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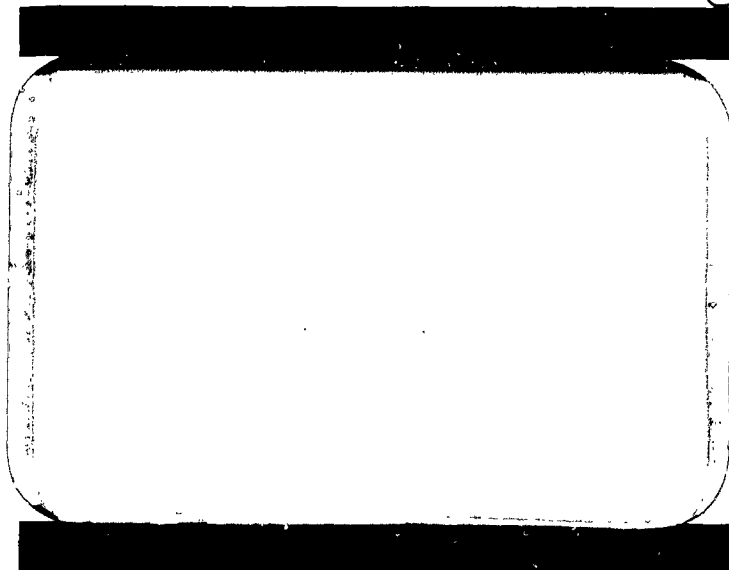


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PREPARATION OF ACCURATE TEST GAS MIXTURES,

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E. R. Bartle and E. A. Meckstroth.

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GENERAL DYNAMICS

ASTRONAUTICS

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By: T. J. B. 6

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I. INTRODUCTION

Present shock tube studies of the chemical kinetics of CO_2 formation using argon diluted mixtures of CO and O_2 require an accurate knowledge of the initial mixture concentration to a high degree of accuracy. Not only are the major constituent's concentrations required, but also traces of minor impurities may play a fundamental role in any proposed reaction schemes. For example, it has been recently reported¹ that the addition of 0.1% H_2 to a 10% O_2 + 20% CO + 70% Ar mixture reduces an "apparent activation energy" from 34 kcal/mole to 21 kcal/mole over the approximate temperature range of 2000°K to 3000°K.

Measurements are now being planned using diminishing amounts of hydrogen added to various mixtures of O_2 , CO, and Ar. These measurements require an accurate preparation of test gas mixtures containing controlled amounts of H_2 varying from 1000 ppm to perhaps 10 ppm. Since the effect of H_2 addition is to be studied, it is important to not only accurately determine the mole concentration of H_2 contained in the mixture but also to be able to produce a fixed amount of H_2 in the test gas mixture. Thus, the immediate task was to develop techniques of preparing test gas mixtures containing previously prescribed concentrations.

A further consideration is to know how soon after initial preparation the test gas mixture is thoroughly mixed, i.e., when homogeneity of the mixture is achieved. It has been determined in obtaining previous measurements² that a two component mixture contained in a 20 gallon tank required at least a 24 hour period before sufficient homogeneity was achieved.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

(a) Test Gas Preparation: The test gas preparation procedures previously described² have been modified somewhat to facilitate the actual preparation,

to decrease possible contamination, to more accurately prepare a desired test gas mixture and to know accurately the resulting mole fractions of the final test gas mixture. In general fractional distillation using a dry ice trap and a liquid nitrogen trap together with a vacuum system permits removal of impurities with very high or very low boiling points by freezing out or pumping off possible contaminants. Thus any undesired contamination due to H_2 , He, CO_2 and H_2O may be effectively minimized. Analyzed reagent grade gases are generally used for mixture preparation. Typical maximum impurity levels anticipated are listed in parts per million Table 1:

Gas \ Impurity	Ar	CO	O_2	CO_2	N_2	H_2	H_2O	Other
Ar	-	1	17	1	25	1	2	1
CO	-	-	25	2000	500	250	5	-
O_2	100	10	-	10	400	50	2	26
CO_2	-	100	10	-	100	10	2	-
N_2	5	-	5	1	-	1	2	11
H_2	-	1	1	1	3	-	2	2
He	-	1	1	1	3	-	2	2

Table 1. Typical maximum impurity levels in parts per million of test gases as stated by the manufacturer.

In general manufacturers have exceeded their specifications. For example, one lot of O_2 supplied by the Matheson Company contained the following impurities:

Ar -	100 ppm
CO ₂ -	1 ppm
N ₂ -	20 ppm
CH ₄ -	14 ppm
H ₂ O - 1t	3 ppm
Others -	12 ppm

Comparison with Table 1 shows that the actual impurities are far less than anticipated.

The test gas mixing and storage system shown in Fig. 1 basically consists of a 20 gallon glass lined storage tank (1)*, a high vacuum pumping system (2a, 3, 4a, 5a), a gas purification section (2b, 5b, 6) and pressure measuring instruments (7, 10). Before any test gases are admitted the entire system is heated using heater tapes to about 120°C and evacuated. The ultimate system pressure after filling all cold traps is 4×10^6 mm Hg. The leak rate of the entire system is shown in Figure 2. Also shown is the leak rate of the system excluding the storage tank (1) and precision mercury manometer (7) sections. The first mentioned leak rate contributes possible contaminants to the first test gas admitted to the storage tank while the second leak rate is a possible source of impurities thereafter.

