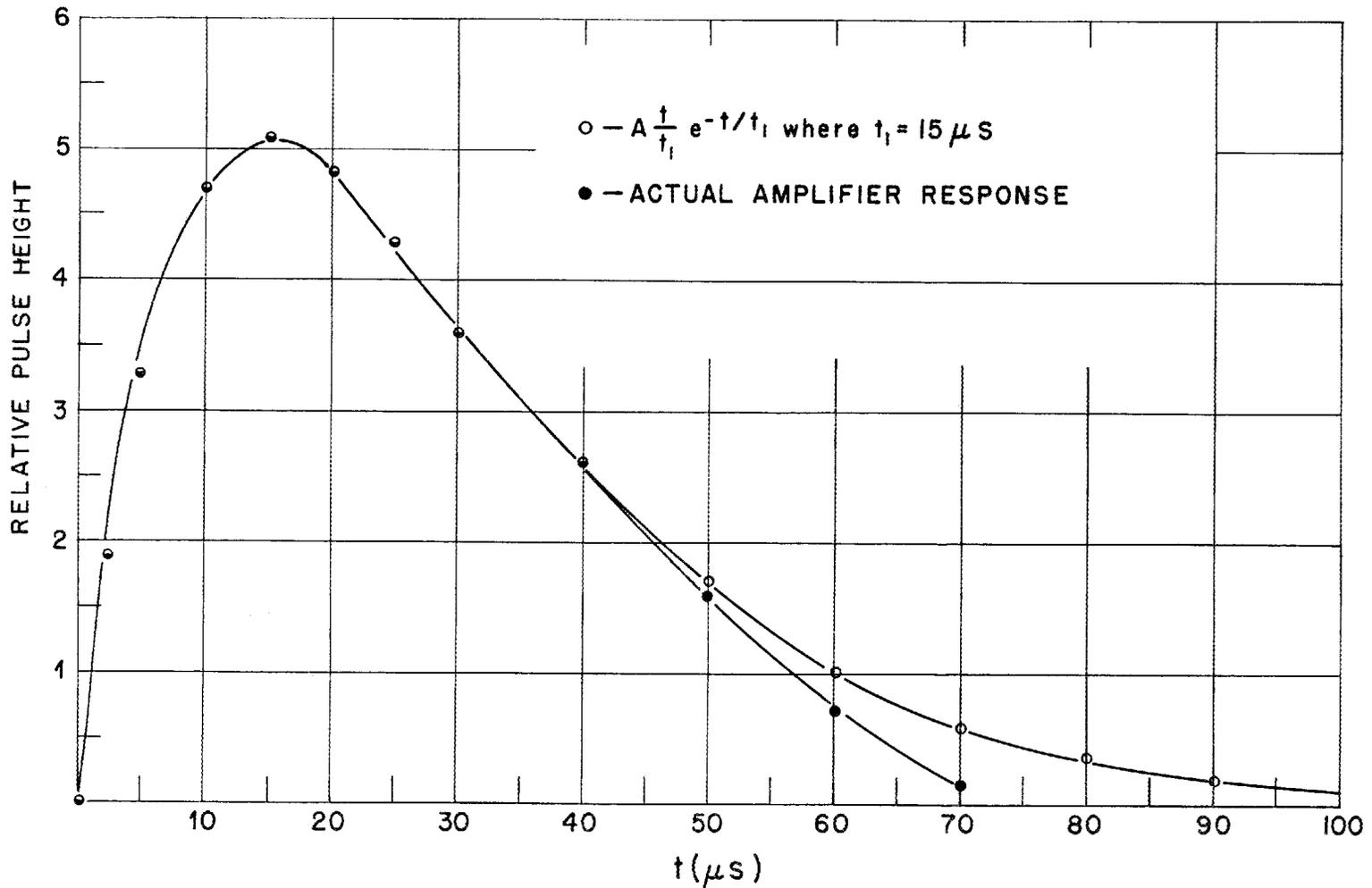
³W. H. Jordan and P. R. Bell, Rev. Sci. Instr. 18, 703 (1947).

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ELECTRON ATTACHMENT APPARATUS

FIG-7



STEP FUNCTION RESPONSE OF MODIFIED A-1 LINEAR AMPLIFIER
FIG-8

Deviation from the idealized response will not, however, affect the pulse height provided the amplifier output pulse peaks in a time τ' less than 50 microseconds. From Eq. (9) it can be seen that

$$\frac{d\tau'}{df} = \frac{-(e^\mu - 1)^2 \tau_0 / \mu^2 + \tau_0 e^\mu}{(e^\mu - 1)^2} \quad (10)$$

where $\mu = (\tau_0 - t_1 f) / t_1$. Now $d\tau' / df < 0$ for all positive f ; therefore, τ' will be greatest for $f = 0$. In this case,

$$\tau' = \frac{\tau_0 e^{\tau_0 / t_1}}{(e^{\tau_0 / t_1} - 1)} \approx (\tau_0 + t_1) \quad (11)$$

We require then that the experiment be performed in such a manner that $(\tau_0 + t_1)$ is always less than 50 microseconds.

Pulse height is measured with a single channel analyzer having a motor-driven base line so that the "window" scans uniformly in time. A display of the analyzer output on a count rate recorder affords a convenient method of pulse height measurement.

The gas purification system must necessarily be adaptable to the particular gases to be purified and to the gases which are to be removed. A drying unit is necessary regardless of the gas to be purified, since water vapor is extremely effective in reducing the pulse height due to electron attachment. Either P_2O_5 -Drierite or anhydronite is used in two inconel traps (in series) 18 in. long and 1.5 in. in diameter.

When feasible, the gases are further purified by distillation (or sublimation) with a simple trap surrounded with liquid N_2 . In other cases, it is helpful to absorb virtually all gases in activated coconut charcoal⁴ held at liquid N_2 temperature. The desired gas may then be released by increasing the temperature of the charcoal.

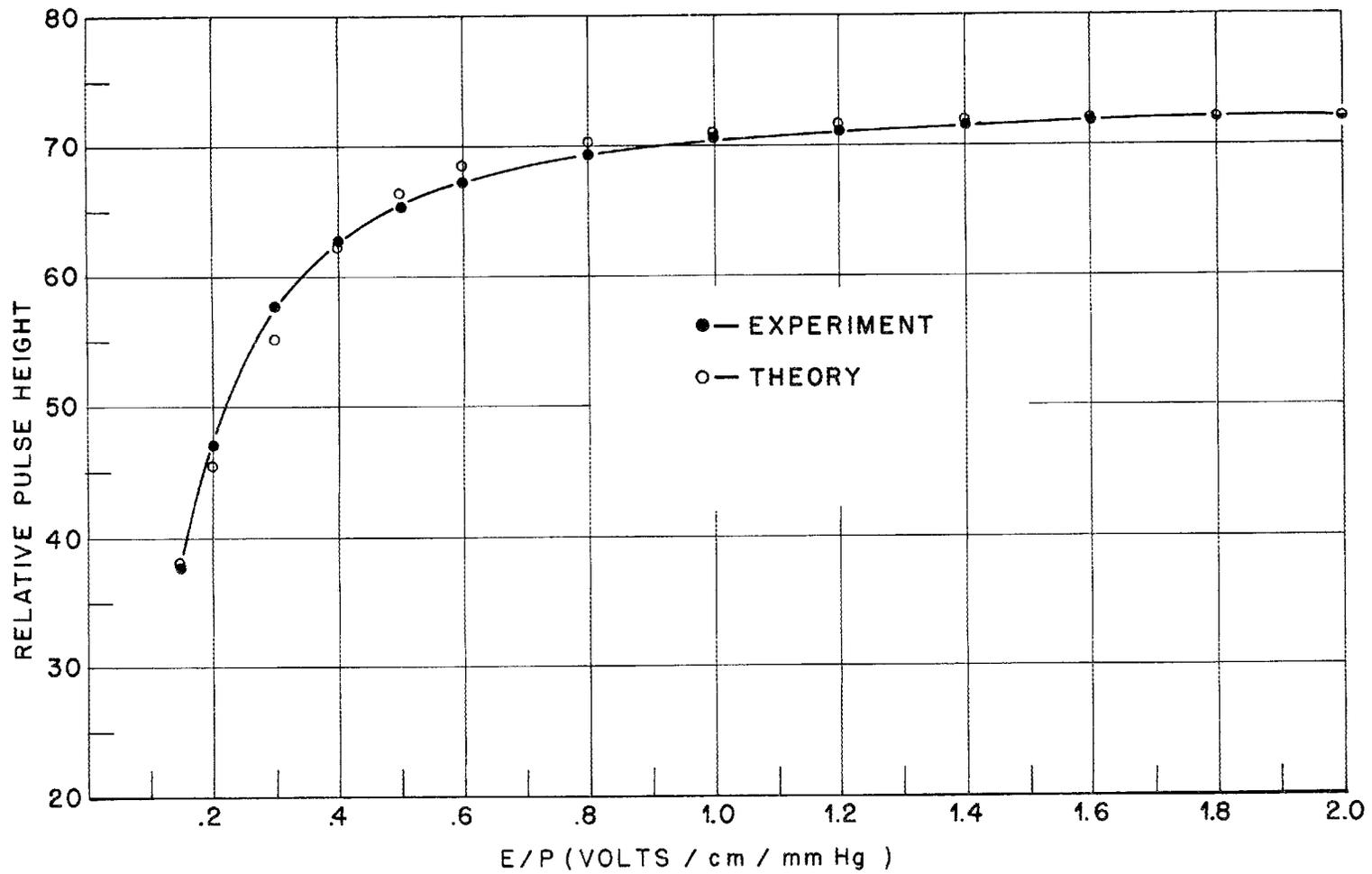
Experimental Check of Dependence of Pulse Height
on τ_0/t_1 Using Pure CO_2

The dependence of pulse height on E/P (volts per cm per mm Hg) was studied in pure CO_2 . In CO_2 the electron drift velocity varies nearly linearly with E/P going from a very low value of 0.1 cm/microsecond at E/P = 0.2 to 1.0 cm/microsecond at E/P = 2.0. For a 6.0-cm source to plate separation corresponding values of τ_0 are 60 and 6 microseconds, respectively. Pulse height measured with an amplifier having a value $t_1 = 15$ microseconds would vary considerably with E/P in CO_2 (see Figure 3 for $f = 0$).

Very careful purification of "bone dry" CO_2 is required. If CO_2 is admitted directly into the chamber, no pulse can be found at any value of E/P (i.e., the pulse height is less than amplifier noise pulses). When the CO_2 is passed through the anhydrous drying traps only, the pulse height is about one-half the value found when the CO_2 is passed through anhydrous and then further purified with a cold trap. The cold

⁴Saul Dushman, Scientific Foundations of Vacuum Techniques (John Wiley and Sons, New York, 1949).

trap is filled with copper turnings and is surrounded with liquid nitrogen. At this temperature sublimation takes place and oxygen can be removed by pumping. When the temperature is increased very pure CO_2 goes into the attachment chamber, giving a highly reproducible pulse height vs E/P . This curve is shown in Figure 9 where a comparison is made with the calculated pulse height curve, obtained by normalization of the $f = 0$ curve in Figure 6 and using the values in Ref. 2 for drift velocity in CO_2 .



PULSE HEIGHT Vs E/P FOR PURE CO₂

FIG-9

CHAPTER III

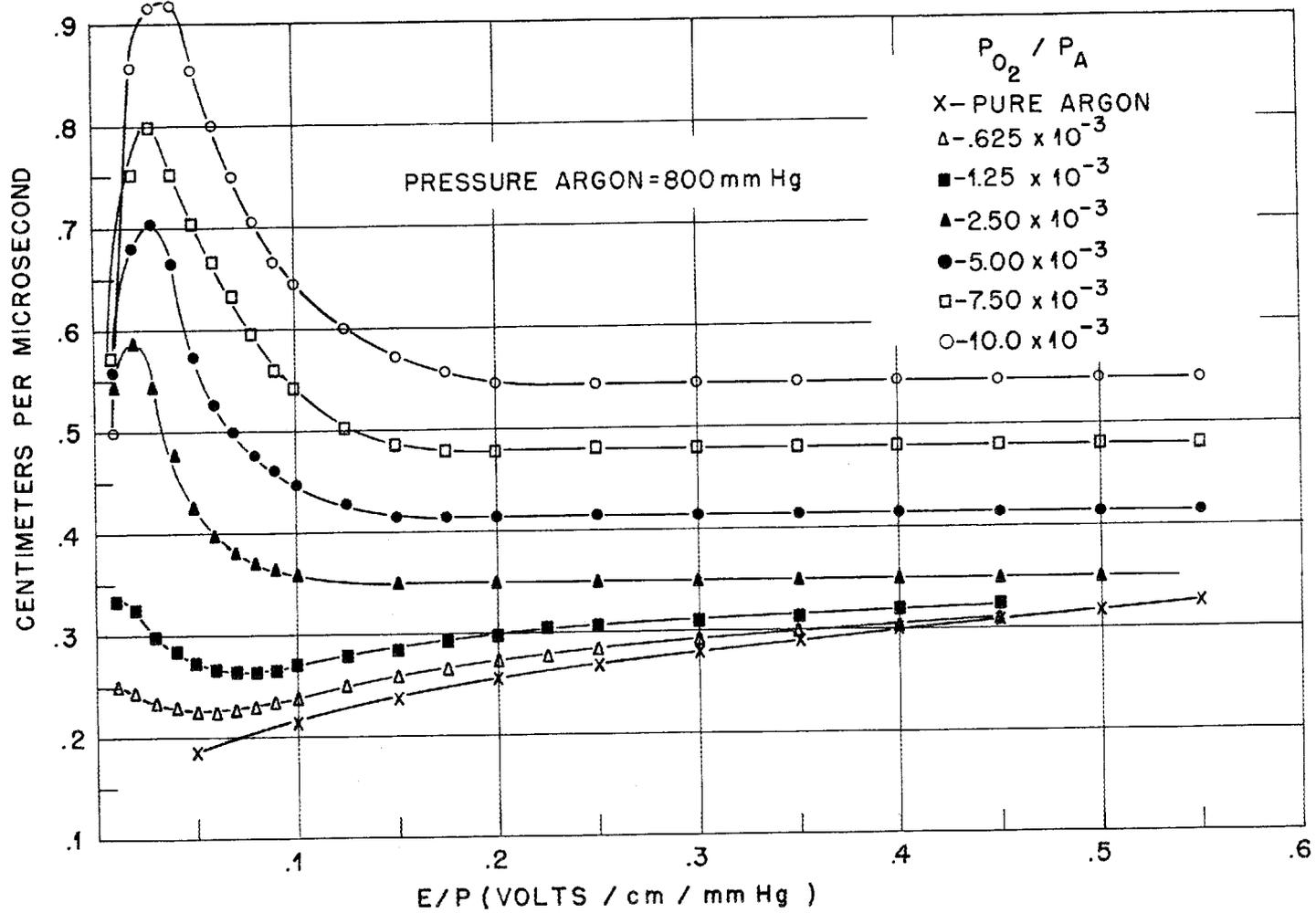
EXPERIMENTAL RESULTS AND INTERPRETATION

Attachment of Electrons in Argon-Oxygen Mixtures

As shown in Chapter II, the attachment coefficient α may be determined by measuring the drift velocity and pulse height due to the motion of free electrons in a plane geometry ionization chamber. In this section we will show results for argon-oxygen mixtures, since for all mixtures examined to date, this is the most simple case.

Drift velocity curves for argon-oxygen mixtures are shown in Figure 10. The behavior of these curves is rather striking, both the shape and magnitude being strongly affected by the addition of less than one part oxygen per 1000 parts argon. The data shown were taken at an argon pressure of 800 mm Hg. Several checks were made by reducing the argon pressure to 600 and 400 mm Hg. The drift velocity at a given E/P and a fixed concentration of oxygen was not affected by total pressure. The increase in drift velocity with the addition of oxygen implies a decrease in the electron agitation energy. According to the usual qualitative argument, if the electron agitation energy is decreased the electric field is more effective in producing a general drift of the swarm in the field direction.

The pulse height was determined as a function of E/P , total pressure, and concentration of oxygen, as shown in Table III and Figures 11, 12, and 13. It was seen early in the work that the attachment



ELECTRON DRIFT RATE IN ARGON AND ARGON-OXYGEN MIXTURES AS INDICATED
FIG-10

TABLE III

PULSE HEIGHT (VOLTS) FOR ARGON-OXYGEN MIXTURES

(ALL PRESSURES ARE mm Hg)

A. PRESSURE ARGON = 400

E/P	Pressure Oxygen						
	0	0.25	0.50	1.0	2.0	3.0	4.0
0.05	65.4	68.7	70.0	72.0	72.0	70.7	68.3
0.1	68.6	69.8	70.5	71.8	72.8	71.9	70.4
0.15	70.0	70.8	71.0	72.4	72.9	72.3	71.6
0.2	70.6	71.3	71.6	72.4	73.0	72.9	72.4
0.25	71.2	71.2	71.0	71.7	72.1	72.8	72.3
0.3	71.4	70.0	68.9	68.5	69.2	70.0	70.5
0.35	71.9	67.2	64.0	62.0	62.0	63.6	65.3
0.4	72.3	62.1	56.5	51.5	50.5	52.5	55.3
0.45	72.4	56.1	47.4	40.4	37.7	39.0	42.5
0.5	72.5	49.3	38.1	30.0	26.0	27.2	30.0

TABLE III (continued)

PULSE HEIGHT (VOLTS) FOR ARGON-OXYGEN MIXTURES

(ALL PRESSURES ARE mm Hg)

B. PRESSURE ARGON = 600

E/P	Pressure Oxygen						
	0	0.375	0.75	1.5	3.0	4.5	6.0
0.05	64.1	67.0	68.4	69.9	68.4	64.3	59.4
0.1	67.2	68.5	69.0	70.0	69.9	67.0	63.8
0.15	68.3	69.2	69.8	70.5	70.4	68.6	66.3
0.2	69.0	69.7	70.0	70.4	70.6	69.2	67.7
0.25	69.8	69.4	69.0	69.2	69.5	69.0	68.0
0.3	70.0	67.9	66.0	65.0	65.5	66.0	66.0
0.35	70.2	63.2	58.7	55.3	55.0	57.0	58.6
0.4	70.5	56.7	49.0	43.0	41.4	43.8	46.8
0.45	70.8	48.3	38.0	30.0	16.6	28.9	32.2
0.5	70.9	39.6	27.8	19.7			

TABLE III (continued)

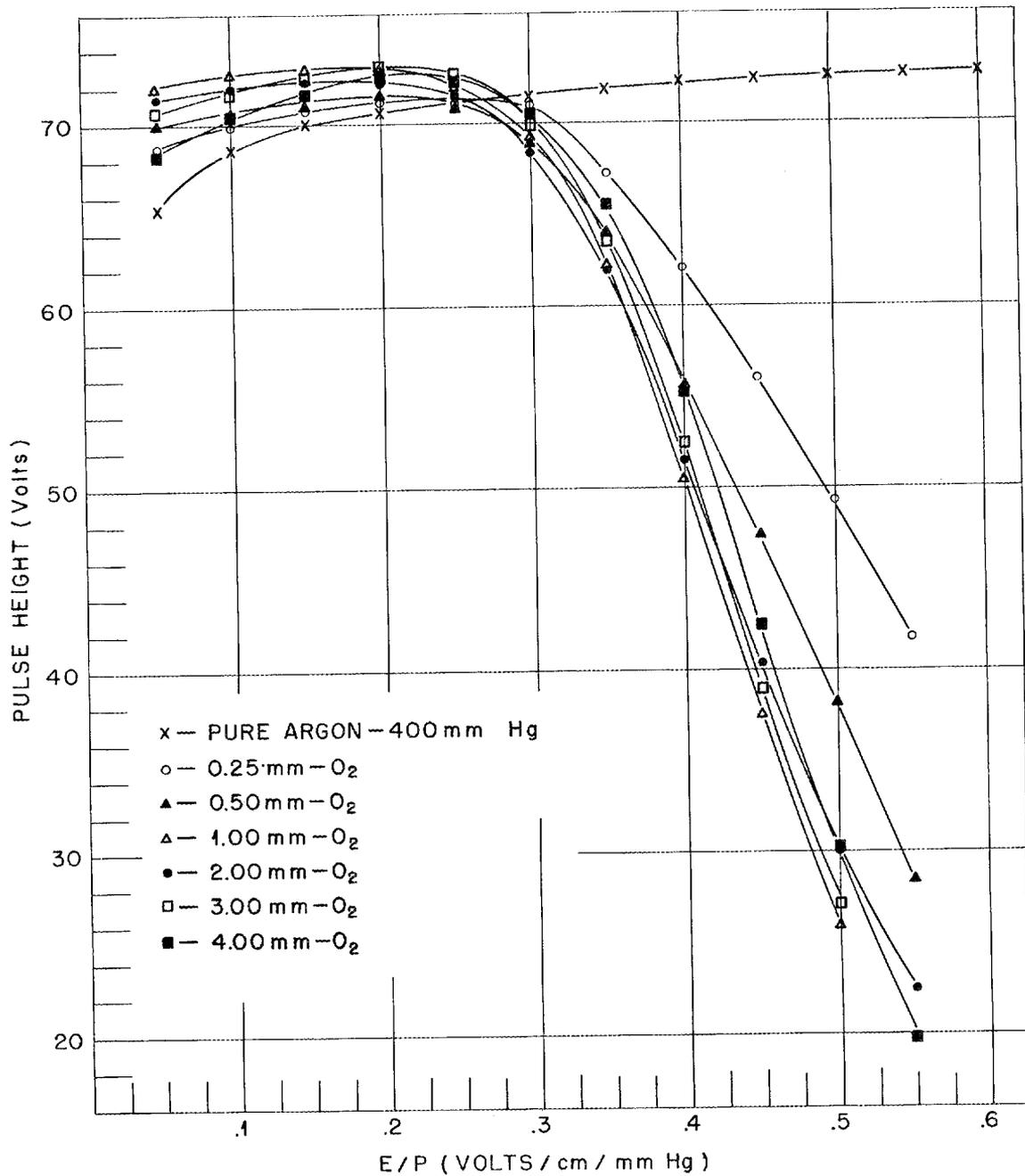
PULSE HEIGHT (VOLTS) FOR ARGON-OXYGEN MIXTURES

(ALL PRESSURES ARE mm Hg)

C. PRESSURE ARGON = 800

E/P	Pressure Oxygen						
	0	0.5	1.0	2.0	4.0	6.0	8.0
0.05	63.0	65.8	67.0	67.8	64.3	57.6	49.8
0.10	66.0	67.3	67.7	68.4	66.7	62.2	56.9
0.15	67.3	67.8	68.4	68.8	68.0	64.7	60.3
0.20	68.3	68.4	68.5	69.1	68.6	66.1	62.8
0.25	68.6	68.0	67.7	67.7	67.5	64.8	63.3
0.30	69.0	65.3	63.0	61.6	61.8	61.6	61.0
0.35	69.3	59.3	54.0	49.8	49.0	50.5	51.4
0.40	69.4	50.9	41.9	34.8	32.8	34.7	38.0
0.45	69.5	41.0	30.0	22.0	19.0	20.0	23.4
0.50	69.6	31.6	20.4				

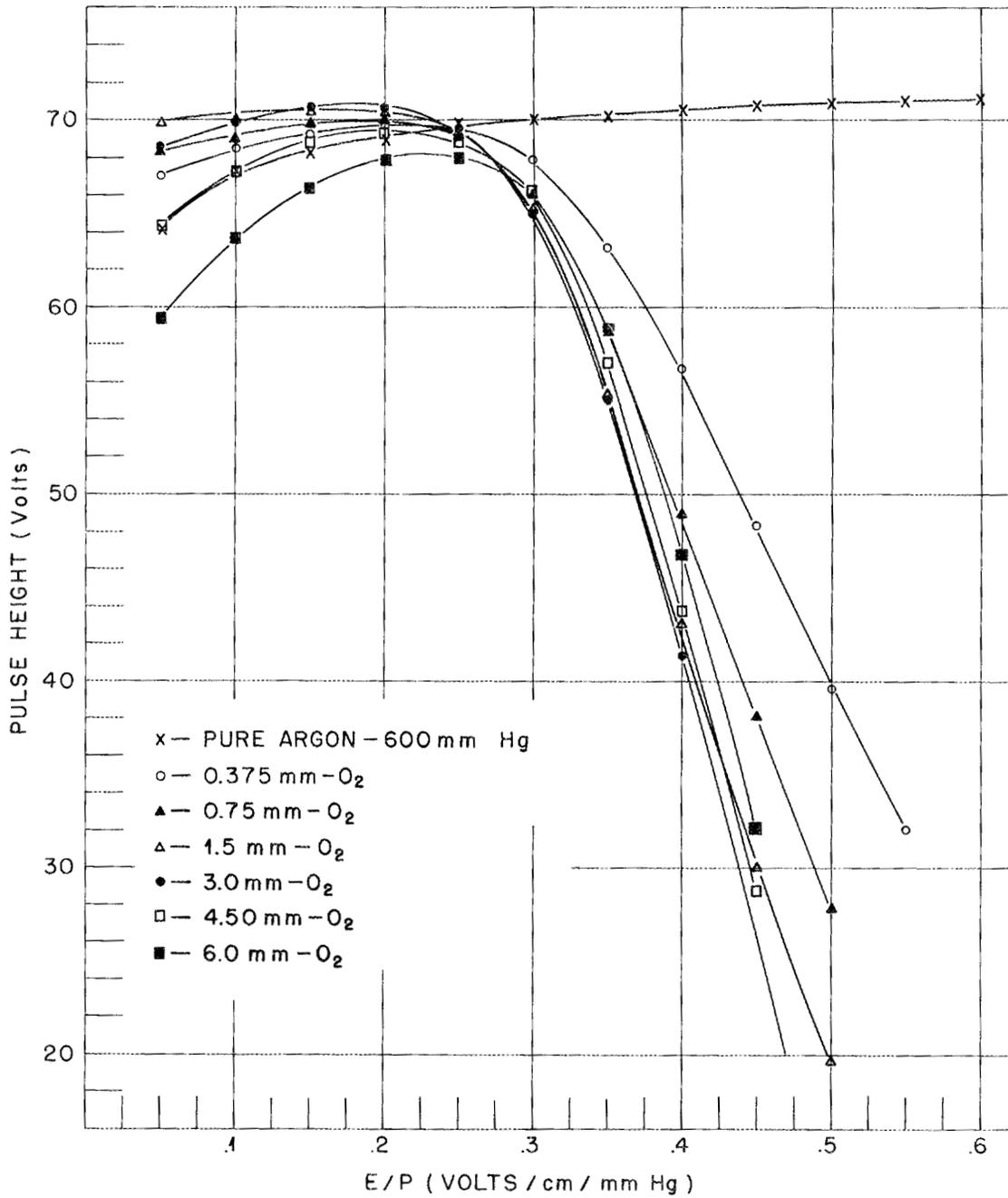
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PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN ARGON AND ARGON-OXYGEN MIXTURES AS INDICATED. ARGON PRESSURE IS 400 mm Hg

FIG-II

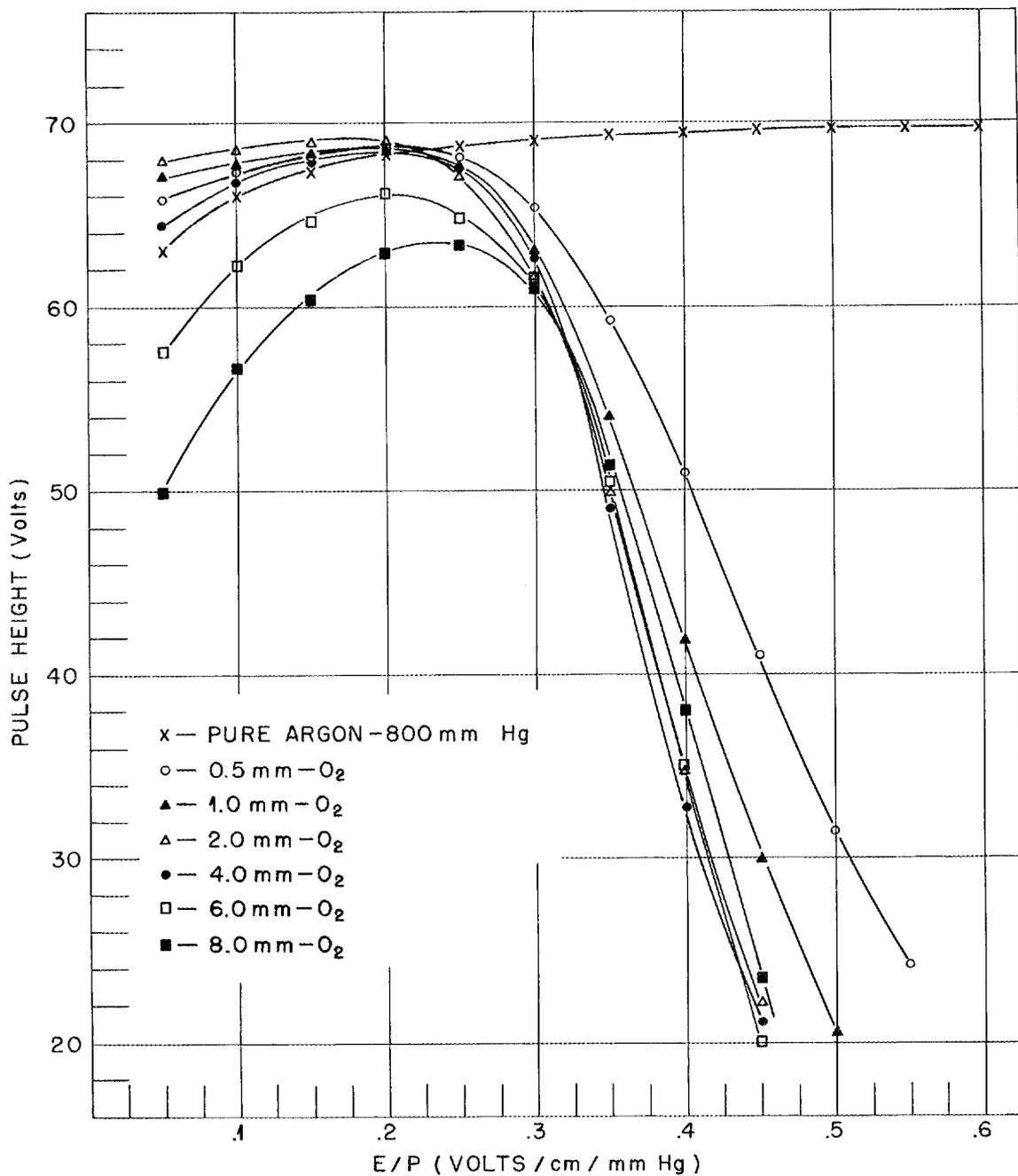
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PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN ARGON AND ARGON-OXYGEN MIXTURES AS INDICATED. ARGON PRESSURE IS 600 mm Hg

