

ACTIVE NITROGEN REACTIONS

Thesis by
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In Partial Fullfillment of the Requirements
for the B.S. Degree

California Institute of Technology
Pasadena, California

1965

ABSTRACT

The nitrogen recombination reaction and the reaction of active nitrogen with methane were studied. The intensity of the nitrogen afterglow was found to be independent of total pressure at pressures less than three millimeters, and first order in total pressure at higher pressure. The radiative efficiency of the recombination reaction was found to be very low; only about one- three hundredth of all recombinations resulted in the emission of a light quantum. The reaction of active nitrogen with methane was found to produce CN radiation. It was found that the rate of emission of this radiation may be expressed in a rate law of the following form:

$$I_{CN} = K P_{total}^2 \cdot P_N^y \left[P_{CH_4} (1 + k P_{CH_4})^{-1} + k' P_{CH_4}^x \right]$$

$$2 < y < 3$$

$$0 < x < 1$$

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INTRODUCTION

In the spring, 1964, quarter, Bob Levin and Wayne Ryback found that when natural gas, which consists mostly of methane, was released into a stream of active nitrogen in the Ch 26 fast-flow apparatus, the intensity of the nitrogen after-glow (a measure of the concentration of nitrogen atoms) decreased sharply a short distance down the reaction tube from the mixing point and a violet glow ~~simultaneously~~ appeared. This indicated that a reaction was taking place between the methane and active nitrogen.

I studied this reaction further during the summer of 1964, with the goal of determining the kinetics of the active nitrogen-methane reaction in general, and of the reaction producing the violet glow in particular.

APPARATUS

Essentially the same apparatus was used as in the Ch 26 laboratory work. Drawings showing its essential features are reproduced on graph pages 1 and 2.

Nitrogen (Linde, 99.99%) flowed from a tank through tubing over a mercury manometer and to a capillary flow meter. At times a pyrex tube containing copper pellets heated to 500°C. was inserted into the gas line between the nitrogen tank and manometer. Methane was introduced into the system in much the same manner. Fittings were arranged so that methane could be

introduced at either S_2 or S_4 . All tubing from tanks to flow meters was neoprene; from flow meters to reaction tube, $1/8$ " copper. Fittings that were not subjected to high vacuum were sealed with Dow-Corning high vacuum grease; those that were, with Apiezon grease.

The total gas pressure in the reaction tube was regulated by valve V_1 . The diffusion pump was not used. A silicon oil absolute manometer was used to measure the pressure in the reaction tube. It was generally found to be necessary to evacuate the system for one half hour with the high speed pump for the manometer to give reproducible readings when the total pressure was varied. This was presumably due to air dissolved in the oil; the matter was not investigated.

The microwave diathermy was powered by a constant voltage transformer. It was necessary to allow the diathermy unit to operate for 15-20 minutes at 70-80% power prior to an experiment in order to avoid variable photometer readings due to drifting of the power in the diathermy unit.

All flow rates and pressures could be maintained almost indefinitely with little or no adjustment.

The photometer was mounted on a dolly running on rails so that it could be moved up and down the tube at a constant distance from it. When the Jarrell-Ash Recording Spectrometer was used, it was placed on a cart that could be rolled up and down beside the tube, with the slit level with the center of the tube and 6.0 cm. from it.

EXPERIMENTAL WORK

I. Initial Spectroscopic Studies.

The first experimental work was concerned with trying to identify excited intermediates in, and products of the methane-active nitrogen reaction. This was attempted by studying the emission spectrum of the gas in the reaction tube, using a photographic quartz spectrograph which was calibrated against standard mercury lines from an AH-4 mercury arc lamp. Exposures of the reaction spectrum were taken with the spectrograph slit about one half cm. from the tube.

Exposures of the two spectra (mercury and reaction) were overlapped on the same negative (i.e., by first making an exposure of the mercury arc with one half of the slit covered, and then making an exposure of the reaction tube on the same negative with the other half of the slit covered). All lines were measured on a comparator, and a calibration curve for the spectrograph was made by matching the ^{observed} comparator readings of the observed lines to their ^{with standard wavelengths} standard wavelengths on a smooth curve. The comparator readings of the reaction bands were then matched to the corresponding wavelengths on the curve (see graph p.5). All comparator readings were made at the centers of the bands on the negative. An exposure of about $\frac{1}{4}$ second through four thicknesses of Kimwipe was found to produce the mercury lines clearly at a slit opening such that fifteen minutes' exposure was enough for the violet glow in the reaction tube to show a distinct spectrum.

Exposures were made both with and without methane present in the reaction tube. In the absence of methane, the following

bands were unambiguously identified:¹

N_2 first positive system ($B^3\Pi \rightarrow A^3\Sigma$)	5804 Å.
	5755 Å.
NO β system ($2\Pi \rightarrow 2\Pi$ ground state)	4041 Å.
	3800 Å.
	3583 Å.
	3386 Å.
	3206 Å.

With methane present, all the above were observed, with the addition of the following:

CN ($2\Sigma \rightarrow 2\Sigma$ ground state)	4216 Å.
	3883 Å.
	3854 Å.

The CN bands were quite clear after an exposure time of about fifteen minutes. No additional bands appeared after an hour's exposure.

At this time a new and later to be significant problem appeared. As the total pressure in the reaction tube was increased to about 10 mm. Hg, a violet glow appeared and the nitrogen afterglow disappeared, both with and without methane present, in much the same way as the afterglow disappears and the violet NO glow appears in the titration of nitrogen atoms with NO. This effect was presumed to be due to the presence of oxygen in either the gas line or the nitrogen tank. Changing from Linde to Mathieson high purity nitrogen (99.996%), and/or inserting a pyrex tube of copper pellets at 500° in the gas line between the nitrogen tank and manometer produced no obvious improvement. The tube with the copper turnings was only about fifteen cm. long; better results might have been obtained ^{had been} ~~if it had been~~ longer, which would ^{have} ~~have~~ kept the oxygen ^{in the tube} (if any were present) in contact with the copper for a longer period of time.

II. Calibration of the Photometer.

A. Calibration of sensitivity changes.

Since the microammeter sensitivities indicated on the gain switch were not very precise, it was necessary to determine more accurately the relative sensitivities at successive settings of this switch. The absolute sensitivities were not of particular interest at the time. The conditions of the calibration were unimportant, since what was being measured was a property of the recorder only. If the absolute rate of nitrogen emission is kept constant (by keeping the power, total pressure, etc., constant) then the relative sensitivity at two settings of the gain switch is the ratio of the recorder deflections at the two settings. The relative sensitivities are as follows:

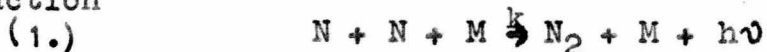
Table I
Relative Sensitivities of Microammeter *

Gain Switch Setting (in μ amps)	Relative Sensitivity
3	0.329
1	1
0.3	3.36
0.1	10.25

* The tabulated ratio of recorder deflections is the average of three such ratios which were obtained by varying the power 10-20%. All are calibrated to 1 μ amp = 100 (recorder deflection).

B. Absolute calibration of the photometer for concentrations of atomic nitrogen.

Nitrogen atoms are presumed to recombine by the overall reaction²

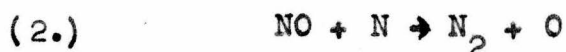


$$(Eq. 1) \quad \frac{dN_2}{dt} = kN^2M$$

$$(Eq. 2) \quad \text{and} \quad I = k_1 k N^2 M = k_1 k P_N^2 P_M$$

where k_1 is a yet to be determined "intensity constant" of the reaction and apparatus.

NO is known to react rapidly and quantitatively according to the reaction³



Consequently, if NO is added to a stream of active nitrogen, the intensity of the nitrogen afterglow diminishes, and finally disappears when the added concentration of NO equals that of nitrogen atoms. Consequently, the absolute concentration of atomic nitrogen may be determined by titration with NO. In addition, the total pressure is very nearly equal to P_M , and the rate constant for the nitrogen recombination reaction is known. Consequently, the intensity constant k_1 may be determined by measuring the intensity of the afterglow, and then titrating with NO to determine the concentration of atomic nitrogen present.

The data and results of experiments to determine k_1 are summarized in Table I:

Table II
Intensity Constant for Nitrogen Recombination

Total Pressure (mm. Hg)	Intensity* (Recorder Deflection)	$P_{NO} \times 10^2$ ** (mm. Hg)	Reaction Rate *** (mm. Hg sec ⁻¹)	$k_1 \times 10^{-3} =$ $\frac{\text{Intensity} \times 10^{-3}}{\text{Reaction Rate}}$ (s.u. sec. mm ⁻¹)
1.5	50.0	1.95	1.43	3.50
1.5	34.5	1.82	1.24	2.78
1.5	22.0	1.24	0.577	3.82
1.5	13.6	0.95	0.339	4.02
2.0	105	3.25	5.29	1.99
2.0	63.5	2.02	2.04	3.11
2.0	42.5	1.68	1.41	3.01
2.0	29.3	1.30	0.846	3.47
3.0	139.5	3.28	8.08	1.73
3.0	105	2.66	5.31	1.98
3.0	78.0	2.35	4.31	1.89
3.0	54.5	1.95	2.85	1.91
4.0	156	3.14	9.86	1.58
4.0	120	3.04	9.24	1.30
5.0	135	2.44	7.45	1.81
6.0	91	1.77	4.71	1.93
Average				2.5 ± 0.8

I cannot explain the fact that the ratio I_0/P_N^2 appears to be independent of total pressure at pressures below 3 mm. Hopefully, work being done in Ch 26 will help to clear up the question of the dependence of the rate of the luminous reaction on total pressure.

* All intensities are corrected to 1 μ amp = 100 (I_0).

** $P_{NO} = \frac{\text{NO flow rate}}{\text{total gas flow rate}} \times \text{total pressure}$

*** Computed from $k = 25 \text{ mm.Hg}^{-2} \text{ sec}^{-1}$

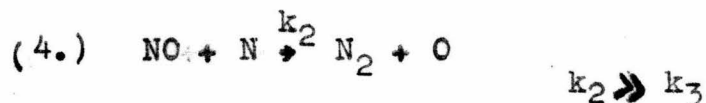
III. Explanation of the Violet (NO) Glow.

As noted earlier, NO bands appeared in the active nitrogen spectrum. This was assumed to be due to the presence of oxygen as an impurity in the system. The glow was quite annoying, since at high pressures it nearly completely extinguished the nitrogen afterglow.⁵

Experimental work described below apparently confirmed the reactions producing the glow to be the following:



k_4 is the intensity constant for the reaction.



From equation 2 and the above,

$$(\text{Eq. 4}) \quad \frac{I_o}{I_v} = \frac{k k_1 P_N^2 P_M}{k_4 k_3 P_N P_O P_M}$$

$$(\text{Eq. 5}) \quad \therefore \frac{I_o^{\frac{1}{2}}}{I_v} = \frac{1}{k_3 k_4 P_O (P_M / k k_1)^{\frac{1}{2}}}$$

Since almost all of the NO present reacts with N to form atomic oxygen, $P_O \approx P_{NO}$, and

$$(\text{Eq. 6}) \quad P_O = \frac{\text{NO flow rate}}{\text{total gas flow rate}} \times \text{total pressure}$$

Therefore, at a given pressure and flow rate of NO, the ratio of $I_o^{\frac{1}{2}}$ to I_v should be constant down the tube; and in general

$$(\text{Eq. 7}) \quad \frac{I_o^{\frac{1}{2}}}{I_v} \times \frac{\text{NO flow rate}}{\text{total gas flow rate}} \times (P_{\text{total}})^{\frac{3}{2}} = \frac{(k k_1)^{\frac{1}{2}}}{k_3 k_4}$$

Experimental Work Concerned with the Origin of the NO Glow

Since the NO-N reaction was known to proceed rapidly, the O concentration was set at a known value by introducing a definite NO flow into the active nitrogen stream. The procedure followed was to introduce NO into the system, take photometer readings in both the orange and violet at various places down the tube in order to determine the constancy of $I_O^{1/2}/I_V$, and to vary the NO flow rate and the total pressure in order to determine the constancy of the product on the left of Eq. 7.

Table III
Determination of $(k_3 k_4)^{1/2}/k_3 k_4$

P (mmHg)	$I_O^{1/2}/I_V^*$	NO flow rate (ml./sec.)	$P^{1/2} \times \text{NO flow rate} \times I_O^{1/2}/I_V \times 10^3$
1.6	0.44	0	
	0.097	0.0173	3.41
	0.053	0.0359	3.9
	0.033	0.0562	3.8
2.1	0.29	0	
	0.053	0.0173	2.8
	0.028	0.0359	3.0
	0.021	0.0562	3.6
3.9	0.100	0	
	0.021	0.0173	2.8
	0.011	0.0359	3.2
	0.0086	0.0562	3.7
6.2	0.044	0	
	0.007	0.0359	3.8

Average 3.4 ± 0.3

(Eq. 8) Therefore $\frac{(k_3 k_4)^{1/2}}{k_3 k_4} = 1.9 \times 10^{-4}$

Using $k_3 = 1.6 \text{ mm}^{-2} \text{ sec}^{-1}^{**}$, $k = 24 \text{ mm}^{-2} \text{ sec}^{-1}$, and
 $k_1 = 2.5 \times 10^3 \text{ s.u. sec. mm}^{-1}$, $k_4 = 8 \times 10^5 \text{ s.u. sec. mm}^{-1}$.

* Averaged over readings at 75, 100, 125, 150, and 175 cm. (Average deviation usually $\sim 5\%$). The measured $I_O^{1/2}/I_V$ has no obvious absolute significance, because the sensitivity of the photometer is different in different spectral regions.

** Taken from work done during school year. Also agrees with accepted value (see footnote 4.)

The intensity constant for the violet was approximately 300 times as large as the intensity constant for the nitrogen afterglow. This indicated that either the photometer was remarkably more sensitive to violet than to orange radiation, or else the nitrogen radiative process was much less efficient than that producing the violet glow. The first of these was unlikely to produce the observed difference in the values for the intensity constants; the second will be discussed later.

The purpose of these experiments was to calculate the per cent of atomic oxygen that, if actually present in the active nitrogen stream, would have been required to produce the observed intensity of the violet glow. With no NO added (see Table III): This per cent was calculated by substituting back into Eq. 7, with $\frac{(k_3 k_4)^{\frac{1}{2}}}{k_3 k_4} = 1.9 \times 10^{-4}$, the intensities being those with "no" NO present (see Table III). The ratio of calculated NO flow rate to the total gas flow rate was then the per cent of atomic oxygen in the active nitrogen flow that would have produced the observed violet glow. The data from Table III gave a value for the per cent oxygen of approximately 0.02%, as compared to the manufacturer's statement that the nitrogen was 99.99 % pure.

To check for consistency, the apparent per cent of atomic oxygen was calculated with data from earlier experiments. It was found that the apparent per cent was relatively high near S_2 , but decreased rapidly and remained essentially constant after about fifty cm. downstream. The anomolous results near the first orifice were probably due somehow to various short-lived

excited nitrogen states, present near the microwave cavity, which have been observed for several years but are not yet well understood.⁶

Table IV
Apparent Per Cent of Atomic Oxygen ($\times 10^2$)

Distance Down Tube (cm.)	Pressure (mm.)		
	1.5	2.0	3.0
3	2.76	4.3	4.1
5	3.4	6.0	4.8
7.5	4.07	7.3	3.8
10	4.9	7.1	2.8
12.5	—	5.4	2.0
15	4.6	3.9	1.6
20	3.2	2.1	1.3
25	2.3	1.7	1.1
50	1.4	1.2	1.1
75	1.4	1.1	1.2
100	1.5	1.3	1.3
125	1.6	1.3	1.3
150	1.6	1.3	1.3
175	1.6	1.3	1.3

The per cent of atomic oxygen calculated was 0.013-0.015 %, which was approximately the manufacturer's limit of impurity in the nitrogen.

IV. Use of Spectrophotometer.

At this point it appeared inadvisable to continue to use the photometer to measure the intensity of the CN glow because of the large interference from the NO glow, which would have been a bother to correct for, at the least. Consequently, a Jarrell-Ash recording spectrograph~~meter~~ was set up so that it could be used to observe the reaction tube. It was placed on a cart that could be rolled up and down beside the tube at a fairly constant distance from it. Reproducibility of readings to 1% or better presented no problem, and recorder readings varied only slightly with the distance of the spectrophotometer from the tube. The spectrograph~~meter~~ was not calibrated with respect to wavelength, in view of the width and small number of bands present. The spectrum of the gas stream, both with and without methane present, was observed (see graph page 24).

Table V
Spectrum of Reaction Tube

Peaks Observed		Identified ⁷
Without Methane	With Methane	As
Present	(Additional)	
3043		3043 NO
3206		3206 NO
3387		3386 NO
3579		3583 NO
3790		3800 NO
3800		
	3845	3854 CN
	3879	3883 CN
	4146	4152 CN

The region of the reaction tube near the spectrophotometer was excited with a tesla coil in an attempt to determine whether or not any excitable species other than CN were formed in significant quantities in the reaction. Heretofore unobserved bands

were found at 3575 and 3800 Å. These were both identified as part of the nitrogen second positive system.⁸

This result was taken to mean that such possible intermediates as NH, CH,...were not present in significant quantities, since the nitrogen second positive system was excited to approximately the same intensity as the CN bands, and other excitable species would have been expected to show up if they had been present in significant quantities. For example, the fairly easily excitable 3360 Å NH system and/or the 4300 Å CH system, etc.

Calibration of the Spectrophotometer

An absolute calibration of the spectrophotometer was attempted in order to determine the total number of molecules of CN and N_2 emitting a quantum of radiation in unit time per cubic centimeter of reaction mixture.

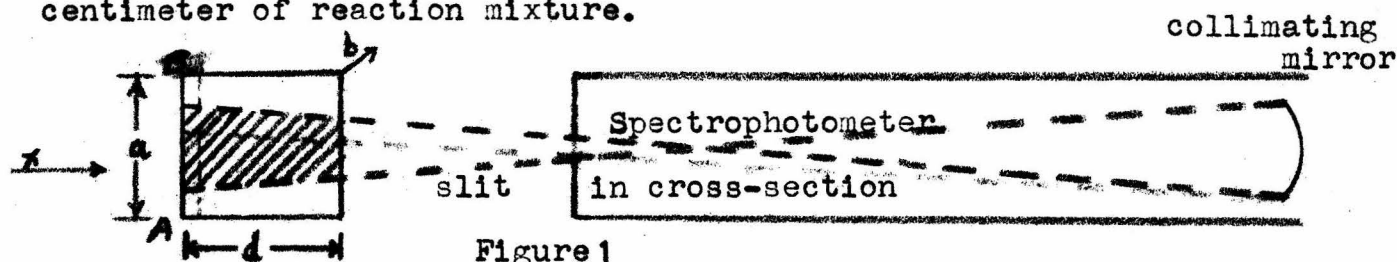


Figure 1

Consider a rectangular volume of radiating gas of thickness a , with the other dimensions sufficiently great to include entirely the "field of vision" of the spectrophotometer (the shaded region in Figure 1). It is not difficult to show that the fraction of the radiation emitted by the molecules in any slice of gas of thickness ϵ and parallel to plane AB, which is received by the collimator mirror, is independent of the location of this slice.

Consequently, if all molecules in the volume abd could be translated in the x -direction and concentrated in the plane AB (without altering their rate of emission) the amount of radiation passing through the spectrophotometer would be unaffected. It is therefore possible to determine the rate of emission of radiation from the volume abd by comparing the radiometer deflection in the situation shown in Figure 1 with that in a situation in which the plane AB is replaced by a suitably illuminated ideal diffuse reflector. Of course, it is necessary to know the rate at which energy in the wave lengths of interest falls on the reflector.

If the radiometer deflection at a given wave length setting of the spectrophotometer is I_g when exposed to radiant gas, and is I_r when exposed to the diffuse reflector illuminated with known intensity I_λ watts $\text{cm}^{-2}\mu^{-1}$, the rate of emission of radiation by a unit volume of gas is given by

$$(Eq. 9) \quad R (\text{watts cm}^{-3}\mu^{-1}) = \frac{I_g}{I_r} \frac{2}{d} I_\lambda A \quad *$$

The factor of two arises from the fact that the gas radiates both in forward and backward directions, while the reflector returns radiation only in the backward direction; the factor A (the albedo) is a correction for an imperfect, though ideally diffusing reflector.