Handling procedures for various gases differ somewhat depending upon the test gas being admitted to the system at the moment. After bake-out and evacuation the purification traps (2b, 5b) are filled. The dry ice trap (5b) is a one liter stainless steel cylinder packed with stainless steel wool and surrounded by crushed dry ice. All test gases are bled

*Numbers in parentheses refer to the items designated in Fig. 1.

slowly through the dry ice trap, keeping the pressure in the trap greater than one atmosphere, and temporarily are stored in the liquid nitrogen trap (2b). By this procedure any possible water and oil vapors existing are greatly diminished.

Following the collection of a test gas in the liquid nitrogen trap, the gas is there solidified (Ar) or liquified (O_2 , CO). At this time part of the trapped test gas is pumped off to remove possible noncondensibles (H_2 , He). The gas is then distilled into the storage tank through a perforated tube extending from the entrance at the top of the tank to the bottom of the tank. By essentially entering the gas at many different positions in the tank, homogeneity is more quickly achieved. The pressure of the gas in the tank is read on a precision mercury manometer. (Wallace-Tierman, FA187). After the tank is sealed the rest of the system is again baked and evacuated. During evacuation the tank pressure and temperature are periodically monitored to find the equilibrium value. When the second component test gas is admitted the same procedure described above is used. When the second and subsequent purified gases are admitted to the tank, they are throttled in slowly, always maintaining a minimum pressure differential of 200 mm Hg to lessen any possible back-diffusion of the previously admitted gas.

The mole percentages of the various gases are determined by using their equilibrium partial and total pressures corrected for any temperature changes, (temperature changes are usually less than $2^{\circ}C$). Experience has shown that monitoring the temperature and pressure after each component gas is added to the tank gives variations in the temperature corrected pressures of ± 0.2 mm Hg. Thus for a final total pressure of 600 mm Hg (the usual approximate amount required for a series of shots in the shock tube) the mole concentrations

are readily determined. Likewise, the error in mole concentrations determination may easily be shown to be

$$\% \frac{\Delta C}{C} = \frac{0.2}{600} \left(\frac{2}{C} + 1 \right) 100\% \quad (1)$$

where C signifies the mole concentration. From this it is seen that for a 1% concentration the error is on the order of 5% and increases to about 700% for concentrations of 100 ppm.

By using a constant volume technique, repetition of a desired small concentration may be obtained. The control volume enclosed by dotted lines in Figure 1 is used for this purpose. The control volume ratio to tank volume ratio was originally estimated by pressure measurements to be about 600. As will be shown later actual concentration measurements using a gas chromatograph established this volume ratio as 632. Thus a 0.1% concentration with a total mixture pressure of 600 mm Hg requires pressurizing the control volume to 379 mm Hg which is read on the precision Wallace Tiernan dial gauge (10). Accuracies of ± 2 mm Hg are attained with this gauge giving a concentration repetition accuracy of about 0.5% for a 0.1% desired concentration or 5% accuracy for a 100 ppm desired concentration.

For these mixtures containing a small H_2 concentration the H_2 is the next to last constituent added to the mixture. The major constituent of the mixture is then added last and acts as a piston, driving the minor constituent ahead of it into the storage tank with a minimum pressure differential of 200 mm Hg always being maintained.

(b) Gas Chromatograph: From the preceding it is apparent that the accurate preparation of a test gas mixture containing small percentages of minor constituents is a non-trivial problem. A Perkin Elmer Model 154D Vapor Fractometer³ is presently being used to obtain mixture composition analyses.

This sensitive laboratory instrument measure the relative concentration of vapors and gases using chromatographic techniques and permits continuous quantitative analyses of the test gas mixtures.

A carrier gas (see Fig. 3) supplied from an external tank is maintained at constant pressure by two pressure regulators; one at the external source and one within the instrument. The sample of the test gas mixture is then introduced into the instrument by means of the four-way valve and passes through a column which separates the components of the sample according to their respective affinities for the material with which the column is filled. After leaving the column the separated components are swept one by one through the sensing chamber of the detector. Matched thermistors in both the sensing and the reference chambers are connected into a bridge circuit. An unbalance in the circuit generates a signal which is proportional to the difference in thermal conductivities of the atmospheres in the two chambers. This signal drives the pen of a Leeds and Northrup Speedomax G strip charge recorder, equipped with a variable full scale voltage selector of from 1 to 10 mv full scale. The chromatograph itself has a range control which attenuates the signal from 1 to 512 by successive factors of 2. This permits utilization of a large recorder scale deflection for even very small concentrations and produces in graphic form a quantitative description of the sample. As shown by Keulemans,⁴ the concentration of each component is proportional to the area traced out on the recorder paper.

The Model 154D chromatograph has a stated analytical reproducibility of $\pm 0.25\%$ for gas analysis. To perform quantitative analyses using chromatography techniques, the main factors to be considered are: the complete

separation of the samples components by the column, the control of sample size, the constancy and purity of the carrier gas flow, the detector and its associated circuitry, and the accurate integration of the areas traced out on the recorder paper. Following these criteria in order to improve and to better adapt for our purposes the basic Model 154D Vapor Fractometer, several modifications have been made.