FIG-12

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PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN ARGON AND ARGON-OXYGEN MIXTURES AS INDICATED. ARGON PRESSURE IS 800 mm Hg

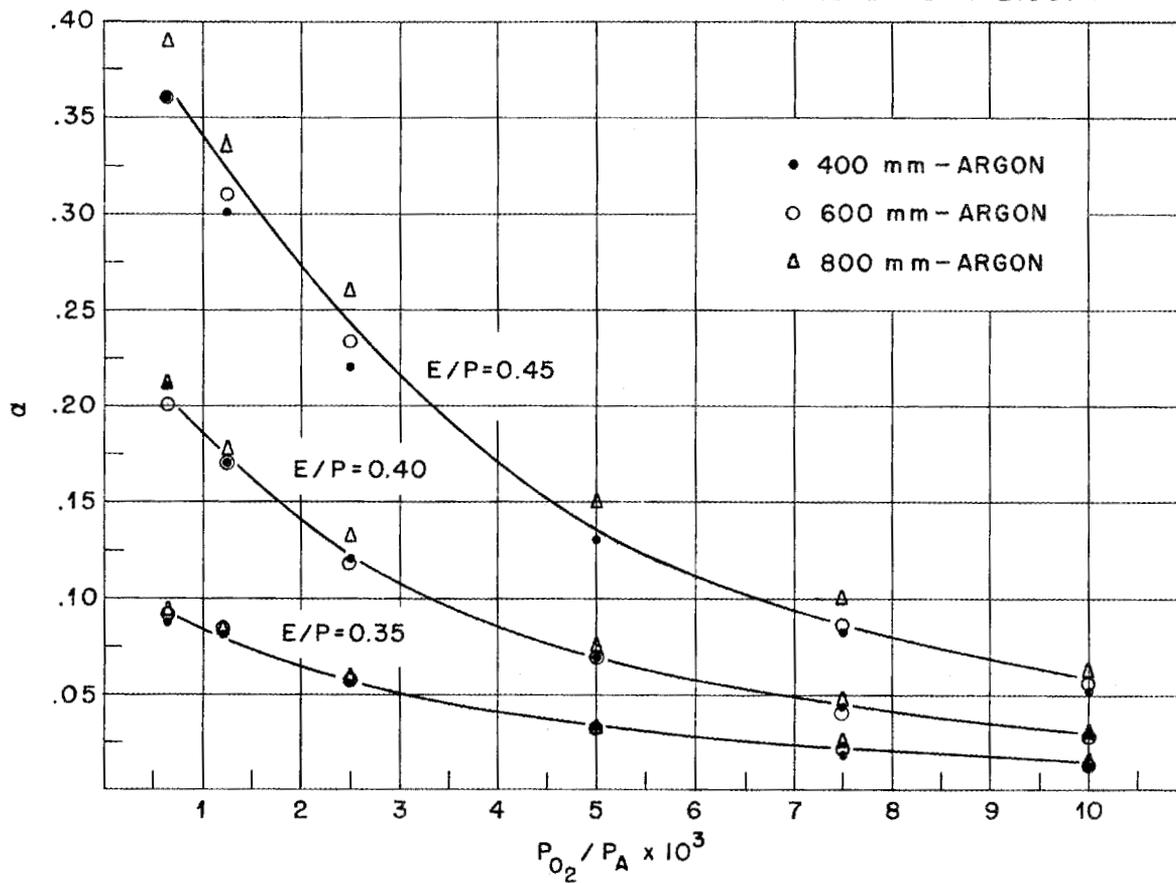
FIG-13

coefficient appeared to depend on pressure; thus data were taken at three pressures of argon (400, 600, and 800 mm Hg) and the pressure of oxygen was varied for each of the argon pressures, but in such a way that sets of fixed fractions $(P_{O_2})/(P_A)$ (called oxygen concentration) could be established. At values of E/P less than 0.3 the pulse height actually increases with the addition of oxygen. This can be accounted for by the increase in drift velocity, but the small values for the attachment coefficients at the low E/P cannot be determined with accuracy since the drift velocity correction on pulse height is so large. A very interesting behavior of practical importance is seen at $E/P = 0.30$ (Figure 11). At this E/P , oxygen (or air) contamination would not appreciably decrease the pulse height in an ionization chamber.

At E/P values greater than 0.30 the attachment coefficient can be calculated. Results are shown in Figure 14 for $E/P = 0.35, 0.40,$ and 0.45 . Curves for α are plotted as a function of oxygen concentration for these E/P values, and for argon pressures 400, 600, and 800 mm Hg. The attachment coefficient depends strongly on E/P and oxygen concentration, but is independent of argon pressure. This behavior of α can be interpreted without difficulty. The attachment reaction which is involved is $O_2 + e \rightarrow O_2^- + O$, since in argon at these E/P values the electron energy is great enough to dissociate the O_2 molecule (dissociation energy of O_2 is 5.09 volts, appearance of O_2^- is energetically possible at electron energy of 3.1 volts).¹

¹L. B. Loeb, Basic Processes of Gaseous Electronics (University of California Press, Berkeley and Los Angeles, 1955), p. 428.

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DEPENDENCE OF α ON THE CONCENTRATION OF OXYGEN IN ARGON
FOR INDICATED ARGON PRESSURES
FIG-14

Figure 14 shows that as E/P decreases, α decreases and since a decrease in E/P must be associated with a decrease in the mean agitation energy, α (in this region of electron energies) decreases with decreasing energy. Electron agitation energy depends on the reduced electric field, E/P , and the nature of the gas. In argon there are no excitation levels less than 10 volts, consequently electrons may be accelerated by the field to energies up to 10 volts while making only elastic collisions with argon atoms. When O_2 is added to argon, the mean electron energy is decreased because electrons make inelastic collision with O_2 . Therefore, for a fixed argon pressure, α will decrease with increasing values of P_{O_2}/P_A . On the other hand, if P_{O_2}/P_A is fixed the electron agitation energy will not depend on total pressure, hence α should not depend on P_A . Therefore, the only assumption which must be introduced to understand all the data in Figure 14 is that the agitation energy of electrons in argon is decreased by the addition of O_2 . As discussed above this is a most reasonable assumption which is further supported by the fact that the drift velocity was observed to increase with the addition of oxygen.

Attachment of Electrons in Nitrogen-Oxygen Mixtures

Data for electron drift velocity in nitrogen have been reported² and are shown in Figure 15. It was found that (a) as much as 2 per cent

²T. E. Bortner, G. S. Hurst, and W. G. Stone, Rev. Sci. Instr. 28, 103 (1957).

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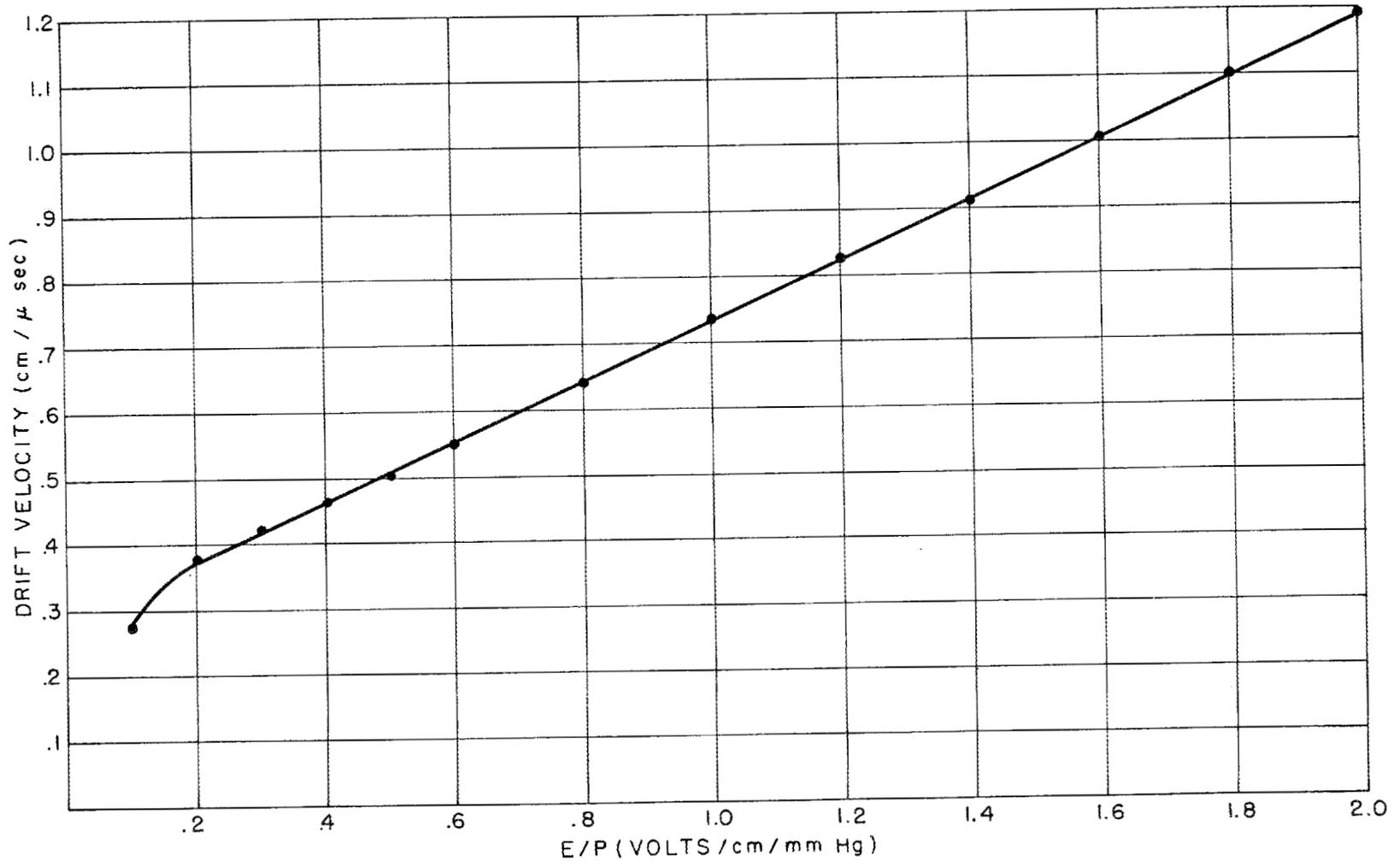


FIG.15 ELECTRON DRIFT VELOCITY IN NITROGEN

oxygen did not affect the measured drift velocity, and (b) the drift velocity of the electrons in the mixtures was a function of E/P but independent of total pressure P . Pulse height data were taken for various pressures of nitrogen and oxygen as a function of E/P ; data for N_2 pressures of 400, 600, 800, 1000, 1200, 1400, and 1600 mm Hg and a range of O_2 pressure of 1-8 mm Hg are shown in Figures 16 through 22, respectively.

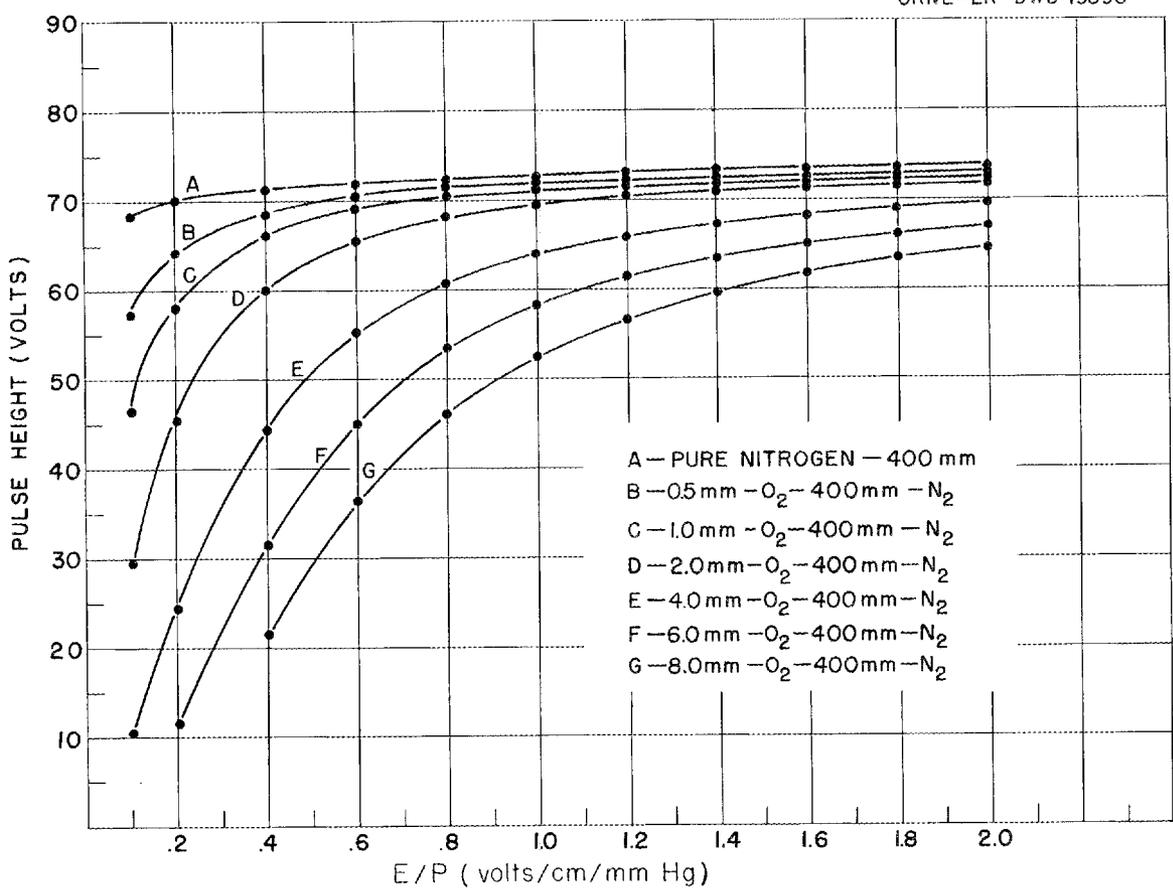
Calculated results for α show dependence on the O_2 pressure, f_1P , as well as the N_2 pressure, f_2P . Figures 23 through 26 show the results for $E/P = 0.20, 0.40, 0.60,$ and 0.80 , respectively. The results are described by the empirical equation,

$$\alpha = Af_1P + Bf_2P + Cf_1Pf_2P \quad (12)$$

where $A, B,$ and C are independent of f_1P and f_2P , but depend on E/P as shown in Table IV. In Figures 23-26 the solid lines are calculated from Eq. (12), adjusted to fit the experimental data points. This is the first case where it is found that the cross section for the formation of stable O_2^- definitely depends on pressure. Bradbury's³ experiment failed to show the dependence of α on oxygen pressure, even with pressure as low as 3.5 mm Hg. It is worth noting, however, that only a meager amount of data were reported for values of E/P less than 2. Earlier work of

³N. E. Bradbury, Phys. Rev. 44, 883 (1933).

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PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN AND NITROGEN-OXYGEN MIXTURE AS INDICATED.

400 mm Hg - NITROGEN
FIG. 16

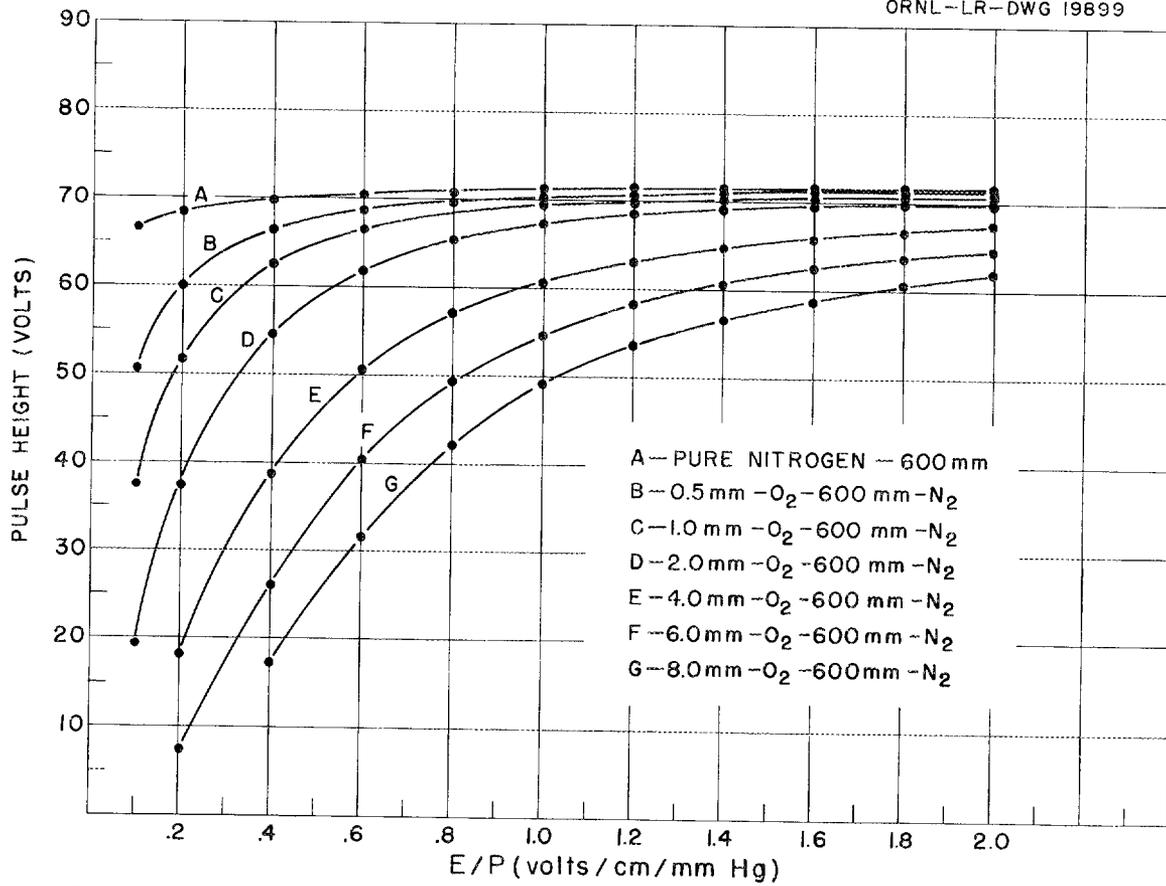
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FIG.17 PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN AND NITROGEN-OXYGEN MIXTURE AS INDICATED.
600 mm Hg - NITROGEN

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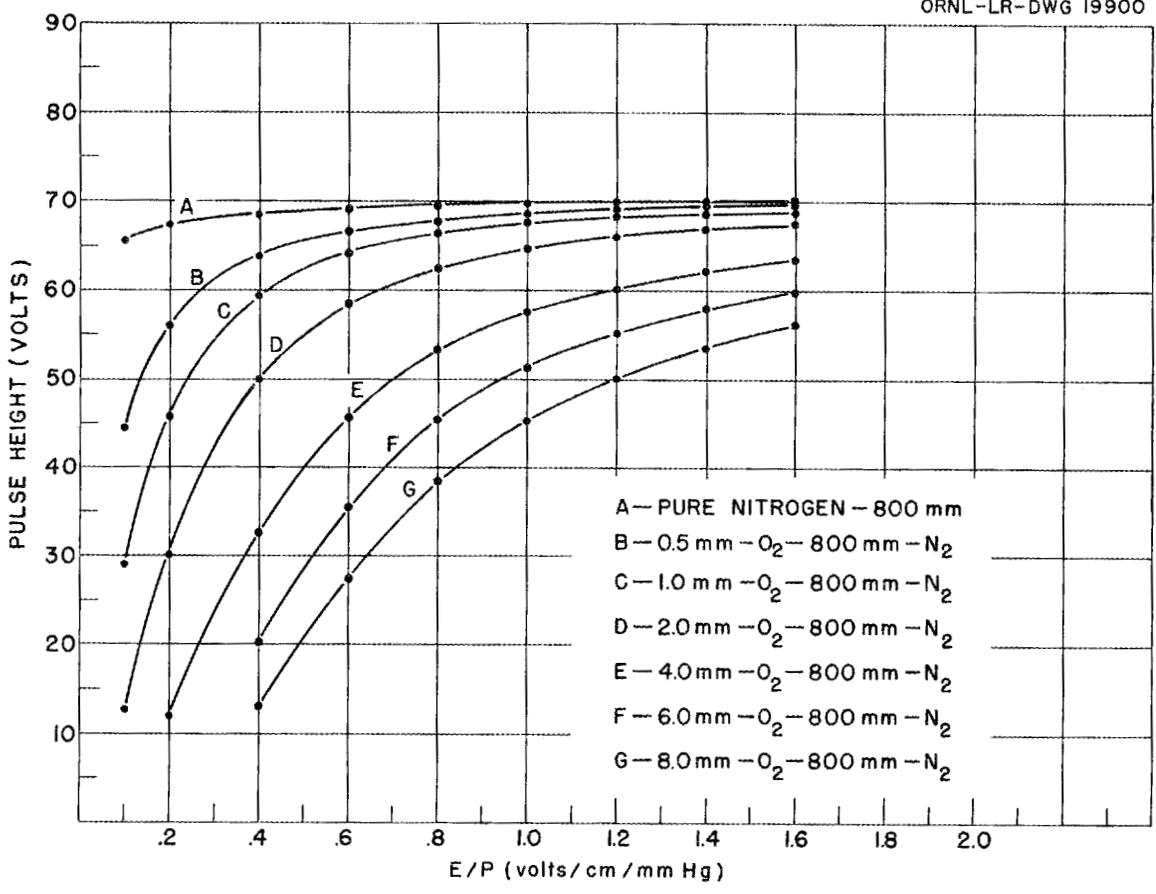


FIG. 18 PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN AND NITROGEN-OXYGEN MIXTURE AS INDICATED.
800 mm Hg - NITROGEN

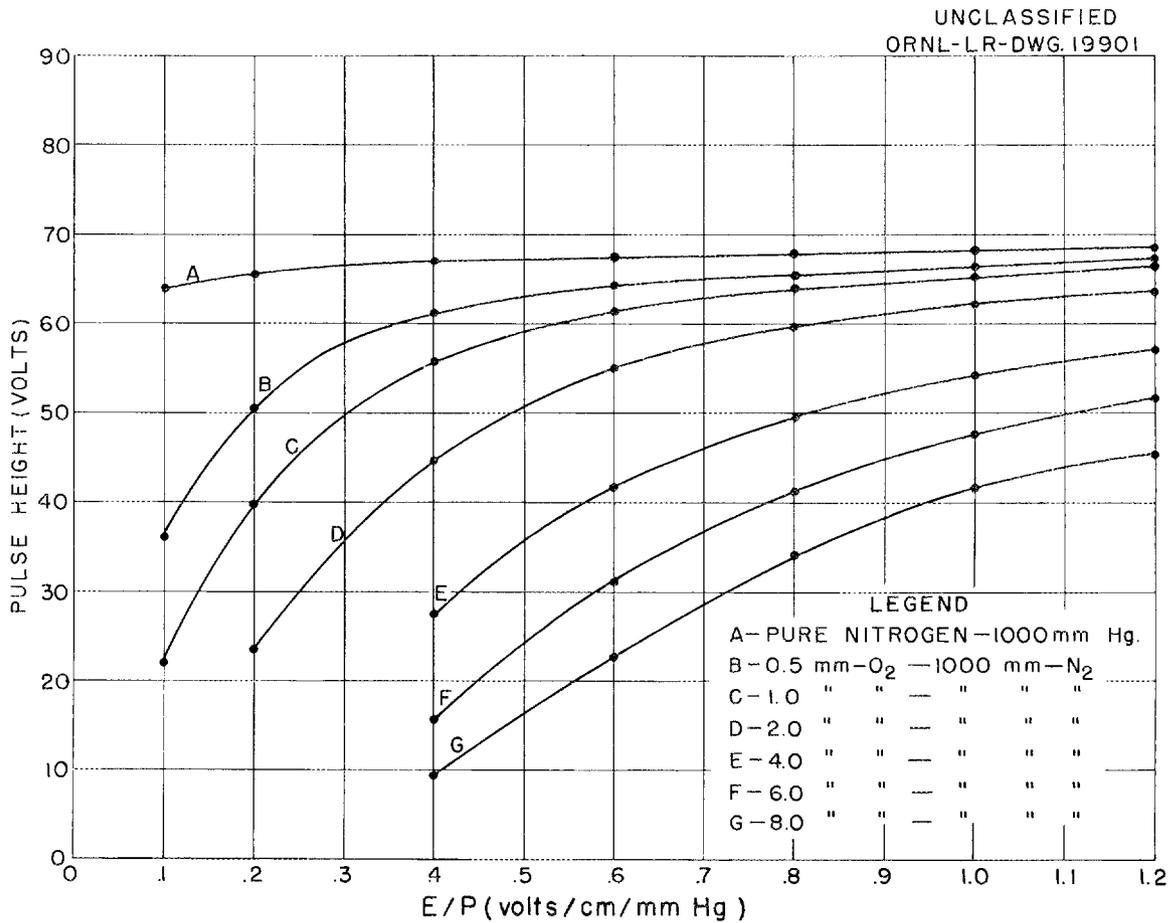


FIG.19 PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN-OXYGEN MIXTURES AS INDICATED.

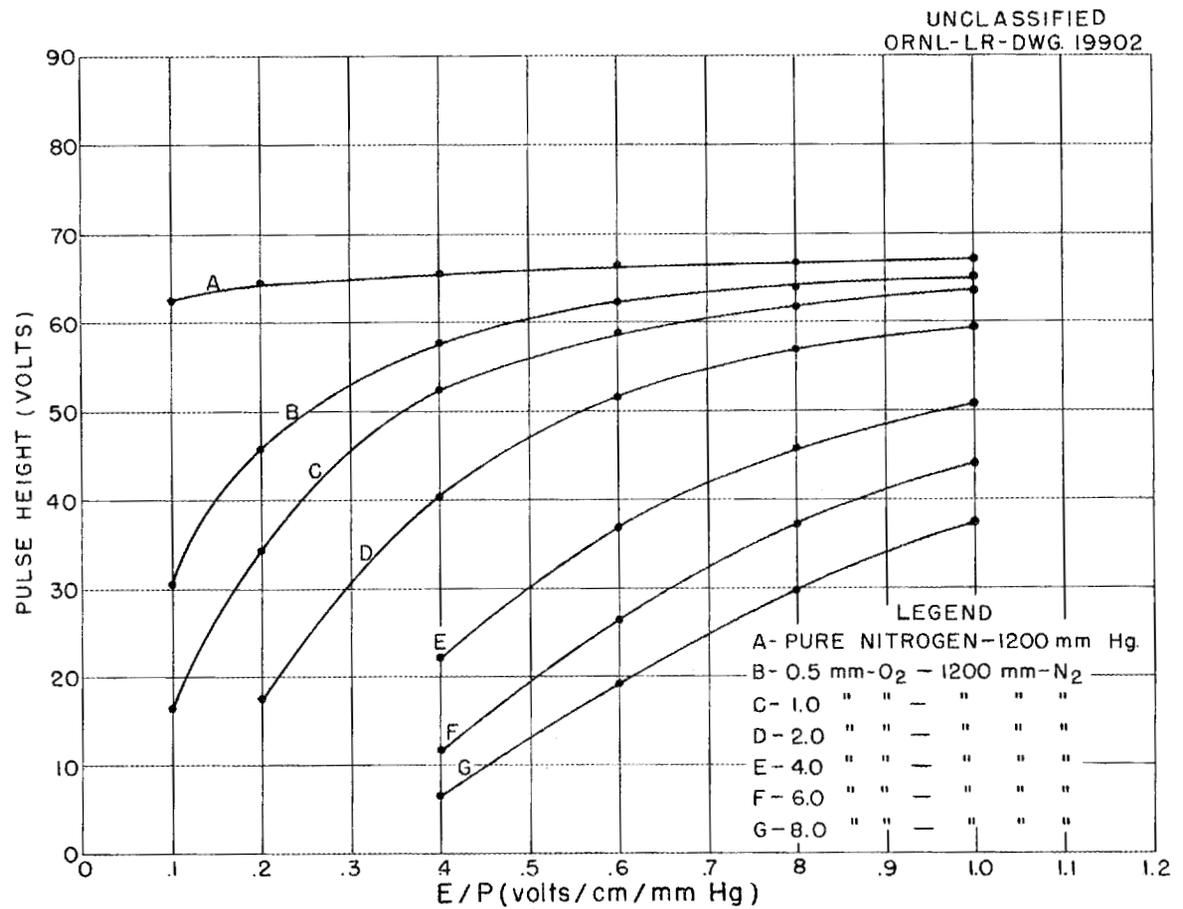


FIG.20 PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN-OXYGEN MIXTURES AS INDICATED.