In applying the above relation to the actual experimental situation the distance d is taken as the diameter of the reaction tube, and the small errors introduced by the non-planarity of boundary surfaces are ignored.

In the calibration experiment, the comparison reflector consisted of an opaque deposit of MgO smoke, which is known to be nearly an ideal diffuse reflector, and has a known albedo.⁹ This was illuminated by a 500 watt Westinghouse tungsten lamp (color temperature 3200°K) of which the emission at various wave lengths was calculated from data taken from the literature. The distance from the spectrophotometer to the reflector was fixed at forty centimeters, although the radiometer readings varied little if the distance were changed. There was also little variation as the orientation of the spectrophotometer relative to the reflector

* In the present case, I_λ is taken to be the intensity at the midpoint of the wavelength region of interest. Also, I_g and I_r are actually $[I_\lambda (\text{recorder deflection})_\lambda d\lambda]$, where $\lambda_1 \rightarrow \lambda_2$ is the wavelength region of interest.

was changed.

Calibration of the nitrogen afterglow.

Nitrogen afterglow emission was observed only in the spectral regions 5325-5425 Å and 5700-5825 Å. Consequently, radiation in only these regions was of interest in attempting to determine the number of quanta being emitted per unit time during the process of nitrogen recombination. The Jarrell-Ash spectrophotometer, utilizing a RCA IP-28 photomultiplier, was used in all intensity measurements.

Equation 9 can be employed if I_λ , the intensity incident upon the reflector, is known. I_λ , in turn, can be calculated if the following are known: temperature of the lamp, emissivity of the tungsten filament, area of the filament, and the angle of the plane of the filament relative to the plane of the reflector. The last of these is taken to be zero.

The "effective area" of the filament can be calculated from the Stefan-Boltzmann law:
(Eq. 10)

$$\text{Total emission of lamp (watts)} = 5.73 (\text{Area}) \cdot T^4 \cdot (\text{total emissivity of tungsten})$$

where the area is in square centimeters and the temperature is in kilodegrees.

The lamp has a color temperature of 3200°K. this corresponds to an actual temperature of 3095°K. (see graph p.7).¹⁰

It is assumed that the emissivity of the lamp filament is close to that of a tungsten strip. The emissivity of the latter

is as follows:¹¹

Table VI					
Emissivity of a Tungsten Strip					
T (°C)	$\lambda(\mu)$				total
2900	0.3	0.38	0.467	0.665	0.345
3000	0.489	0.472	0.456	0.417	
3200	0.488	0.470	0.455	0.415	
3400	0.486	0.468	0.452	0.411	
	0.484	0.465	0.450	0.407	

Therefore, if the total emission of the lamp is 500 watts, (Eq. 11)

$$\text{area} = \frac{500}{5.73 \times (3.095)^4 \times 0.345} \text{ cm}^2 = 2.76 \text{ cm}^2$$

The rate of emission of the lamp in a given wavelength region is equal to the rate of emission of a perfect black body of the same area at the same temperature as the filament of the lamp times the emissivity of the tungsten filament at that wavelength and temperature.

The total hemispherical radiation of a black body in the interval $d\lambda$ may be calculated from the relation

$$\text{(Eq. 12)} J_{\lambda} d\lambda = c_1 \lambda^{-5} \left(e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1} d\lambda \quad 12$$

where $c_1 = 3.703 \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1}$, $c_2 = 1.433 \text{ cm}^\circ\text{K}^{-1}$, and λ is measured in centimeters.

Since J_{λ} does not change much with λ in the wavelength interval to be considered, J_{λ} is calculated only at the midpoint of the region of interest and this value is multiplied by the width of the region in order to obtain the total hemispherical radiation of the black body in that region.

For $T=3095^\circ\text{K}$, $\lambda = 5765 \text{ \AA}$, $J_\lambda = 185 \text{ watts cm}^{-2}\mu^{-1}$. Therefore, the total radiation received in the wavelength region 5700-5825 $\text{\AA}$ by one square centimeter of the diffuse reflector at a distance r from the lamp is

$$(Eq. 13) \quad I = 2\pi \times \frac{185 \text{ watts}}{\text{cm}^2} \times 2.10 \text{ cm}^2 \times 0.0125 \times 0.432 \times \frac{1.41^*}{4\pi r^2} = \frac{0.47 \text{ watts}}{r^2 \text{ cm}^2}$$

A graph was made experimentally of radiometer deflection v. wavelength for radiation from both the reflector and the nitrogen afterglow in the reaction tube (such as graph p. 24). The area under each tracing was found (in arbitrary units). The radiation reflected from the calibrating reflector yielded an area of 2.524×10^4 units at a distance r from the lamp to the reflector of 100 cm.; the radiation from the nitrogen afterglow, 325 units under the conditions $P_{\text{total}}=5\text{mm.}$ and $I_0=204$ at $I_{\text{amp}}=100$.

Taking the albedo of the reflector as 0.95,¹³ and the inside diameter of the reaction tube as 3.72 cm., formula 9 was employed to obtain

$$(Eq. 14) \quad R (\text{watts cm}^{-3}) = \frac{325}{2.524 \times 10^4} \times \frac{2}{3.72} \times 0.96 \times \frac{0.47}{10^4} \text{ watts cm}^{-3} = 3.12 \times 10^{-7}$$

The energy per quantum emitted is given by

$$(Eq. 15) \quad E = \frac{hc}{\lambda} = 3.45 \times 10^{-12} \frac{\text{erg}}{\text{quantum}}$$

Therefore, the number of quanta being emitted per second was

$$(Eq. 16) \quad N = \frac{3.12 \times 10^{-7} \text{ watts cm}^{-3}}{3.45 \times 10^{-12} \text{ erg}} \times \frac{10^7 \text{ erg}}{\text{watt-sec}} = 0.9 \times 10^{12} \frac{\text{quanta}}{\text{cm}^3 \text{ sec.}}$$

Similar calculations for the 5325-5425 $\text{\AA}$ region yielded for the number of quanta emitted in this region $N_{5325-5425} = 2 \times 10^{12} \frac{\text{quanta}}{\text{cm}^3 \text{ sec}}$

Therefore, under these conditions, about 3×10^{12} quanta

* The factor 1.41 is a correction for the fact that the lamp filament lies nearly in a plane and thus does not emit in a spherically symmetric manner. (more light is emitted perpendicular than parallel to the plane of the filament).

per second were emitted in the process of nitrogen recombination.

It is possible to calculate the expected rate of emission per cubic centimeter if each nitrogen recombination resulted in the production of a light quantum. The experimental conditions used in obtaining the tracings of radiometer deflection v. wavelength were $I_0 = 204$ at $S = 1$ amp, and a total pressure of 5 mm. Using the previously determined expression for obtaining P_N ,

$$(Eq. 17) \quad P_N = (2.5 \times 10^2)^{-1} \sqrt{\frac{I_0}{P_{tot}}} = 2.6 \times 10^{-2} \text{ mm.}$$

$$(Eq. 18)* \quad \frac{d N_2}{dt} = 2.85 \times 10^{15} \frac{\text{molecules}}{\text{cm}^3 \text{ sec.}}$$

Using the accepted value for the rate constant, $2 \times 10^{-32} \frac{\text{cm}^6}{\text{molecule}^2 \text{ sec}}$,¹⁴

Thus it appears that only a very small fraction of nitrogen recombinations lead to emission of radiation.

V. Study of the Methane-Active Nitrogen Reaction.

A. Initial Photometric Studies (not using spectrophotometer).

Methane was introduced into the stream of active nitrogen at the first orifice (52). The intensities of the orange (nitrogen) and violet (CN plus NO) glows were observed down the tube with the photometer. The results (see graph page 23a) may be summarized as follows:

The intensity of the nitrogen afterglow dropped by as much as a factor of two or three about 5-10 cm. past the mixing point, depending on the total pressure and flow rates of the nitrogen and methane. This drop occurred with methane comprising only about 1% of the total gas concentration, so the effect was not due merely to pressure change. The difference between the intensities of the nitrogen glow with and without methane present decreased virtually to zero about fifty cm. down the tube.

The violet (CN plus NO) glow rose abruptly as the nitrogen glow dropped, and then decreased with distance down the tube. It appeared that the violet glow dropped to a relative minimum at about 20 cm. down the tube, then rose 10-30% over a distance of about 20 cm., and finally decreased slowly for the remainder of the tube's length.

B. Work Done Using the Spectrophotometer.

It was desired to learn the dependence of the rate of CN emission upon each of the parameters (i.e., nitrogen atom concentration, methane concentration, and total pressure). A series of experiments was done in order to isolate the effect of varying each of the parameters. All readings were taken at $x = 68$ cm., about five cm. downstream from the orifice where the methane was introduced. It was assumed that only a small fraction of the methane had reacted by the time the gas reached this point; i.e., that the methane concentration was the same as at the orifice where it was introduced. The plausibility of this assumption was shown at least partially by the fact that only about 2-3% of the total CN emission occurs in the first five cm. past the orifice (graph page 8.)

I. Dependence on nitrogen atom and methane concentration.

The nitrogen atom concentration was varied at constant methane concentration and total pressure by varying the diathermy power. The procedure followed was to introduce a given methane flow rate, and make a series of recorder readings in both the orange (photometer) and violet ($\lambda = 3880 \text{ \AA}$ with the spectrophotometer) at a number of settings of the diathermy power. The methane flow rate was then changed and the procedure repeated. The intensity of the CN glow was then plotted against the square and the cube of the nitrogen atom concentration, which was calculated using Formula 17 (See graph pages 9-21). The intensity of the CN glow was found to vary between " the square " and " the cube of " the nitrogen atom concentration, depending upon the methane concentration and the total pressure.

It appeared that no simple " P_N^X " (X an unknown constant) relationship would fit the experimental data.

The dependence of the intensity of the CN glow upon the methane concentration was determined by plotting I_{CN} versus P_{CH_4} at an arbitrary P_N ($P_N = 1.5 \times 10^{-2}$ mm. was used for convenience), taking I_{CN} from the graphs of I_{CN} v. P_N^2 .

The curves determined at different pressures (see graph page 22) show no simple relationship to one another. This is due at least partly to the fact that some of the experiments determining them were done on different days, and the system seems not to be perfectly reproducible from day to day. However, the curves do exhibit a common shape, which is the following:

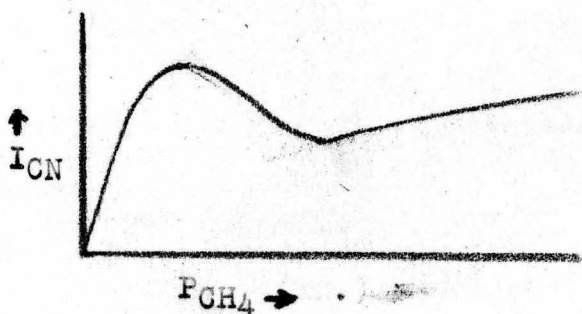


Figure 2

2. Dependence on total pressure.

The dependence of the intensity of the CN glow on total pressure may be found in two separate ways. The first is to find I_{CN} as a function of the total pressure from the previously determined graphs of I_{CN} v. P_{CH_4} (graph page 22). It appears that the intensity of the CN glow varies with the total pressure, but there is no obvious relationship between the two.

The second way was employed in a separate experiment. The total pressure was varied and the diathermy power was adjusted so that $I_0/P = \text{constant}$ ($P_N = \text{constant}$) and the methane flow rate was adjusted so that $P \times (\text{CH}_4 \text{ flow rate}) = \text{constant}$ ($P_{CH_4} = \text{constant}$). The CN intensities were then found at varying pressures.

Table VII
Variation of I_{CN} on Total Pressure

Trial	P (mm.)	I_0	CH ₄ flow (ml./sec.)	I_{CN}
Trial 1	1.5	30.5	0.41	1.4
	3.0	61.5	0.205	5.6
	6.0	122	0.10	26.5
Trial 2	1.5	27.2	0.48	1.2
	3.0	55.5	0.24	5.0
	6.0	112	0.12	21.0

The observed result was that the intensity of the CN glow varied very nearly as the square of the total pressure, the atomic nitrogen and methane concentrations being held constant.

Interpretation and Conclusions

I. Pressure dependence of the nitrogen afterglow.

Some controversy exists as to the pressure dependence of the rate of the nitrogen recombination reaction. It has been asserted that the intensity of the nitrogen afterglow is independent of the total pressure, if the nitrogen atom concentration is held constant.¹⁵ On the other hand, there is a large body of evidence suggesting that the afterglow intensity is directly proportional to the total pressure.¹⁶ Two sections of my work have some bearing on this question.

A. Intensity constant for the nitrogen afterglow reaction. (p.7)

I found that the the ratio $I_0/P_N^2 \cdot P_{total}$ was essentially constant at pressures varying from three to six millimeters. This indicates that the rate law for the recombination reaction is first order in the total pressure.

B. Origin of the NO glow. (p.9)

I found that $I_0^{1/2} P_{total}^{3/2} / I_v$ was essentially constant at a constant NO flow rate at pressures ranging from 1.6 to 6.2 millimeters. This constant factor was derived using $I_0 \propto P_N^2 \cdot P_{total}$. Assuming that the afterglow intensity is independent of the total pressure ($I_0 \propto P_N^2$) one would expect the constant factor to involve the square of the total pressure. This was not found.

These two results, plus the work done during the school year, lead me to believe that the rate law is first order in the total pressure, and in fact

$$I_0 \propto P_N^2 \cdot P_{total}$$

II. Radiative efficiency of nitrogen recombination.¹⁷

The experimental data contains essentially all that I know. It appears that only a small fraction of nitrogen recombinations lead to emission. It is interesting to note that the ratio of the NO to the nitrogen intensity constants (p.10) is (possibly coincidentally) approximately the same as the calculated fraction of excited nitrogens that emit. Perhaps this indicates that a large fraction of the NO's produced by combination of atomic nitrogen and oxygen actually emit. Since my knowledge of collision theory is negligible, I am not prepared to offer an explanation for that possibility. Possibly a collision of an excited NO with an inert molecule tends to produce a radiative state more often than does one of an excited N_2 .

III. Kinetics of the methane-active nitrogen reaction.

It is possible to express the observations of the dependence of the rate of CN emission upon the various parameters in a very imprecise rate law. The rate law must have the following characteristics:

A. The rate of CN emission is proportional to the square of the total pressure.

B. The rate of CN emission is between second and third order in the nitrogen atom concentration.

C. It appears quite likely that there are at least two possible reaction paths, in view of the unusual dependence of the rate of CN emission upon the methane concentration. It is difficult for me to imagine any simple single reaction path that would give the

observed results. Probably the simplest expression would be to assume the intensity of the CN emission to be proportional to

$$\frac{P_{CH_4}}{1 + k(P_{CH_4})^2} + k'(P_{CH_4})^x \quad 0 < x < 1$$

This sort of relationship would fit the experimental data fairly

well: $I_{CN} = K P_{total}^2 \cdot P_N^y \left[P_{CH_4} (1 + k P_{CH_4}^2)^{-1} + k' P_{CH_4}^x \right]$ $\begin{matrix} 2 < y < 3 \\ 0 < x < 1 \end{matrix}$

Winkler and his co-workers studied the methane-active nitrogen reaction several years ago.¹⁸ When the final products of the reaction were condensed, separated, and identified, they found only hydrogen cyanide and a trace of hydrogen. No ammonia or other products which might be associated with NH-type intermediates were found.

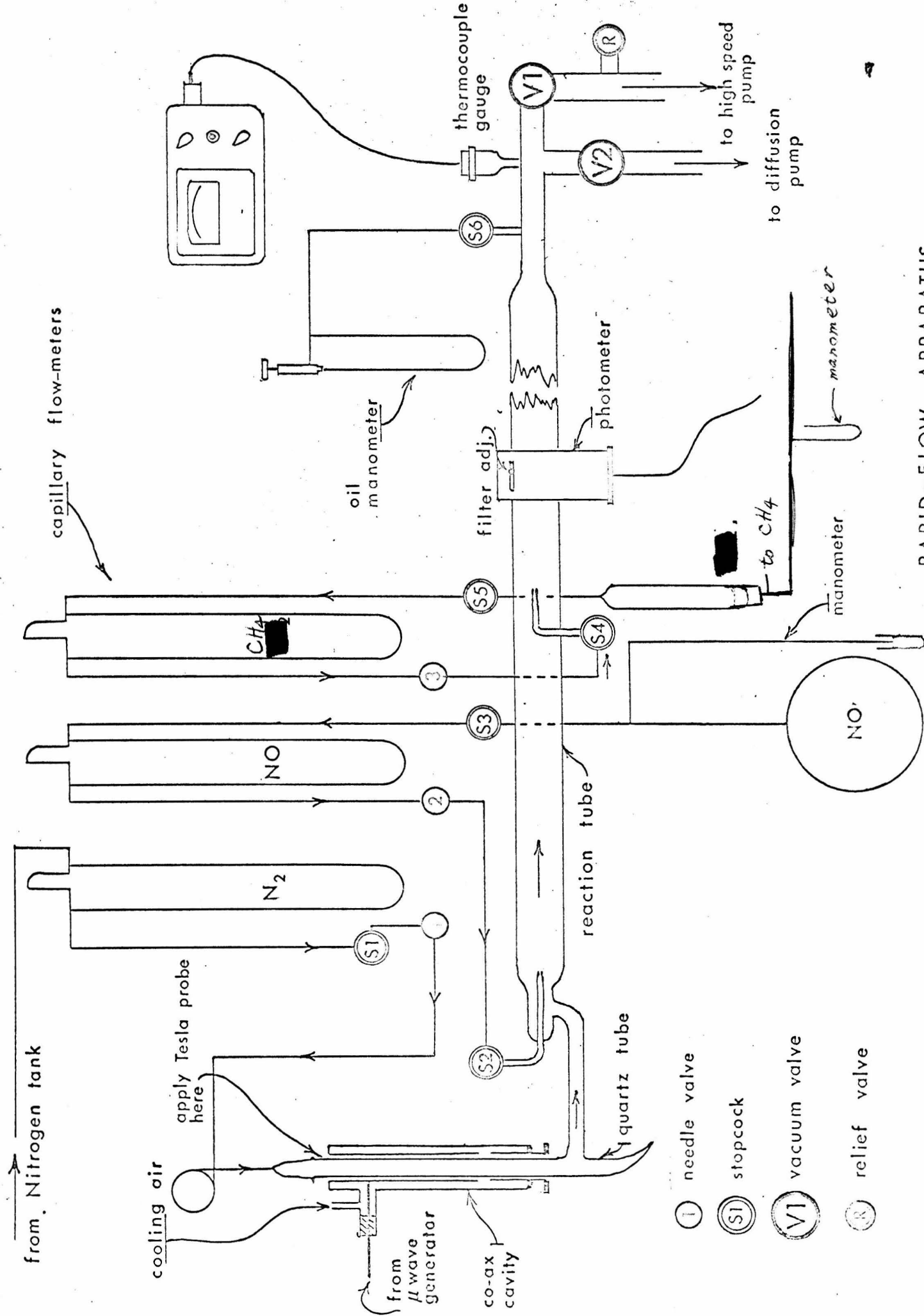
If one accepts their observations (if not their conclusions as to the mechanism of the reaction), one rapidly reaches an impasse when trying to think of a plausible mechanism to fit the kinetic characteristics that I have observed. Unfortunately, I have not yet seen a way out. If this research is carried further in the future, it might be usefull to use the Ch 26 ESR apparatus to identify various radicals undoubtedly present in the reaction mixture.