Three different columns have been fabricated using 2 meter long X 6.4 mm O.D. X 0.5 mm wall stainless steel tubing packed with screened adsorbents (0.4 mm to 0.7 mm particle size). The adsorbents used were activated charcoal,⁵ silica gel⁶ and zeolite (molecular sieve)⁷ which permit separation and resolution of all test gas components anticipated. The oven enclosing the column and detector is thermostatically controlled to $\pm 0.1^{\circ}\text{C}$. However on-off power cycling was detected on the zero base line portrayed on the strip chart of the recorder. To eliminate this effect the tubing was wrapped with asbestos sleeving and covered with aluminum foil. Its size was compacted by using the quadruple U-shape indicated by Figure 3. These precautions eliminated any detectable oven temperature cycling effects.

A four-way valve was designed and fabricated for the purpose of introducing a sample of the test gas mixture to the chromatograph. One side of the valve permits continuous flow of the carrier gas. The other side of the valve is initially evacuated to at least 10 microns Hga. Then the sample to be analyzed is purged through the system flushing out any residual contaminants. Its pressure is adjusted and read using the 0 to 40 in. Hga manometer. By turning the four-way valve 60 degrees, a trapped fixed volume sample (15 c.c.) is then forced by the carrier gas into the chromatograph. This method of sample introduction is known to be both

repetitious and accurate.⁸ Although the trapped sample volume is fixed, the mass of the actual sample added may be conveniently varied by varying the pressure of the sample gas that is trapped. The instrument response for either calibration of a particular gas or analysis of a test gas mixture thus may be expressed as a function of sample pressure.

As the carrier gas drives components of the sample out of the column, it carries them into the sensing side of the detector. The detector is a dual thermal conductivity cell using a thermistor bridge circuit to measure the thermal conductivities of the atmospheres in the detector chambers. In the normal resistance bridge circuit any variation in the voltage supplied to the bridge gives the same percent variation in the output voltage from the bridge. For the present purpose of quantitative analysis in a routine manner of minute concentrations of test gas mixture components, variations of the dry cell voltage supplying the bridge circuit was very noticeable. This was particularly true in trying to reproduce results on a day to day basis. To eliminate this difficulty a small solid state D.C. voltage supply was designed, fabricated and installed. This power supply and the associated measurement circuitry is shown in Fig. 4. It is conservatively estimated that a constant supply voltage of 8 V is now maintained within $\pm 0.1\%$ at all times.

Quantitative analysis is based upon the time-response history as components of a test gas mixture emerge from the column. For a particular column and a given set of operating conditions, the retention time for each component is a characteristic unique to that substance and serves to identify it and evaluate its concentration. The concentration of any component is directly proportional to the area of its peak obtained from the recorded

fractogram. An integrator for this purpose has been designed and fabricated. The counter being utilized is a Beckman Time Interval Meter Model 7270R. At present the circuit is adjusted to give a maximum counting rate of 1131 cts/sec. This gives a convenient calibration number of 5000 cts/in.². The linearity of the integrator has been experimentally established as $\pm 0.5\%$ in terms of cts/sec/recorder scale division. The present counting rate is better than an order of magnitude greater than the commercially supplied accessory integrator. If it were desirable the present counting rate could be even further increased by yet another factor of 10. For present purposes, however, this counting rate yields at least 4 digit numbers for H₂ component concentrations as small as 50 ppm using sample pressures of 25 in. Hga. The integrator circuit is not included at the present time due to a pending patent application.

As has been stated previously, calibration may be expressed as a linear function of pressure, i.e.,

$$R = AP \quad (2)$$

where R signifies the area response (in.²) and P signifies the pressure (in. Hga) of the trapped sample. Thus A is a unique constant for each gas component when operating the chromatograph at a given set of conditions. Some typical calibration plots are shown in Fig. 5. Calibrations for two columns operating at different conditions are shown in Table 2.

Column Material	Carrier gas flow rate	Column Temp.	Carrier gas	gas	Start of elution	$A = \frac{\text{in.}^2}{\text{in. Hg sec}}$
Charcoal	8.00 div.	40.0°C	Argon	H ₂	44 sec	161.0
				He	56 sec	97.04
				O ₂	156 sec	15.82
				CO	224 sec	12.44
				N ₂	167 sec	13.60
Molecular Sieve (Zeolite)	9.00 div.	30.0°C	Argon	H ₂	44 sec	108.0
				He		
				O ₂	62 sec	10.66
				N ₂	76 sec	9.202
				CO	118 sec	9.153

Table 2. Typical calibration values.

In Table 2, the carrier gas flow rate is given in terms of indicated scale divisions on the mass flow meter. Full scale of 15 divisions is equivalent to a flow rate of 400 ml/min. Argon was chosen as the carrier gas for two reasons; one, there is no known column material that will simply separate O₂ and Ar and two, there is a comparatively large difference in the thermal conductivities of H₂ and Ar thereby giving a more sensitive determination of H₂ content in a test gas mixture. Under the conditions shown the charcoal column completely separates all the components listed with the exception of O₂ and N₂ depending somewhat upon the relative concentrations. That is for a large concentration of say He the base line is so broadened as to overlap the H₂ elution. The molecular sieve column will separate O₂ and N₂ completely for concentration ratios as high as 5:95% mixtures under the conditions shown.

However, it yields calibration constants 50% smaller than the charcoal column due to the different operating conditions required.