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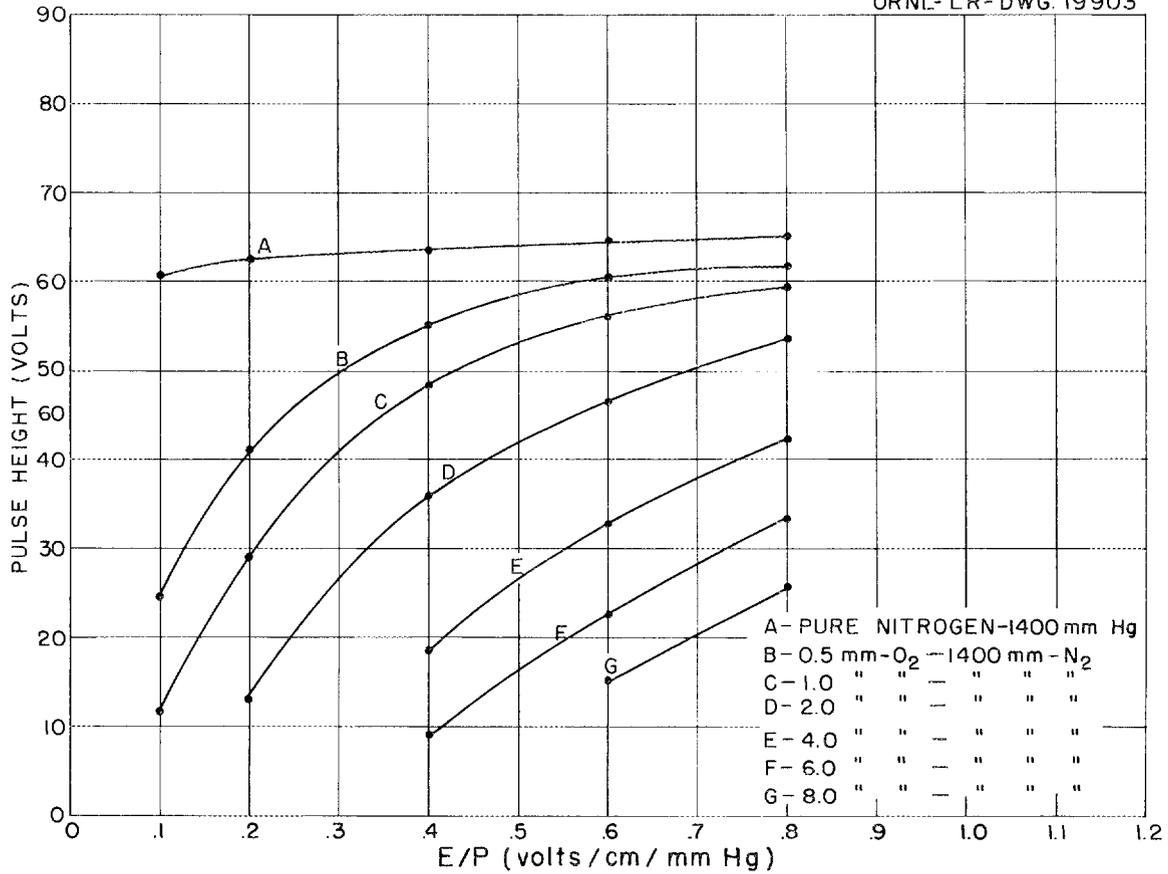
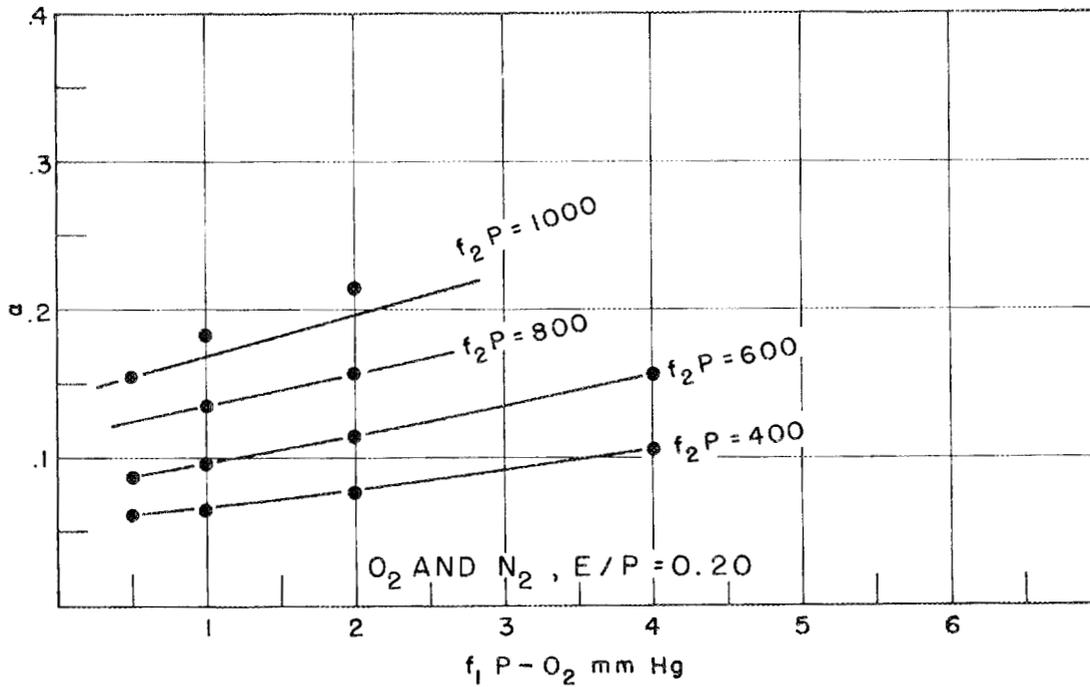
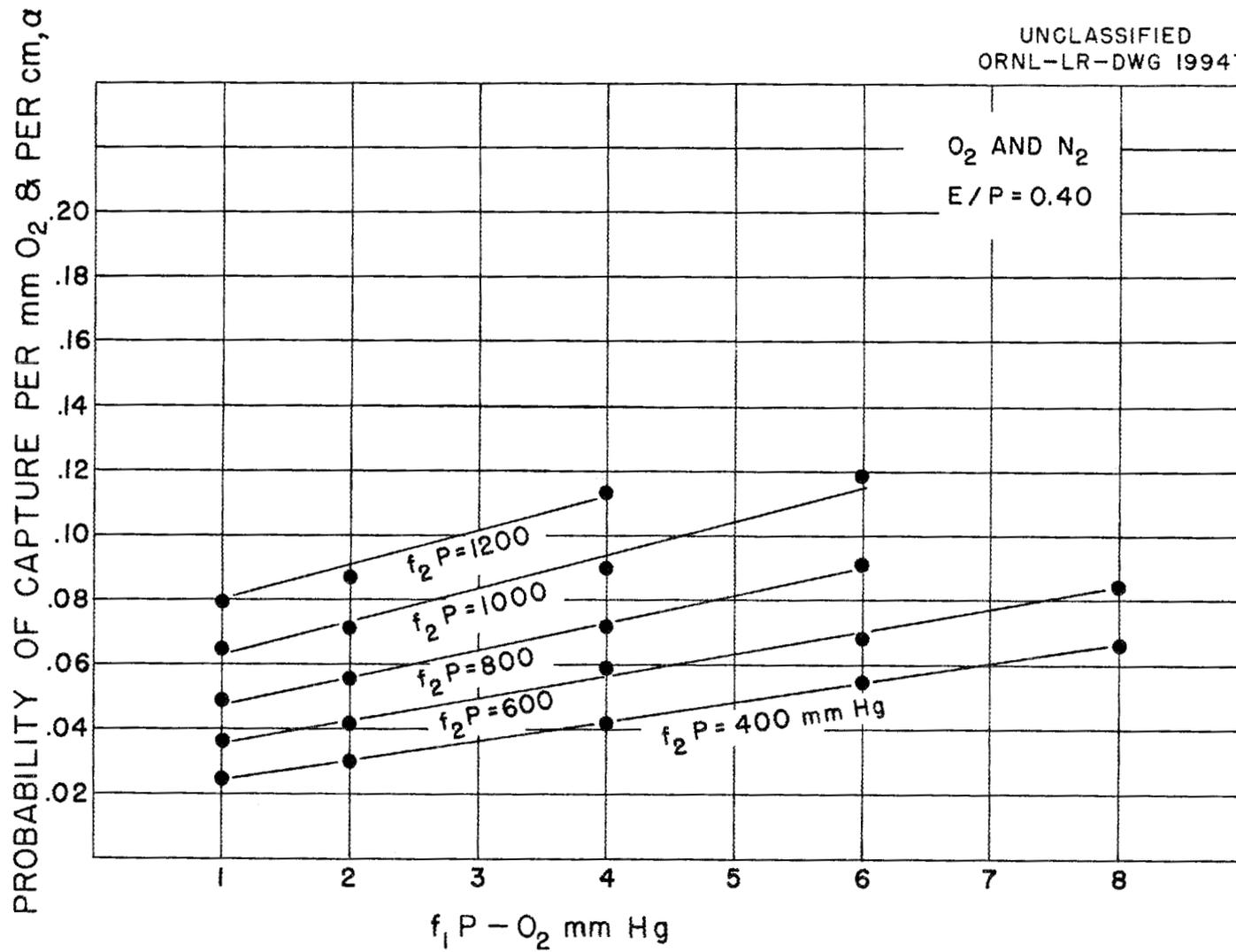


FIG.21 PULSE HEIGHT VERSUS THE ELECTRICAL FIELD IN NITROGEN-OXYGEN MIXTURES AS INDICATED.

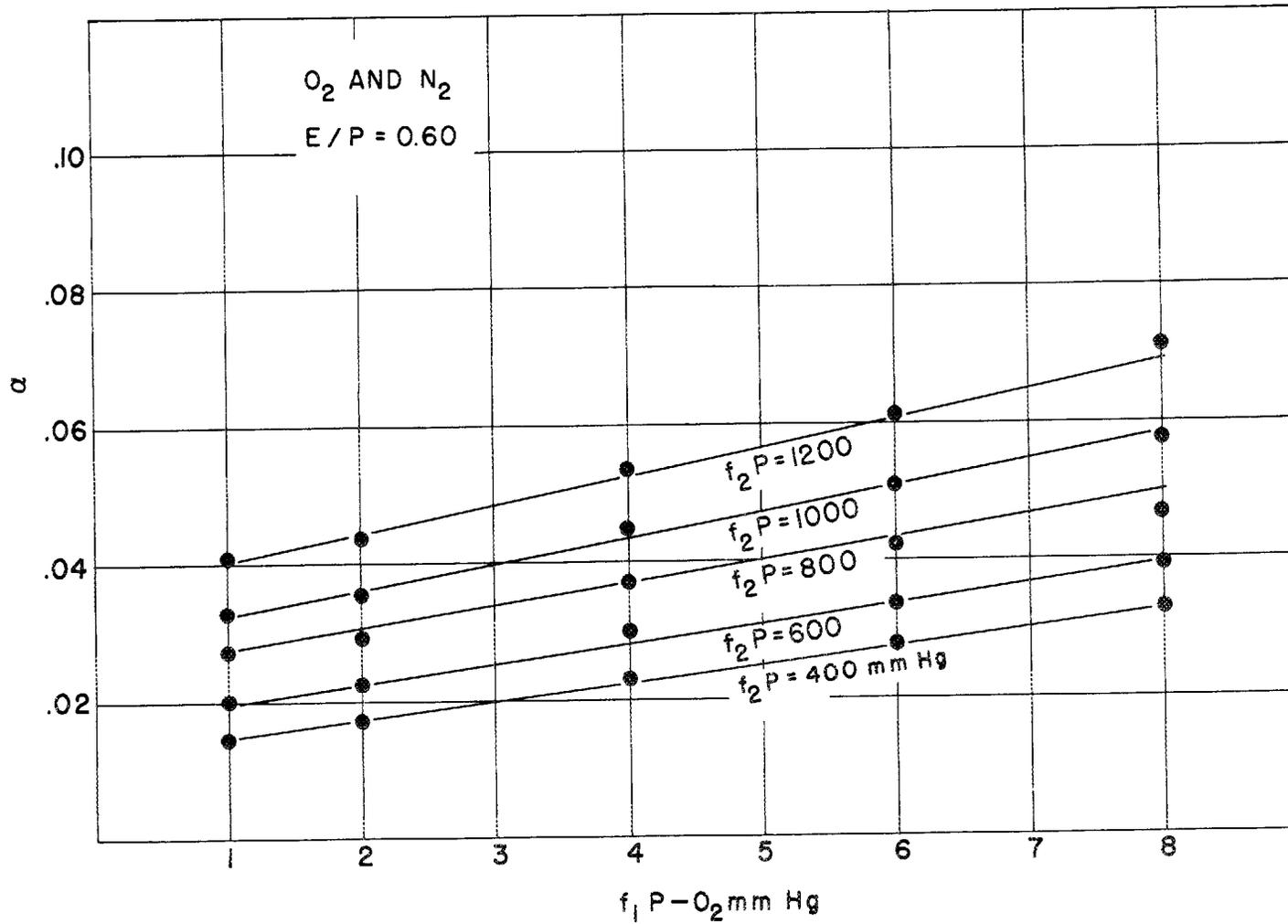
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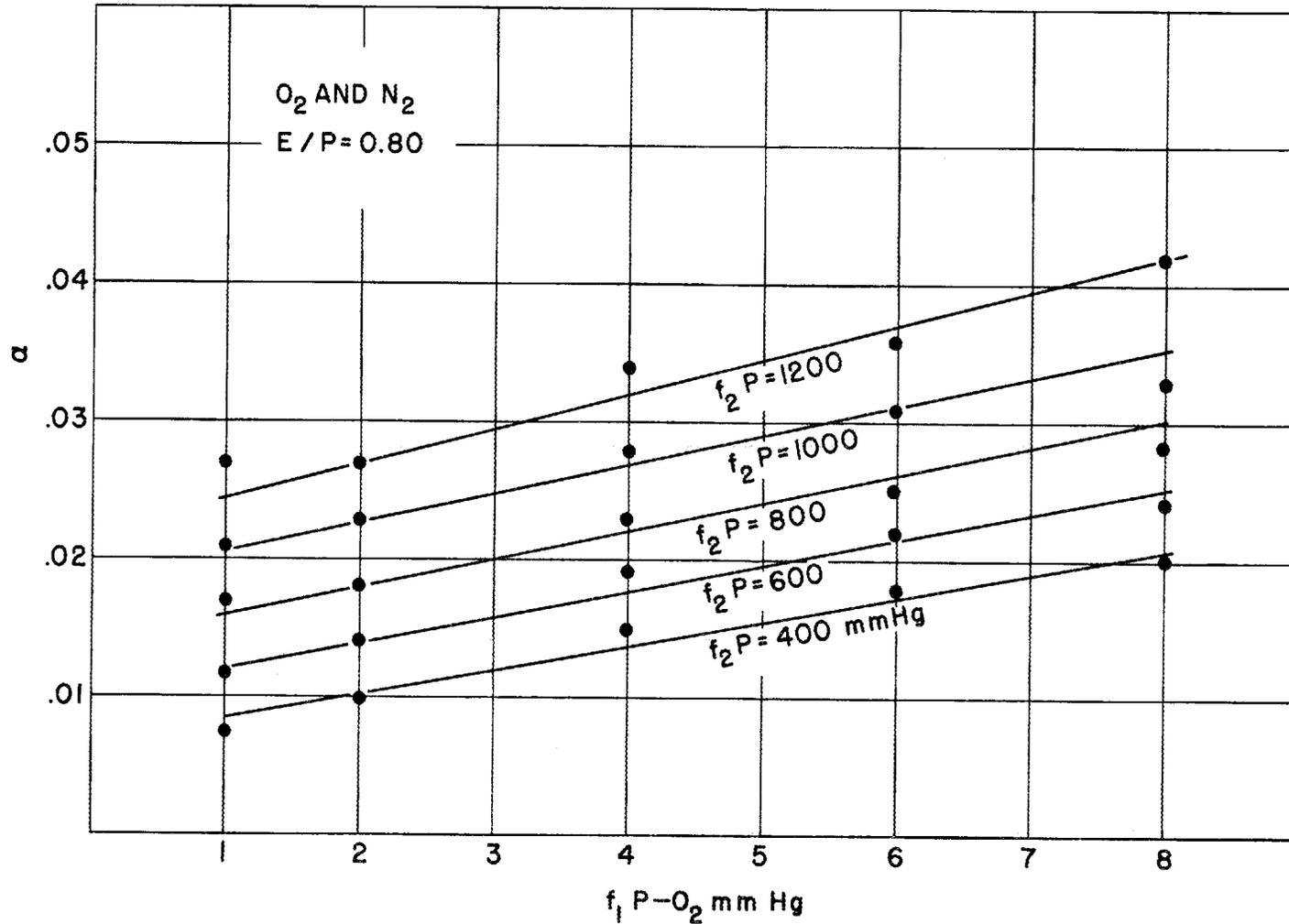
DEPENDENCE OF α ON PRESSURE OF O_2 AND N_2
FOR $E/P = 0.20$
FIG. 23



DEPENDENCE OF α ON PRESSURE OF O₂ AND N₂ FOR E/P = 0.40
FIG. 24



DEPENDENCE OF α ON PRESSURE OF O_2 AND N_2 FOR $E/P = 0.60$
FIG. 25



DEPENDENCE OF α ON PRESSURE OF O_2 AND N_2 FOR $E/P = 0.80$

FIG. 26

TABLE IV

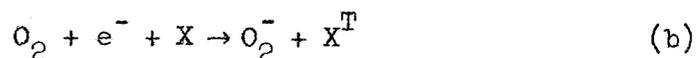
EMPIRICAL CONSTANTS A, B, AND C AS A FUNCTION OF E/P FOR
ELECTRON ATTACHMENT IN O₂-N₂ MIXTURES

E/P	A	B	C
0.2	4.5×10^{-3}	1.4×10^{-4}	2.2×10^{-5}
0.4	2.4×10^{-3}	5.3×10^{-5}	7.6×10^{-6}
0.6	1.5×10^{-3}	2.9×10^{-5}	2.4×10^{-6}
0.8	1.3×10^{-3}	1.8×10^{-5}	9.0×10^{-7}

Cravath⁴ did, in fact, indicate a dependence of attachment cross section on oxygen pressure, which was more pronounced at low values of E/P.

Because of the complexity of the results obtained for α , data were taken for two different source-to-plate separations, d. The values for α were the same for the normal separation of 6.0 cm and for a 9.0 cm separation. This rules out the possibility of a non-uniform rate of attachment. Such an effect could arise for example because of the finite distance required for the electrons created by the α particles to slow down to the equilibrium energy distribution characterized by the E/P ratio and the nature of the gas.

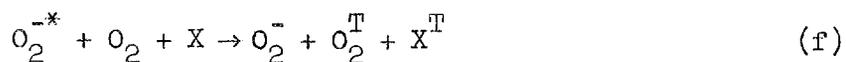
To understand the pressure dependence of α , we will develop a model for the formation of stable O_2^- , which follows to some extent the original ideas of Bloch and Bradbury. Two primary reactions are assumed to lead to the formation of unstable O_2^{-*} according to



where X is the non-attaching member of the binary mixture, and the superscript T designates an excited state. The * indicates that the O_2^- ion has enough excitation energy (either electronic or vibrational) to make the reverse of process (a) possible. The absence of the * does not

⁴A. M. Cravath, Phys. Rev. 33, 605 (1929).

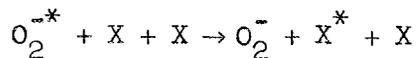
mean that O_2^- is in its ground state, but merely that the ion is energetically stable. A reaction like (b) but where another O_2 replaces X would not be of importance since in general $f_1P \ll f_2P$. We further postulate that O_2^{*-} may be stabilized by the reactions,



or the electron may be spontaneously emitted by the reaction,



It may be noted here that a reaction of the type



may be anticipated, but as will be seen later, the experimental data does not require it.

The number of electrons, dn_a , which react to form O_2^{*-} (process a)

while n electrons are moving a distance dx is given by

$$dn_a = -\beta n f_1 P dx \quad (13)$$

where β is a constant. The number of electrons dn_b attached by process (b) is given similarly by

$$dn_b = -kn f_1 P f_2 P dx \quad (14)$$

where k is a constant. On the other hand, the coefficient of attachment α is defined by Eq. (1). Clearly then, $dn = f_s dn_a + dn_b$ where f_s is the fraction of the number of O_2^{-*} which are stabilized. Thus,

$$\alpha = f_s \beta + k f_2 P \quad (15)$$

where the fraction f_s is determined by processes (c) through (g).

To evaluate f_s assume that the passage of the n electrons through an element of distance dx leaves behind $N_0 O_2^{-*}$ ions. Of these, N_s are stabilized by processes (c), (d), (e), and (f) while $N_0 - N_s$ re-emit the electron by process (g). Thus,

$$f_s = \frac{N_s}{N_0} = -\frac{1}{N_0} \int_0^{\infty} \left[\left(\frac{dN}{dt} \right)_c + \left(\frac{dN}{dt} \right)_d + \left(\frac{dN}{dt} \right)_e + \left(\frac{dN}{dt} \right)_f \right] dt \quad (16)$$

Defining the rates for processes (c), (d), (e), (f), and (g) by

$$\begin{aligned} \left(\frac{dN}{dt}\right)_c &= -\lambda_1 N, & \left(\frac{dN}{dt}\right)_d &= -C_1 N f_1 P \\ \left(\frac{dN}{dt}\right)_e &= -C_2 N f_2 P, & \left(\frac{dN}{dt}\right)_f &= -K N f_1 P f_2 P \end{aligned} \quad (17)$$

and

$$\left(\frac{dN}{dt}\right)_g = -\lambda_2 N$$

leads to f_s such that

$$\alpha = \left(\frac{\lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P}{\lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P + \lambda_2} \right) \beta + k f_2 P \quad (18)$$

Equation (18) reduces to the form required for the O_2-N_2 case (Eq. 12) if λ_1 is assumed to be negligible in the numerator of the first term and if $\lambda_2 \gg \lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P$. Then,

$$\alpha = \frac{C_1}{\lambda_2} \beta f_1 P + \left(\frac{C_2 \beta}{\lambda_2} + k \right) f_2 P + \frac{K}{\lambda_2} \beta f_1 P f_2 P \quad (19)$$

which is the form required by the experimental data, Eq. (12). The

condition that λ_1 be small is reasonable since Biondi⁵ has shown that only at thermal energies can an appreciable part of the attachment cross section be attributed to radiation stabilization. The condition that λ_2 be larger than the pressure dependent terms in the denominator of Eq. (18) would hold only at "low" pressures. The values of the empirical constants A, B, and C, Table I, may now be equated to

$$\frac{C_1}{\lambda_2} \beta, \quad \left(\frac{C_2}{\lambda_2} \beta + k \right), \quad \text{and} \quad \frac{K}{\lambda_2} \beta, \quad \text{respectively.}$$

In the original Bloch-Bradbury interpretation it was assumed that the excited ion O_2^{-*} was simply the first vibrational level in the ground state (${}^2\Pi_g$) of O_2^- . If this is the case, the rate constant C_1 depends only on the cross section, σ_1 , for the transfer of vibrational energy from O_2^{-*} to O_2^- . We may now see what values of σ_1 are required to explain the present values of $(C_1/\lambda_2)\beta$.

The ratio β/λ_2 is closely related to the ratio of the transition probability for capture T_{12} to the transition probability for the reverse process, T_{21} . This ratio is given directly from the principle of detailed balance, i.e., $T_{12}/T_{21} = \rho_2/\rho_1$, where ρ_1 and ρ_2 are the numbers of initial and final states per unit of energy interval, respectively. The cross section for electron capture σ_c is given by $\frac{T_{12}}{v_0} f(E^*)$, where

⁵M. A. Biondi, Phys. Rev. 84, 1072 (1951).

v_o is the mean electron velocity and $f(E^*)$ is the energy distribution function evaluated at the energy E^* , at which capture takes place. Now β is equal to $\sigma_c N_o \frac{v_o}{w}$, where N_o is the number of oxygen molecules per cm^3 at 1 mm Hg, and w is the drift velocity of the electrons. The rate of electron emission λ_2 is just T_{21} . Thus,

$$\frac{\beta}{\lambda_2} = \sigma_c N_o \frac{v_o}{w} \frac{1}{T_{21}} = \frac{N_o}{w} \frac{T_{12}}{T_{21}} f(E^*) = \frac{N_o}{w} \frac{\rho_2}{\rho_1} f(E^*) \quad (20)$$

Since the initial states refer to the free electron, ρ_1 is determined from quantum statistics as follows,

$$\rho_1 = 2 \times \frac{4\pi}{8\pi^3 \frac{1}{h^3}} P^{*2} \frac{dP^*}{dE^*} = \frac{m^2 v^*}{\pi^2 \frac{1}{h^3}} \quad (21)$$

where P^* is the electron momentum at which the transition occurs and $\frac{1}{h}$ is Planck's constant divided by 2π , and m is the mass of the electron.

Thus

$$\frac{\beta}{\lambda_2} = \pi^2 \frac{1}{h^3} \frac{N_o}{w} \frac{f(E^*)}{m^2 v_o} \rho_2 = \frac{N_o}{w} \frac{2\pi^2 \frac{1}{h^3} f(E^*)}{(2m)^{3/2} (E^*)^{1/2}} \rho_2 \quad (22)$$

where ρ_2 is 2 or 4, depending on whether the final state is $O_2^-(^2\Pi_g)$ or $O_2^-(^4\Sigma_u)$, Figure 3.

The only uncertainty in evaluating β/λ_2 lies in the distribution function $f(E)$ and the energy E^* . If the Bloch-Bradbury values for these are used and if $\rho_2 = 2$, the cross section σ_1 , based on our experimental values for $C_1(\beta/\lambda_2)$ is approximately $3 \times 10^{-15} \text{ cm}^2$ (Table V); thus, larger than gas kinetic cross sections.⁶ The maximum value (corresponding to $k = 0$) of the cross section for process (e), $\sigma_{2 \text{ max}}$, is approximately $6 \times 10^{-17} \text{ cm}^2$. Calculations by Vogt and Wannier⁷ show that the cross section for "close collisions" between an O_2^- ion and an O_2 molecule may be a factor of 100 larger than the cross section for collision of two O_2 molecules. This effect originates from the Coulomb interaction between the ion and the dipole induced in the molecule. Thus, one can readily understand how σ_1 can be larger than the gas kinetic cross section. The reason for the large ratio $\sigma_1/\sigma_{2 \text{ max}}$ deserves further comment. The discussion of this fact must be made in connection with the potential energy diagram for O_2^- , which unfortunately is not well determined (see Chapter I, p 15).

In the Bloch-Bradbury interpretation of Bradbury's data it was assumed that O_2^{-*} was simply the first vibrational level in the ground state (${}^2\Pi_g$) of O_2^- . By an argument based on the quantum mechanical transition probability it was shown that the order of magnitude of the

⁶In relating the rate constant C_1 to cross section σ_0 , we used the convention of A. C. G. Mitchell and M. W. Zemansky, Resonant Radiation and Excited Atoms (Cambridge University Press, London, 1934).

⁷E. Vogt and G. H. Wannier, Phys. Rev. 95, 1190 (1954).

TABLE V

CROSS SECTIONS σ_1 AND $\sigma_{2 \max}$ AND THE RATE CONSTANT $K \frac{\beta}{\lambda_2}$
FOR O_2-N_2 MIXTURES

E/P	$A = \frac{C_1 \beta}{\lambda_2}$	$\sigma_1 (\text{cm}^2)$	$B = \frac{C_2 \beta}{\lambda_2} + k$	$\sigma_{2 \max} (\text{cm}^2)$	$C = \frac{K \beta}{\lambda_2}$
0.2	4.5×10^{-3}	2.1×10^{-15}	1.4×10^{-4}	6.4×10^{-17}	2.2×10^{-5}
0.4	2.4×10^{-3}	3.0×10^{-15}	5.3×10^{-5}	6.8×10^{-17}	7.6×10^{-6}
0.6	1.5×10^{-3}	3.1×10^{-15}	2.9×10^{-5}	5.9×10^{-17}	2.4×10^{-6}
0.8	1.3×10^{-3}	3.2×10^{-15}	1.8×10^{-5}	4.4×10^{-17}	9.0×10^{-7}

results obtained by Bradbury could be understood only if O_2^- is vibrating in its first state. Bates and Massey,⁸ however, have pointed out that the electron affinity for O_2 as obtained from thermochemistry is approximately 1 volt, while the Bloch-Bradbury theory requires approximately 0.1 volt. These two facts are brought into harmony by assuming that electrons may be captured into the ($^4\Sigma_u^-$) state of O_2^- and the ($^2\Pi_g$) state lies nearly 1 volt lower.