FOOTNOTES

1. R.B.W. Pearse., and A.G. Gaydon, The Identification of Molecular Spectra, John Wiley and Sons, New York, 1941, .p. 137, 74.
2. G.G. Mannella, Chemical Reviews, 63, p. 3, (1963)
3. ibid, p. 3.
4. ibid, p.11.
5. This is not a new phenomena; see Mannella, op. cit., p.2.
6. Y. Tanaka, F.R. Innes, and A.S. Jursa, J. Chem Phys., 42, 1183 (1965)
7. Pearse and Graydon, op. cit., p. 145.
8. Pearse and Graydon, op.cit., p. 139.
9. American Institute of Physics Handbook, McGraw-Hill, New York, 1963, 6-124.
10. International Critical Tables, McGraw-Hill, New York, 1929, V, p.246.
11. W.E. Forsythe and E.Q. Adams, J. Opt. Soc. Am. 35, 108 (1945).
12. International Critical Tables, op. cit., p. 238.
13. American Institute of Physics Handbook, op. cit., p.6-124.
14. Mannella, op. cit., p. 11.
15. R.A. Young and R.L. Sharpless, J. Chem. Phys., 39, 1071 (1963).
16. Mannella, op. cit., p.11.
17. R.A. Young and R.L. Sharpless, J. Chem. Phys., 41, 1497 (1964).
18. P.A. Gartaganis and C.A. Winkler, Can. J. Chem., 34, 1457 (1956).

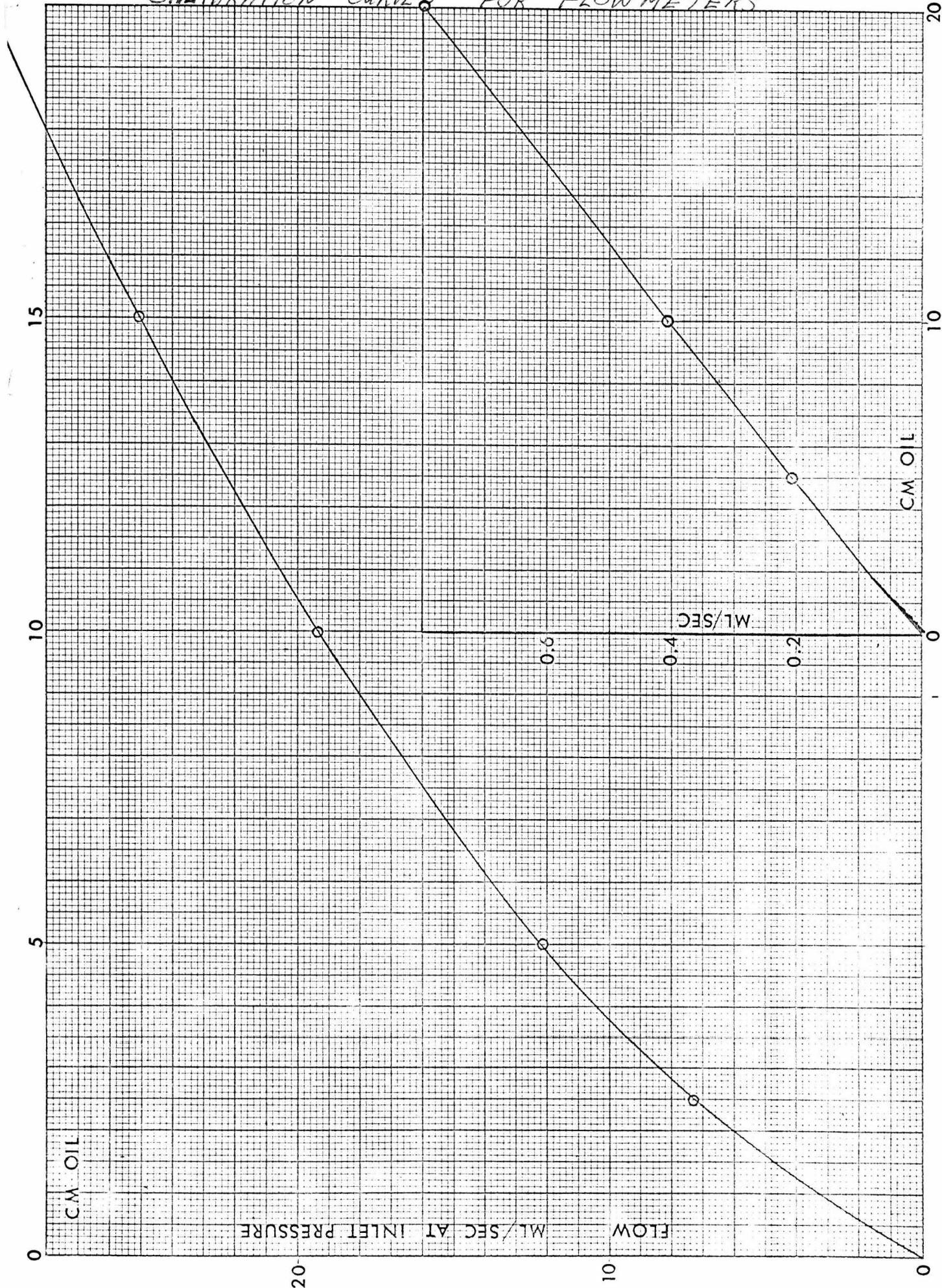
Graphs and Diagrams

SUBJECT	PAGE
Rapid-flow apparatus.....	1-2
Calibration curves for flow meters.....	3
Negatives of mercury and reaction spectra.....	4
Comparator readings versus wavelength.....	5
Calculated %O as a function of x.....	6
Color temperature versus true temperature (W).....	7
Variation of I_{CN} with x.....	8
Variation of I_{CN} with P_N^2 and P_N^3	9-21
Variation of I_{CN} with P_{CH_4}	22
Effect of CH_4 added to active nitrogen stream as a function of distance down the reaction tube.....	23
Spectrum of reaction tube with and without methane present.....	24



RAPID-FLOW APPARATUS

CALIBRATION CURVES FOR FLOW METERS

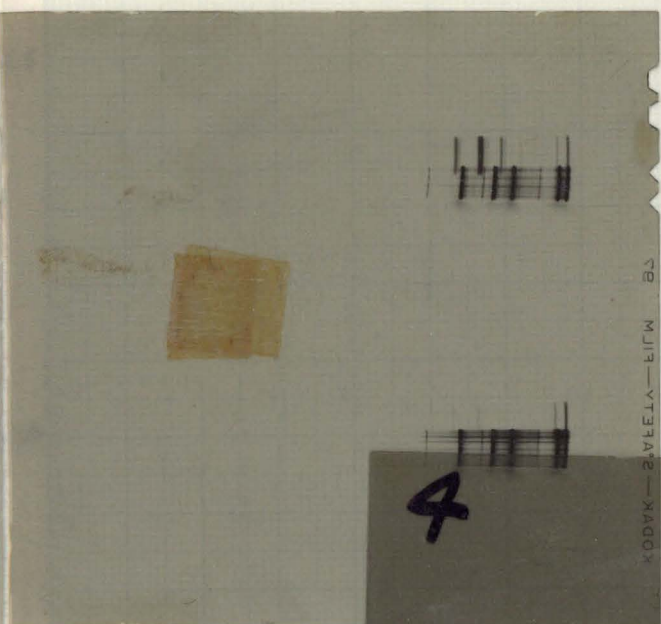


Negatives of Mercury Arc, Active Nitrogen, and Active Nitrogen Plus Methane Spectra

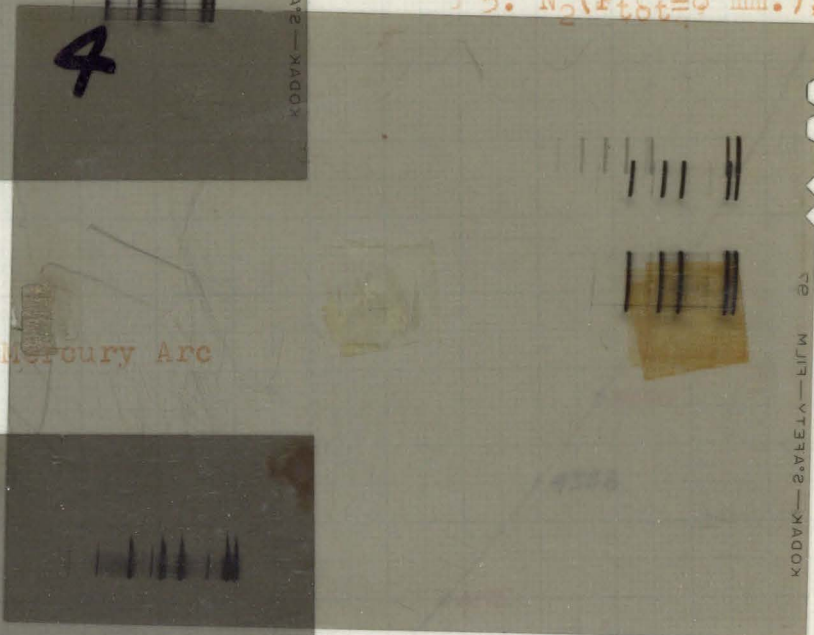
- 2. Lower: Active Nitrogen; mercury
- Upper: Active Nitrogen plus methane; mercury



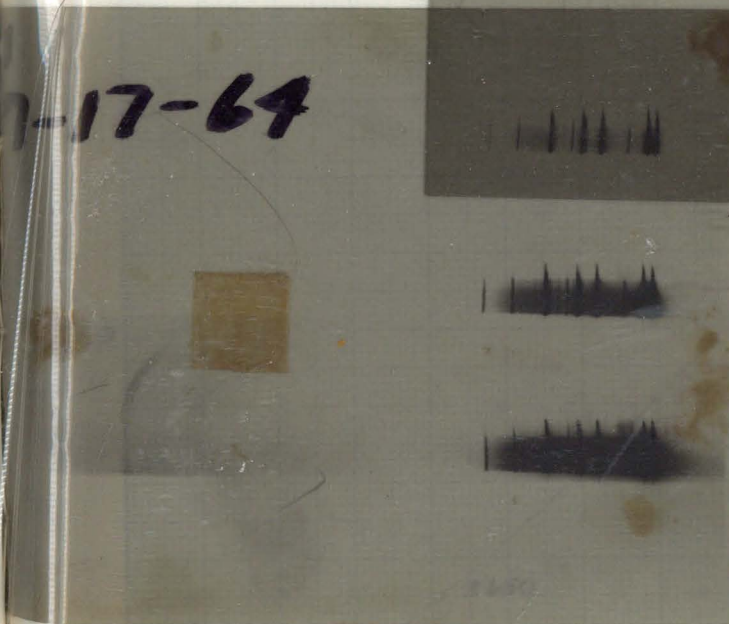
5. N_2 ($P_{tot}=8$ mm.); mercury



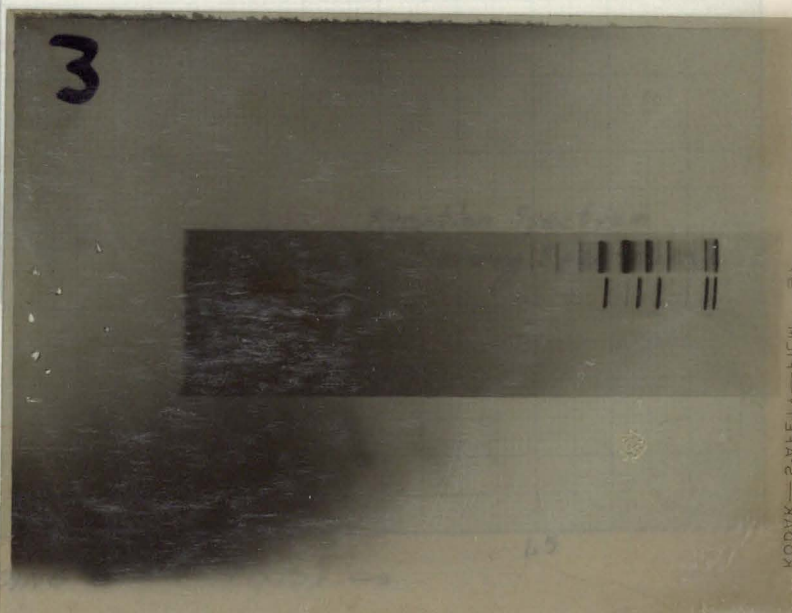
1. Spectrum of Mercury Arc



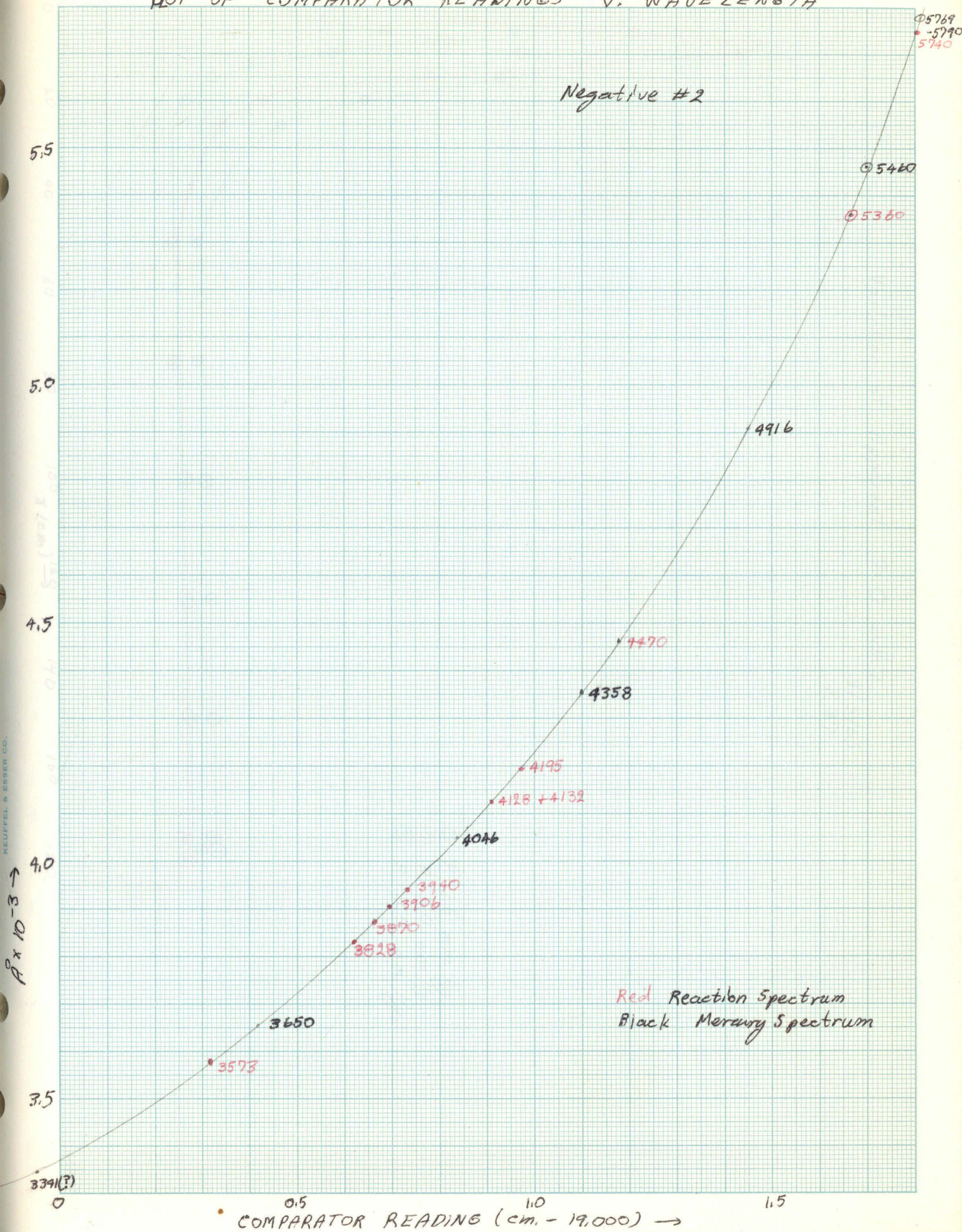
4. CH_4+N_2 ($P_{tot}=8$ mm.); mercury.



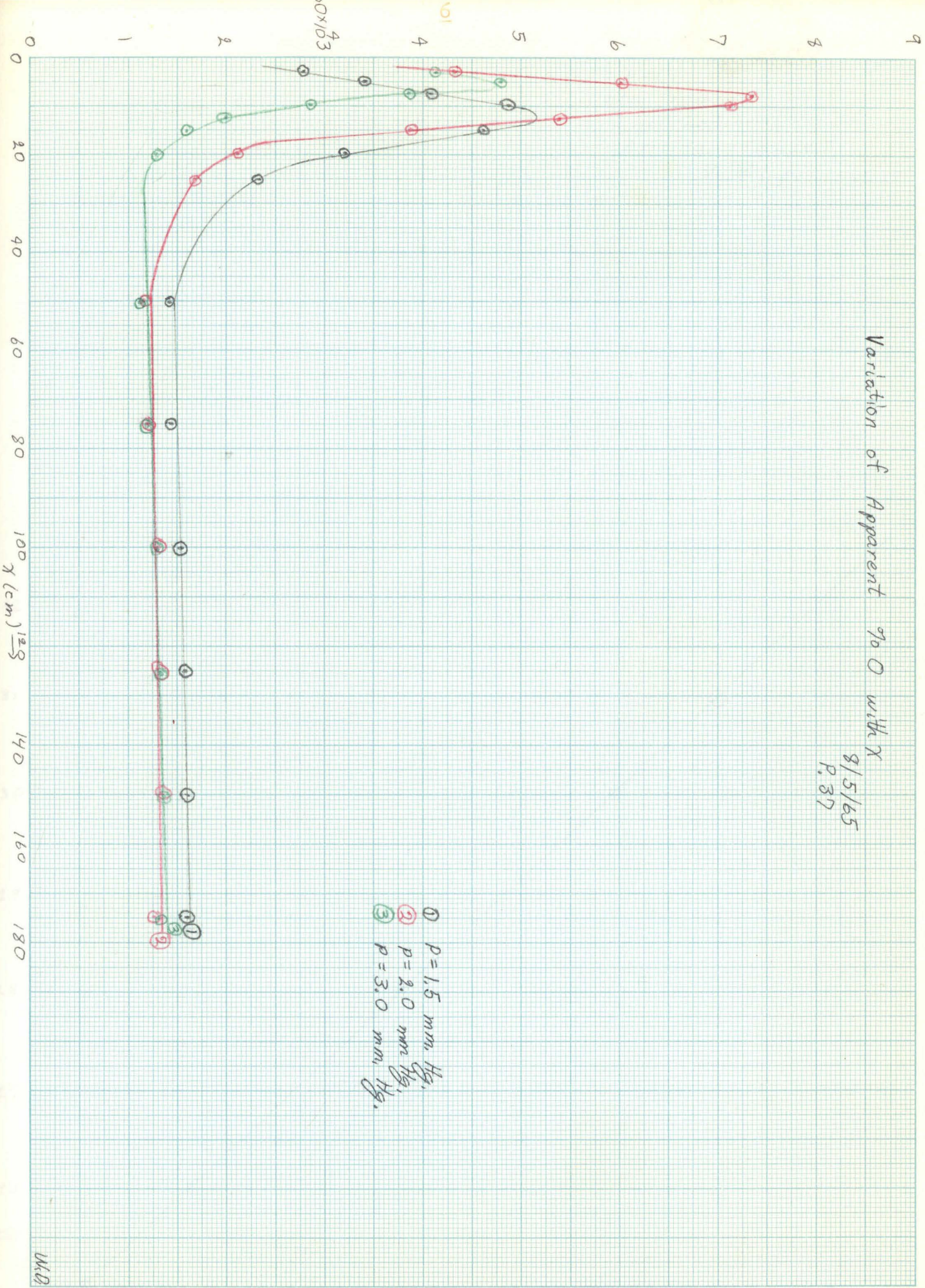
3. Active Nitrogen plus methane; mercury