Values of A were determined by using both pure gases and prepared mixtures at a series of different sample pressures. Least square fits to eqn. 2 gave the values of A tabulated in Table 2. The constancy of the calibration constant is indicated by the periodic data points shown in Fig. 5. Overall deviation from the least square fits is on the order of 1%. Thus the use of these calibrations to analyze a test gas mixture should be accurate to within 2% for concentrations of H₂ as small as 50 ppm.

III. RESULTS AND DISCUSSION

The first application of the chromatographic analyses was the investigation of mixing time histories using only diffusion to achieve homogeneity. Concentrations of the components of a prepared test gas mixture are determined by

$$C = R_1/AP \quad (3)$$

where R_1 signifies the response of a particular component and P represents the pressure of the sample. On a Friday, CO, O₂ and Ar were added to the storage tank in that chronological order. After leaving the tank sealed for the weekend, concentration time histories of CO and O₂ were measured. Since both the filling port through which the individual components were added and the sampling exit port are located at the top of the tank some stratification of the components was expected. Concentration time histories shown in Figure 6 bear this out. As may be seen, following a 64 hour mixing period, the measured concentrations were 88% and 94% of the final measured concentrations for CO and O₂ respectively and 99% homogeneity was not obtained for over 100 hours. These results, indeed, indicate a strong tendency for the components of the test gas mixture to stratify according

to the chronological order of their admittance to the storage tank.

Following this, a filling tube was added to the mixing system storage tank. This is a 1/2 inch perforated stainless steel tube that extends from the top filling port to the bottom of the tank. These perforations are approximately 1 mm in diameter and were drilled through the tube at 25 mm intervals. While a component gas is being admitted to the storage tank, it is effectively added at all levels of the tank instead of just at the top. Furthermore, the small diameter perforations in the filling tube restrict the inlet test gas flow and form a series of jets which give a turbulent mixing action to the test gas mixture being prepared. Subsequent to the installation of the perforated filling tube, gas chromatographic analyses of the concentration time histories have shown a weekend mixing period gives at least 99% homogeneity for 4 component test gas mixtures.

As seen from Eqn. 1, the mole concentrations of a prepared test gas mixture should be determined within 1% for mole concentrations greater than 7% using partial pressure measurements. Analyses using the gas chromatographic techniques described are conservatively estimated to be accurate within 2% for concentrations as small as 50 ppm. Indeed, if the calibration constants have been determined within 0.1%, gas chromatographic analysis should be accurate within 1%.

Some typical argon diluted mixtures of O_2 , CO, and H_2 that have been used in the shock tube program, are shown in Table 3.

Mixture Number	%O ₂			%CO			%H ₂	
	by P.P.	by G.C.	E-%	by P.P.	by G.C.	E-%	by P.P.	by G.C.
33	9.98	10.19	+2.1	20.01	20.39	+1.9	.107±.067	.127±.003
36	10.00	10.00	0	9.91	9.91	0	.102±.067	.128±.003
37	19.98	20.11	.6	10.05	10.04	- .1	.077±.067	.129±.003
37*	19.98	20.05	+ .4	10.05	10.12	+ .7	.077±.067	.129±.003
38	9.96	10.04	+ .8	19.94	20.17	+1.1	.077±.067	.0109±.0002
* Analysis using molecular sieve column.								

Table 3. Comparison of concentration determinations between partial pressure measurements and gas chromatographic analyses.

The indicated concentrations were determined by partial pressure measurements (P.P.) and gas chromatographic analyses (G.C.) using the activated charcoal column, except as noted.* The deviation between the concentration determinations is indicated by E, where E is defined by

$$\%E = \frac{\% \text{ by G.C.} - \% \text{ by P.P.}}{\% \text{ by P.P.}} \times 100. \quad (4)$$

The average deviation between the two methods of concentration determination for CO and O₂ is less than 1%. Both methods agree well within their estimated errors and the two G.C. analyses for Mixture 37 using two different columns agree extremely well. There is considerable difference for the case of H₂ concentration determinations as the partial pressure method becomes extremely inaccurate for these small concentrations.

Examination of the G.C. results shown in Table 3 suggest a consistent trend indicating about 0.4% less argon was added to the mixture than the partial pressure measurements indicate. This 0.4% less argon may of course be accounted for by error limitations, however, it may be due to unaccounted temperature effects as the once solidified argon warms up to the temperature

of the mixture and the final temperature and pressure of the mixture then determined. A possible systematic error of effectively 1.5°C would account for this apparent lack of argon. G.C. analyses of several nitrogen diluted mixtures of CO and O_2 do not show any trend similar to that just discussed.

Mixtures 33, 36, and 37 were prepared with the object of maintaining a constant H_2 concentration and varying the CO-O_2 concentrations from stoichiometric to O_2 -rich and O_2 -lean using Ar as a diluent. The nominal values of 10, 20 and 0.128% were achieved within 2% using the mixture preparation and analysis procedures described previously. Mixture 38 is the result of attempting to prepare a mixture containing 100 ppm H_2 . Although there is a 9% deviation from the desired concentration, it is felt that the constant volume H_2 addition technique will permit close duplication of say 110 ppm, as illustrated by the great success in duplicating the nominal 0.128% H_2 mixtures.