The details of the reactions (d), (e), and (f) are by no means clear, but we may list several possibilities. If electrons are captured into the ($^4\Sigma_u^-$) state there are at least three possibilities for stabilization of O_2^{-*} by process (d): (1) vibrational energy transfer, (2) electron transfer from O_2^{-*} to O_2 , and (3) transfer of electronic excitation from O_2^{-*} to O_2 leaving O_2 in the ($^1\Delta_g$) state. If electrons are captured into the ($^2\Pi_g$) state, possibilities (1) and (2) only remain. Since N_2 is not electronegative, and since the energy condition rules out stabilization by electronic excitation transfer, process (e) represents only vibrational energy transfer, regardless of the state of excitation of O_2^- . In either case the reason for the large ratio $\sigma_1/\sigma_{2 \max}$ is explained. If capture takes place in the ($^2\Pi_g$) state, σ_1 arises from possibilities (1) and (2) for reaction (d), while $\sigma_{2 \max}$ arises from process (e), possibility (1) only. If capture takes place in the ($^4\Sigma_u^-$) state, σ_1 arises from possibilities (1), (2), and (3) for reaction (d), while

⁸D. R. Bates and H. S. W. Massey, Phil. Trans. A239, 269 (1943).

$\sigma_2 \text{ max}$ again arises from process (e), possibility (1) only.

The most surprising result of fitting the above model of electron capture to the experimental data is the large value of the constant K representing the rate of process (f). The usual kinetic theory criterion for three body collisions⁹ fails completely. A possible reason may be that O_2^{-*} and N_2 first combine to form $O_2^{-*}-N_2$ with a lifetime against dissociation which is long compared to the time for electron emission. This point is treated in more detail in Appendix 1.

In Table V it is seen that the cross section σ_1 is nearly independent of E/P (and hence the electron agitation energy) as, of course, it should be if we are dealing with the same excited states in O_2^{-*} . The fact that σ_1 is not entirely independent of E/P can easily be explained by our lack of knowledge of $f(E)$ and E^x . The fact that $\sigma_2 \text{ max}$, obtained by neglecting process (b) does depend on E/P may be taken as evidence that k, representing the rate constant for process (b) is not negligible in the O_2-N_2 mixtures.

Attachment of Electrons in Ethylene-Oxygen Mixtures

An investigation, similar to the one conducted for O_2-N_2 mixtures, was carried out for $C_2H_4-O_2$ mixtures. Drift velocity data have been reported² and are shown in Figure 27. Pulse height data for total

⁹R. C. Tolman, Statistical Mechanics with Application to Physics and Chemistry (Chemical Catalog Co., Inc., New York, 1927).

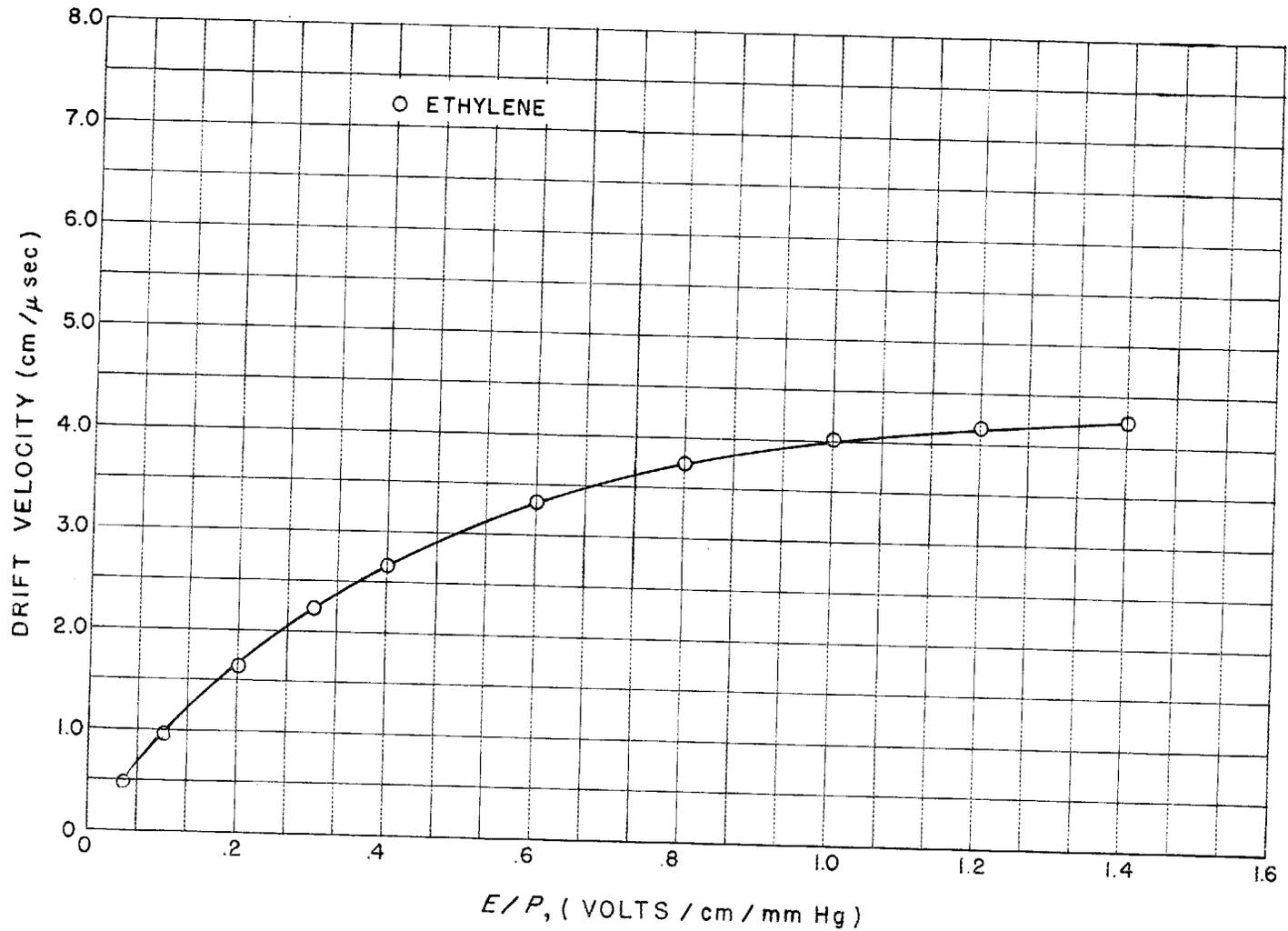


FIG.27 ELECTRON DRIFT VELOCITY IN ETHYLENE

ethylene pressures of 250, 300, 400, 500, and 600 mm Hg and various oxygen pressures as a function of E/P are shown in Figures 28 through 32, respectively.

Calculated values for α are shown in Figures 33 through 58 for E/P = 0.10; similar sets were calculated for E/P values 0.20, 0.30, 0.40, 0.50, 0.60, 0.80, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0. In this series odd figure numbers show α plotted against oxygen pressure for various values of the ethylene pressure. Even figure numbers give the values for α averaged over values of oxygen pressure as a function of ethylene pressure. In all cases α was independent of the O_2 pressure f_1P , but did depend on the C_2H_4 pressure. At all values of E/P the curve of α against f_2P is a straight line, which has a positive intercept for $f_2P = 0$. All the data can be represented with the simple empirical equation,

$$\alpha_o = \alpha_o + k'f_2P \quad (23)$$

where α_o and k' are independent of pressures f_1P and f_2P but do depend on E/P, Figure 59.

Although the dependence of α on f_1P and f_2P for the case of $O_2-C_2H_4$ is rather different from the case of O_2-N_2 it is possible to retain the model which was postulated for the O_2-N_2 case. Assume that all the reactions (a) through (g) hold for $O_2-C_2H_4$ mixtures, i.e., let a C_2H_4 molecule replace the X molecules in every process. The attachment

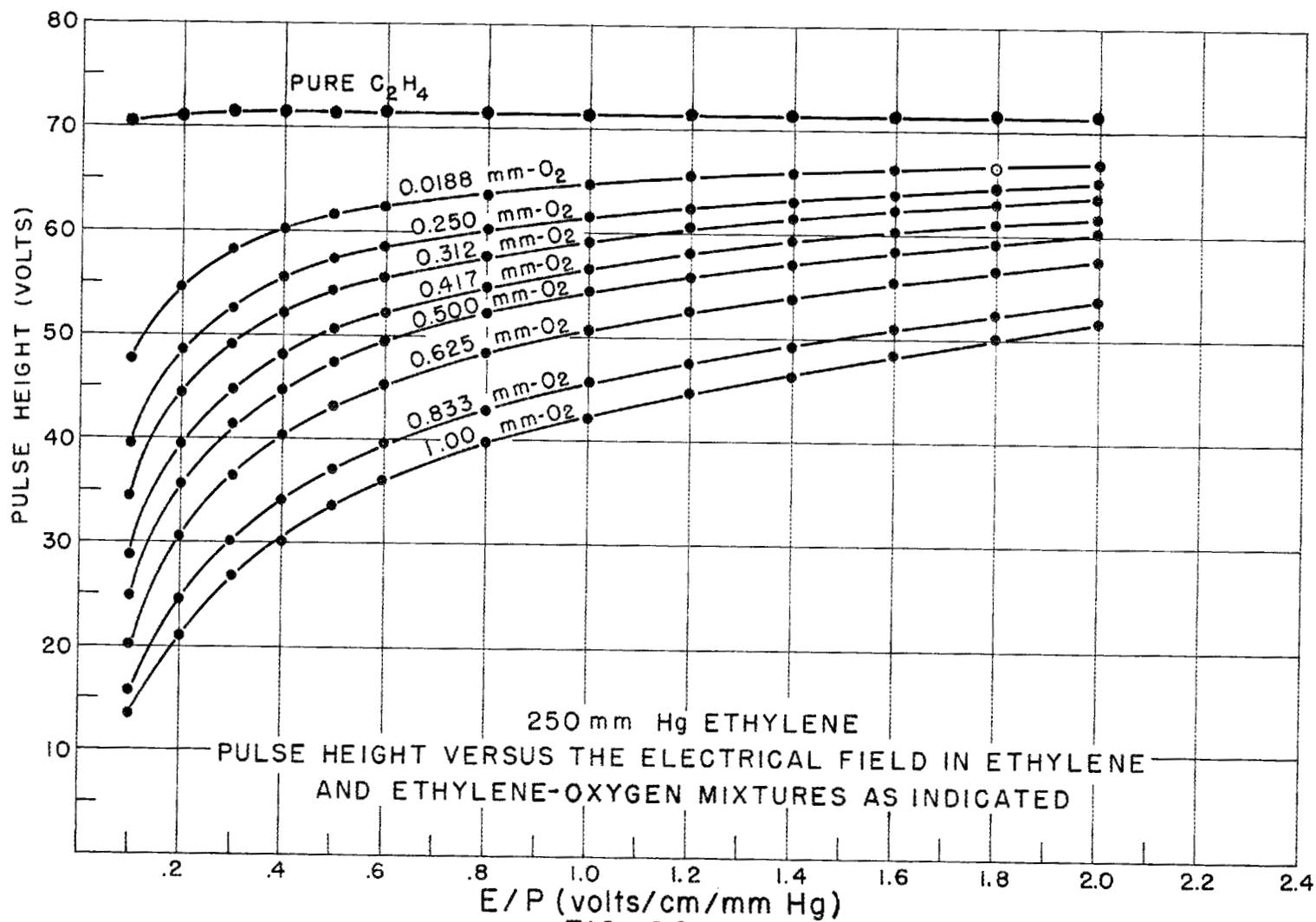
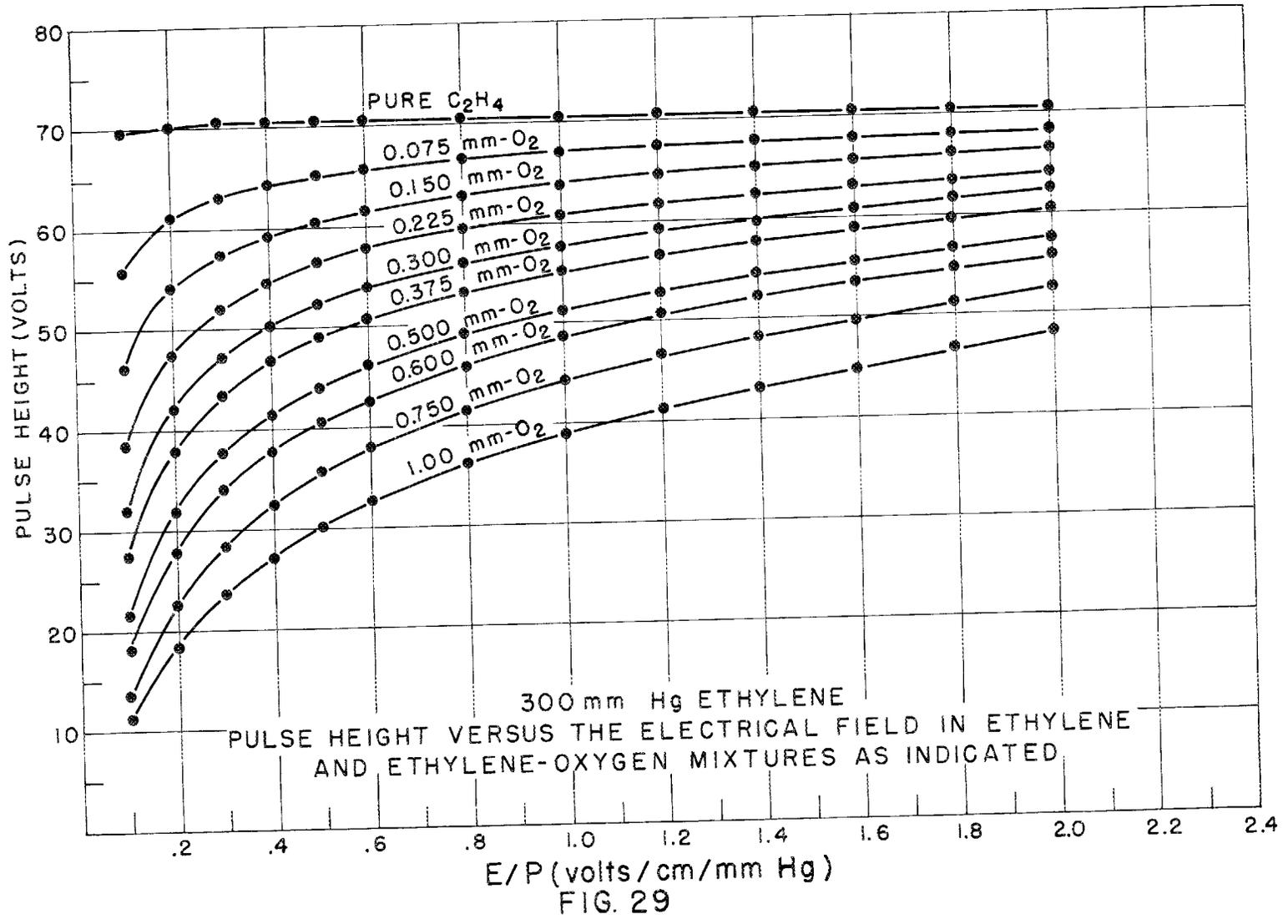


FIG. 28



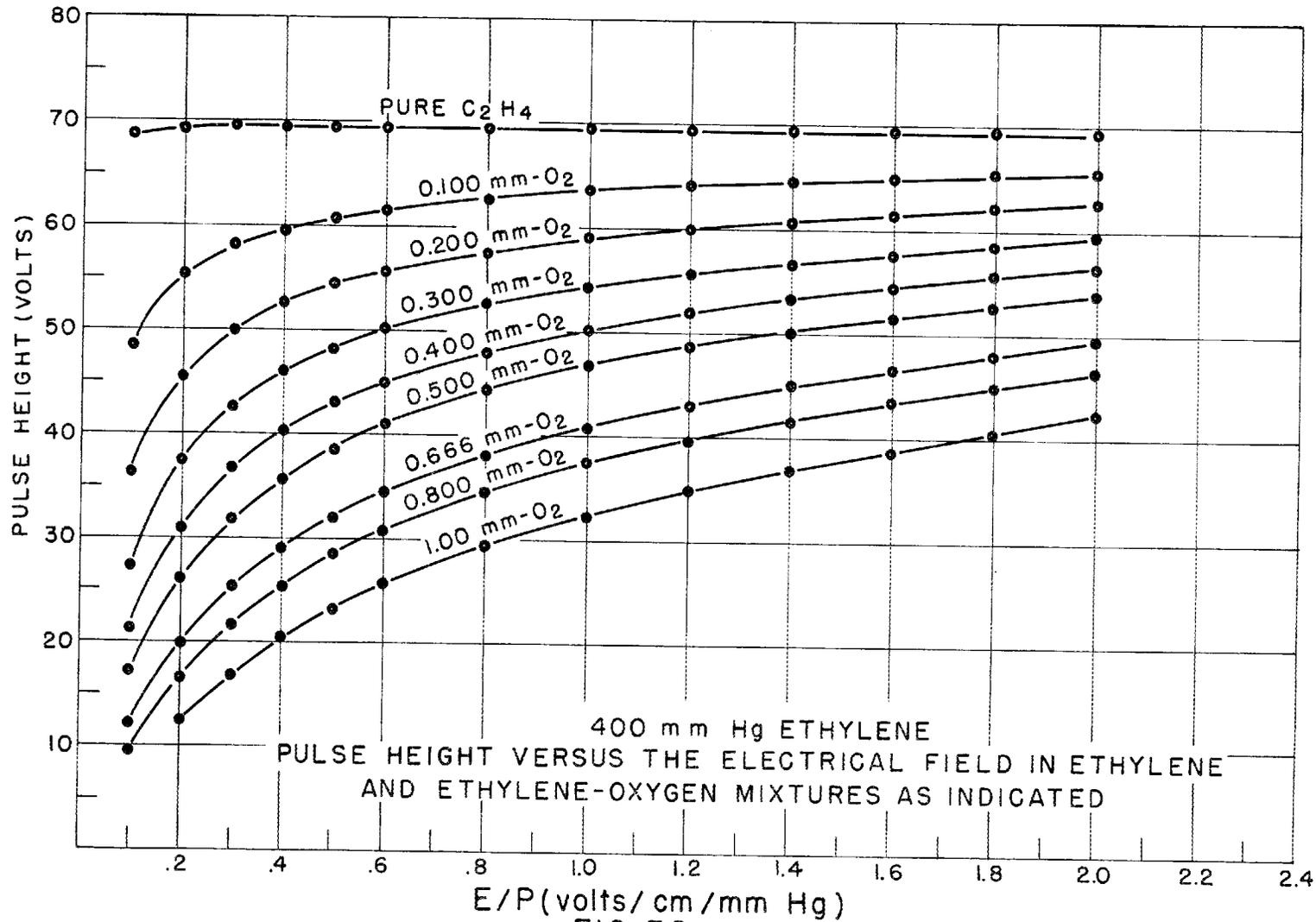


FIG. 30

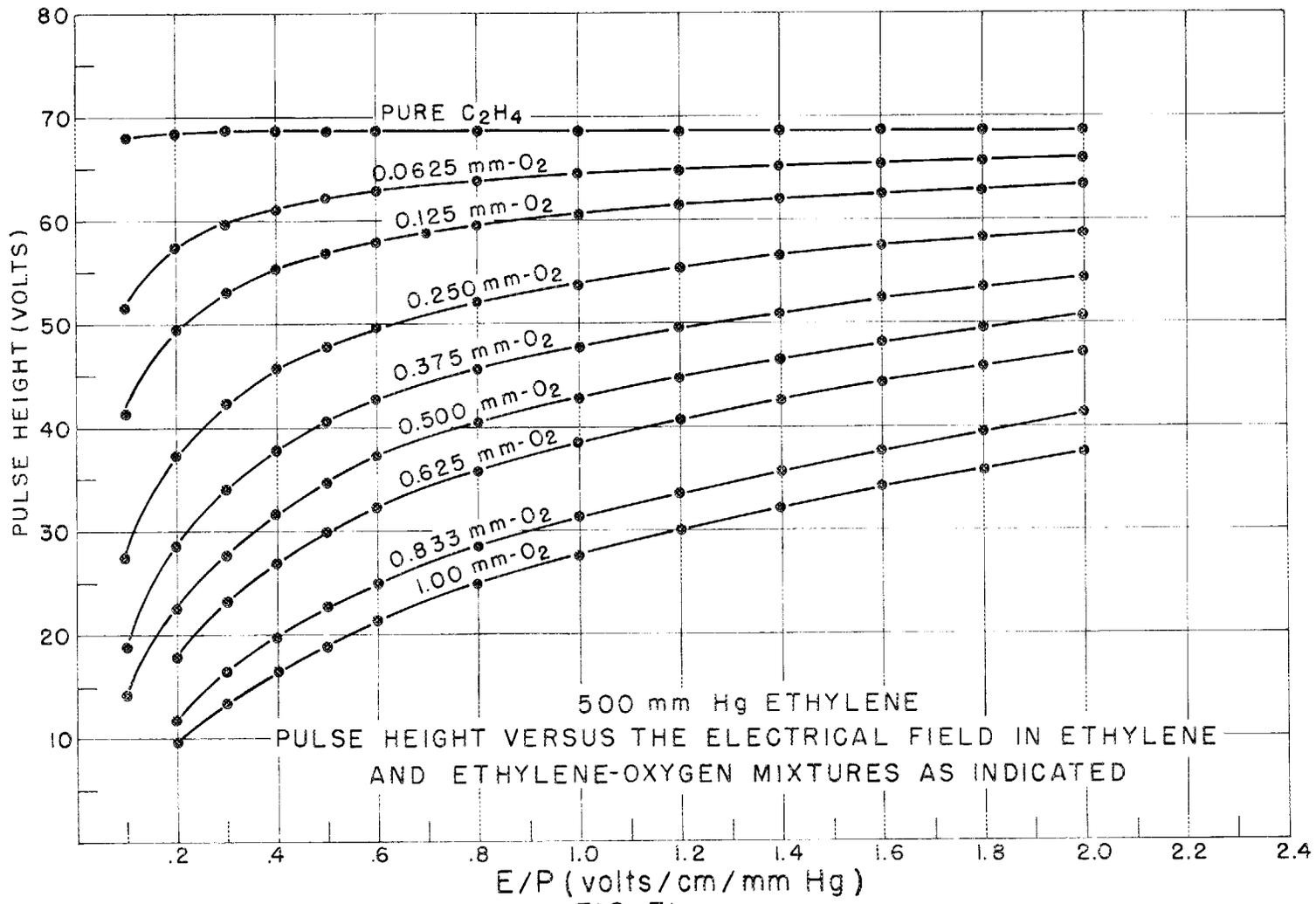


FIG. 3I

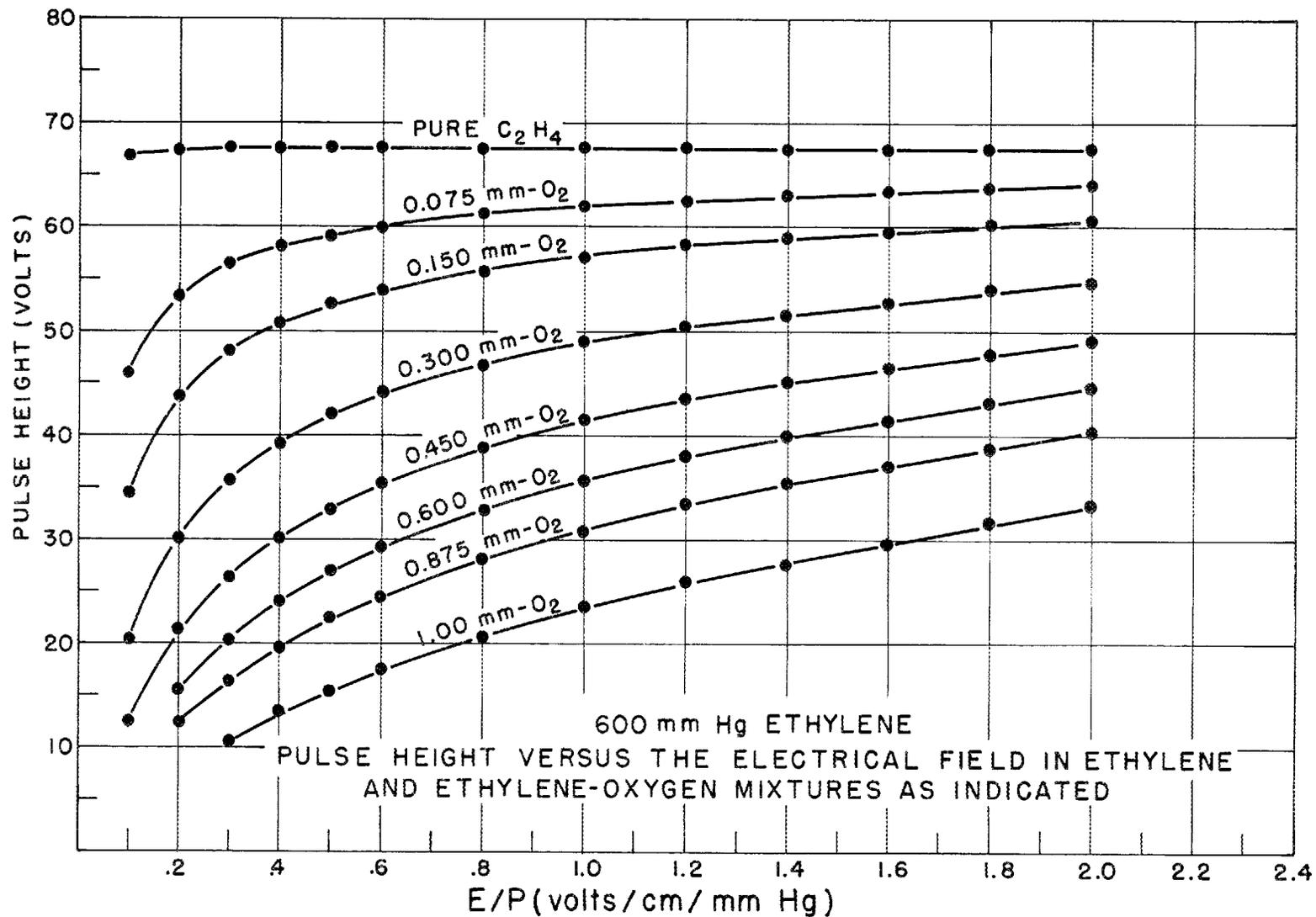
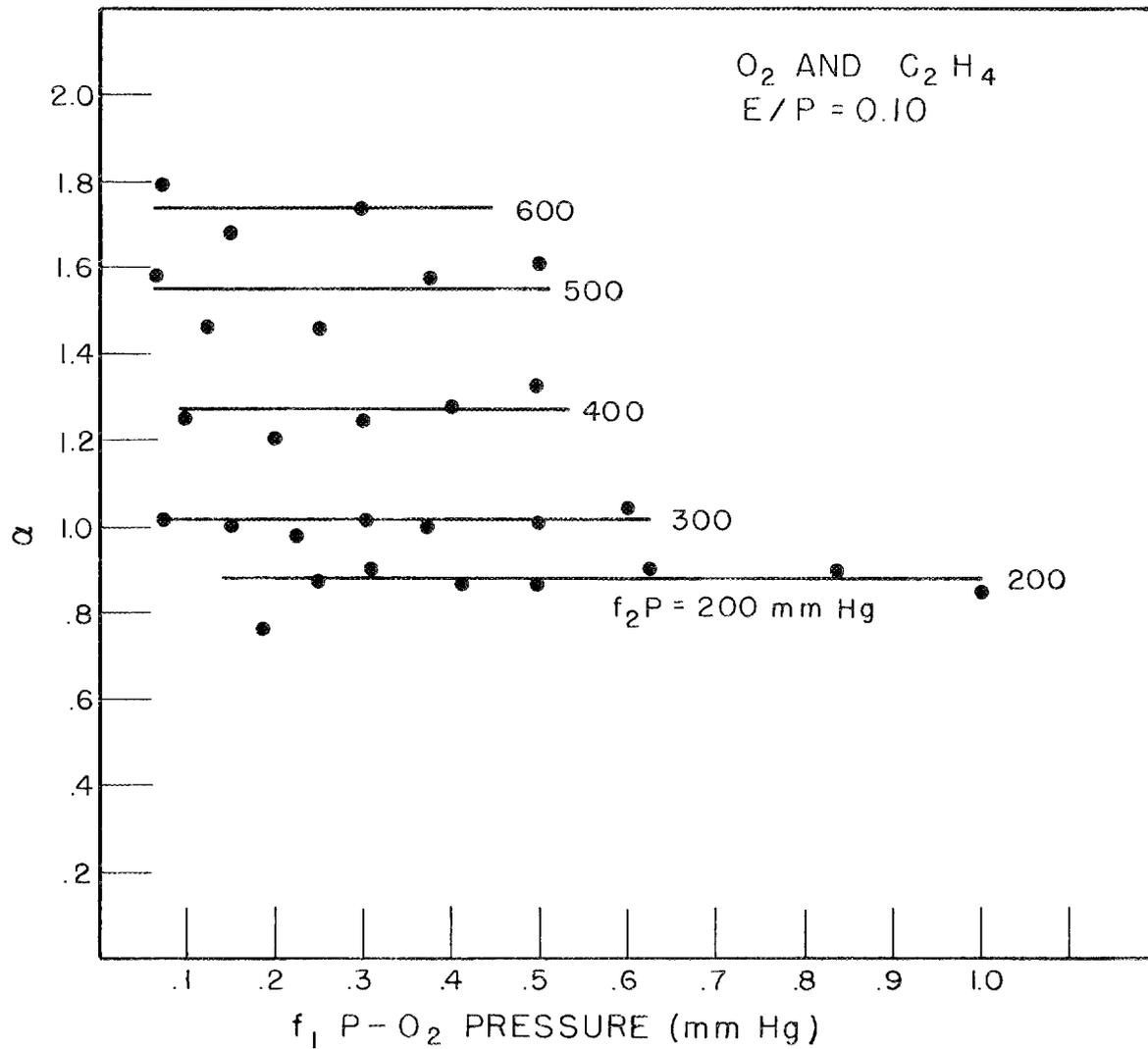