PLOT OF COMPARATOR READINGS V. WAVELENGTH



Variation of Apparent η with x
 8/5/65
 P. 37



COLOR TEMPERATURE V. TRUE TEMPERATURE FOR TUNGSTEN

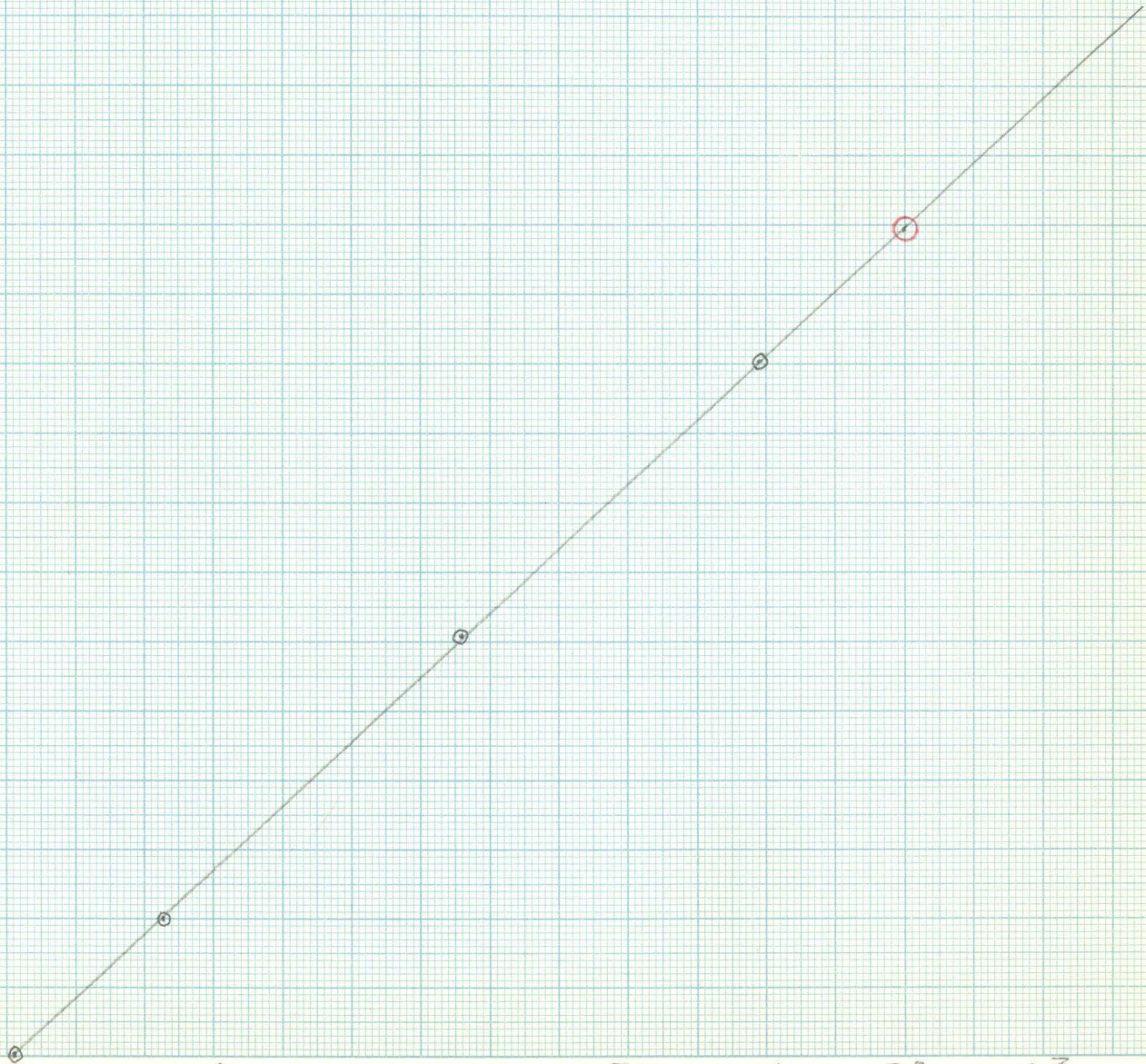
Data from
International
Critical Tables
V. V, p.

TRUE TEMPERATURE ($^{\circ}\text{C} \times 10^{-2}$)

25
26
27
28
29
30
31
32

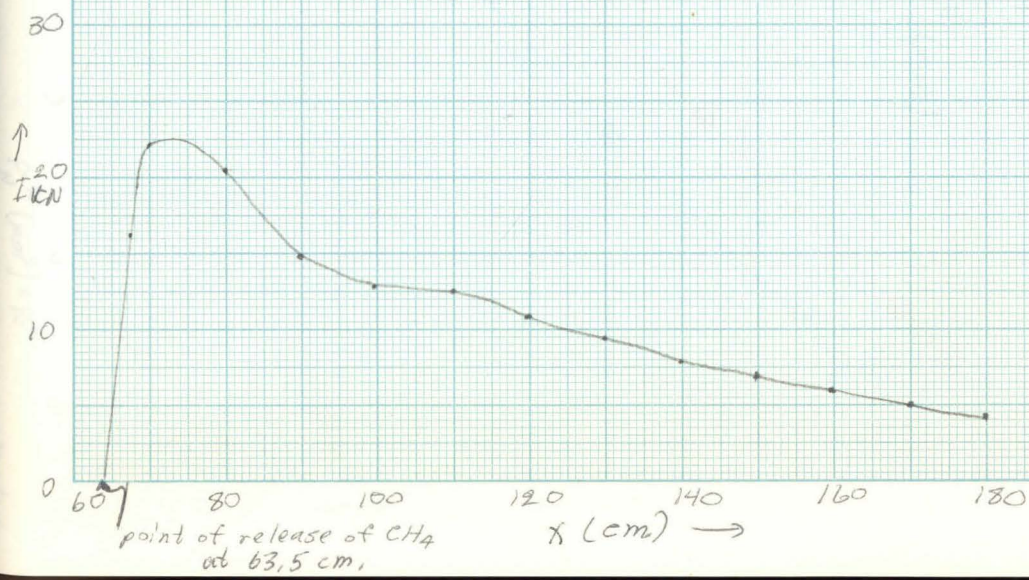
25 26 27 28 29 30 31 32 33

Color Temperature ($^{\circ}\text{C} \times 10^{-2}$)



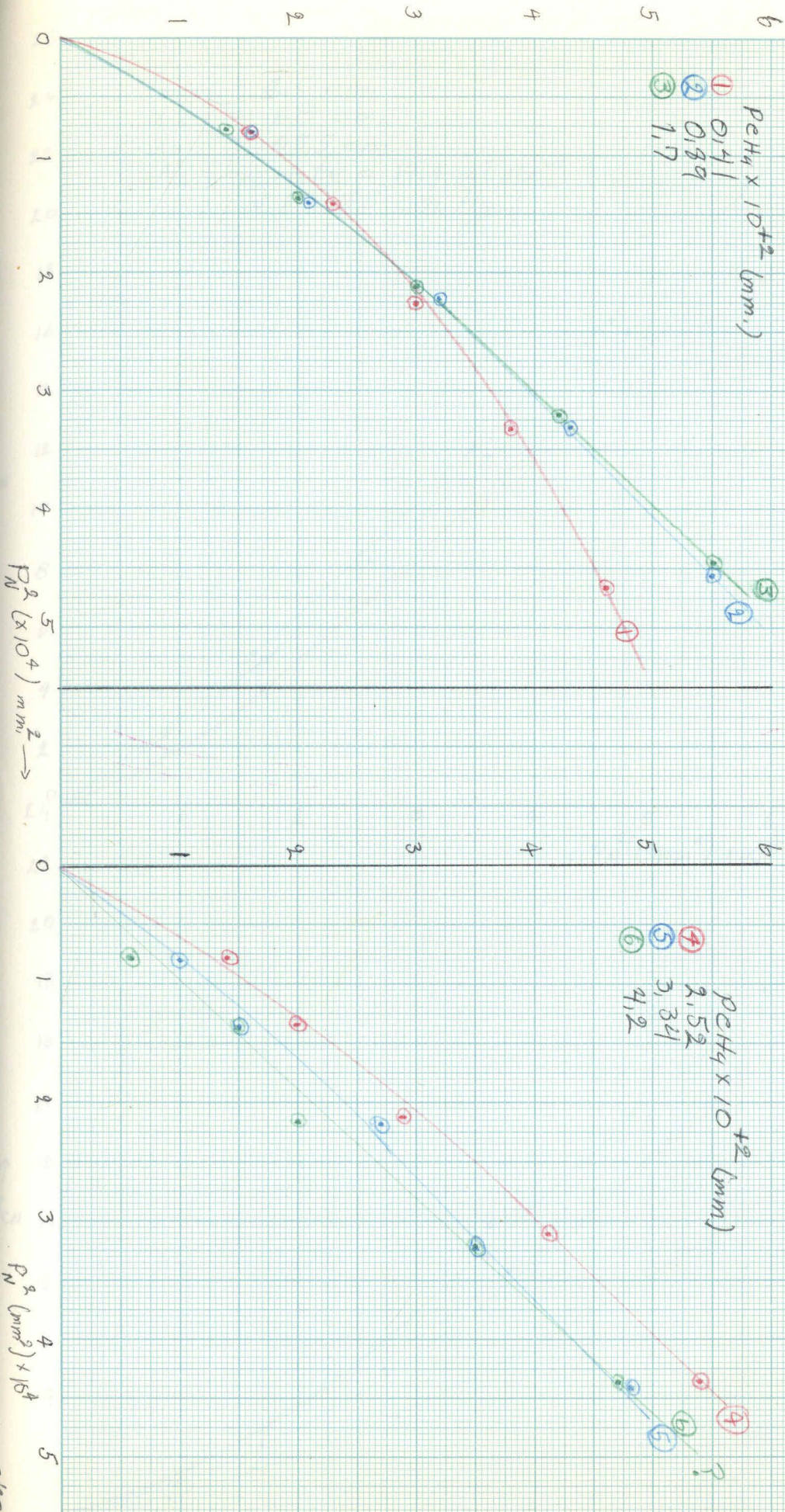
VARIATION OF I_{CN} WITH x

$P_{total} = 4,0 \text{ mm.}$
Other conditions
are unimportant



VARIATION OF I_{ex} WITH P_N^2

$P = 2.0 \text{ mm.}$
 $X = 6.8 \text{ cm.}$
 $X_0 = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml./sec.}^{-1}$
 $\Delta P = 85 \text{ cm. Hg}$



VARIATION OF I_{CN} with P_N^2

26

24

22

20

18

16

14

12

10

8

6

4

2

24

22

20

18

16

14

12

10

8

6

4

2

0

 $P_{total} = 40 \text{ mm.}$
 $x = 68 \text{ cm.}$
 $x_0 = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec.}^{-1}$
 $Q P = 85 \text{ cm. Hg.}$
 $P_{CH_4} \times 10^2 (\text{mm.})$

⑤ 3.4

⑥ 5.1

⑦ 6.7

⑧ 8.45

 $P_N^2 (\text{mm}^2) \times 10^4$
 P_N^2
 $P_{CH_4} \times 10^2 (\text{mm.})$

① 0.41

② 0.82

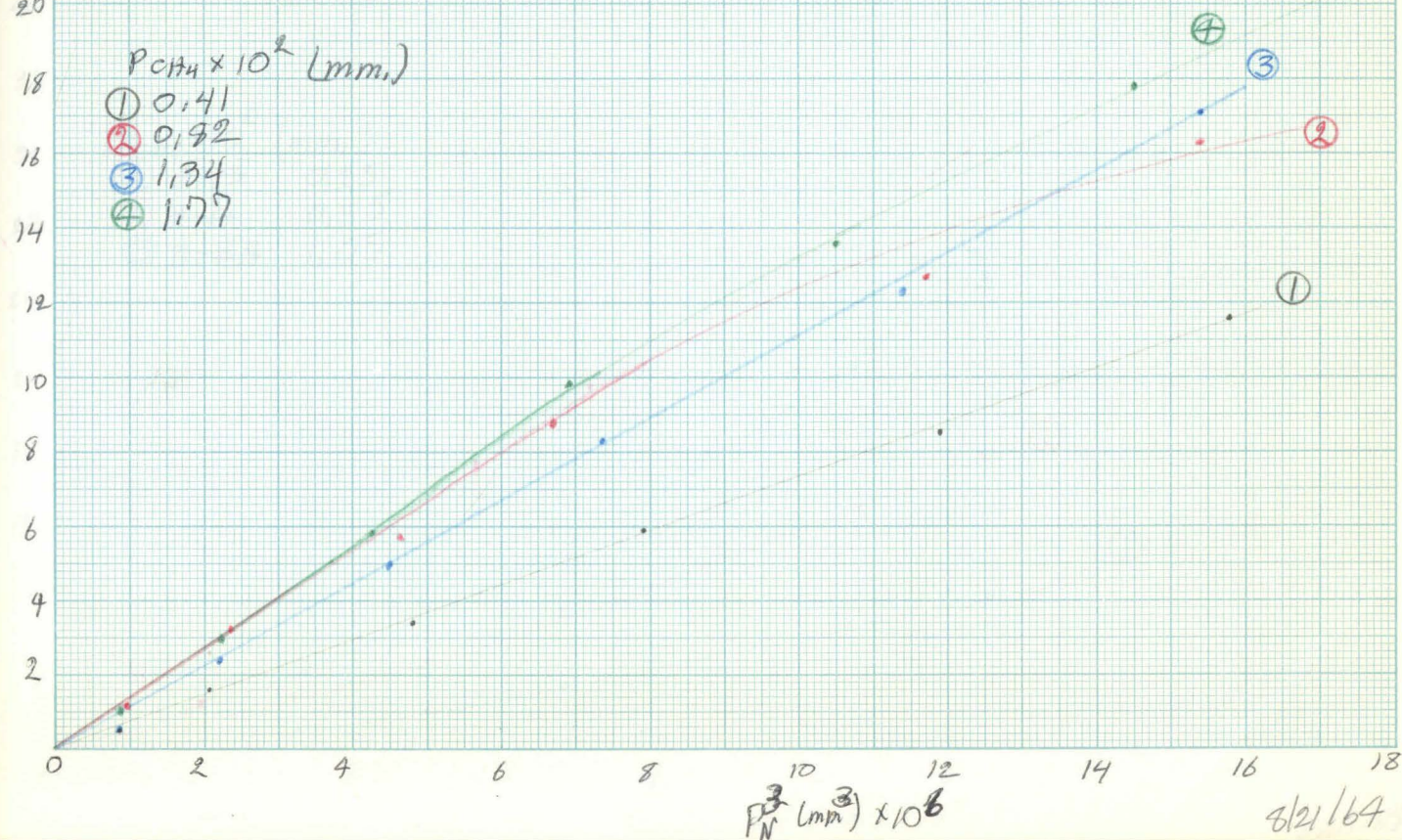
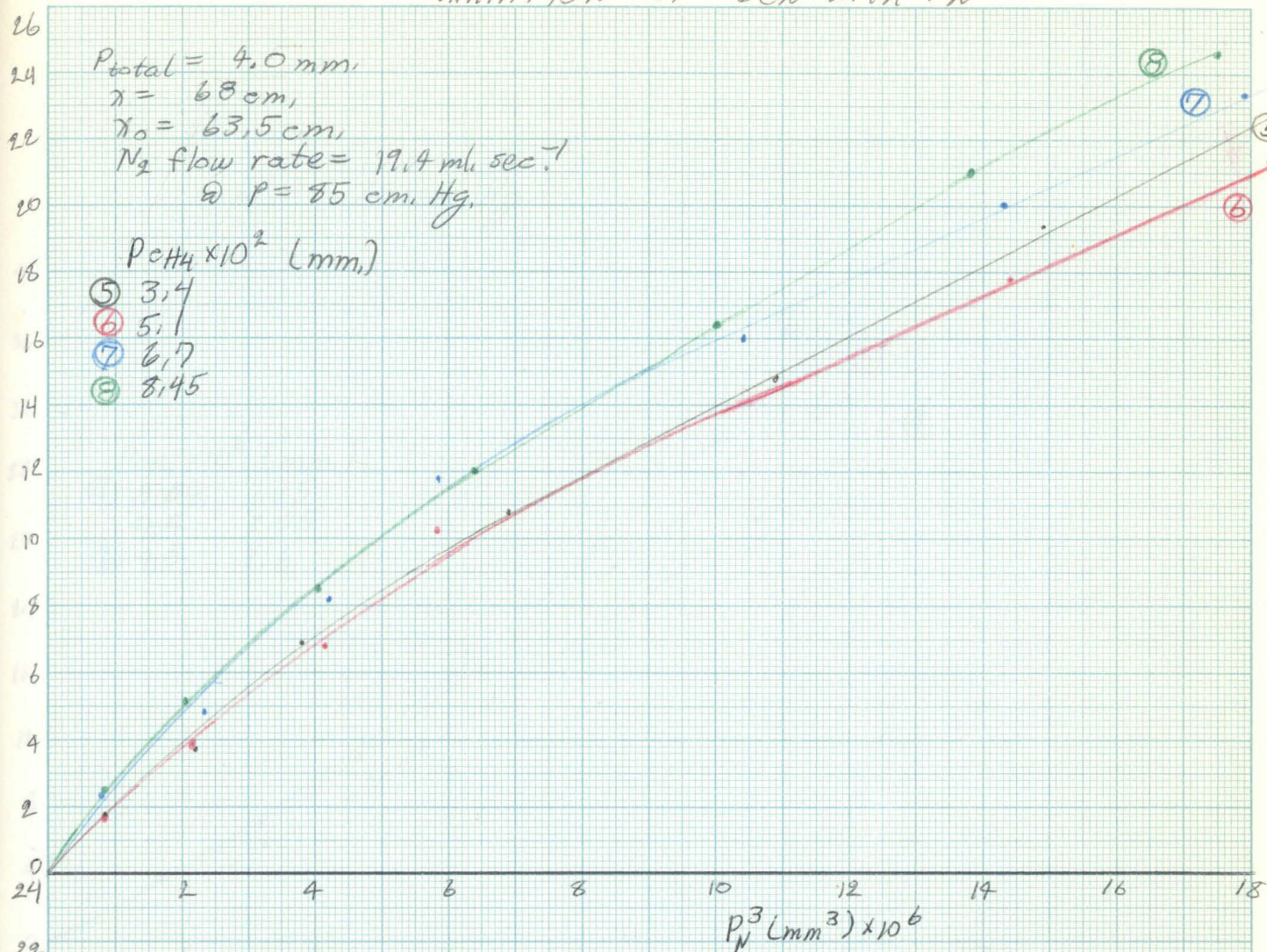
③ 1.34