IV. SUMMARY

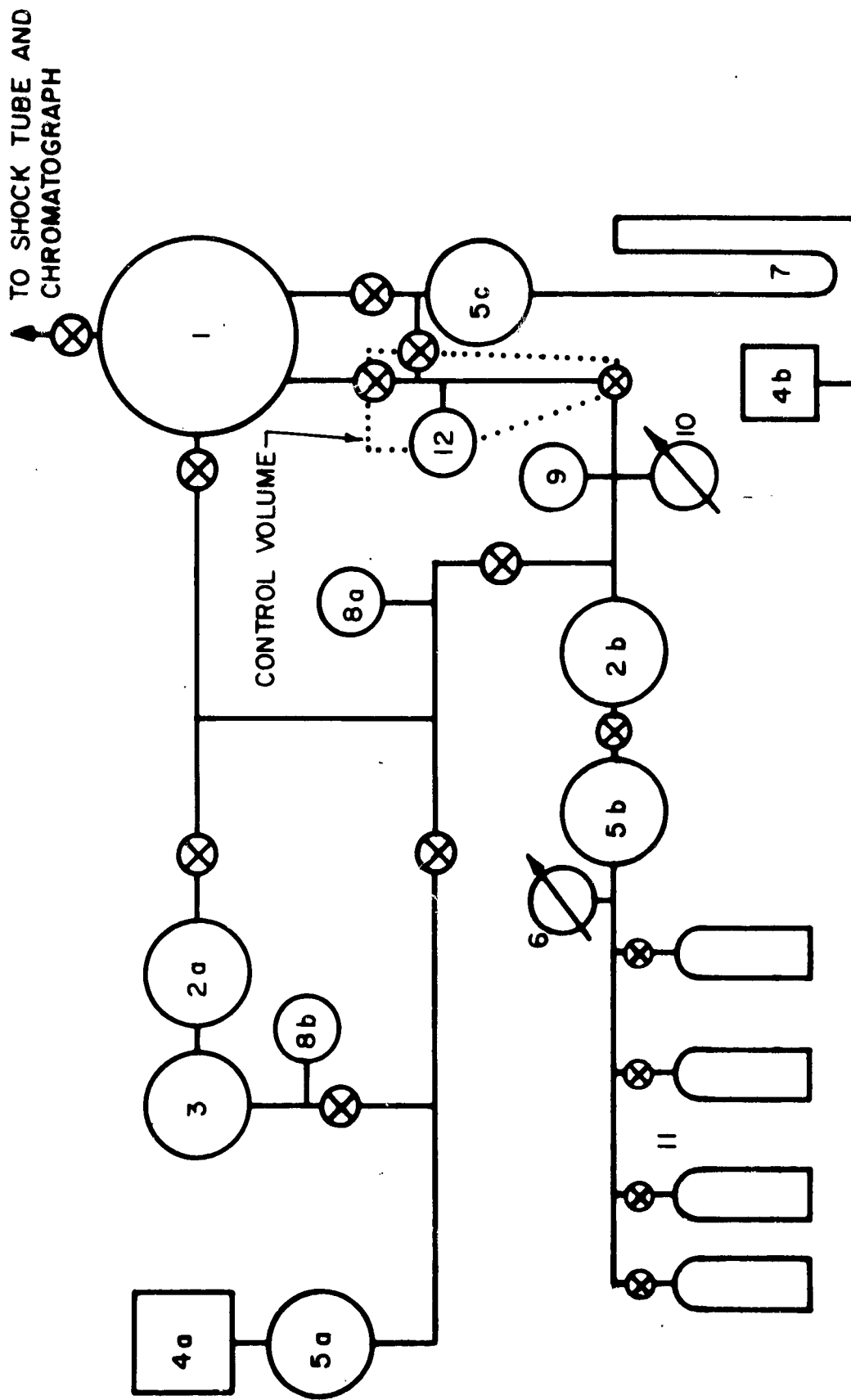
Chemical kinetic studies of CO_2 formation led to the requirement of preparing accurately known, prescribed test gas mixtures. Techniques ~~have been~~^{were} developed for the purification ~~of~~^{of} reagent grade gas components to minimize undesirable impurities, the accurate determination of the resulting mole concentrations and the ability to add very small prescribed minor constituents to a test gas mixture. Concentrations may be determined within 1% using partial pressure measurements for $C > 7\%$ and within 2% using gas chromatographic analysis for $C > 50$ ppm. A series of test gas mixtures of argon diluted CO , O_2 and H_2 have been prepared and the concentrations found to be within 2% of that desired. Presently mixtures are being prepared where the H_2 concentration will be held constant and equal to 110 ppm.

V. ACKNOWLEDGMENT

The authors gratefully acknowledge the suggestions and guidance of Mr. K. G. P. Sulzmann who originated the shock tube studies of CO_2 formation and demonstrated the effect of small amounts of H_2 on the apparent activation energy of CO_2 -formation.