FIG. 32

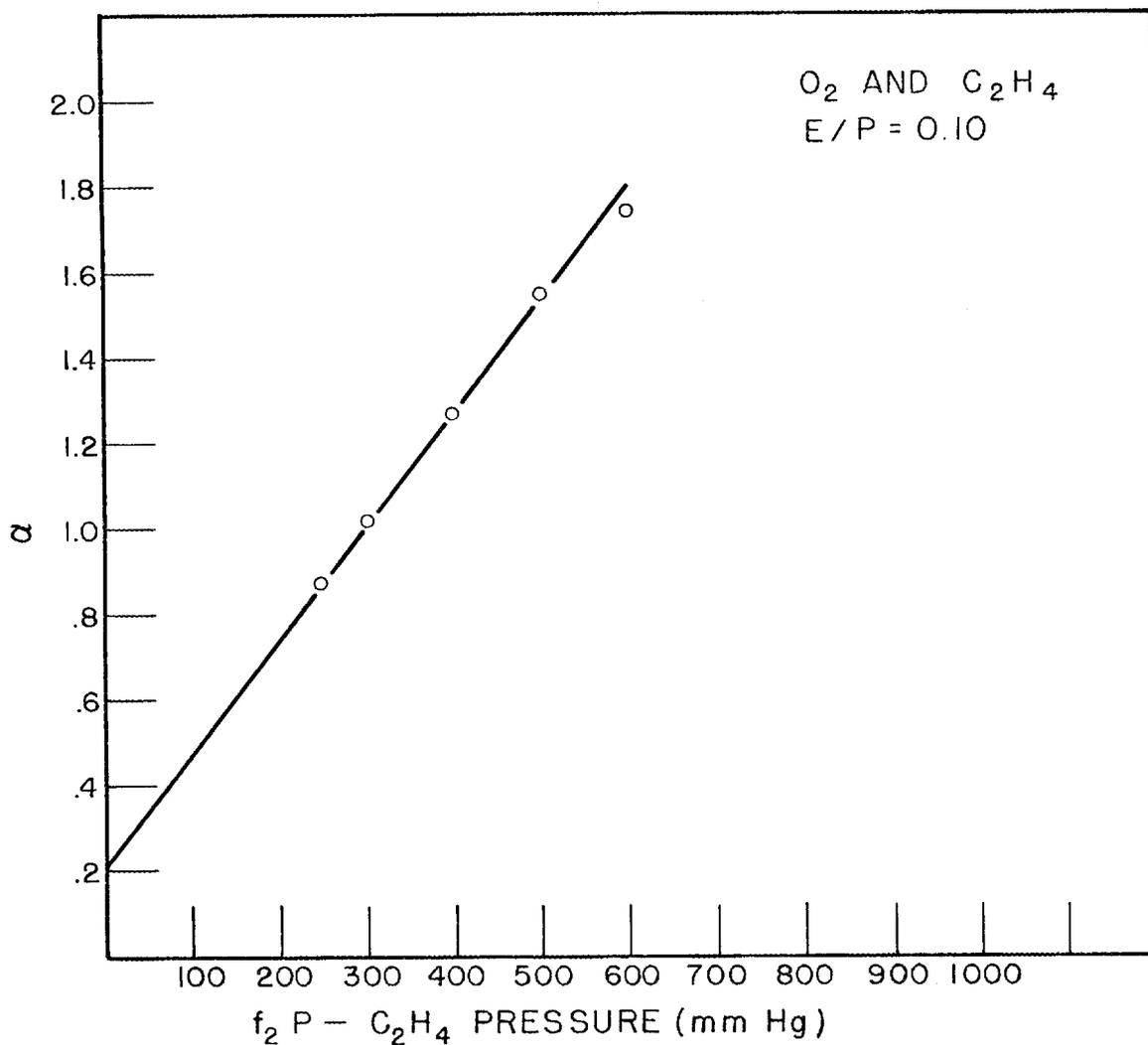
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR $E/P = 0.10$

FIG. 33

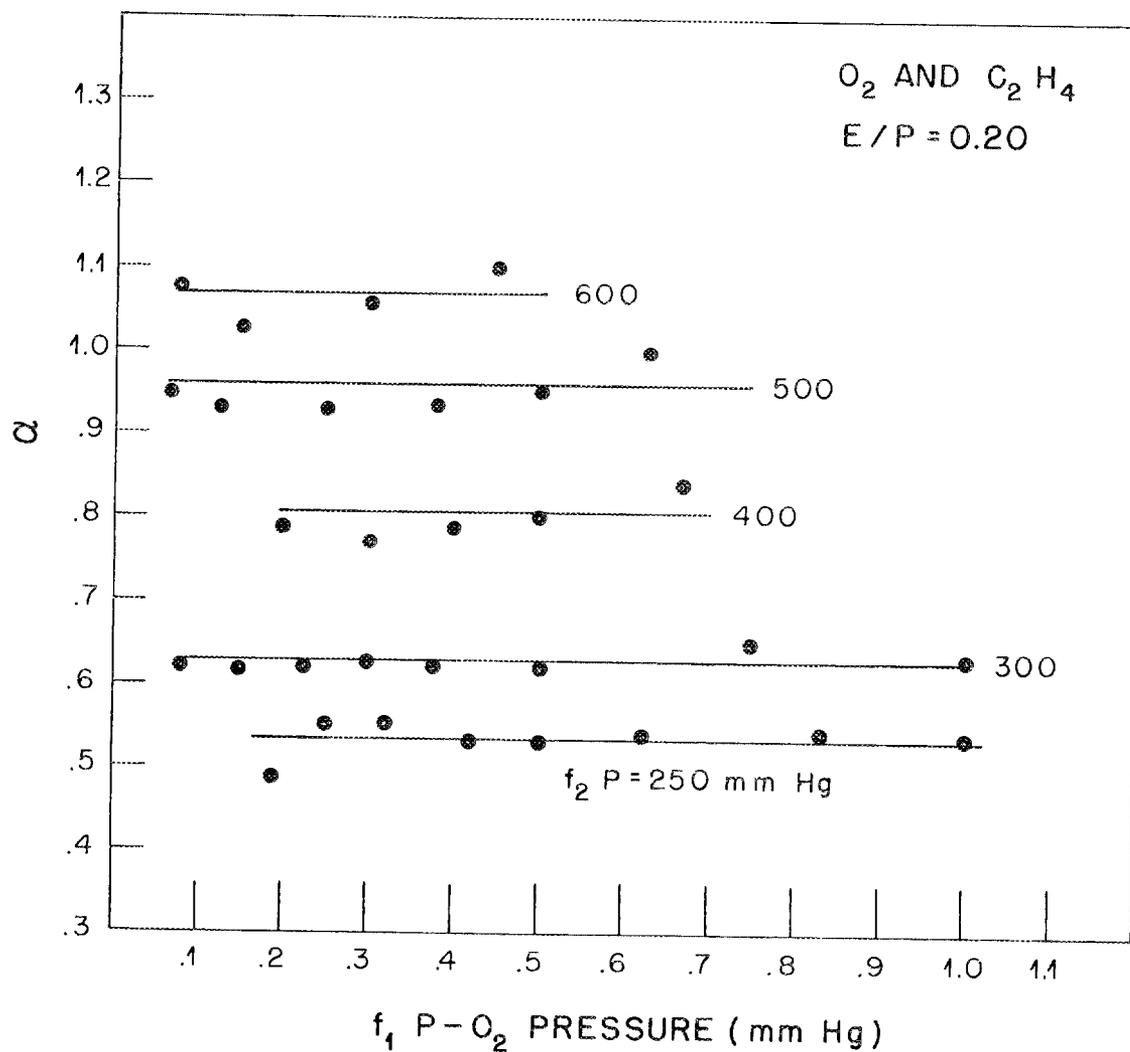
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 0.10

FIG. 34

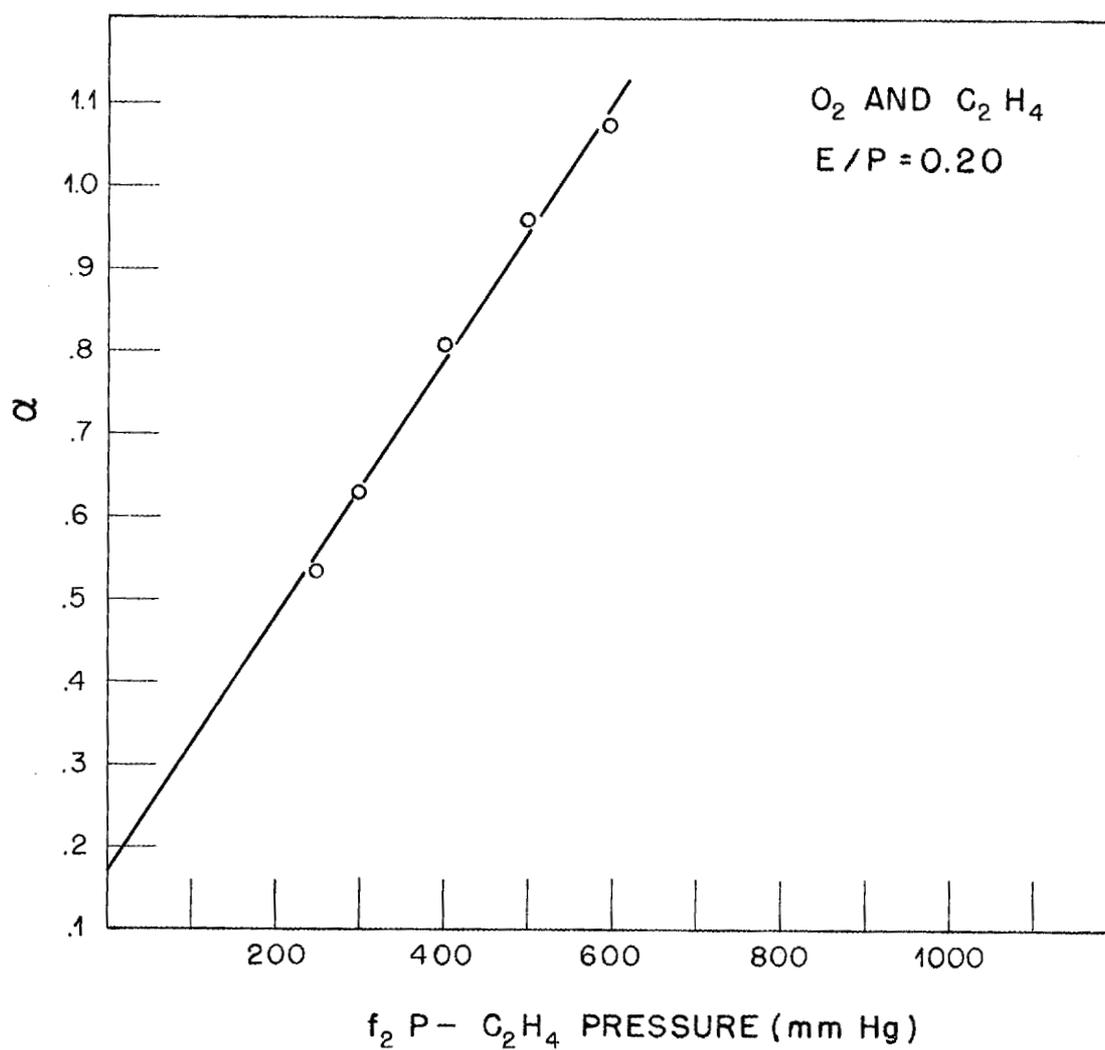
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE - OXYGEN PRESSURE FOR E/P = 0.20

FIG. 35

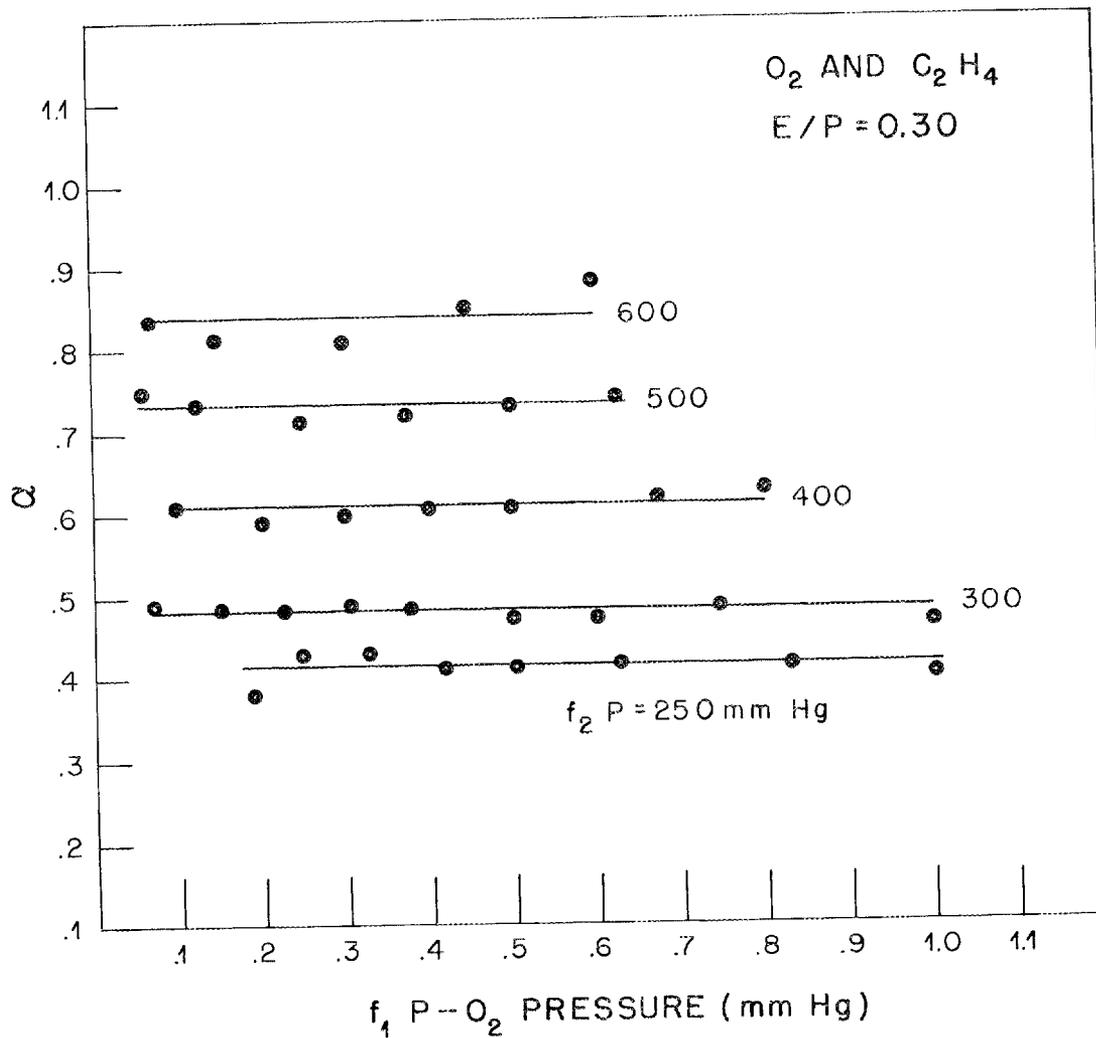
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 0.20

FIG. 36

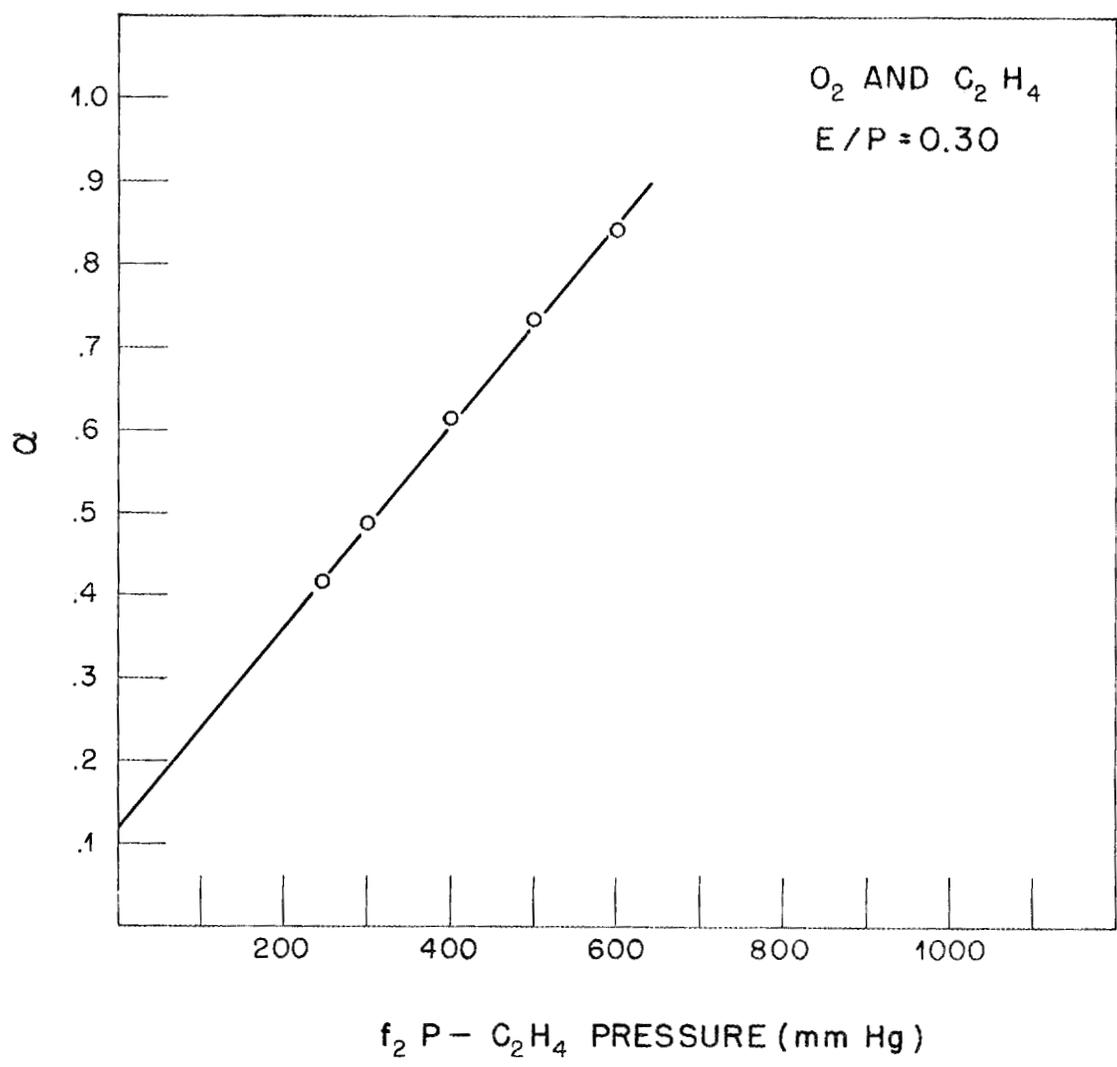
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 0.30

FIG. 37

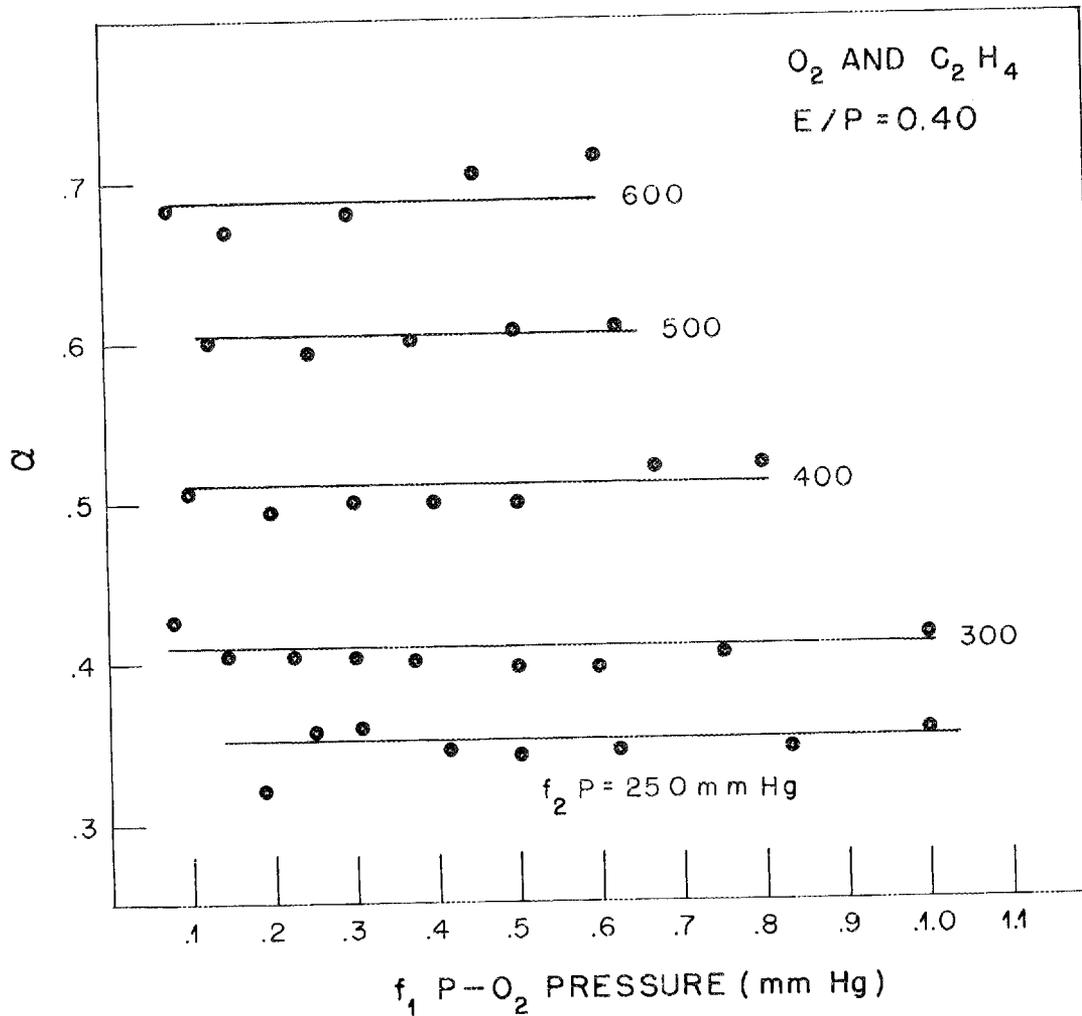
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 0.30

FIG. 38

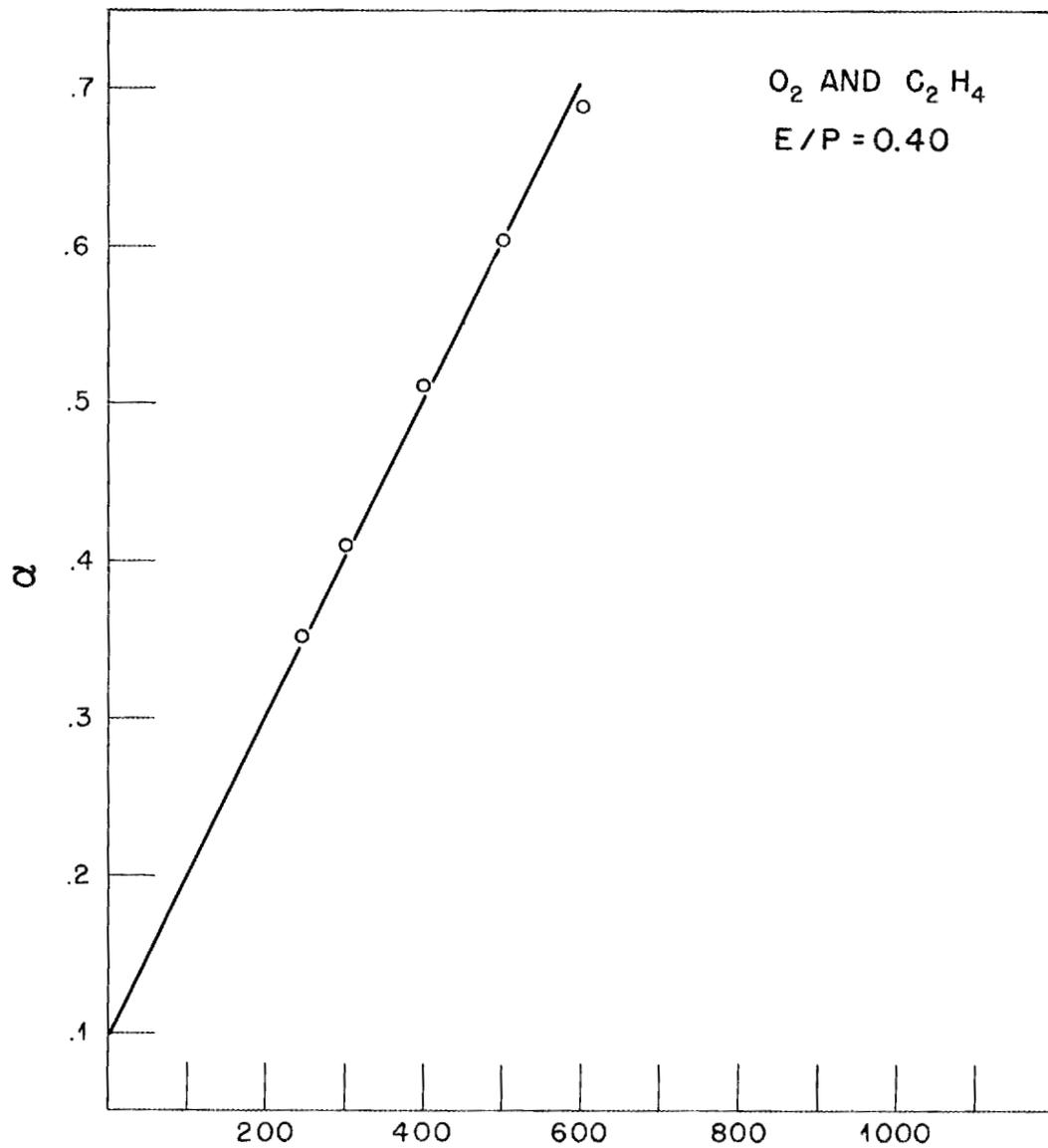
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 0.40

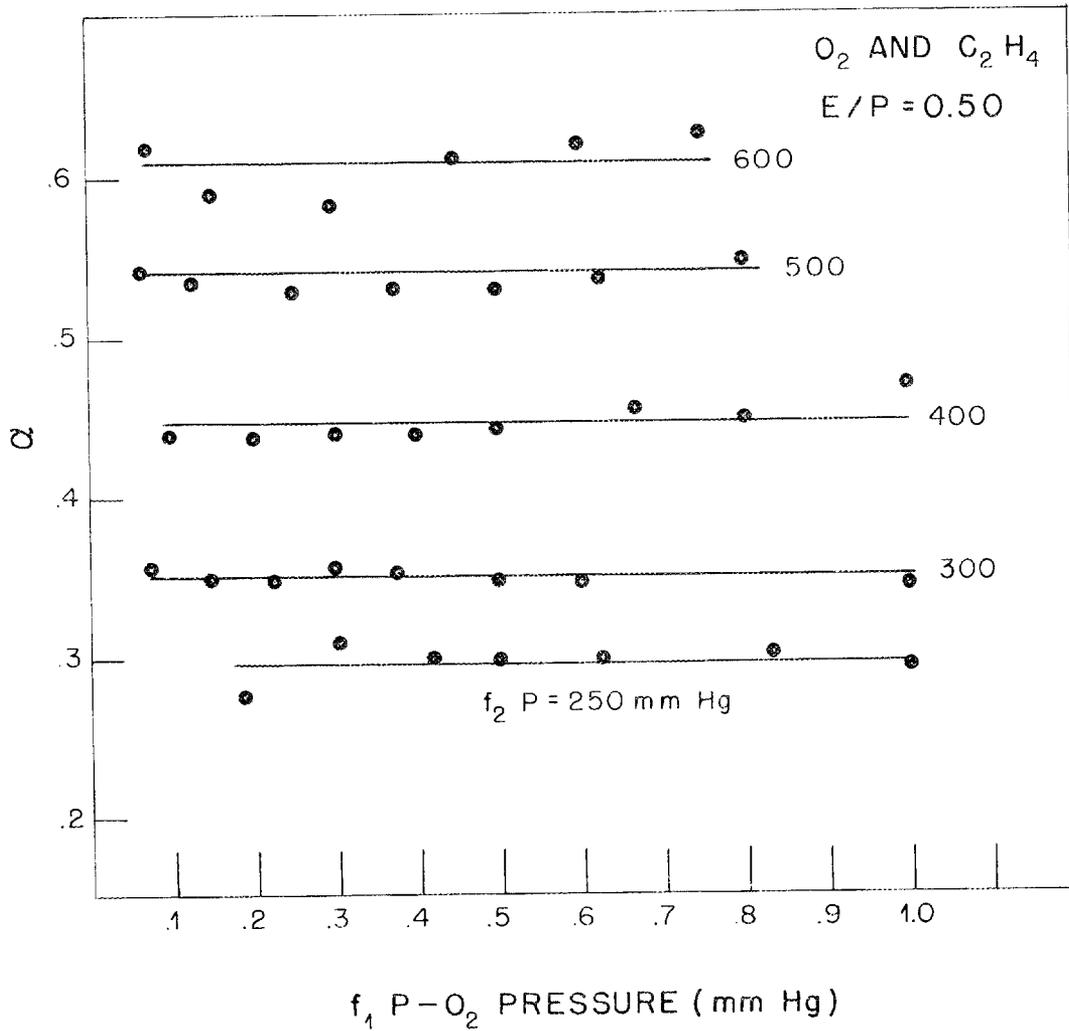
FIG. 39

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f₂ P - C₂H₄ PRESSURE (mm Hg)
THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 0.40
FIG. 40