④ 1.77

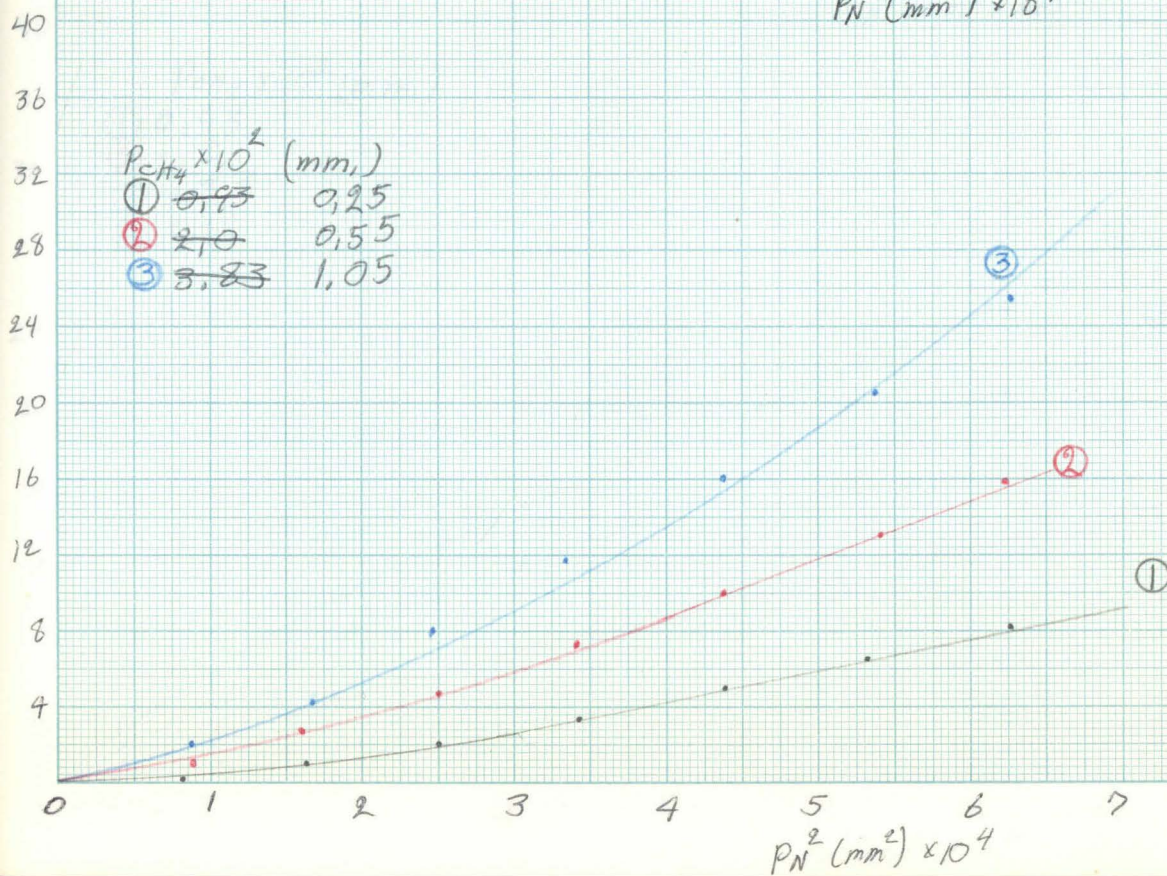
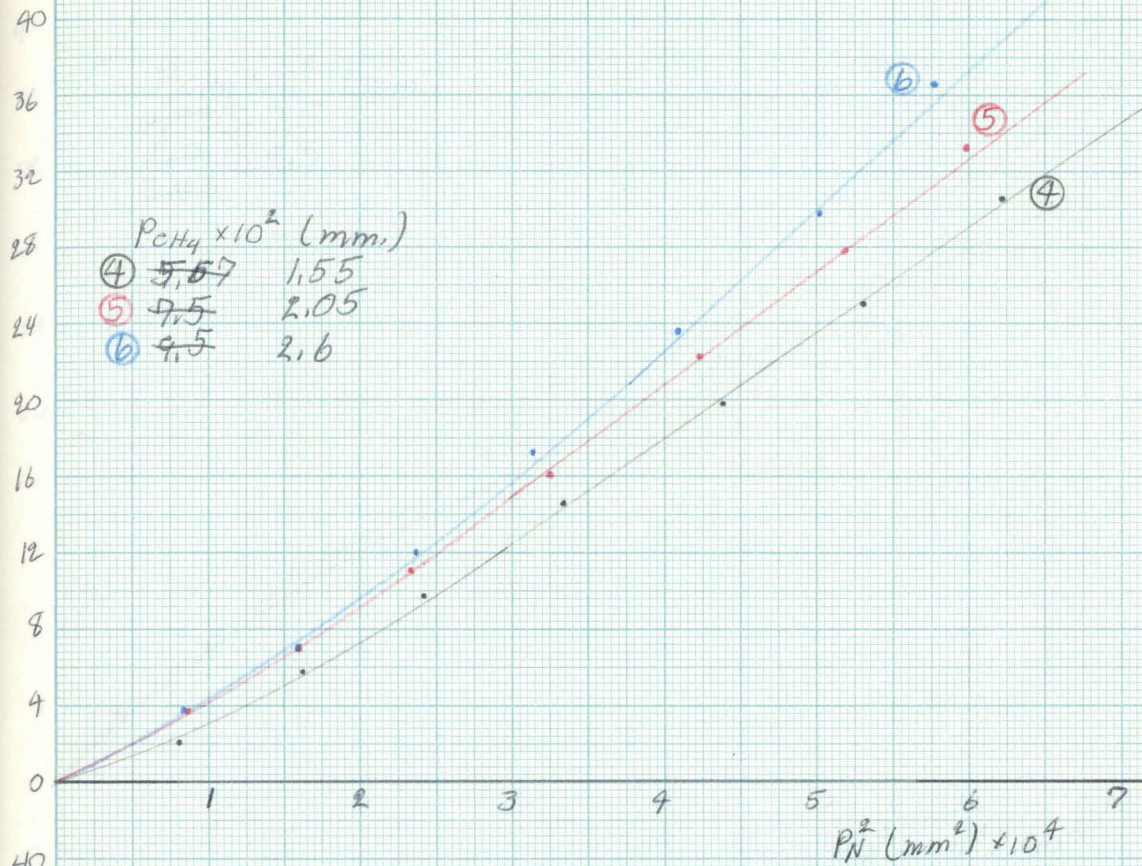
 $P_N^2 (\text{mm}) \times 10^4 \rightarrow$

5/21/64

VARIATION OF I_{CN} WITH P_N^3



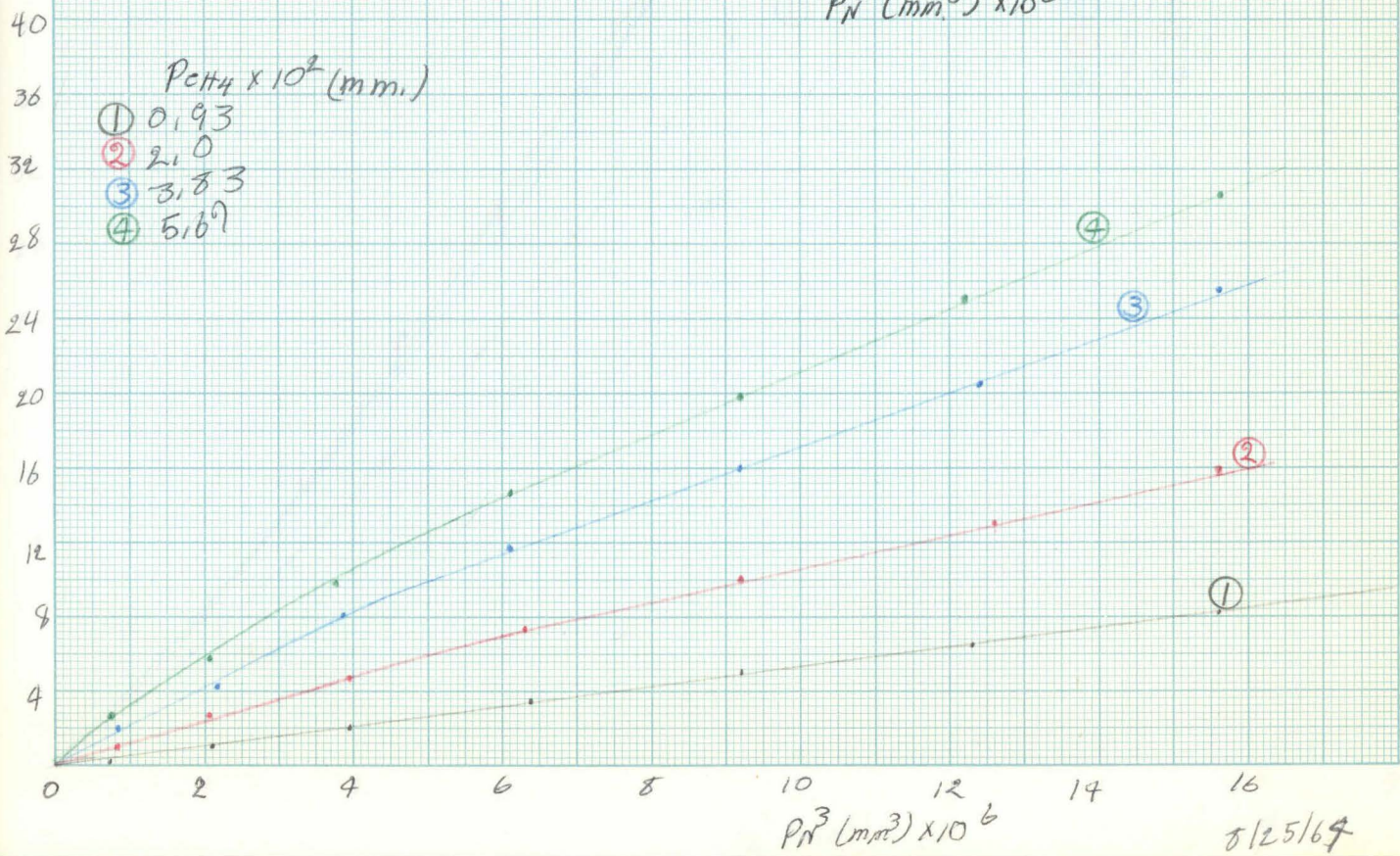
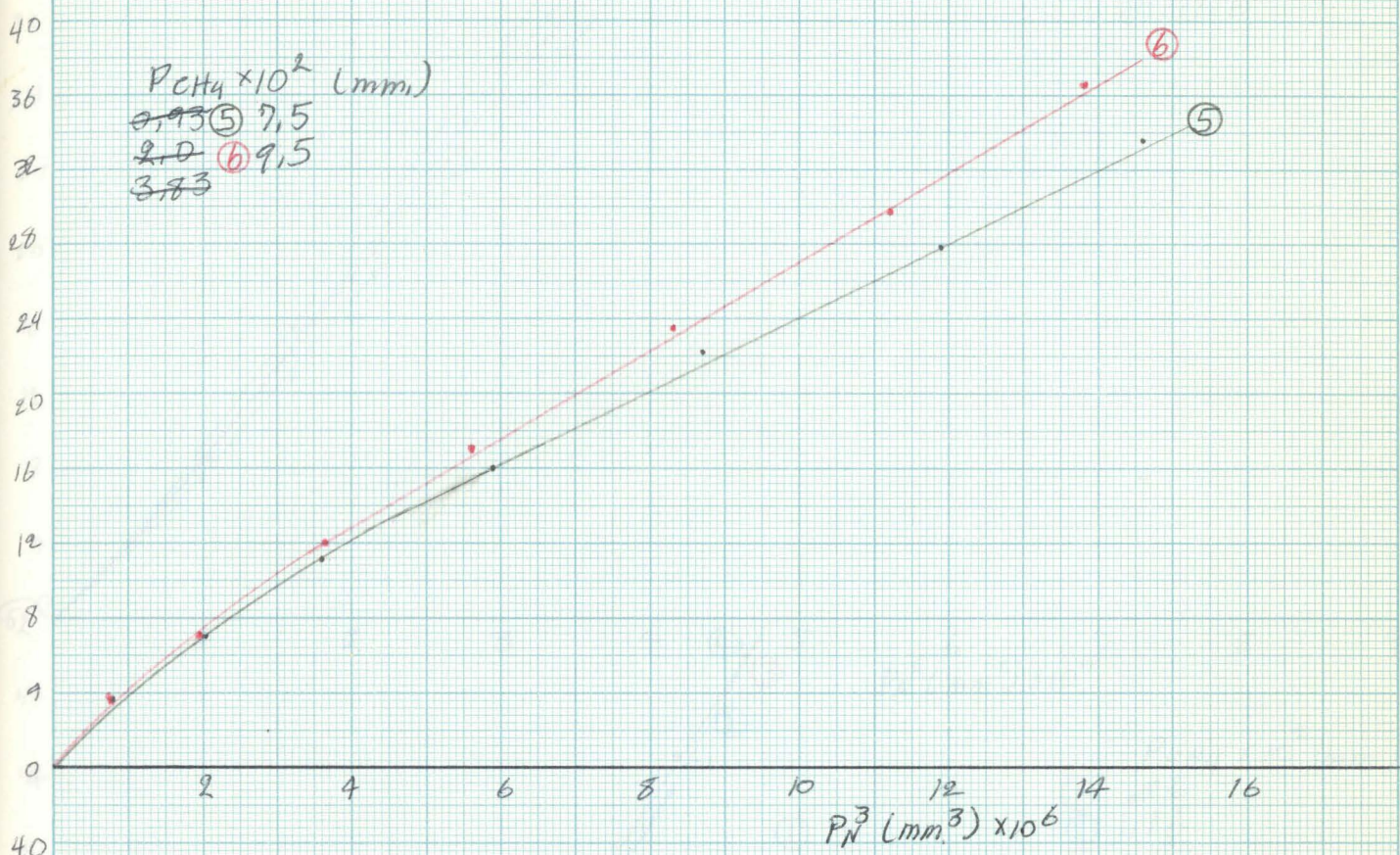
8/21/64

VARIATION OF I_{CN} WITH P_N^2 $P_{total} = 4.5 \text{ mm.}$ $\lambda = 68 \text{ cm.}$ $X_0 = 63.5 \text{ cm.}$ $N_2 \text{ flow rate} = 19.4 \text{ ml. sec.}^{-1}$ $\textcircled{2} P = 35 \text{ cm. Hg.}$ 

8/25/64

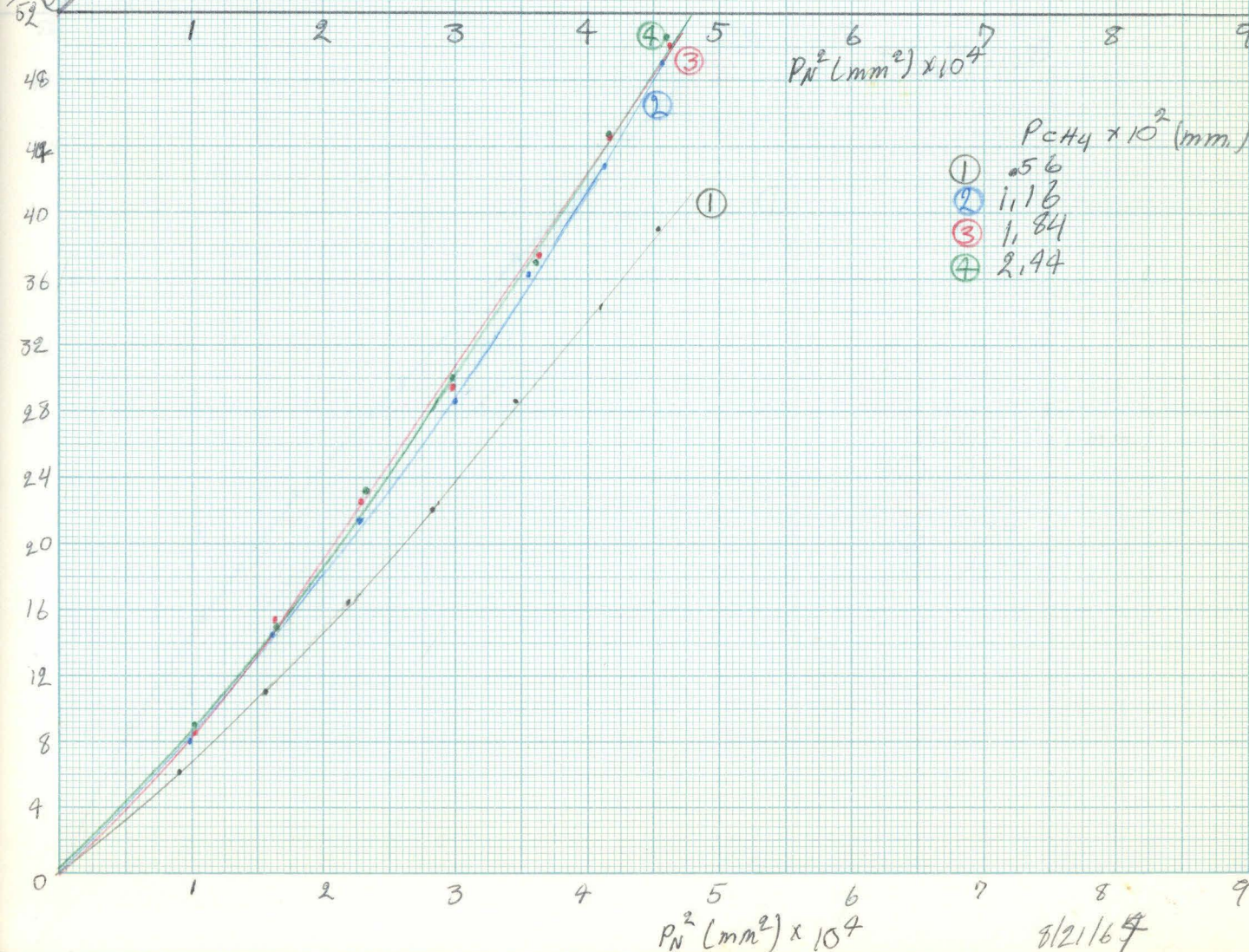
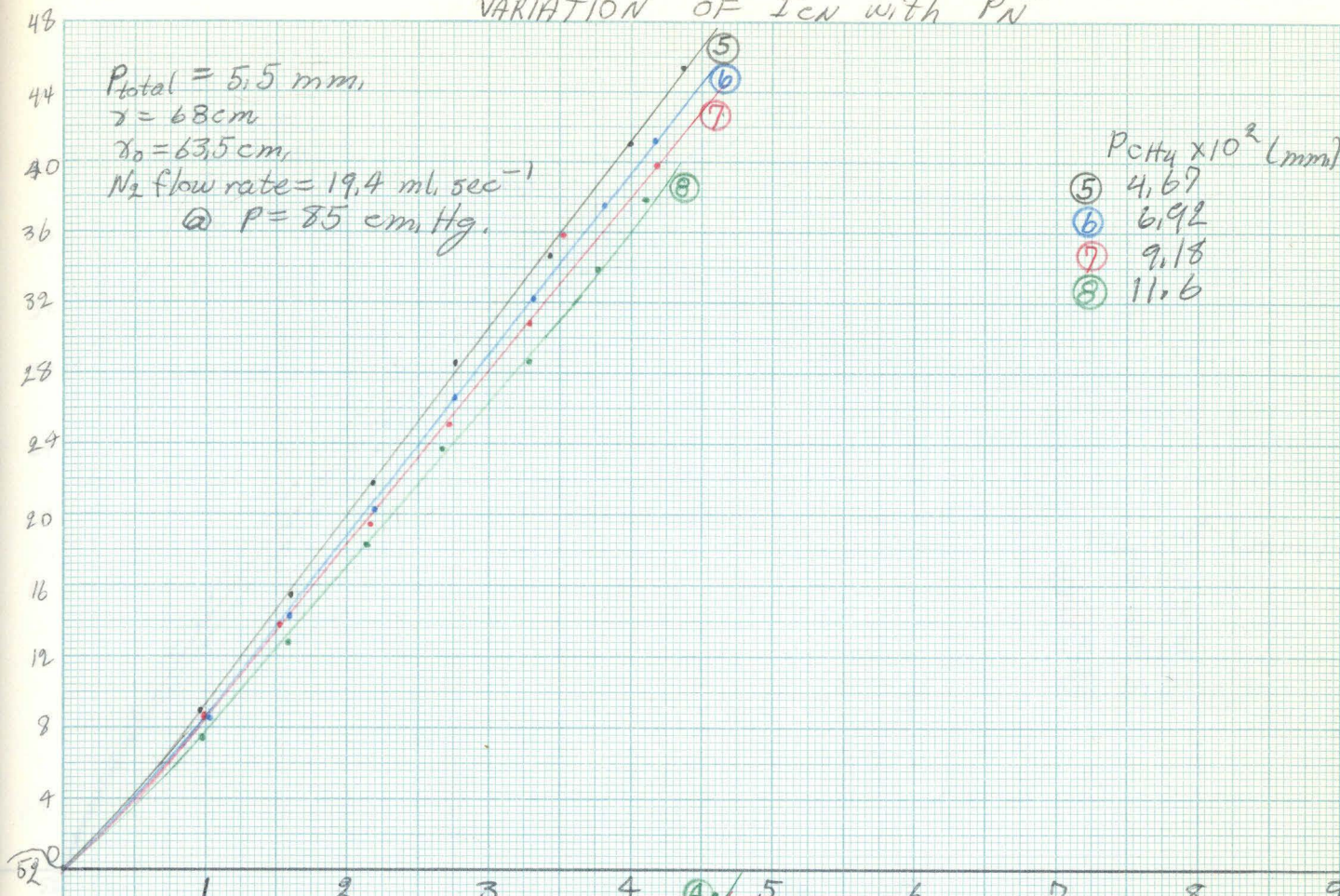
VARIATION OF I_{CN} with P_N^3