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1. GLASS LINED MIXING TANK
2. LN₂ TRAPS
3. OIL DIFFUSION PUMP
4. MECHANICAL VACUUM PUMPS
5. DRY ICE TRAPS
6. VACUUM PRESSURE GAUGE
7. PRECISION MERCURY MANOMETER (0-800 mm Hga)
8. THERMOCOUPLE GAUGES
9. HOT FILAMENT ION GAUGE
10. PRECISION DIAL GAUGE (0-800 mm Hga)
11. RESEARCH GASES
12. PHILIPS VACUUM GAUGE

FIG. 1 : TEST GAS MIXING AND STORAGE SYSTEM (SCHEMATIC)

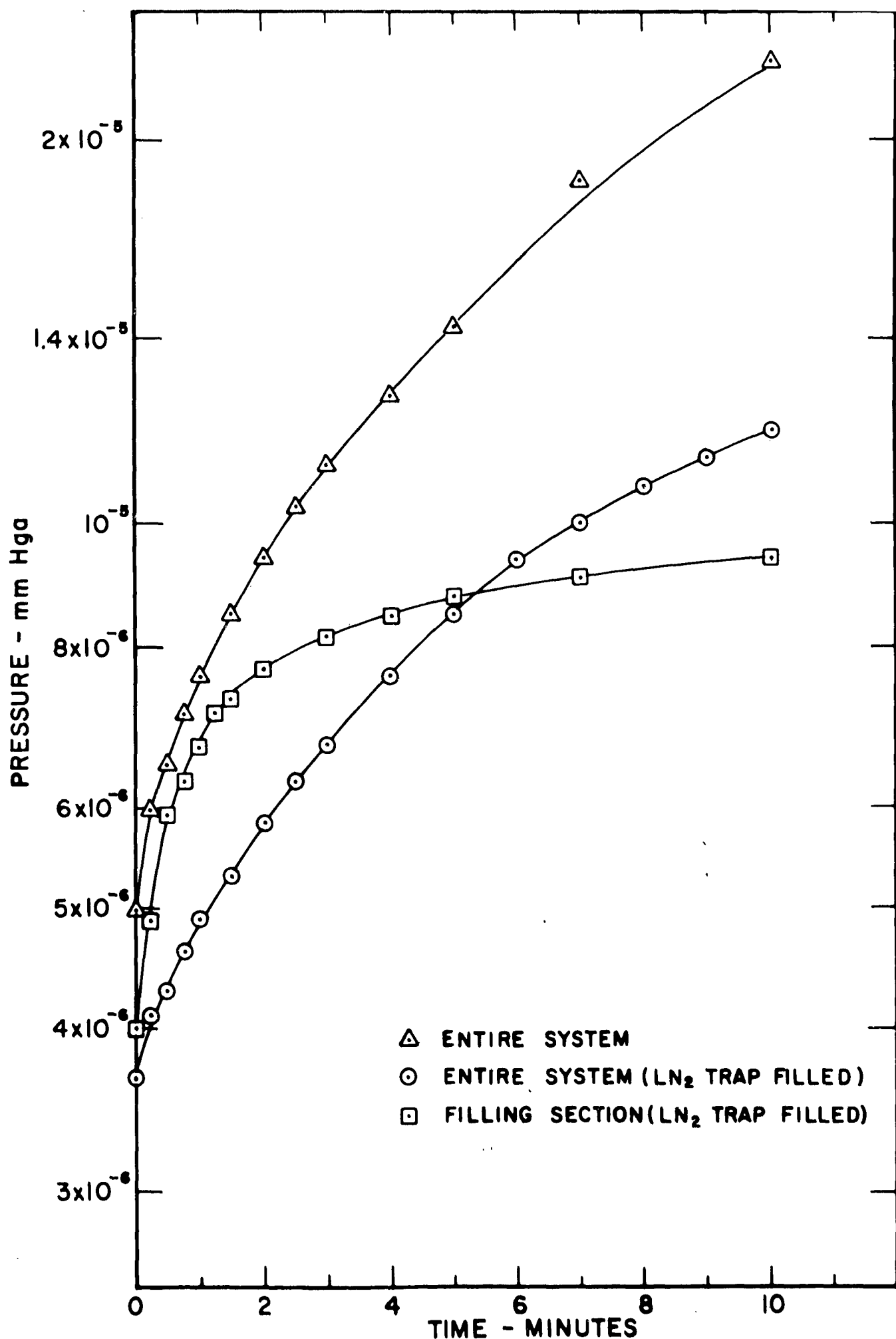


FIG. 2 : LEAK RATES OF MIXING AND STORAGE SYSTEM .