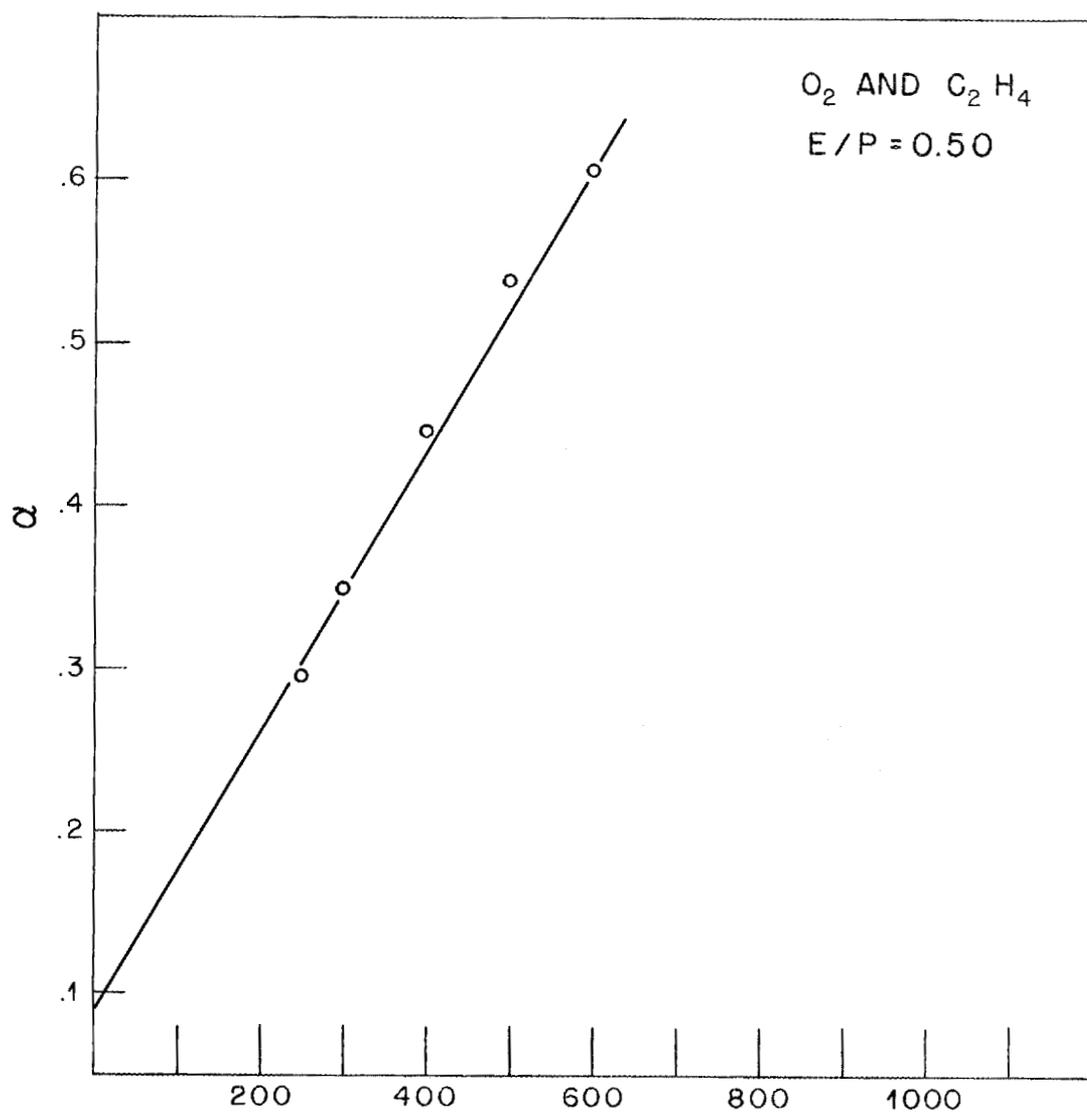
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE - OXYGEN PRESSURE FOR E/P = 0.50

FIG. 41

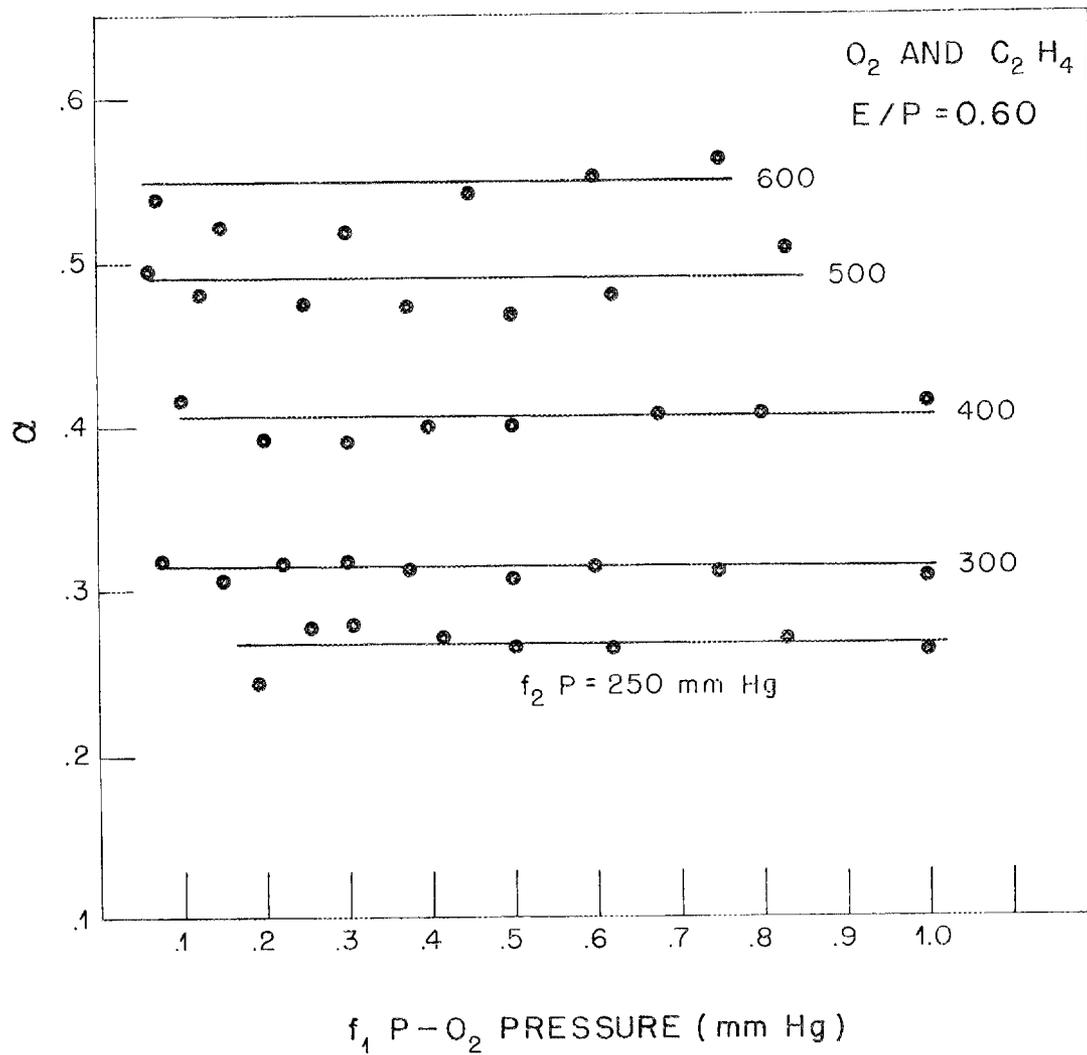
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$f_2 P - C_2H_4$ PRESSURE (mm Hg)
THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 0.50$

FIG. 42

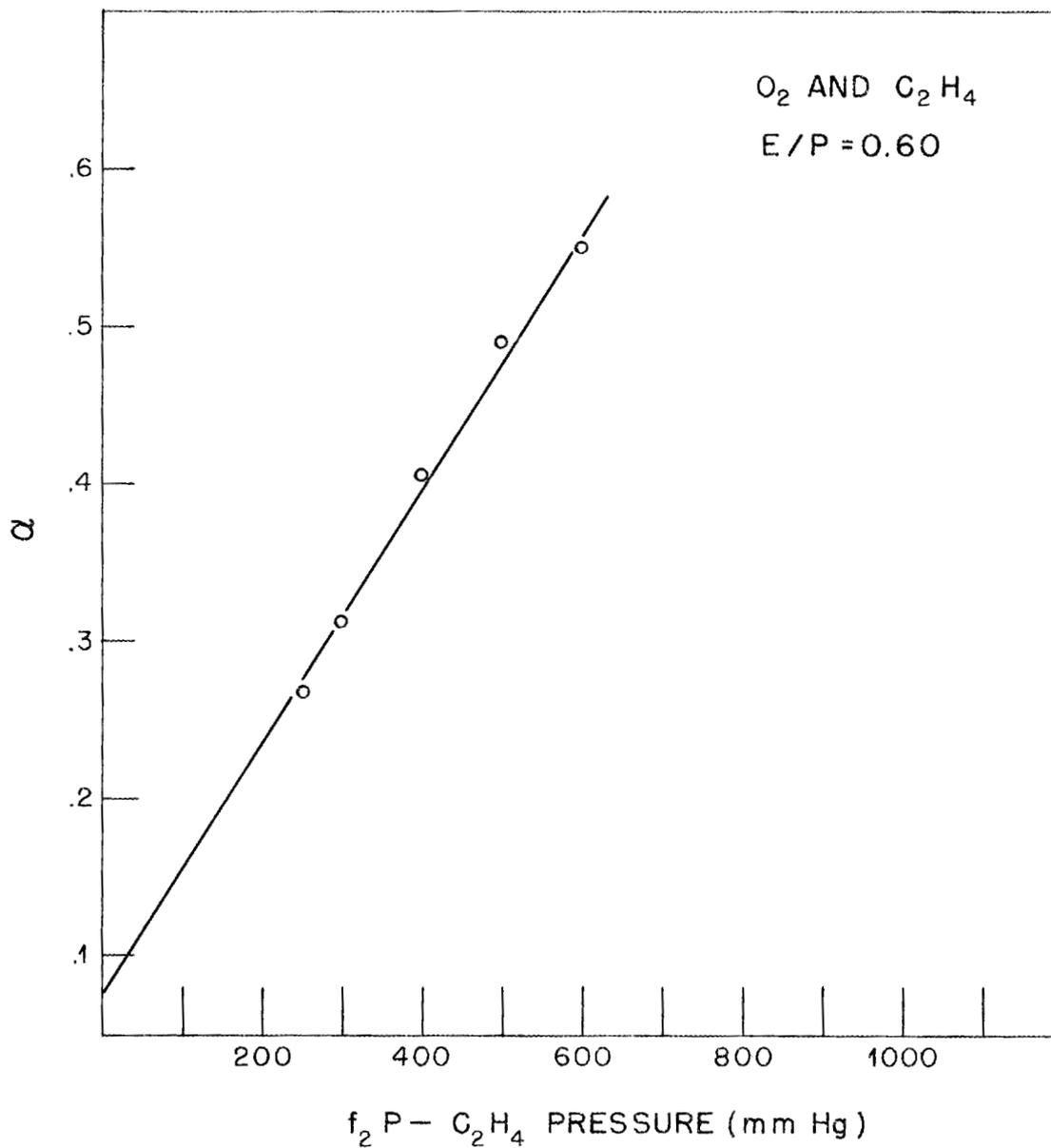
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 0.60

FIG. 43

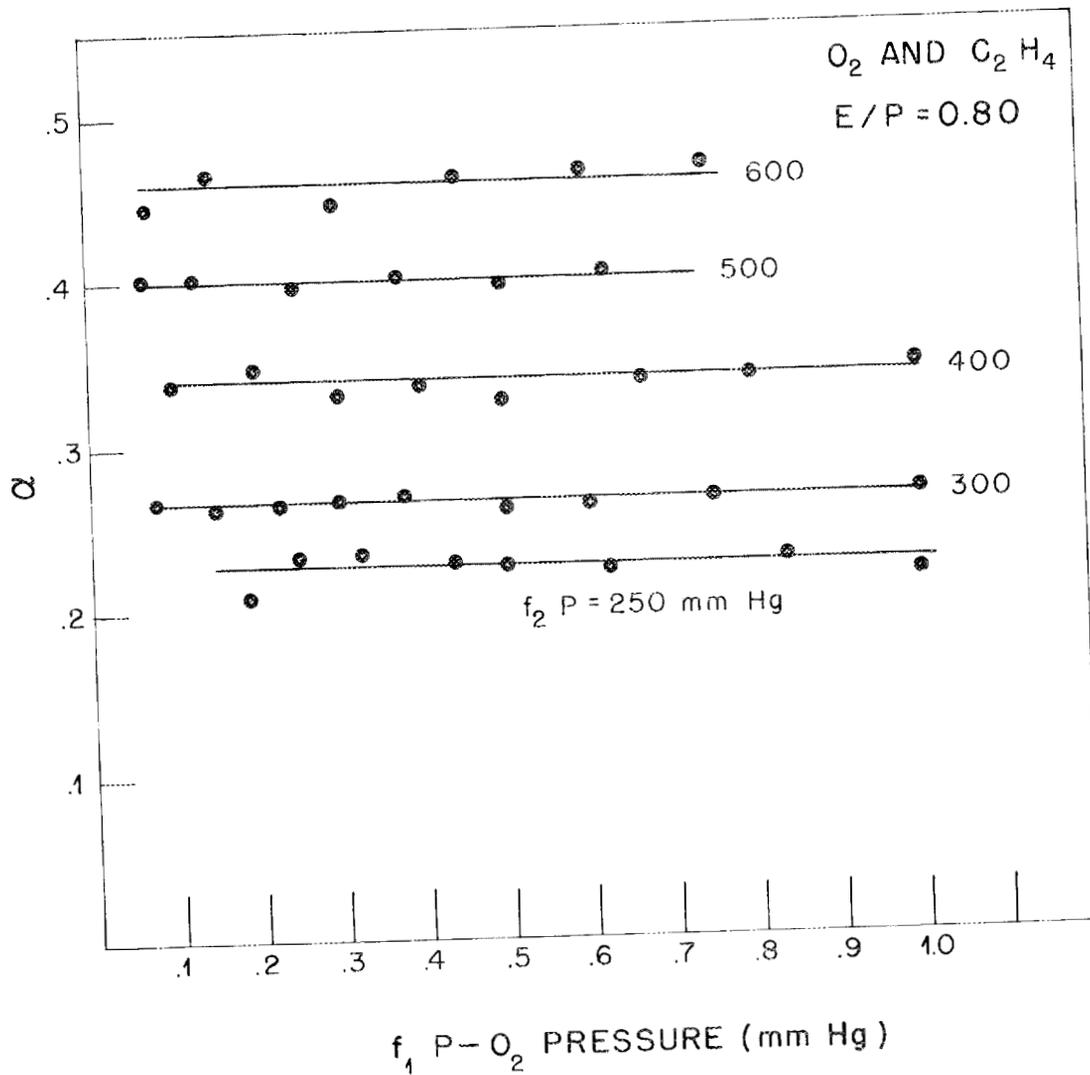
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 0.60$

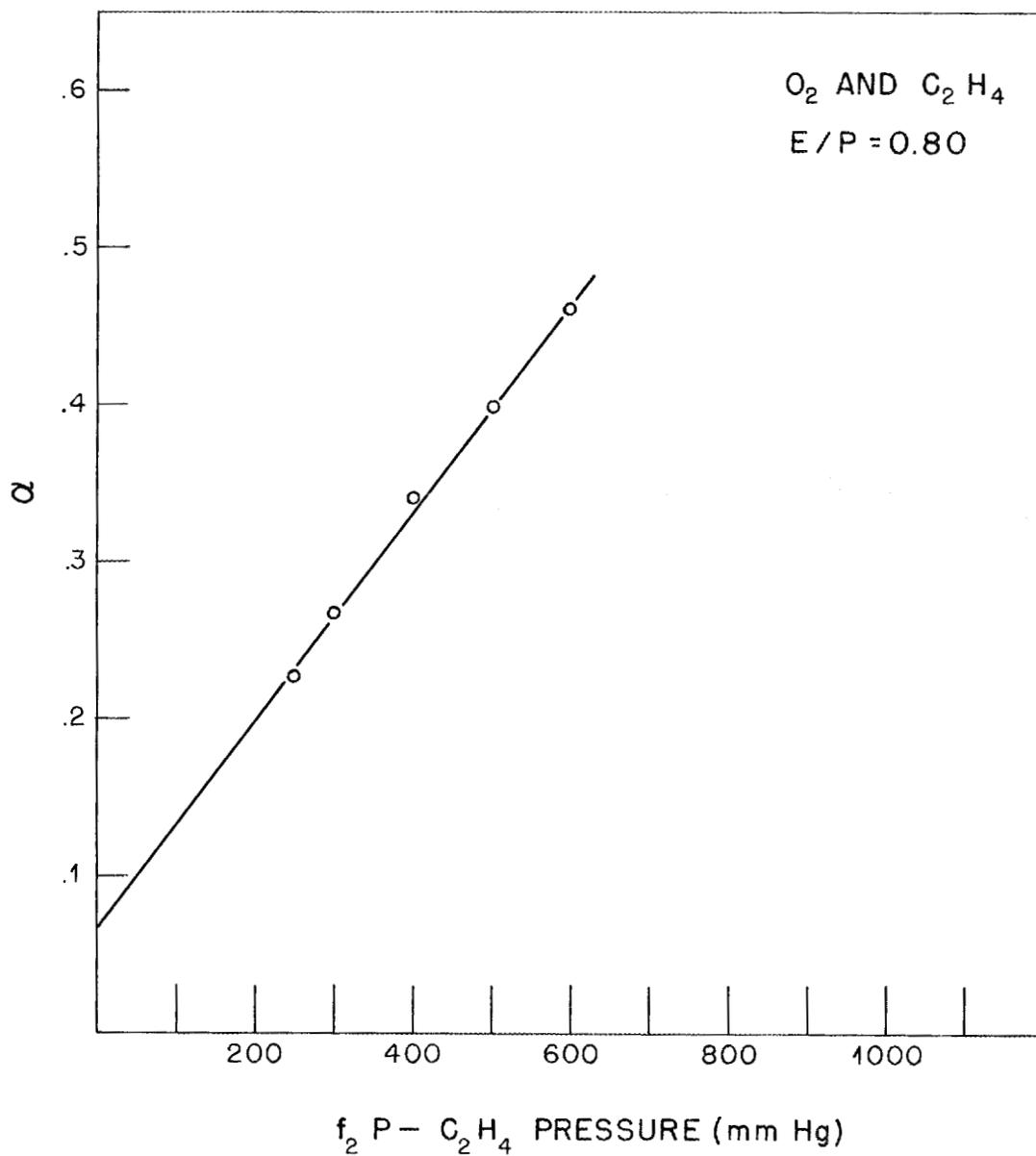
FIG. 44

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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 0.80
FIG. 45

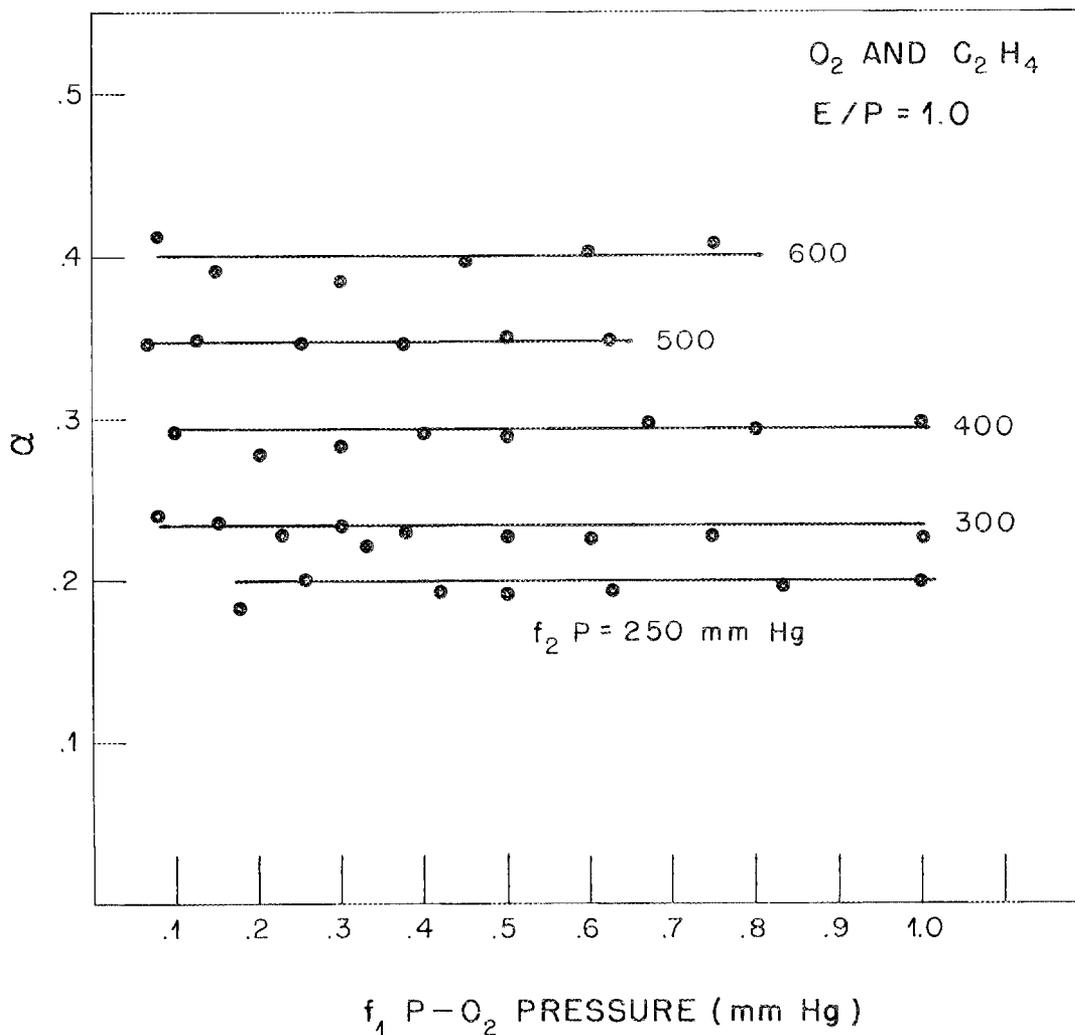
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 0.80

FIG. 46

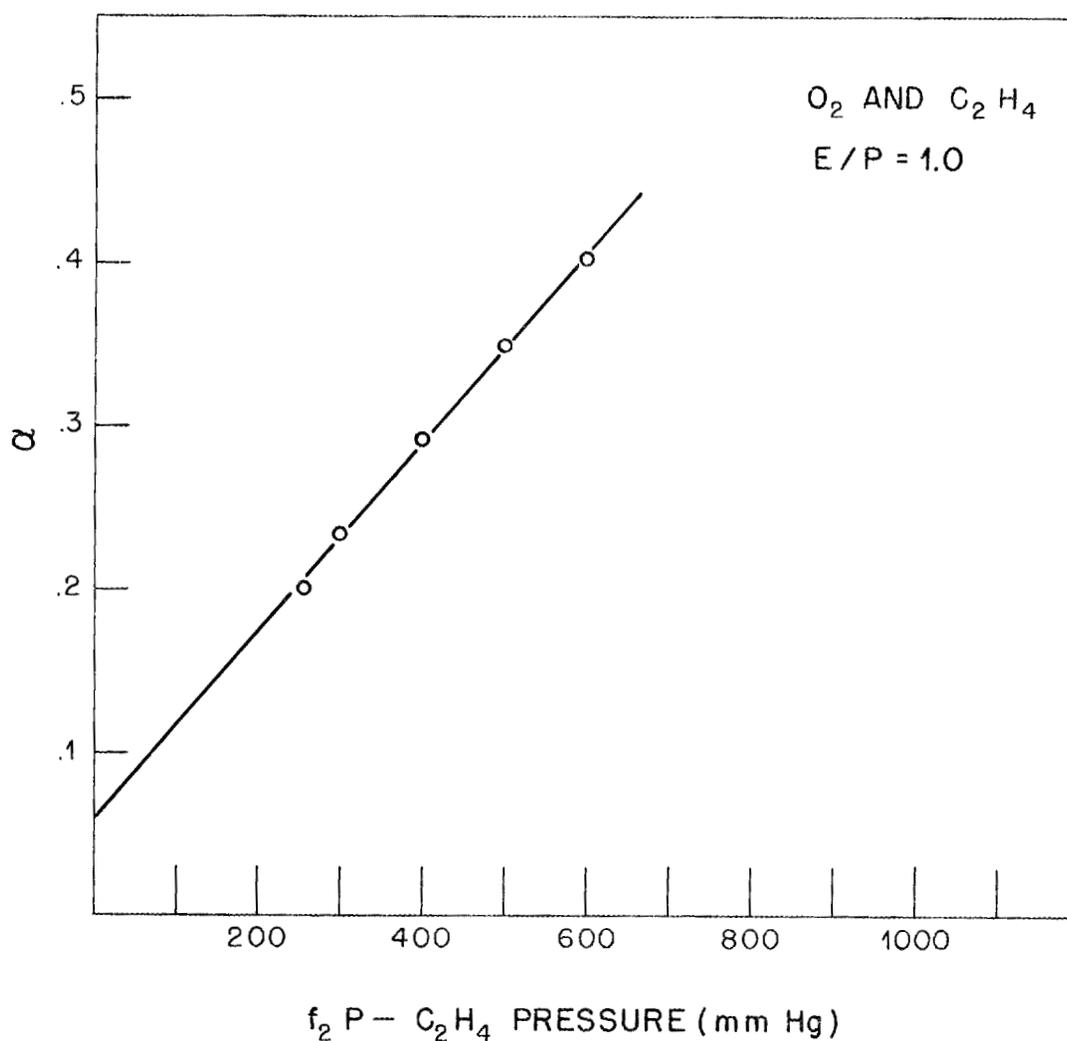
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 1.0

FIG. 47

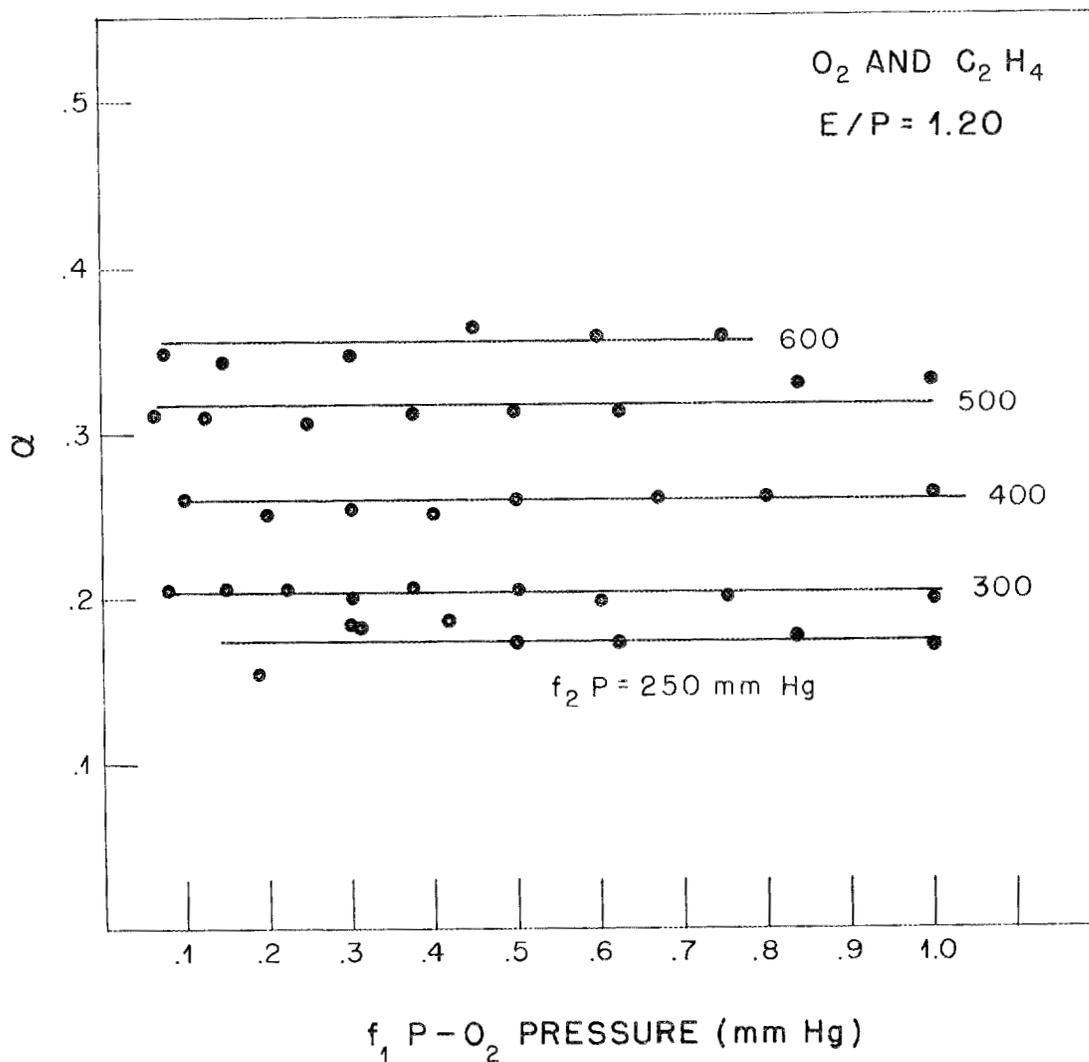
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P=1.0