$P_{total} = 4.5 \text{ mm.}$
 $r = 6.8 \text{ cm.}$
 $r_0 = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec}^{-1}$
 $\bar{p} = 85 \text{ cm. Hg.}$



8/25/69

VARIATION OF I_{CN} WITH P_N^2



8/21/64

15 VARIATION OF I_{CN} WITH P_N^3

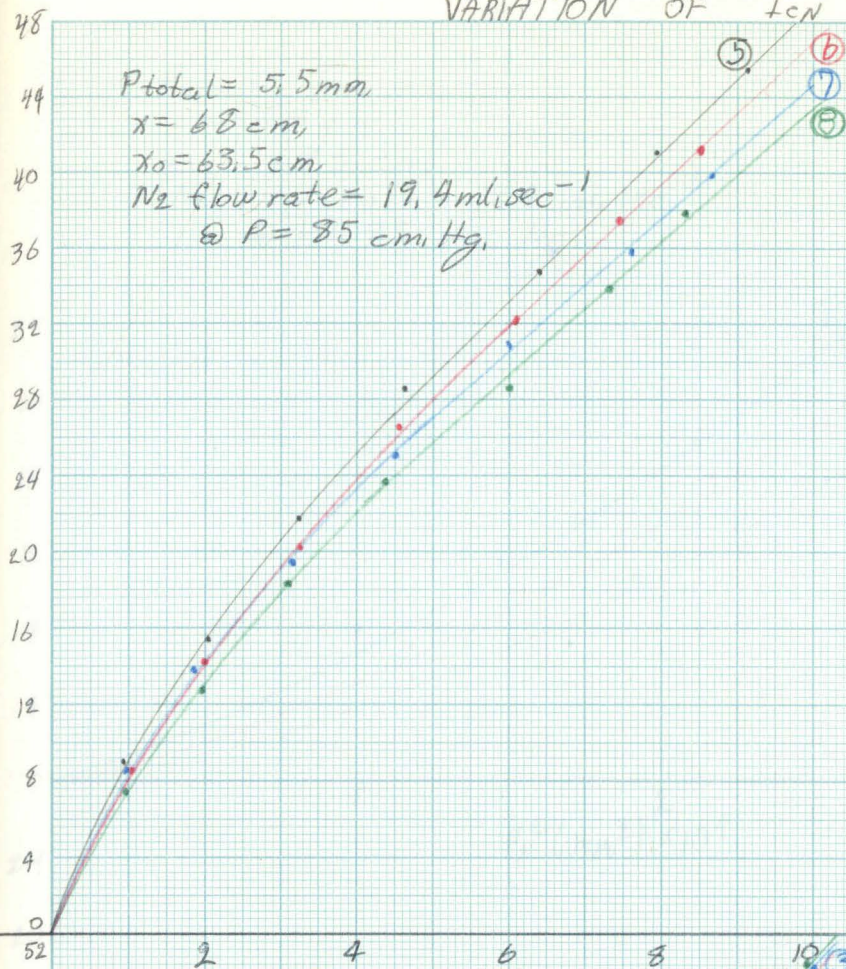
$P_{total} = 5.5 \text{ mm}$

$x = 68 \text{ cm}$

$x_0 = 63.5 \text{ cm}$

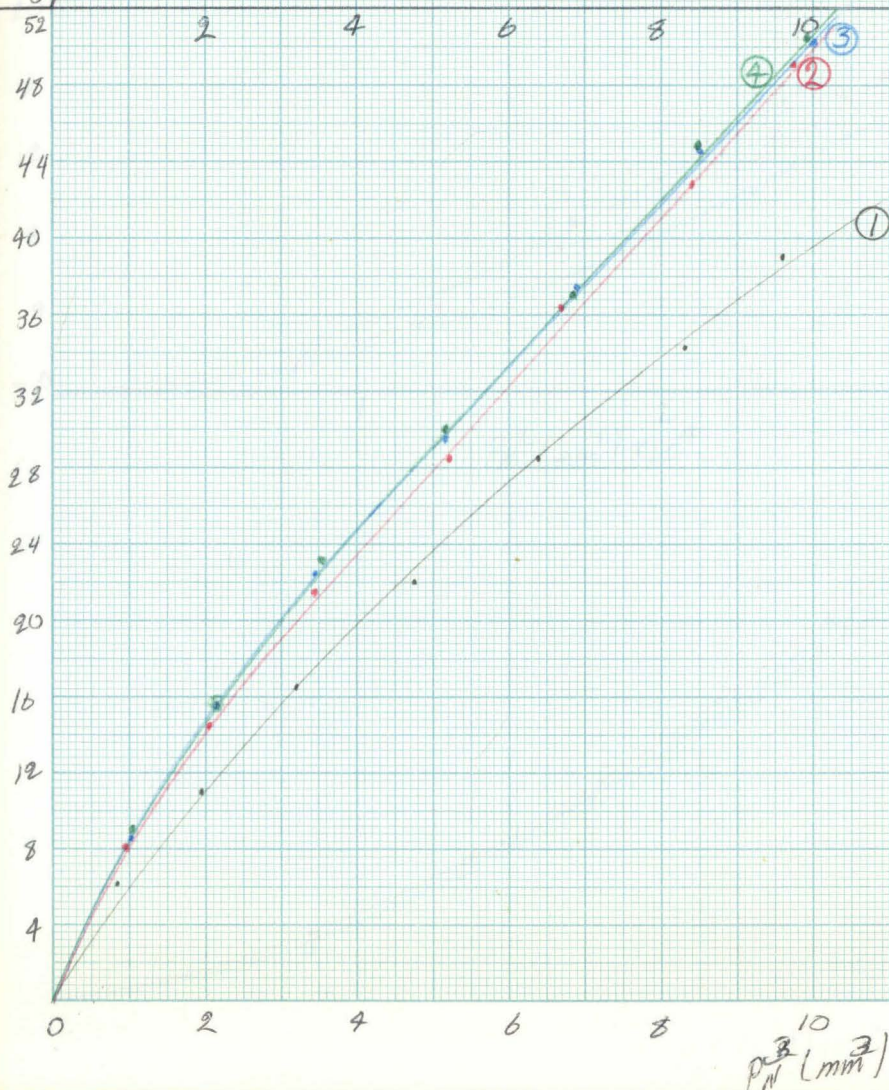
$N_2 \text{ flow rate} = 19.4 \text{ ml/sec}^{-1}$

@ $P = 85 \text{ cm Hg}$



$P_{CH_4} \times 10^2 \text{ (mm.)}$

(5)	4.67
(6)	6.92
(7)	9.18
(8)	11.6



$P_N^3 \text{ (mm}^3\text{)} \times 10^6$

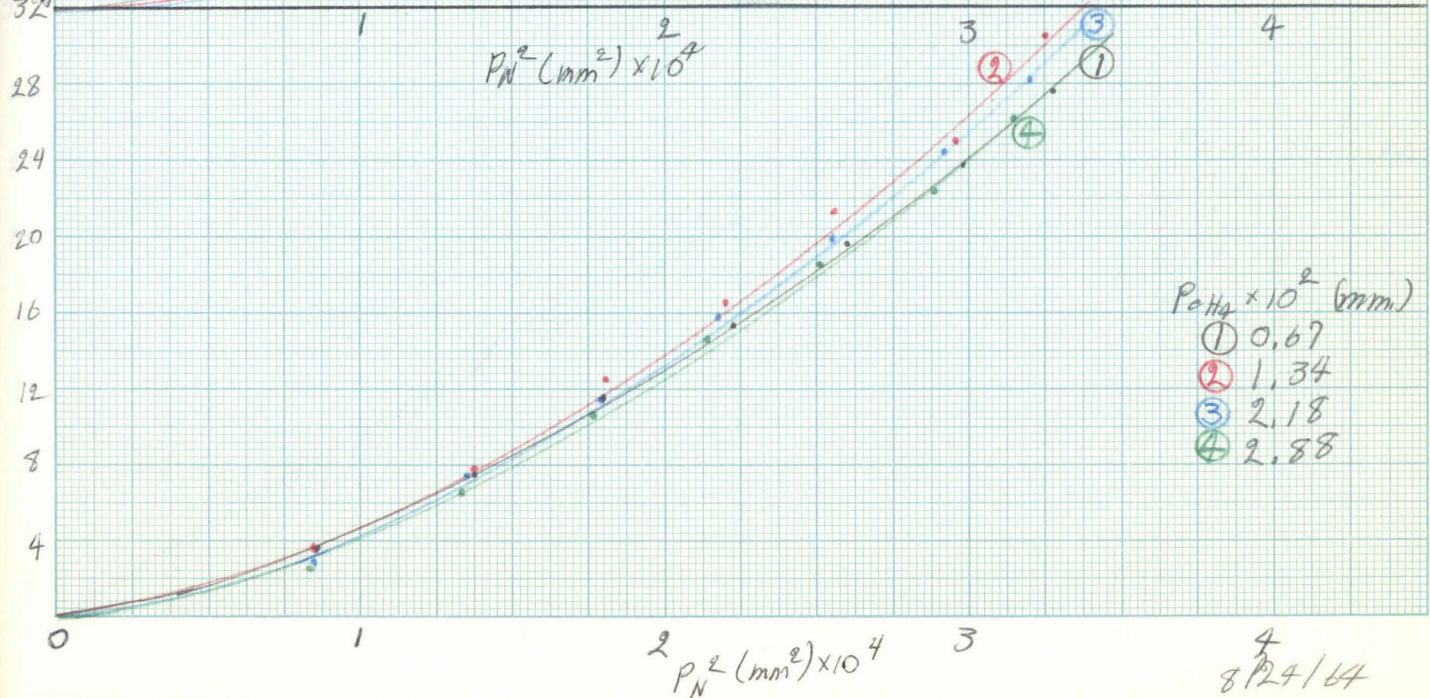
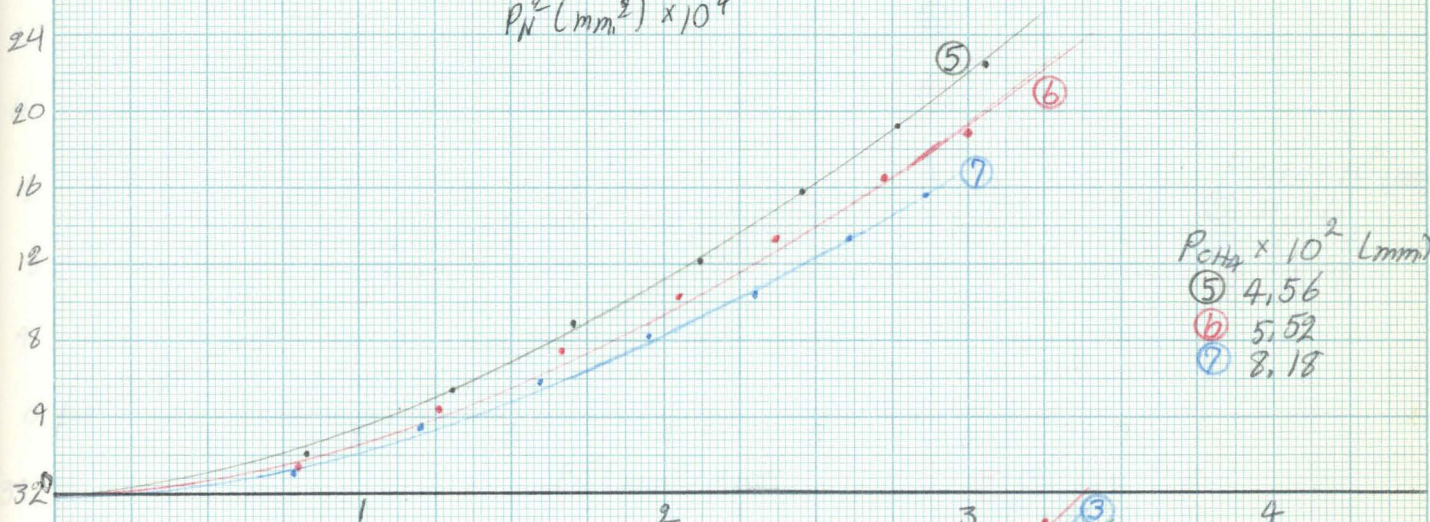
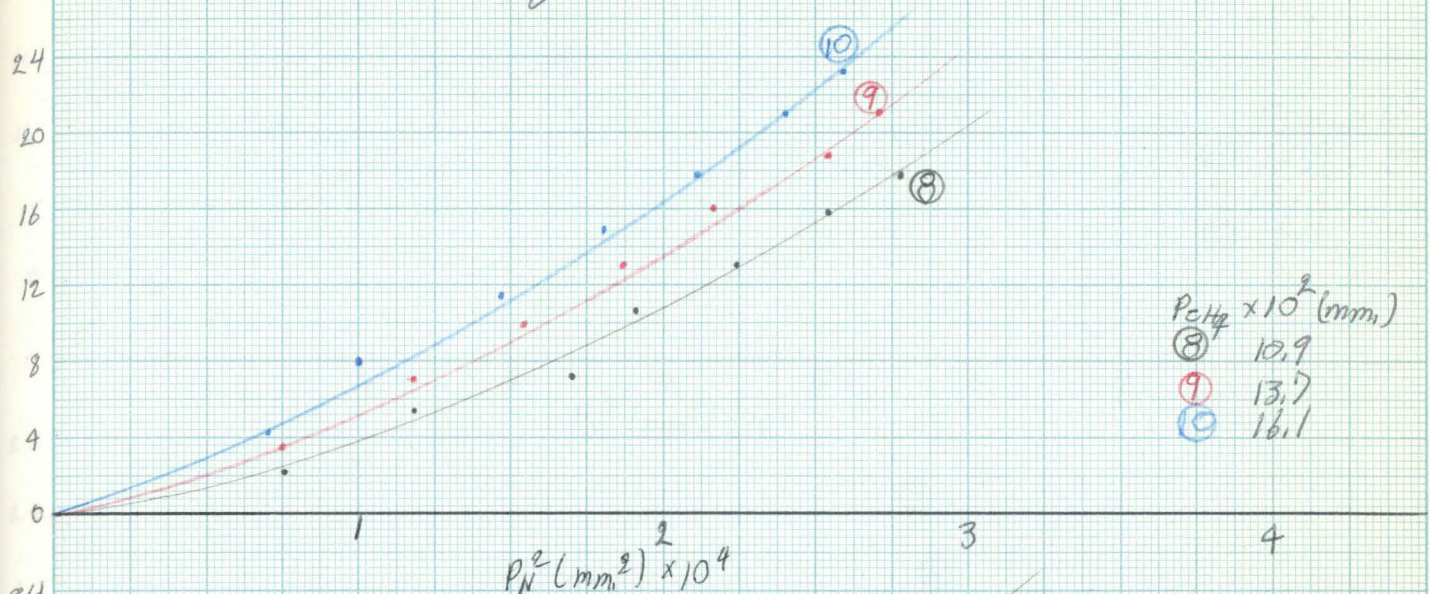
$P_{CH_4} \times 10^2 \text{ (mm.)}$

(1)	0.56
(2)	1.16
(3)	1.84
(4)	2.44

8/21/69

16 VARIATION OF I_{CN} WITH P_N^2

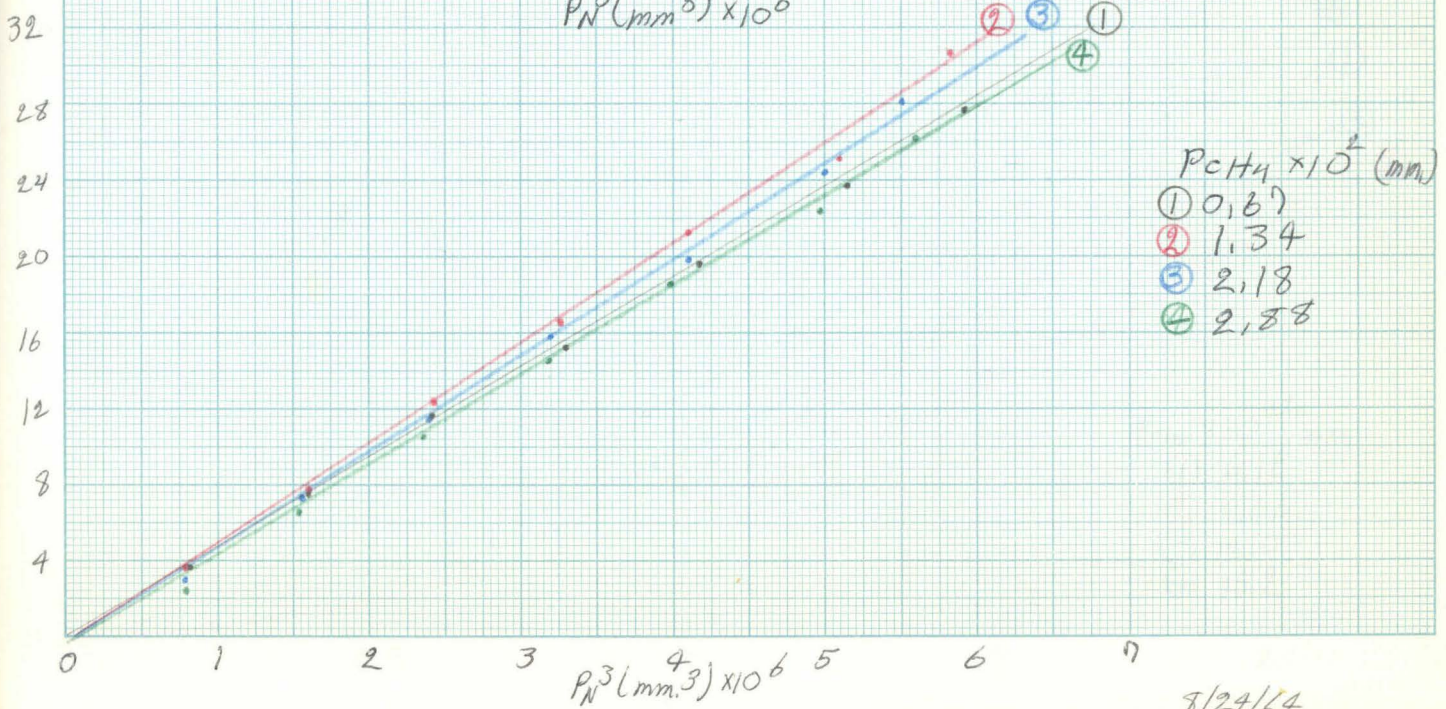
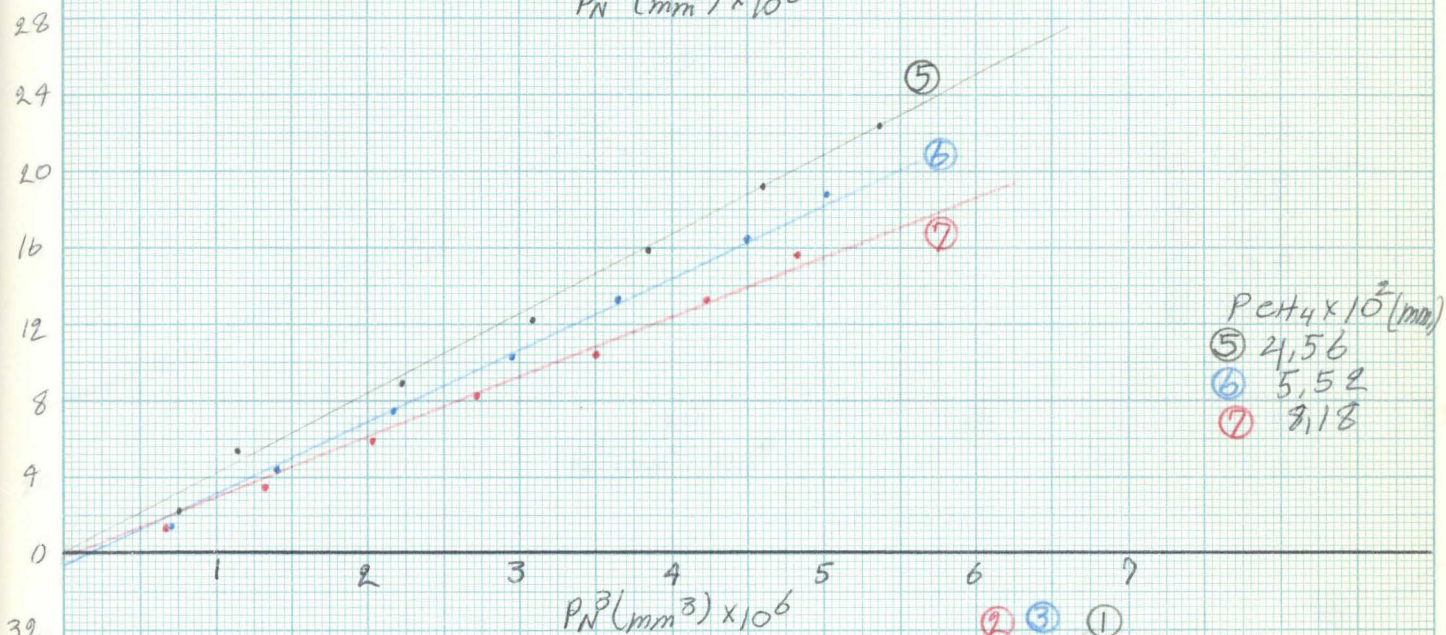
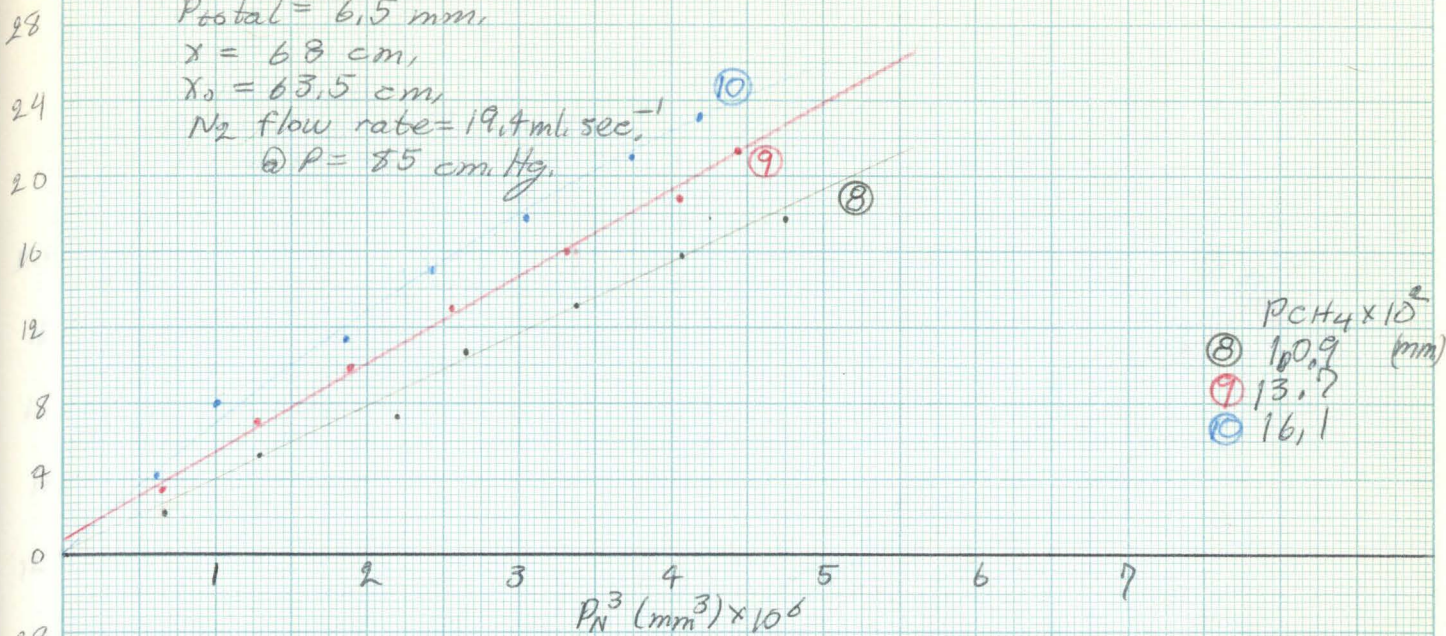
$P_{total} = 61.5 \text{ mm}$
 $x = 6.8 \text{ cm}$
 $x_0 = 63.5 \text{ cm}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec.}^{-1}$
 $@ P = 85 \text{ cm. Hg.}$