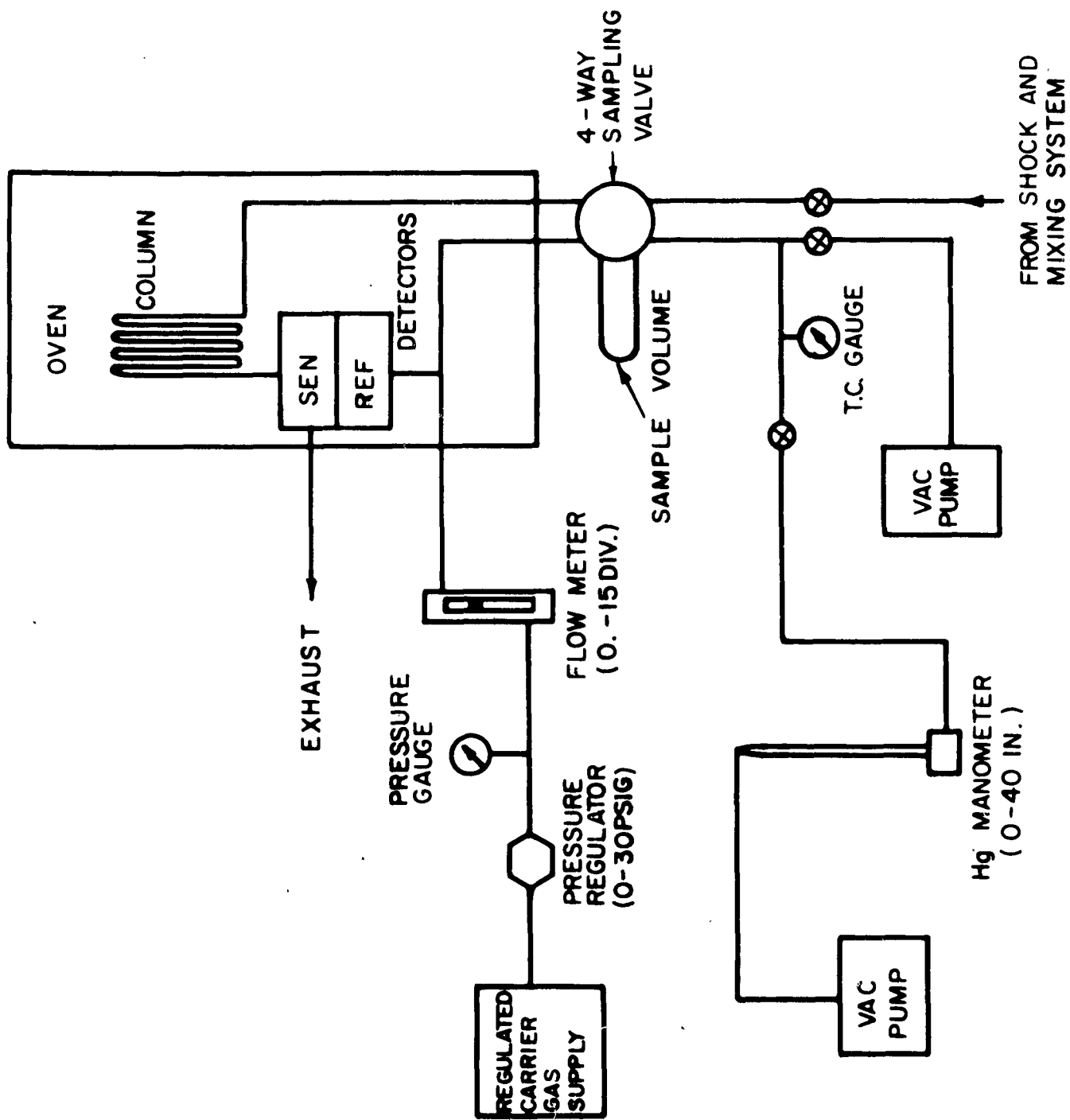


FIG. 3 : FLOW SCHEMATIC OF GAS CHROMATOGRAPH.