FIG. 48

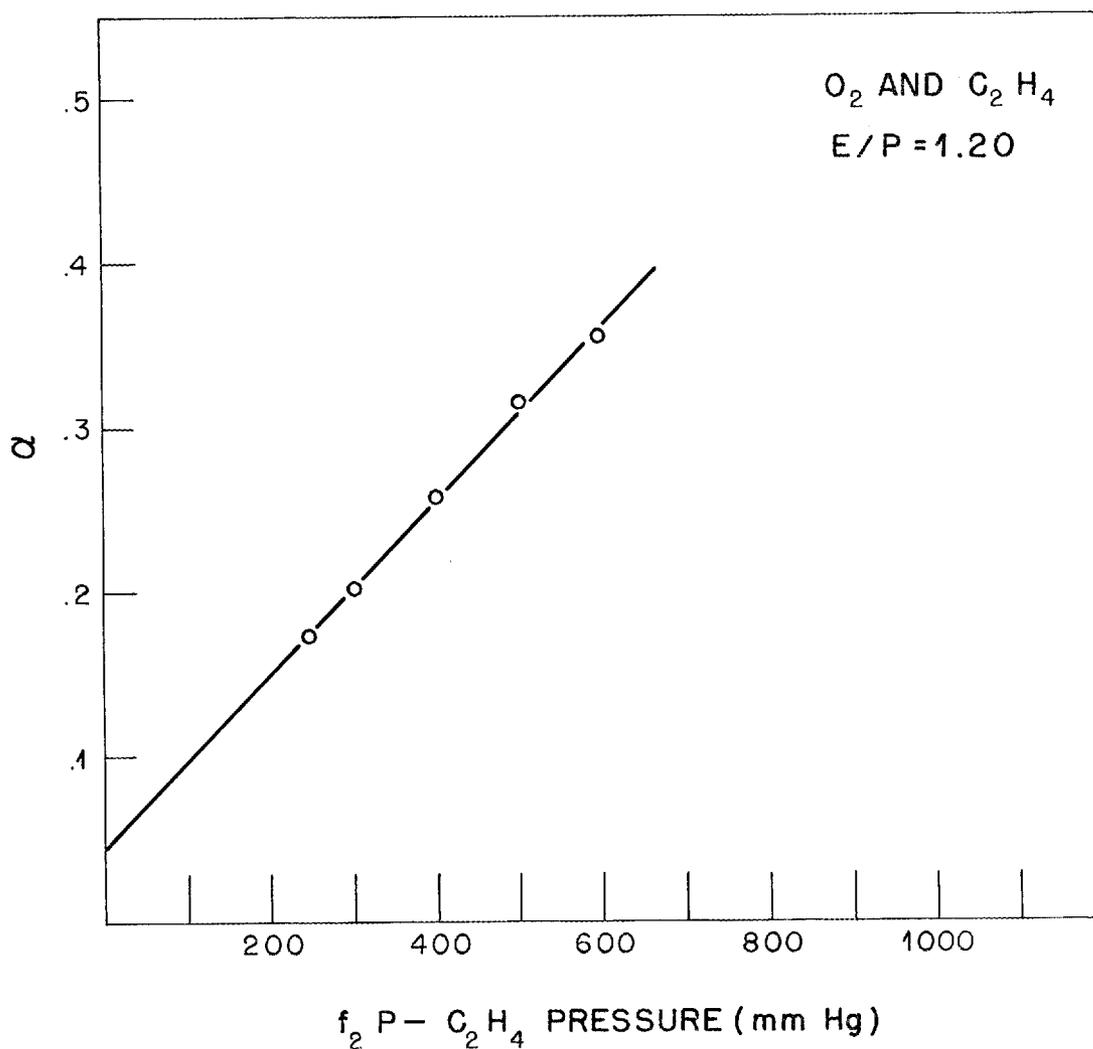
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE - OXYGEN PRESSURE FOR $E/P = 1.20$

FIG. 49

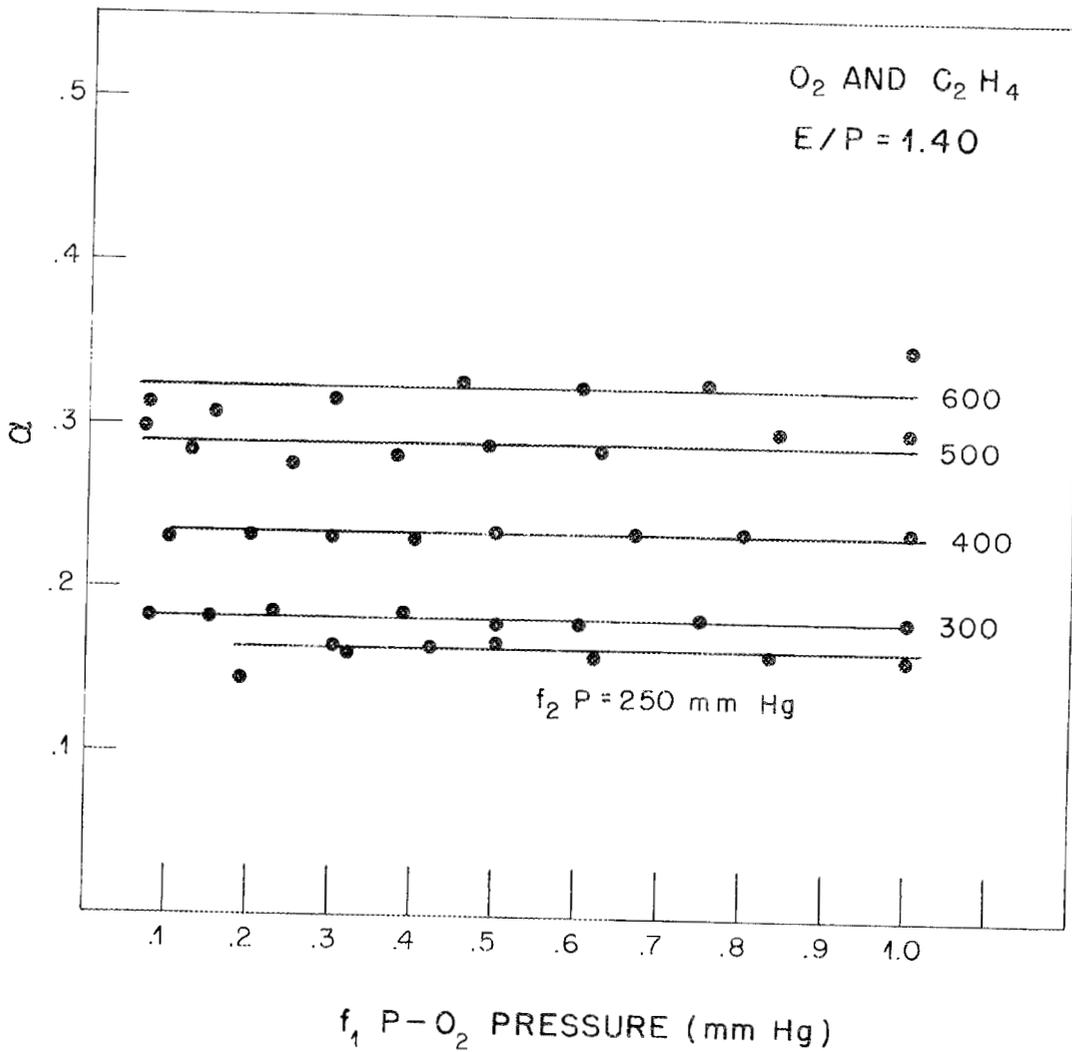
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 1.20$

FIG. 50

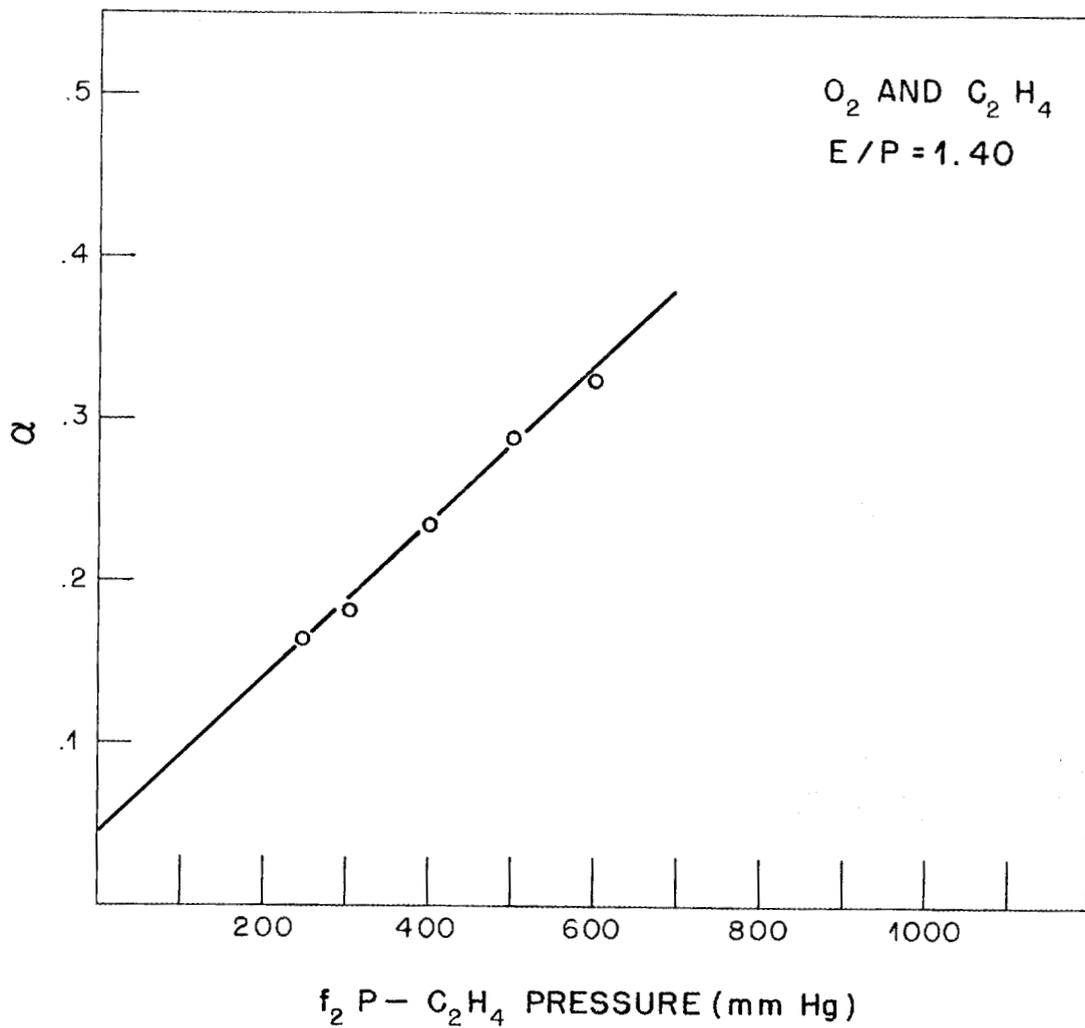
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE - OXYGEN PRESSURE FOR E/P = 1.40

FIG. 51

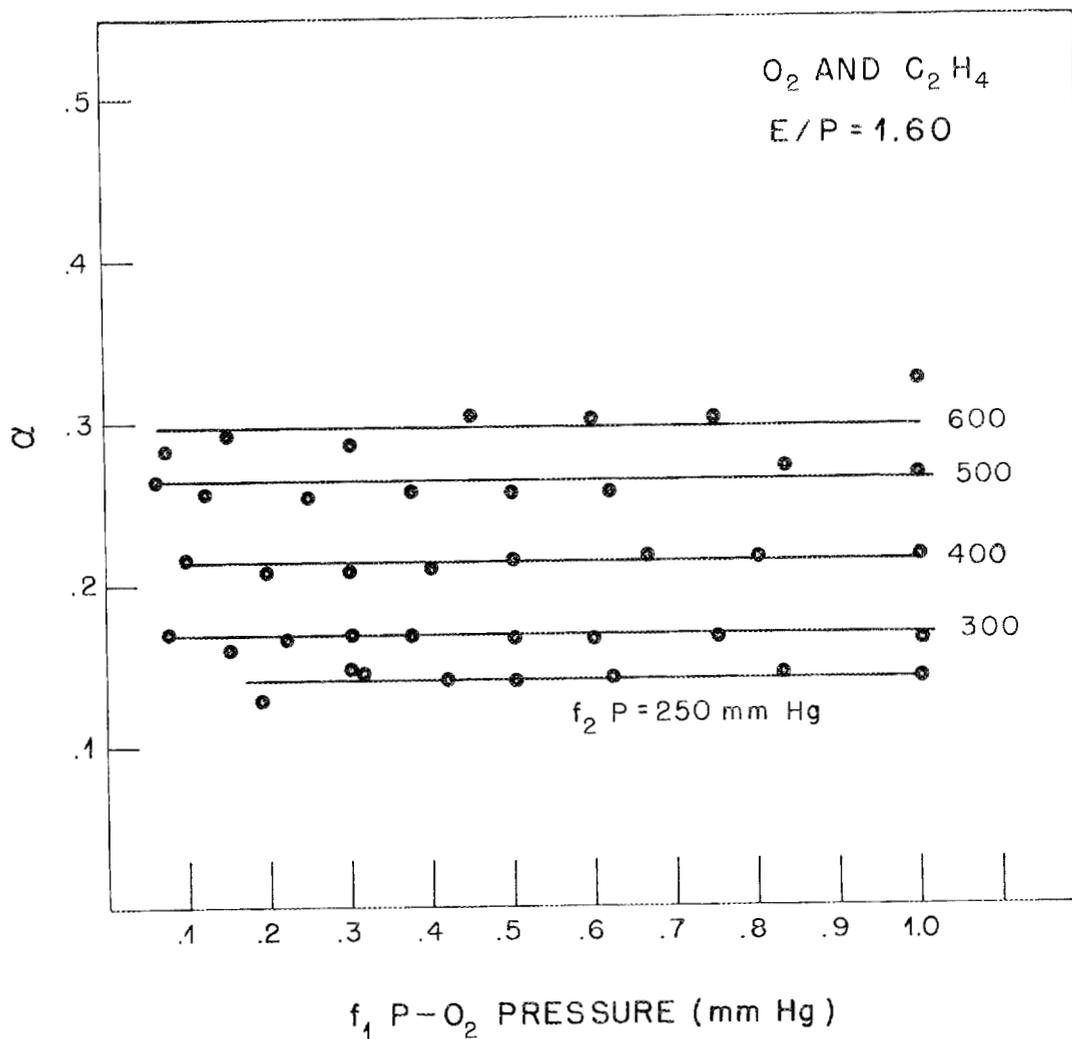
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 1.40$

FIG. 52

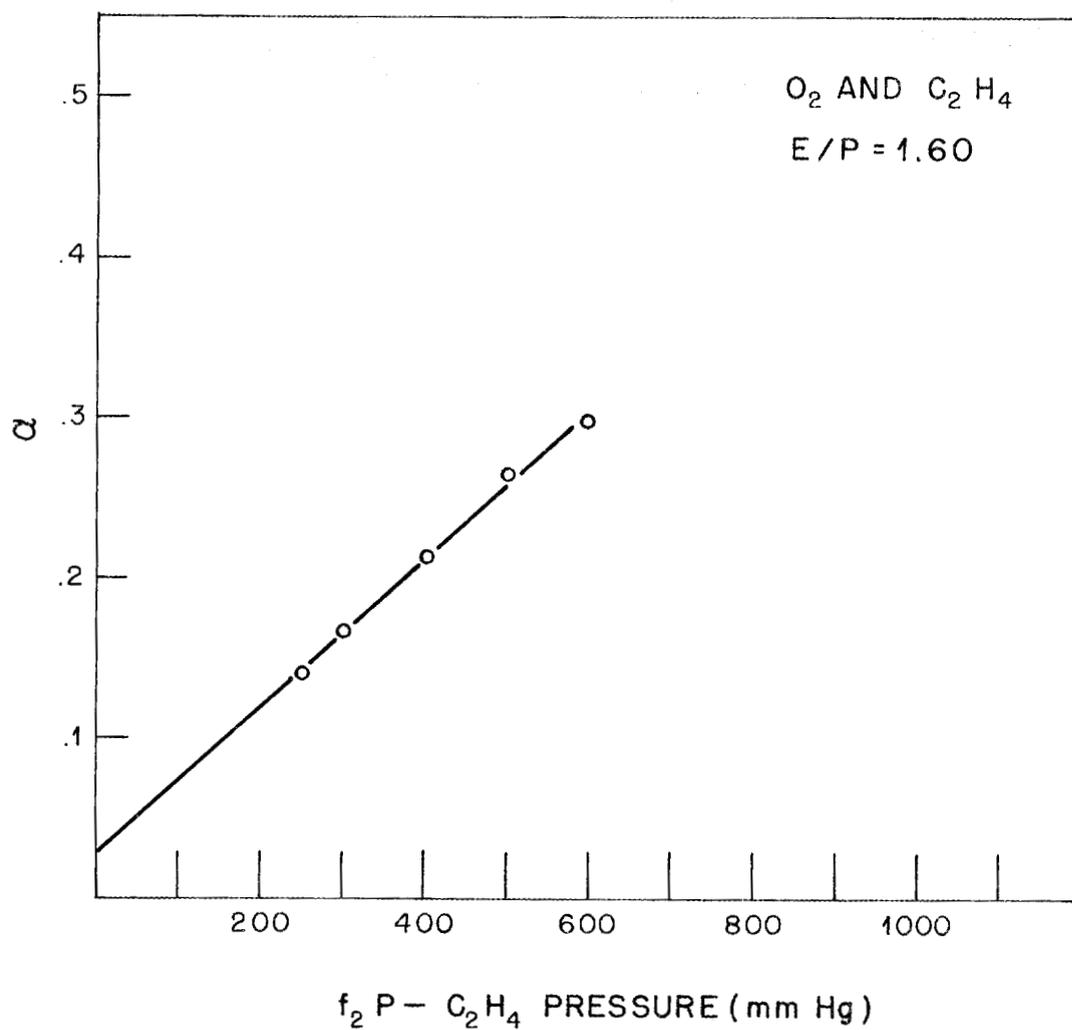
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE -OXYGEN PRESSURE FOR E/P = 1.60

FIG. 53

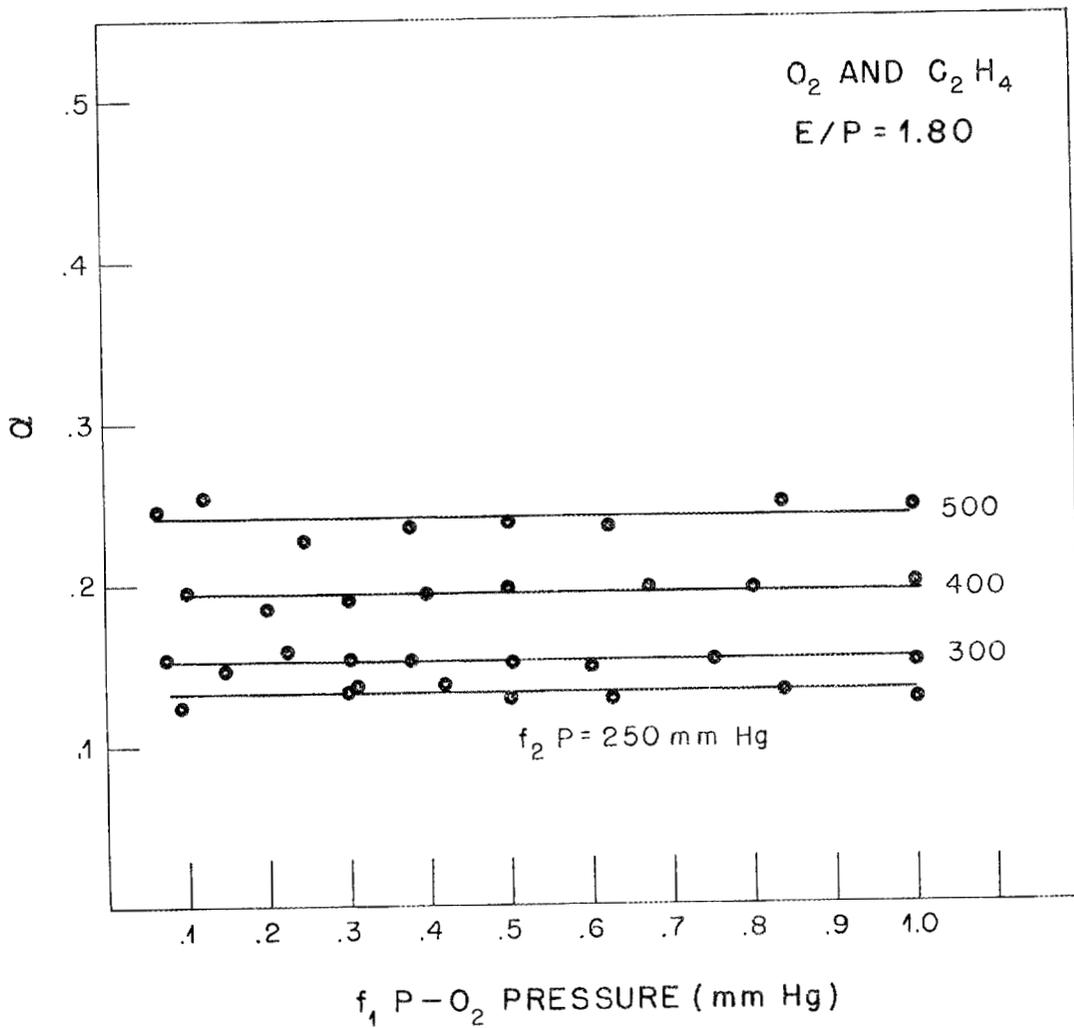
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 1.60$

FIG. 54

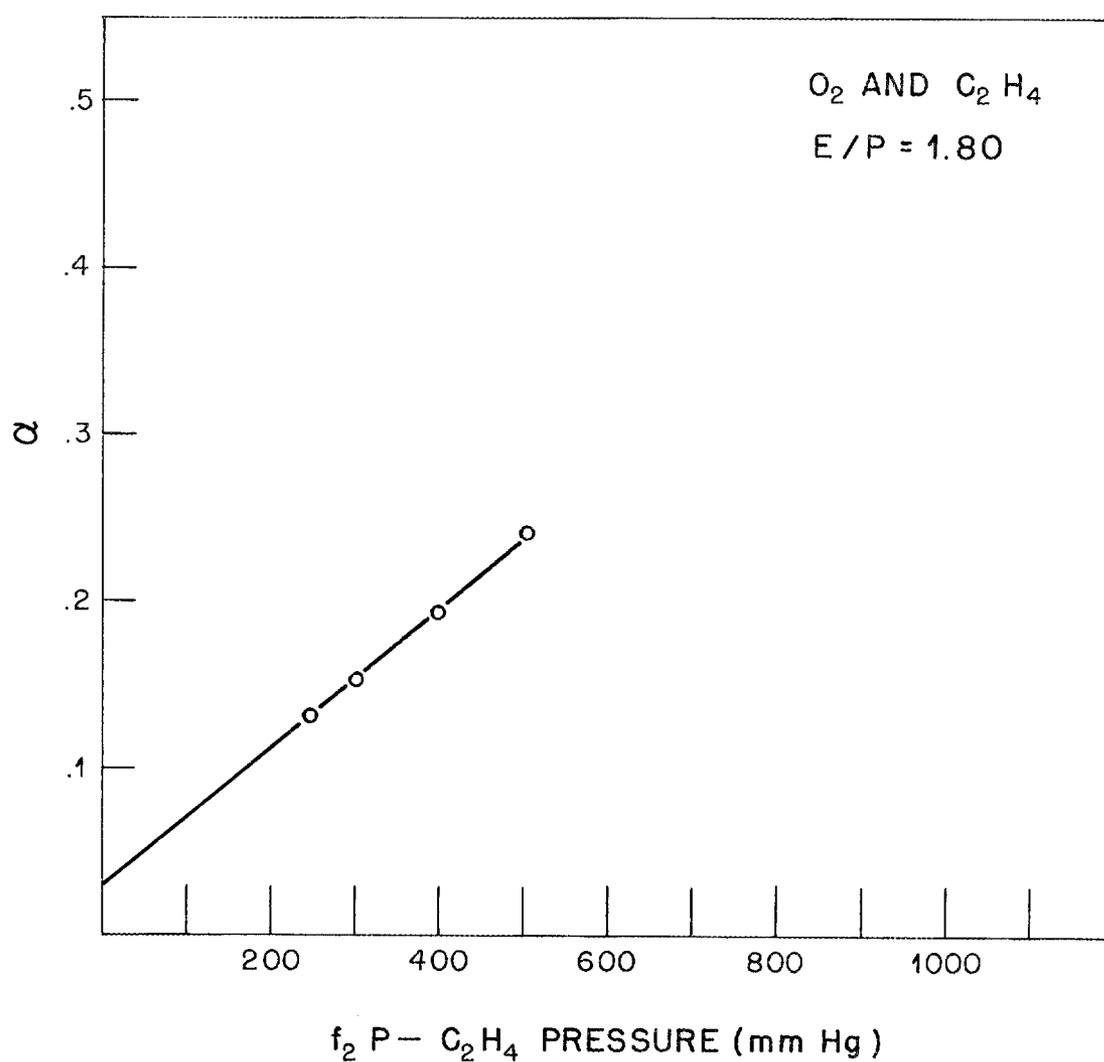
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THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR $E/P = 1.80$

FIG. 55

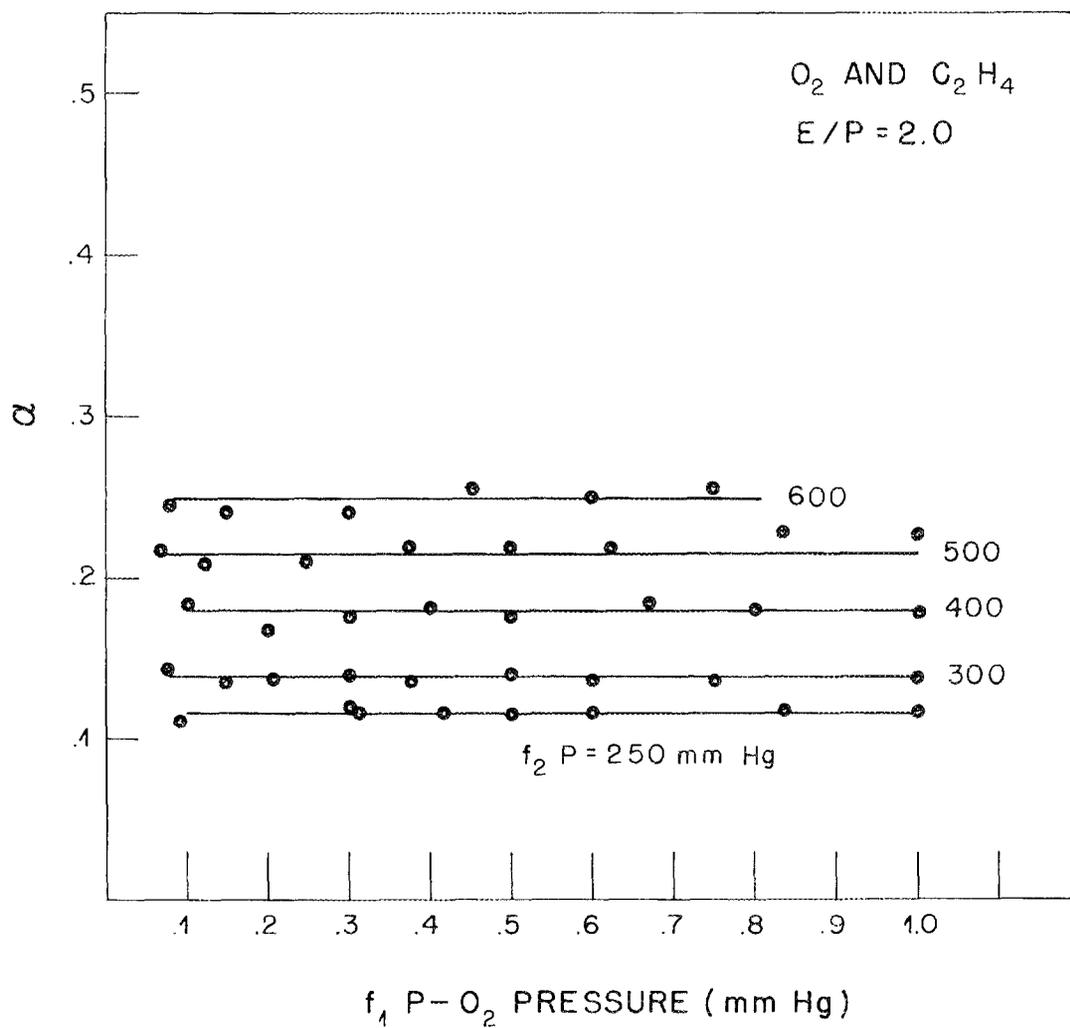
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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR E/P = 1.80