8/24/64

VARIATION OF I_{CN} WITH P_N^3

$P_{total} = 6.5 \text{ mm.}$
 $x = 6.8 \text{ cm.}$
 $x_0 = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec}^{-1}$
 $@ P = 85 \text{ cm. Hg.}$



VARIATION OF I_{CN} WITH P_N^2

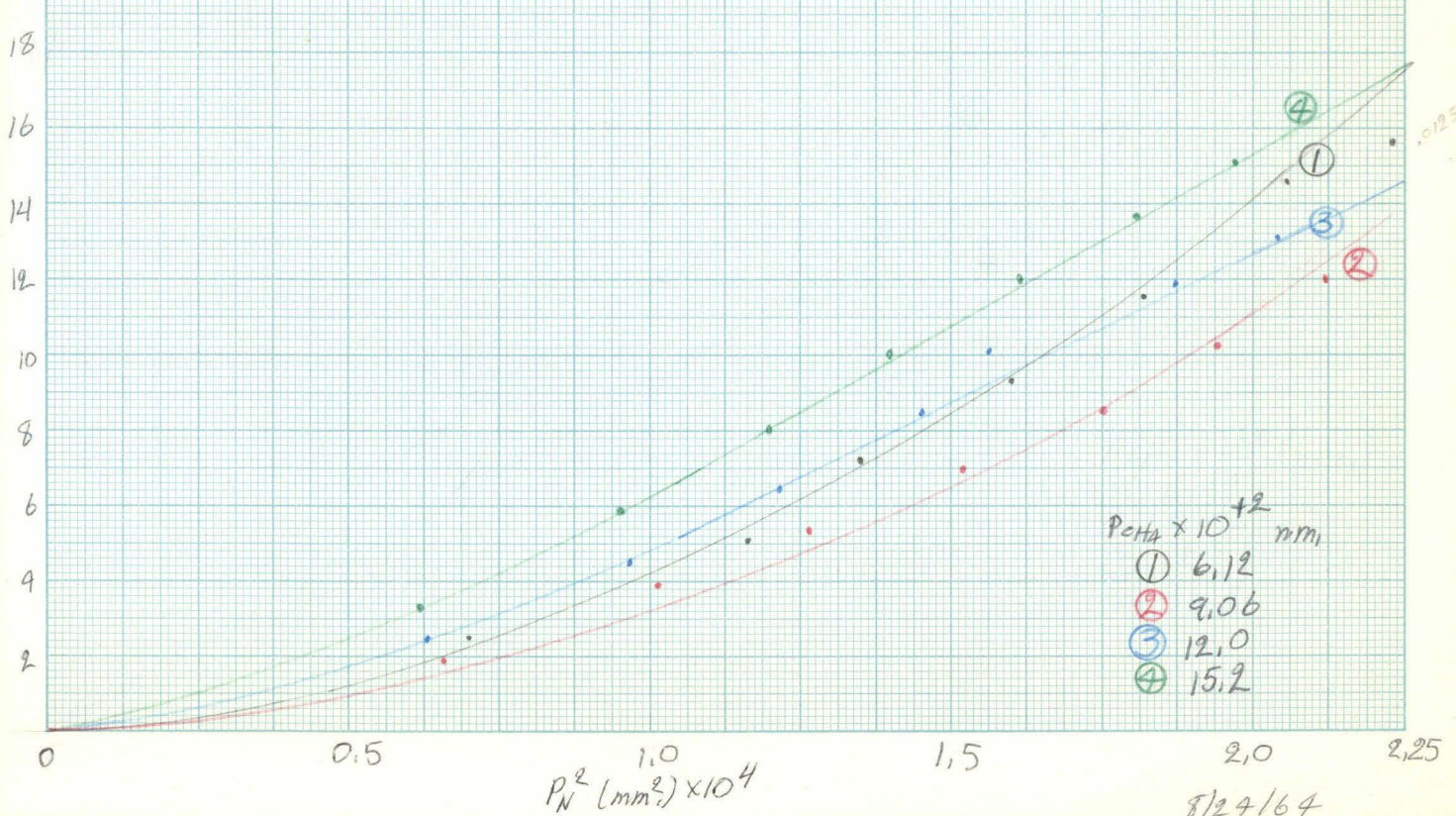
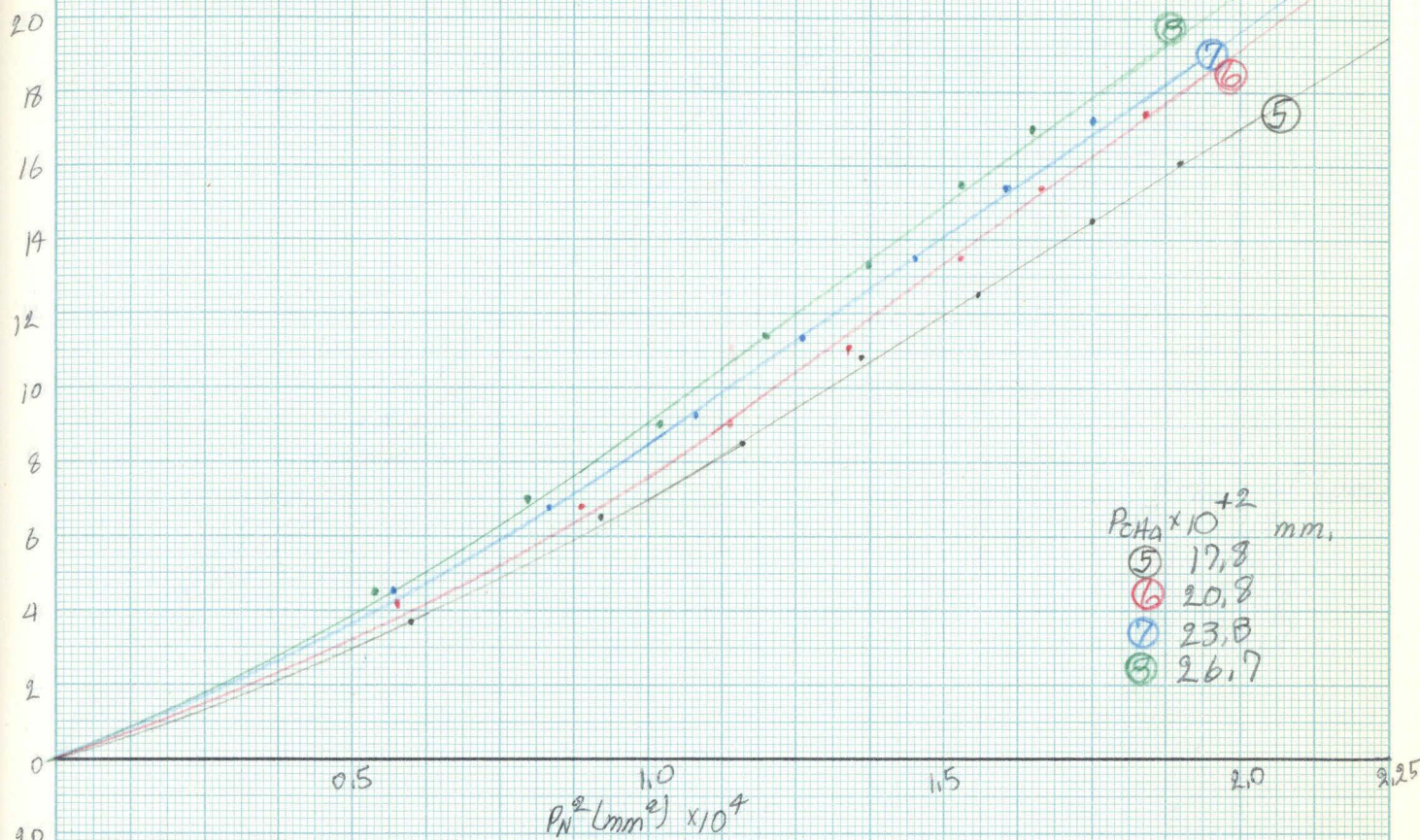
$$P_{total} = 7.2 \text{ mm}$$

$$x = 68 \text{ cm}$$

$$x_0 = 63.5 \text{ cm}$$

$$N_2 \text{ flow rate} = 19.4 \text{ ml sec}^{-1}$$

$$P = 85 \text{ cm Hg.}$$



8/24/64

VARIATION OF I_{CN} WITH P_N^3

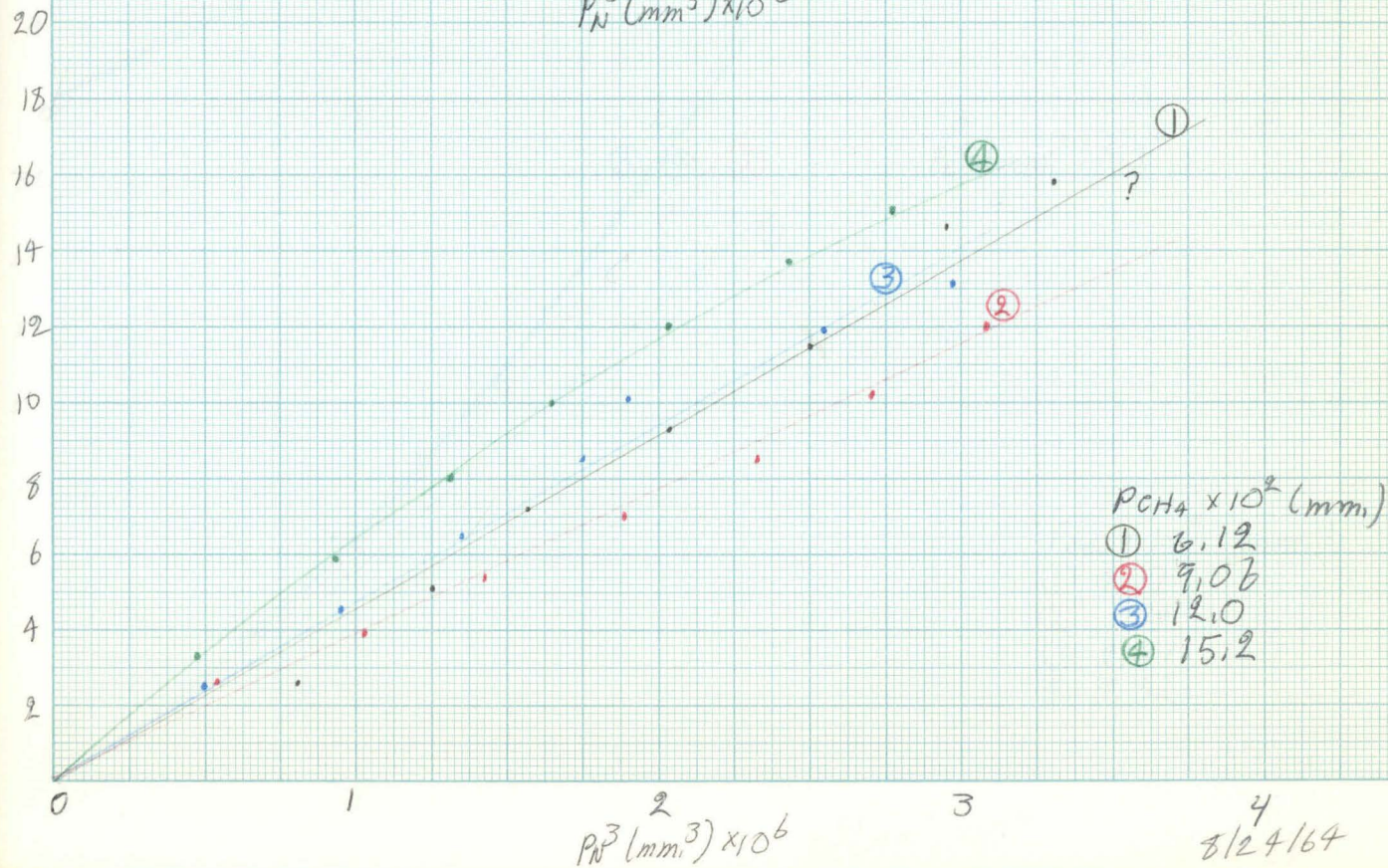
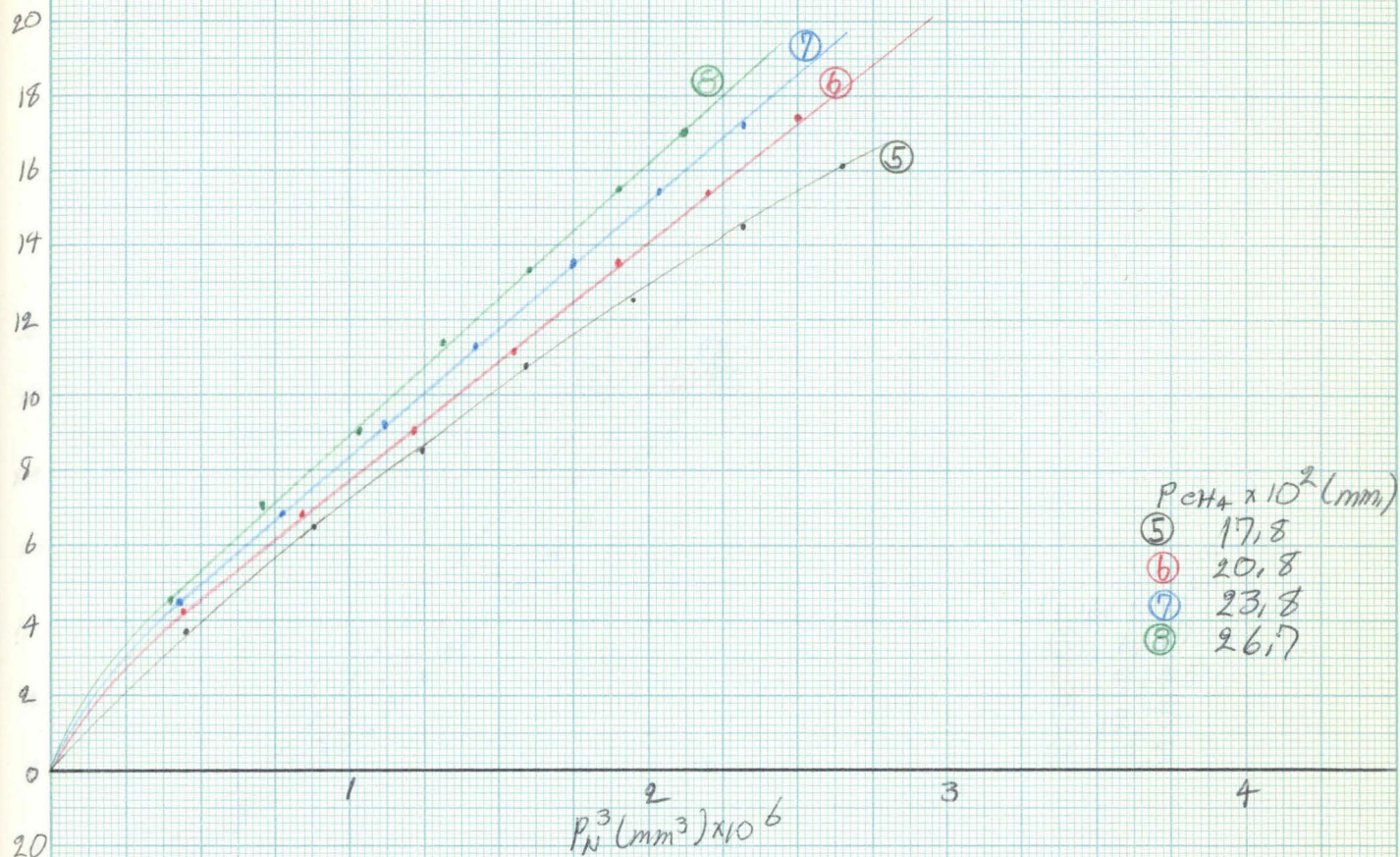
$$P_{total} = 7.2 \text{ mm}$$

$$r = 68 \text{ cm}$$

$$r_0 = 63.5 \text{ cm}$$

$$N_2 \text{ flow rate} = 19.4 \text{ ml. sec}^{-1}$$

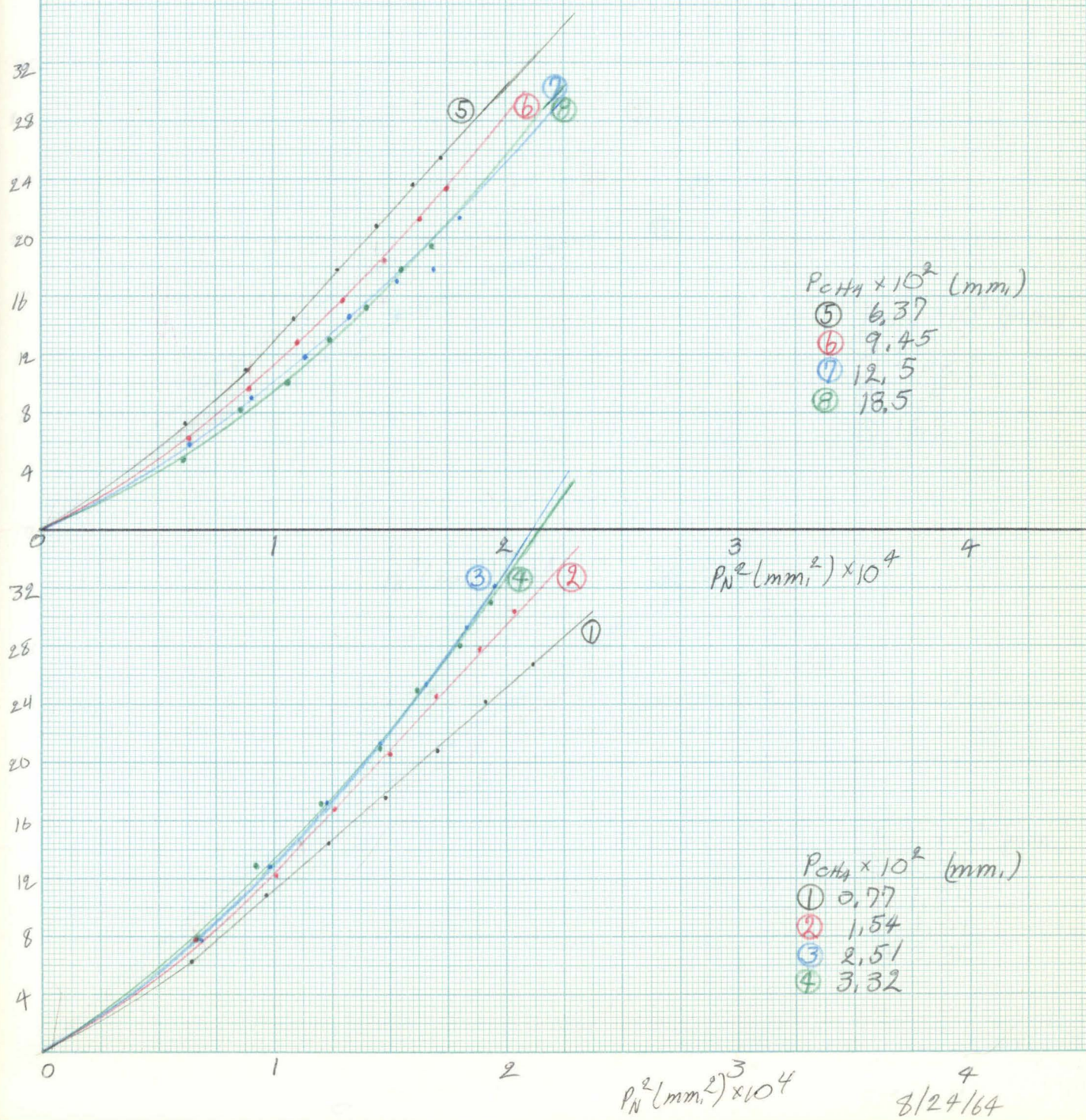
$$a) P = 85 \text{ cm. Hg.}$$



8/24/64

VARIATION OF I_{CN} with P_N^2

$P_{tot} = 7.5 \text{ mm.}$
 $x = 68 \text{ cm.}$
 $x_s = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec.}^{-1}$
 $\text{at } P = 85 \text{ mm. Hg.}$



8/24/64

VARIATION OF I_{CN} WITH P_N^3

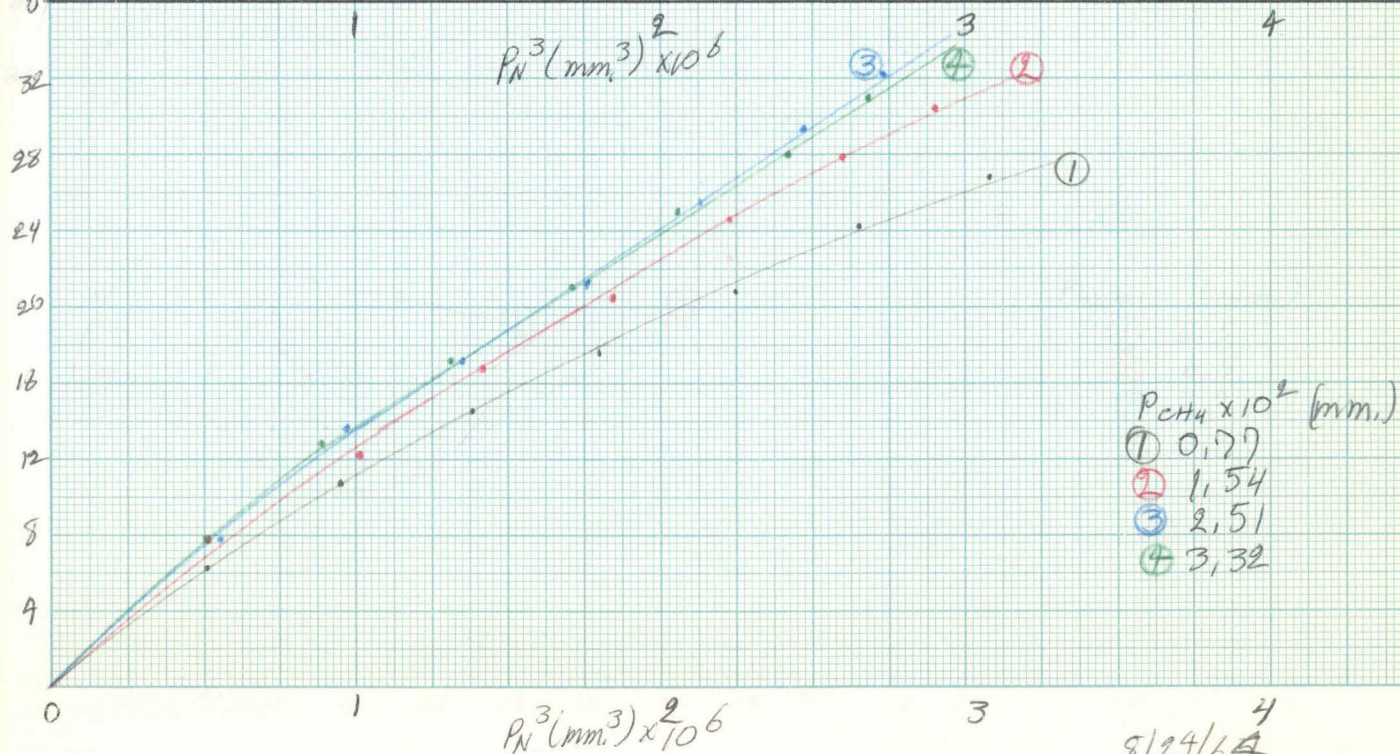
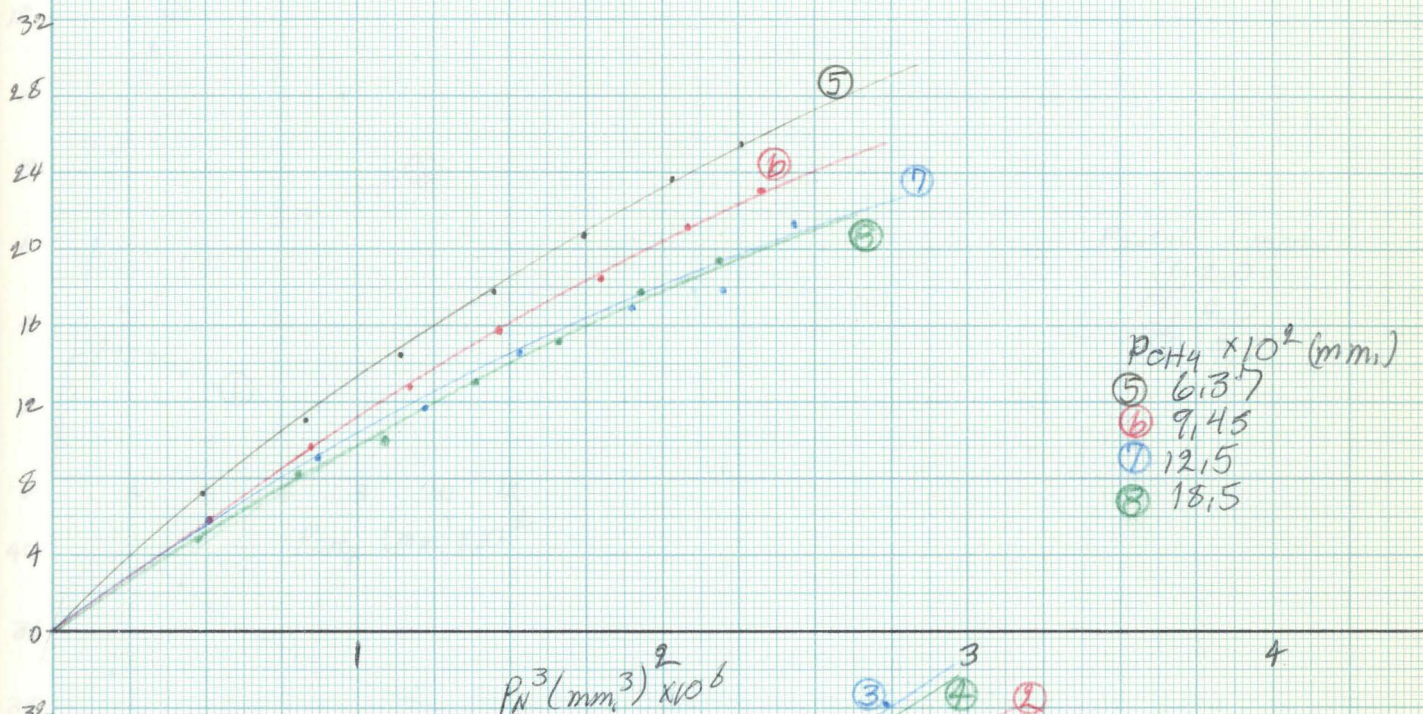
$$P_{tot} = 7.5 \text{ mm.}$$

$$x = 68 \text{ cm.}$$

$$x_s = 63.5 \text{ cm.}$$

$$N_2 \text{ flow rate} = 19.4 \text{ ml. sec.}^{-1}$$

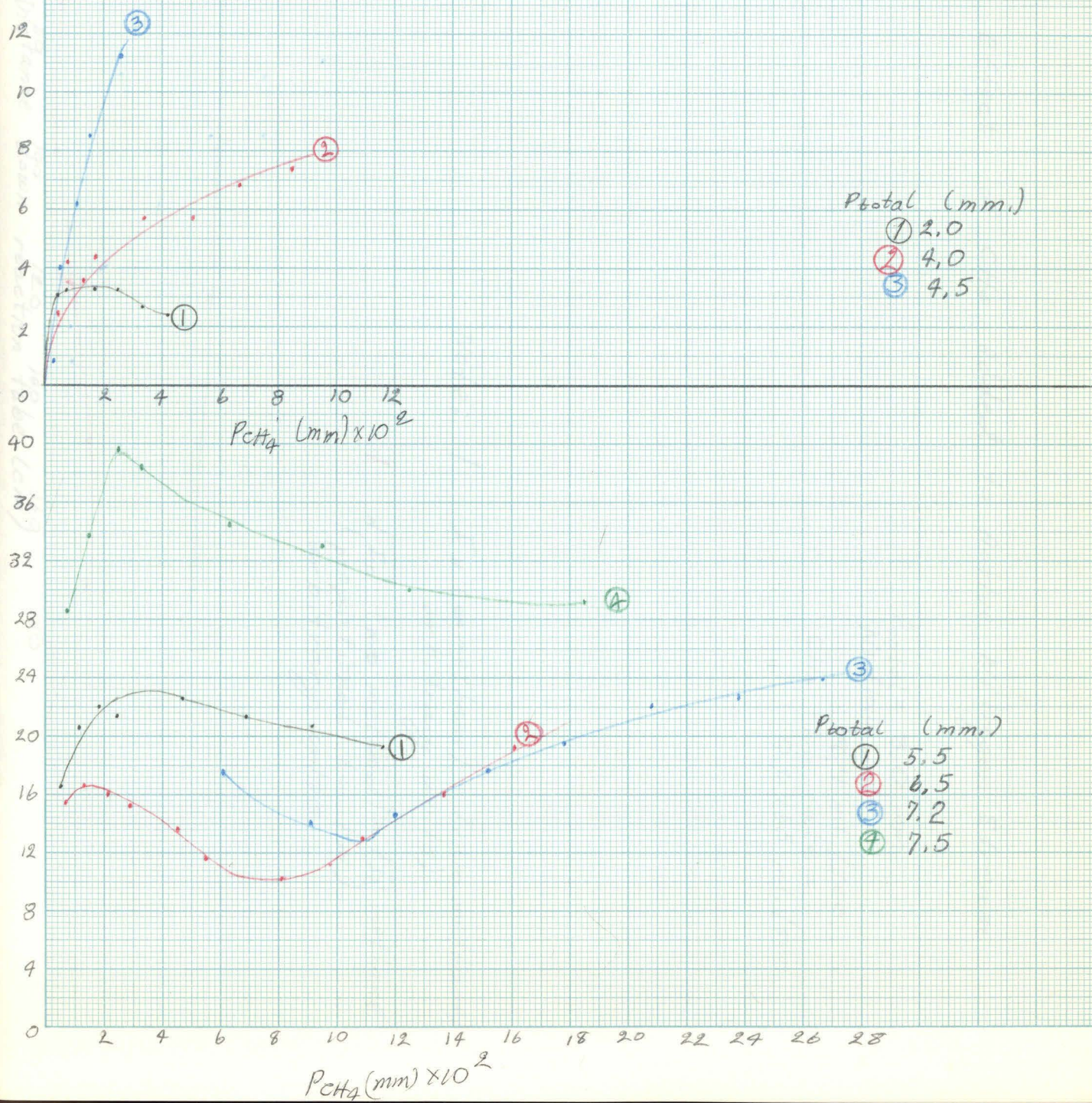
$$\text{at } P = 85 \text{ cm. Hg.}$$



8/24/64

VARIATION OF I_{CN} WITH P_{CH_4}

$x = 68 \text{ cm.}$
 $x_0 = 63.5 \text{ cm.}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml. sec}^{-1}$
 $P = 85 \text{ cm. Hg.}$
 $P_N = 1.5 \times 10^{-2} \text{ mm.}$



Effect of CH₄ Added to Active Nitrogen Stream

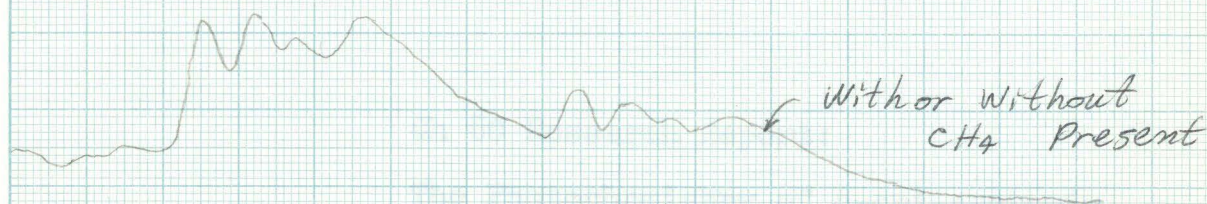
$P_{\text{total}} = 3.0 \text{ mm}$
 $N_2 \text{ flow rate} = 19.4 \text{ ml/sec}$
 $CH_4 \text{ flow rate} = 0.0465 \text{ ml/sec}$



Note: 1 I_v (no methane) - I_0 (no methane)
 arbitrary units
 1 I_0 (no methane) - I_0 (methane)
 (proportional to P_{CH_4})
 arbitrary units

SPECTRUM OF REACTION TUBE
WITH AND WITHOUT METHANE PRESENT
(Observed with Jarrell-Ash Recording Spectrograph)

$P_{\text{total}} = 5 \text{ mm.}$
 $\text{H}_2 \text{ flow rate} = 19.4 \text{ ml./sec.}$
 $I_0 = 201 = 2,01 \text{ mamp.}$

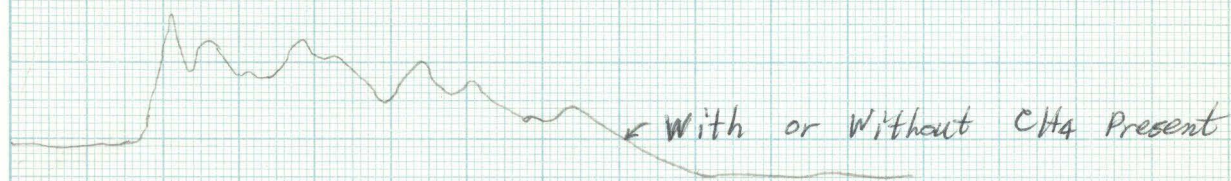


5800

Wavelength ($\text{\AA}$) $\rightarrow$

5750

5700

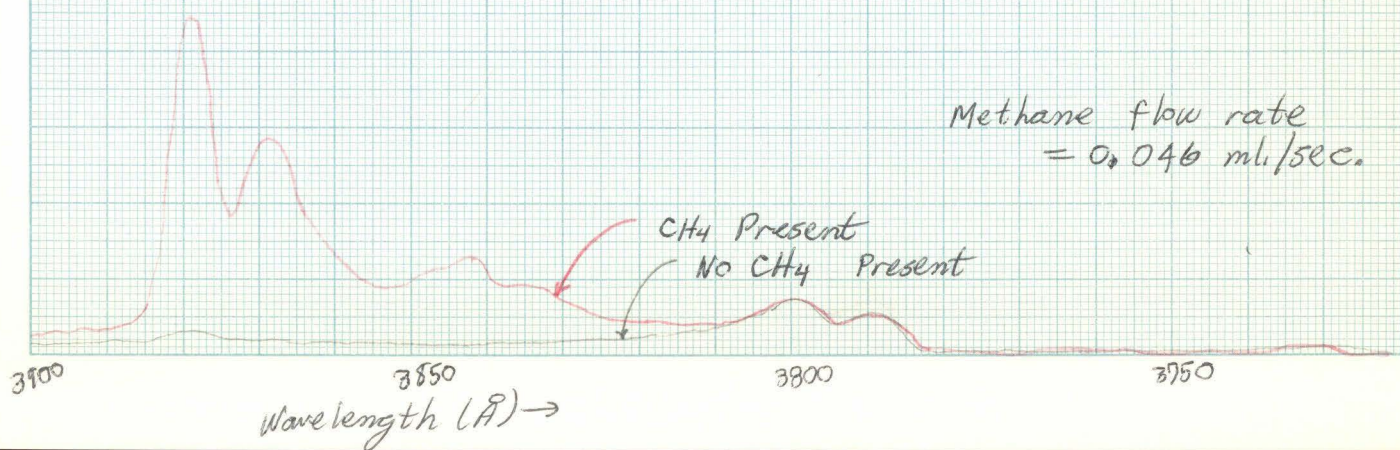


5400

Wavelength ($\text{\AA}$) $\rightarrow$

5350

5300



3900

3850

3800

3750

Wavelength ($\text{\AA}$) $\rightarrow$