FIG. 56

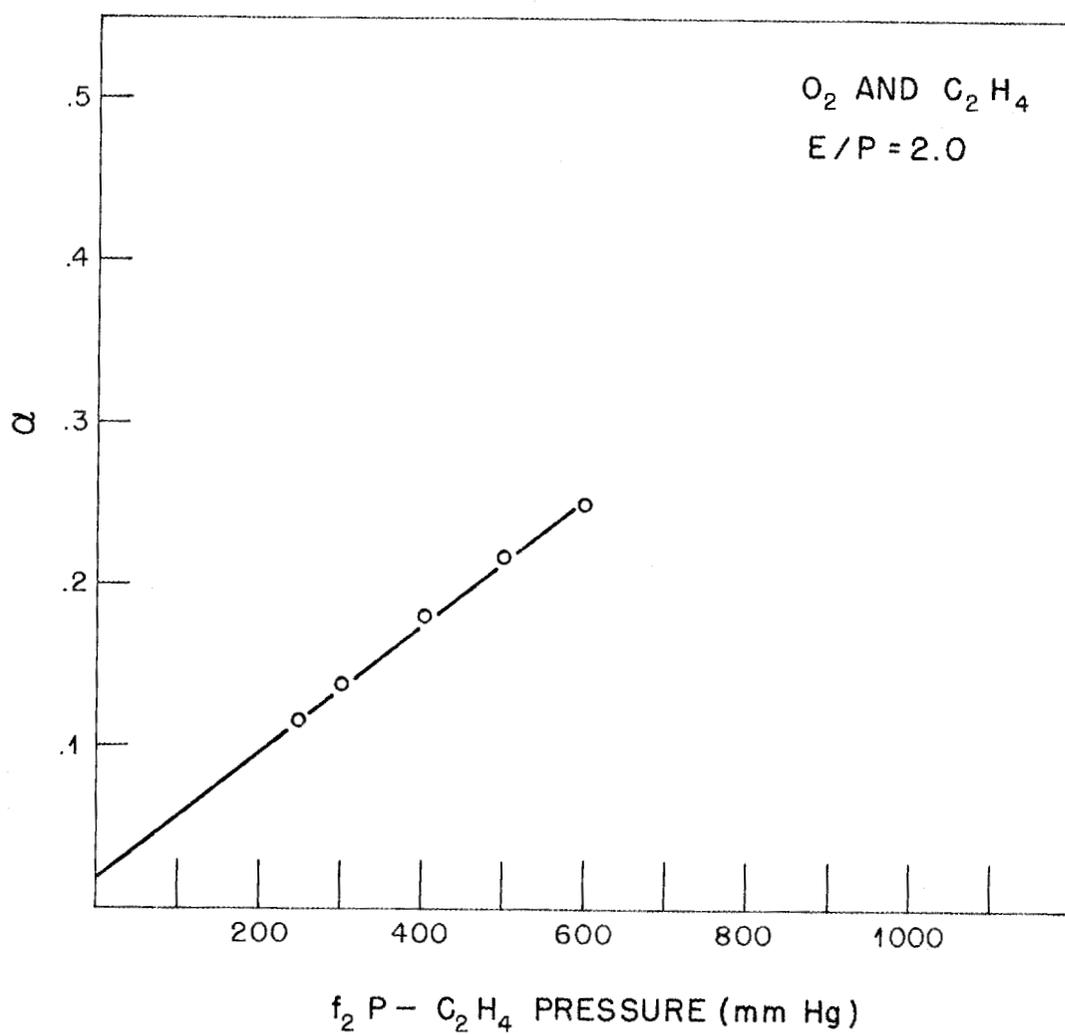
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ORNL-LR-DWG. 37474



THE ATTACHMENT COEFFICIENT α AS A FUNCTION OF
ETHYLENE-OXYGEN PRESSURE FOR E/P = 2.0

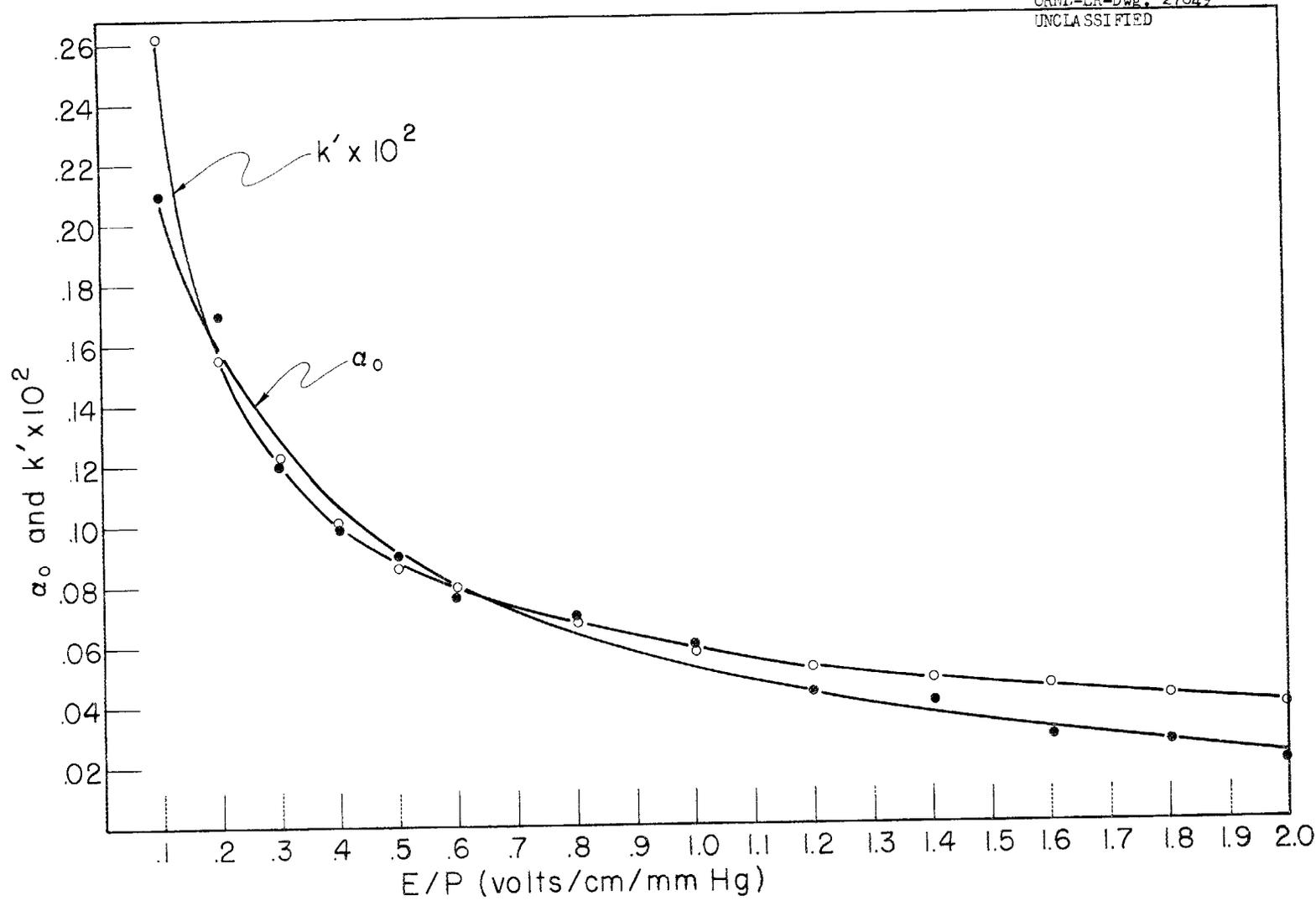
FIG. 57

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THE MEAN ATTACHMENT COEFFICIENT α AS A FUNCTION
OF ETHYLENE PRESSURE FOR $E/P = 2.0$

FIG. 58



COEFFICIENTS α_0 AND k' FOR $O_2-C_2H_4$ AS A FUNCTION OF E/P
FIG. 59

coefficient, α , given by Eq. (18), reduces to the form required by experiment, Eq. (23), with either of two conditions:

(a) $\lambda_1 \gg C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P$, or (b) $\lambda_2 + \lambda_1 \ll C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P$.

For condition (a),

$$\alpha = \frac{\lambda_1}{\lambda_1 + \lambda_2} \beta + k f_2 P \quad (24a)$$

while condition (b) gives

$$\alpha = \beta + k f_2 P \quad (24b)$$

We have shown in connection with the O_2-N_2 data that $\frac{\lambda_1}{\lambda_1 + \lambda_2} \ll 1$; thus if condition (a) holds, α_0 (in Eq. 23) would have to be less than β by a large factor. On the other hand, if condition (b) holds, α_0 would be of the same order as β . When Bradbury's value of h , the probability of capture per collision, is extrapolated to an electron energy of 0.08 volts (corresponding to $E/P = 1.2$ in C_2H_4) and used to obtain α , we find $\alpha = 4 \times 10^{-3}$ as compared to $\alpha_0 = 4 \times 10^{-2}$ at $E/P = 1.2$. Thus β as determined from the Bradbury data is smaller than α_0 by a factor of 10, and one can conclude that condition (b) holds and the value of α , as determined from extrapolating Bradbury's results is a factor of 10 smaller than β . Condition (b) will, of course, not hold at low values of $f_1 P$ and

f_2P , but appears to hold over the entire pressure range covered by the present experiment (f_1P ranged from 0.19 to 1.0 mm Hg, and f_2P ranged from 250 to 600 mm Hg).

CHAPTER IV

CONCLUSION

A study of the processes of electron capture to O_2 was carried out for the cases of O_2 mixed with A, N_2 , and C_2H_4 . The behavior of the attachment coefficient, α , was observed to be complex, i.e., its magnitude depended on the pressures of the two gases in the binary mixture and on the nature of the non-attaching gases.

In the case of O_2 -A, electron capture is due to the process $O_2 + e \rightarrow O_2^- + 0$ since the energy of the electrons, even for $E/P < 0.5$, is large enough to produce dissociation. True pressure dependence for this case was not observed, but it was found that in the region of $0.3 \leq E/P \leq 0.5$, α decreased with increasing P_{O_2}/P_A . This implies that in this region of electron energy α is a decreasing function of energy, and that the mean electron energy decreases with increasing P_{O_2}/P_A .

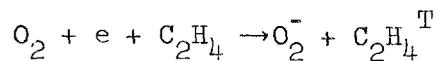
For the case of O_2 - N_2 , α depends on the pressure of O_2 ($f_1 P$) and the pressure of N_2 ($f_2 P$). The complete expression for α was found to be $\alpha = Af_1 P + Bf_2 P + Cf_1 P f_2 P$. These results were interpreted in terms of an extension of the Bloch-Bradbury mechanism where the initial capture leads to an unstable ion O_2^{-*} . An analysis of the results leads to the cross section for the collisional stabilization of O_2^{-*} by O_2 and by N_2 ; the values were found to be $3 \times 10^{-15} \text{ cm}^2$ for O_2 and $6 \times 10^{-17} \text{ cm}^2$ for N_2 . The magnitude of the experimental constant C could not be understood on the basis of the usual gas kinetic theory for three-body

collisions. It was suggested that the complex $O_2^-N_2$ is formed having a life time which is long compared to the vibration time of the molecule, and is long compared to the time for electron emission from O_2^{-*} .

The results for α in the case of $O_2-C_2H_4$ mixtures were expressed as

$$\alpha = \alpha_0 + kf_2P$$

where α_0 and k are pressure independent and f_2P is the pressure of C_2H_4 . These results were shown to be a special case of the detailed model used to explain the O_2-N_2 results. The physical interpretation of the results is as follows: The constant term α_0 arises from the fact that at the lowest C_2H_4 pressure all of the O_2^{-*} have been stabilized by collisions with C_2H_4 molecules. The term kf_2P arises as a result of direct formation of stable O_2^- by reactions of the type



where the T designates the transfer of energy to a C_2H_4 molecule.

BIBLIOGRAPHY

- Bailey, V. A. "On the Attachment of Electrons to Gas Molecules," Phil. Mag., 50 (1925), 825-43.
- Bannon, J., and Brose, H. L. "The Motion of Electrons in Ethylene," Phil. Mag., 6 (1928), 817-24.
- Barbieri, D. "Energy Distribution, Drift Velocity, and Temperature of Slow Electrons in Helium and Argon," Phys. Rev., 84 (1951), 653-58.
- Bates, D. R. and Massey, H. S. W. "The Negative Ions of Atomic and Molecular Oxygen," Phil. Trans. A239 (1943), 269-304.
- Biondi, M. A. "Attachment of Thermal Electrons in Oxygen," Phys. Rev., 84 (1951), 1072.
- Bloch, F. and Bradbury, N. "On the Mechanism of Unimolecular Electron Capture," Phys. Rev., 48 (1935), 689-695.
- Bortner, T. E. and Hurst, G. S. "An Apparatus for Measuring Electron Attachment: Results for Oxygen in Argon," Health Physics, 1 (1958), 39-45.
- Bortner, T. E., Hurst, G. S., and Stone, W. G. "Drift Velocities of Electrons in Some Commonly Used Counting Gases," Rev. Sci. Instr., 28 (1957), 103-108.
- Bowe, J. C., "Drift Velocity of Electrons," Argonne National Laboratory Report ANL-5829 (1958), 14-29.
- Bradbury, N. E. "Electron Attachment and Negative Ion Formation in Oxygen and Oxygen Mixtures," Phys. Rev., 44 (1933), 883-90.
- Branscomb, L. M. "Negative Ions," in Advances in Electronics and Electron Physics. Volume 9. New York: Academic Press, Inc., 1957.
- Brose, H. L. "The Motion of Electrons in Oxygen," Phil. Mag., 50 (1925), 536-46.
- Burch, D. S. and Geballe, R., "Ionic Drift Velocities and Electron Attachment Coefficients in Oxygen," Phys. Rev., 106 (1957), 183-87.
- Chanin, L. M. and Biondi, M. A. "Electron Attachment in Oxygen at Low Energies," Westinghouse Research Laboratories Report 6-94439-7-R5 (1957).

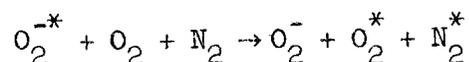
- Craggs, J. D., Thorburn, R., and Tozer, B. A. "The Attachment of Slow Electrons in Oxygen," Proc. Roy. Soc. (Lond.), A240 (1957), 473-83.
- Cravath, A. M. "The Rate of Formation of Negative Ions by Electron Attachment," Phys. Rev., 33 (1929), 605-13.
- Doehring, A. "Messung der Anlagerungswahrscheinlichkeit von Elektronen an Sauerstoff Mittels Einer Laufzeitmethode," Z. Naturforschung, 7a (1952), 253-70.
- Dushman, Saul. Scientific Foundations of Vacuum Techniques. New York: John Wiley and Sons, 1949.
- Geballe, R. and Harrison, M. A. "Negative Ion Formation in Oxygen," Phys. Rev., 85 (1952), 372-73.
- Hagstrum, H. D. and Tate, J. T. "Ionization and Dissociation of Diatomic Molecules by Electron Impact," Phys. Rev., 59 (1941), 354-70.
- Harrison, M. A. and Geballe, R. "Simultaneous Measurement of Ionization and Attachment Coefficients," Phys. Rev., 91 (1953), 1-7.
- Healey, R. H. and Kirkpatrick, C. B. in The Behaviour of Slow Electrons in Gases. Australasia: Amalgamated Wireless Ltd., 1941.
- Herreng, P. "Mesure de la Mobilite des Electrons Dans L'Oxygene et de Leur Probabilite de Fixation Sur Les Molecules de ce Gaz," Cah. Phys., 38 (1952), 6-16.
- Holstein, T. "Energy Distribution of Electrons in High Frequency Gas Discharge," Phys. Rev., 70 (1946), 367-384.
- Huxley, L. G. H. and Zaazou, A. A. "Experimental and Theoretical Studies of the Behaviour of Slow Electrons in Air," Proc. Roy. Soc. (Lond.), A196 (1949), 402-26.
- Jordan, W. H. and Bell, P. R. "A General Purpose Linear Amplifier," Rev. Sci. Instr., 18 (1947), 703-05.
- Loeb, L. B. Basic Processes of Gaseous Electronics. Berkeley and Los Angeles: University of California Press, 1955.
- Loeb, L. B. "Formation of Negative Ions," in Handbuch der Physik. Volume 21. Berlin: Springer-Verlag, 1956.

- Lozier, W. W. "A Study of the Velocities of H^+ Ions Formed in Hydrogen by Dissociation Following Electron Impact," Phys. Rev., 36 (1930), 1285-92.
- Lozier, W. W. "The Heats of Dissociation of Hydrogen and Nitrogen," Phys. Rev., 44 (1933), 575-81.
- Lozier, W. W. "The Heat of Dissociation of CO and the Electron Affinity of O," Phys. Rev., 46 (1934), 268-76.
- Magee, J. L. and Burton, M. "Elementary Processes in Radiation Chemistry. II. Negative Ion Formation by Electron Capture in Neutral Molecules," J. Am. Chem. Soc., 73 (1951), 523-32.
- Massey, H. S. W. Negative Ions. London: Cambridge University Press, 1950.
- Mitchell, A. C. G. and Zemansky, M. W. Resonant Radiation and Excited Atoms. London: Cambridge University Press, 1934.
- Rice, O. K. "On Collision Problems Involving Large Interactions," Phys. Rev., 38 (1931), 1943-60.
- Tate, J. T. and Lozier, W. W. "The Dissociation of Nitrogen and Carbon Monoxide by Electron Impact," Phys. Rev., 39 (1932), 254-77.
- Tate, J. T. and Smith, P. T. "The Efficiencies of Ionization and Ionization Potentials of Various Gases Under Electron Impact," Phys. Rev., 39 (1932), 270-77.
- Tolman, R. C. Statistical Mechanics with Application to Physics and Chemistry. New York: Chemical Catalog Co., Inc., 1927.
- Townsend, J. S. and Bailey, V. A. "The Motion of Electrons in Gases," Phil. Mag., 42 (1921), 873-91.
- Townsend, J. S. and Bailey, V. A. "The Motion of Electrons in Argon and in Hydrogen," Phil. Mag., 44 (1922), 1033-52.
- Townsend, J. S. and Tizard, H. T. "The Motion of Electrons in Gases," Proc. Roy. Soc. (Lond.), A88 (1913), 336-47.
- Vogt, E. and Wannier, G. H. "Scattering of Ions by Polarization Forces," Phys. Rev., 95 (1954), 1190-98.
- Zener, C. "Interchange of Translational, Rotational, and Vibrational Energy in Molecular Collisions," Phys. Rev., 37 (1931), 556-69.

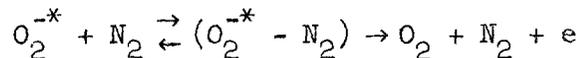
APPENDIX 1

CONSIDERATION OF THE PROCESS $O_2^{-*} + O_2 + N_2 \rightarrow O_2^- + O_2^* + N_2^*$

In this appendix further consideration will be given to the three-body stabilization process,



It is known that ion molecule reactions take place with large cross sections,¹ and that the duration of these collisions may be many times as long as molecular vibration times.² The origin of both of these effects is the long range Coulomb force which comes into play when an ion approaches a molecule having an appreciable polarizability. This force is approximately equal for the pairs $O_2^{-*} - O_2$ and $O_2^{-*} - N_2$. In view of this fact, and because the N_2 pressure was always about 100 times the O_2 pressure, it is reasonable to assume that the intermediate complex is



Assume that this complex is a case of weak interaction between O_2^{-*} and

¹E. Vogt and G. H. Wannier, Phys. Rev. 95, 1190 (1954).

²M. Burton and J. L. Magee, J. Phys. Chem. 56, 842 (1952).

N_2 and thus the decay time against electron emission is the same as for the case of O_2^{-*} alone, i.e., λ_2^{-1} . Assume, further, that the duration of the collision against molecular dissociation, τ , is much greater than λ_2^{-1} .

The equilibrium concentration n_1 , number of $(O_2^{-*} - N_2)$ complexes per cm^3 , is determined by setting the rate of collisions of O_2^{-*} with N_2 (at concentrations n_1 and n_2 , respectively) equal to the rate of electron emission, i.e.,

$$\sigma_{12} v_{12} n_1 n_2 = \lambda_2 n_1 \quad (A-1)$$

where σ_{12} is the cross section for collisions of O_2^{-*} with N_2 and v_{12} is the mean relative velocity of the colliding partners. If σ_{i3} is the cross section for stabilizing collisions of O_2 with $(O_2^{-*} - N_2)$, the rate of these collisions is

$$R = \sigma_{i3} v_{i3} n_1 n_3 \quad (A-2)$$

where σ_{i3} is the average relative velocity of $(O_2^{-*} - N_2)$ and O_2 , and n_3 is the concentration of O_2 .

Combining Eqs. (A-1) and (A-2) gives

$$R = n_1 n_2 n_3 v_{12} v_{i3} \sigma_{12} \sigma_{i3} \lambda_2^{-1} \quad (A-3)$$

The rate of stabilization was defined in Eq. (17) in terms of the experimental constant K . Equating these two rates gives

$$n_1 n_2 n_3 v_{12} v_{i3} \sigma_{12} \sigma_{i3} \lambda_2^{-1} = K n_1 f_1 P f_2 P \quad (\text{A-4})$$

where K and n_1 are pressure independent.

Since $n_2 = N_o \frac{f_1 P}{760}$ and $n_3 = N_o \frac{f_2 P}{760}$, where N_o is the number of molecules per cm^3 of gas at standard temperature and pressure, we finally obtain

$$\lambda_2^{-1}(\text{sec}) = \left(\frac{760}{N_o} \right)^2 \frac{K}{v_{12} v_{i3} \sigma_{12} \sigma_{i3}} = \frac{1.9 \times 10^{-43} K}{\sigma_{12} \sigma_{i3}} \quad (\text{A-5})$$

The average value of K determined from experiment and from β/λ_2 as before is $5 \times 10^4 \text{ sec}^{-1} (\text{mm Hg})^{-2}$ if the state of O_2^- is (${}^2\Pi_g$) or is $2.5 \times 10^4 \text{ sec}^{-1} (\text{mm Hg})^{-2}$ if the state of O_2^- is (${}^4\Sigma_u$). The cross section σ_{12} should be set at about 10^{-14} cm^2 , which is typical for an ion-molecule collision. The cross section σ_{i3} is not as easy to decide since it represents the product of a cross section for collision with the probability for energy transfer.

The upper limit for σ_{i3} is 10^{-14} cm^2 and a reasonable lower limit is 10^{-15} cm^2 , the latter being based on the fact that the cross section

for stabilization of O_2^{-*} with O_2 is more than 10^{-15} cm². The range of values of λ_2^{-1} is then $5 \times 10^{-11} \leq \lambda_2^{-1} \leq 5 \times 10^{-10}$ sec. This is in interesting agreement with the order of magnitude estimate by Bloch and Bradbury³ which gave 10^{-10} sec.

Now let us examine the condition $\tau \gg \lambda_2^{-1}$. Eyring's⁴ statistical mechanical theory of reaction rates has been extended by Magee⁵ and applied to the case of ion-molecule reactions. Burton and Magee² give an approximate formula for the life time of a complex as

$$\tau(\text{sec}) = 10^{-13} \left(1 - \frac{E_B}{E} \right)^{1-\alpha} \quad (\text{A-6})$$

where E_B is the binding energy of the complex, E is the actual relative energy of the complex, approximately equal to $E_B + kT$, and α is the number of vibrational internal degrees of freedom which may be excited in the complex. The maximum value for α is $3n-6$, where n is the number of atoms in the complex.

The binding energy E_B for O_4^- may be estimated by adding the polarization energy to the potential energy curve for O_4 . The polarization energy, V_p , may be expressed as

³F. Bloch and N. Bradbury, Phys. Rev. 48, 689 (1935).

⁴H. Eyring, J. Chem. Phys. 3, 107 (1935).

⁵J. L. Magee, Proc. Nat'l. Acad. Sci. 38, 764 (1952).

$$V_P = \frac{-e^2 P}{2r^4} \quad (\text{A-7})$$

where P is the polarizability and is equal to $1.6 \times 10^{-24} \text{ cm}^3$ for O_2 and is $1.8 \times 10^{-24} \text{ cm}^3$ for N_2 .⁶ When V_P is added to the potential for O_4 , used by Salow and Steiner⁷ in interpreting the absorption spectra for O_4 , it is found that the minimum occurs at 3.0 \AA and E_B is 0.10 volt. If the potential energy curve for O_4 is first adjusted so that it is equal to zero at a distance equal to the diameter of O_2 as determined from gas kinetic theory, i.e., 2.96 \AA ,^{7,8} and then the V_P term is added to this curve, its minimum occurs at 2.7 \AA and E_B is 0.17 volt. Thus, the approximate range of values for E_B which should be considered in estimating τ is $0.10 \leq E_B \leq 0.20$ volt. Since the polarization term is dominant in determining E_B and since the gas kinetic diameters for O_2 and N_2 are nearly equal, this range of E_B will also be considered for ($\text{O}_2^* - \text{N}_2$).

Table A-1 shows the results when Eq. (A-6) is evaluated for the various values of α and values of E_B in the region of interest. For the case of excitation of all degrees of freedom, i.e., $\alpha = 6$, theory gives

⁶J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954), p. 950.

⁷H. Salow and W. Steiner, Zeit. f. Physik 99, 137 (1936).

⁸E. H. Kennard, Kinetic Theory of Gases (McGraw Hill Book Company, Inc., New York, 1938), p. 224.

Table A-1

LIFETIMES (IN SEC) FOR (O₂-N₂) OR O₄ FOR VARIOUS VALUES OF α AND E_B

E _B (volts)	Degrees of Freedom, α				
	2	3	4	5	6
0.050	3×10^{-13}	9×10^{-13}	2.7×10^{-12}	8.1×10^{-12}	2.4×10^{-11}
0.075	4×10^{-13}	1.6×10^{-12}	6.4×10^{-12}	2.6×10^{-11}	1.0×10^{-10}
0.10	5×10^{-13}	2.5×10^{-12}	1.2×10^{-11}	6.0×10^{-11}	3.0×10^{-10}
0.15	7×10^{-13}	4.9×10^{-12}	3.4×10^{-11}	2.4×10^{-10}	1.7×10^{-9}
0.20	9×10^{-13}	8.1×10^{-12}	7.3×10^{-11}	6.6×10^{-10}	6.0×10^{-9}
0.25	1.1×10^{-12}	1.2×10^{-11}	1.3×10^{-10}	1.5×10^{-9}	1.6×10^{-8}
0.30	1.3×10^{-12}	1.7×10^{-11}	2.2×10^{-10}	2.9×10^{-9}	3.8×10^{-8}

$3.0 \times 10^{-10} \leq \tau \leq 6 \times 10^{-9}$ sec for $0.10 \leq E_B \leq 0.20$ volts. Thus the condition $\tau \gg \lambda_2^{-1}$ can be met since the range for λ_2^{-1} is 5×10^{-11} to 5×10^{-10} sec.

Another condition has been imposed on λ_2 . In the development of the stabilization model (p. 57 and following) it was assumed that

$$\lambda_2 \gg \lambda_1 + C_1 f_1 P + C_2 f_2 P + K f_1 P f_2 P$$

The evaluation of the right hand side for $f_1 P = 10$ mm Hg and $f_2 P = 10^3$ mm Hg gives

$$3 \times 10^8 \text{ sec}^{-1} \quad \text{or} \quad \lambda_2^{-1} \ll 3 \times 10^{-9} \text{ sec}$$

The inequalities are best satisfied if λ_2^{-1} is about 5×10^{-11} , and τ is about 6×10^{-9} sec, corresponding to $E_B = 0.2$ ev and $\alpha = 6$. One final condition on λ_2 should be examined, i.e., $\lambda_2^{-1} \ll$ time between collisions, t_{bc} , of O_2 with $(O_2^{-*} - N_2)$. This condition is not demanding since at 10 mm Hg, $t_{bc} = 6 \times 10^{-23} / \sigma_{i3}$ and $\lambda_2^{-1} = 5 \times 10^{-25} / \sigma_{i3}$.

Conditions similar to the above would be violated in at least one respect if the intermediate state were assumed to be O_2^{-*} (unstable against electron emission), $O_2^{-}N_2$ (stable against electron emission), or O_2^{-} (stable against electron emission); thus the above model is preferred. A set of values which leads to internal consistency is then $\tau = 6 \times 10^{-9}$ sec corresponding to $E_B = 0.2$ ev and $\alpha = 6$, $\lambda_2^{-1} = 5 \times 10^{-11}$

sec, compared to the Bloch-Bradbury value = 10^{-10} sec, and $\sigma_{13} = 10^{-14}$ cm².

The large value of σ_{13} indicates that essentially every collision of O₂ with the complex leads to a transfer of energy, presumably electronic excitation, from the distorted O₂⁻(⁴Σ_u) state. On this basis it may be inferred that the perturbation of the energy level due to the loosely coupled N₂ molecule is responsible for the increase in the energy transfer cross section.

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