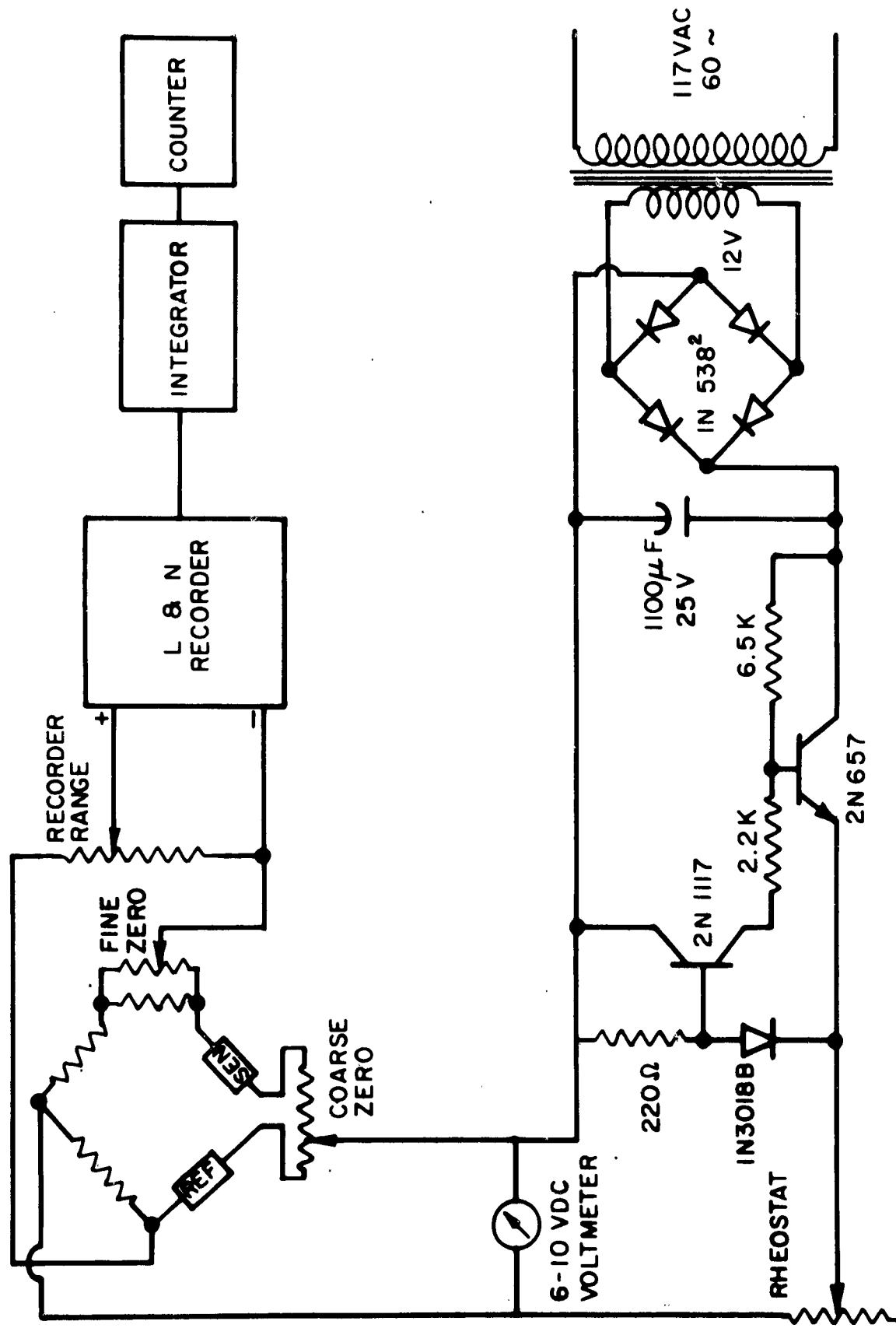


FIG. 4 : SCHEMATIC DIAGRAM OF CHROMATOGRAPH MEASUREMENT CIRCUIT.

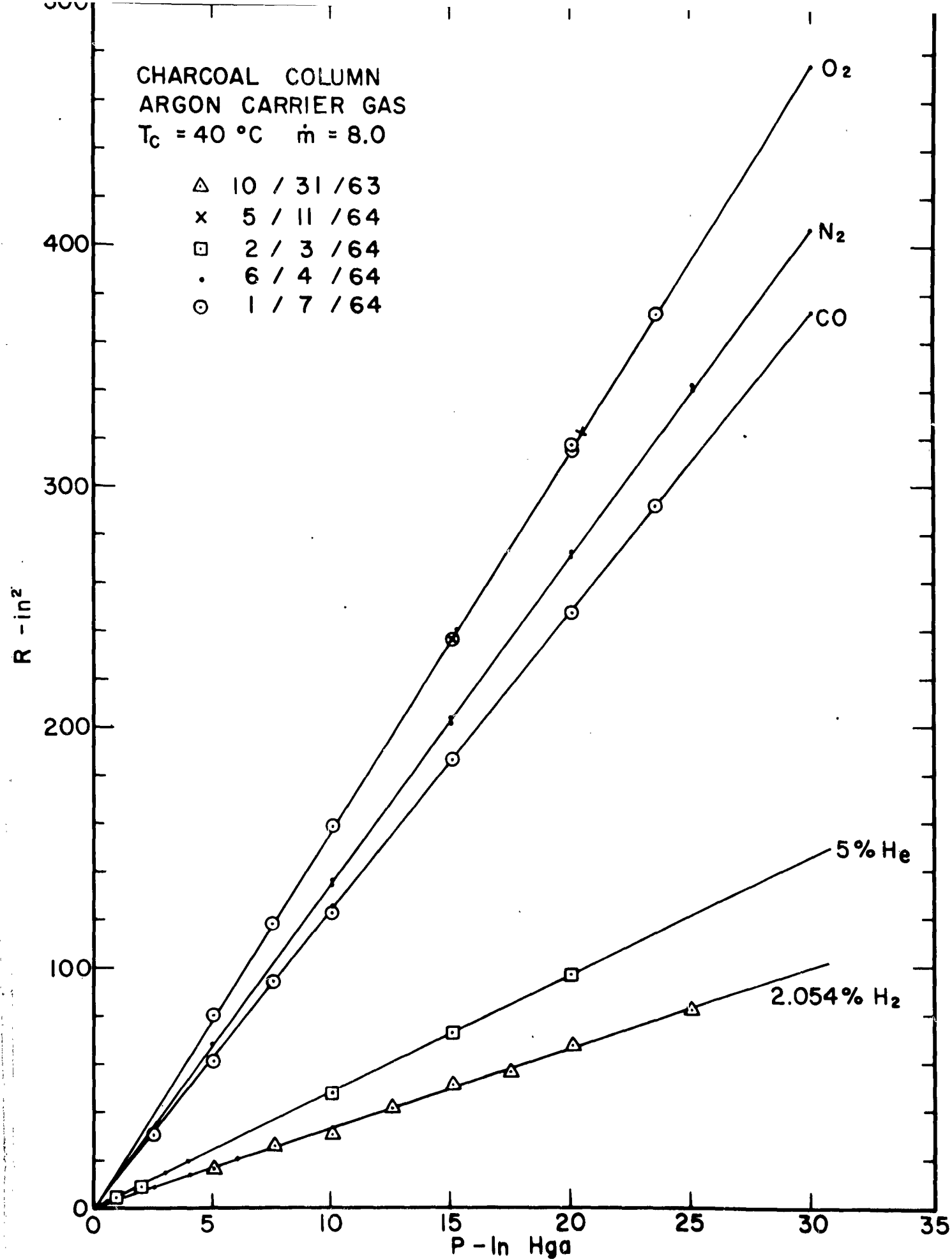


FIG. 5 : TYPICAL CALIBRATION PLOTS

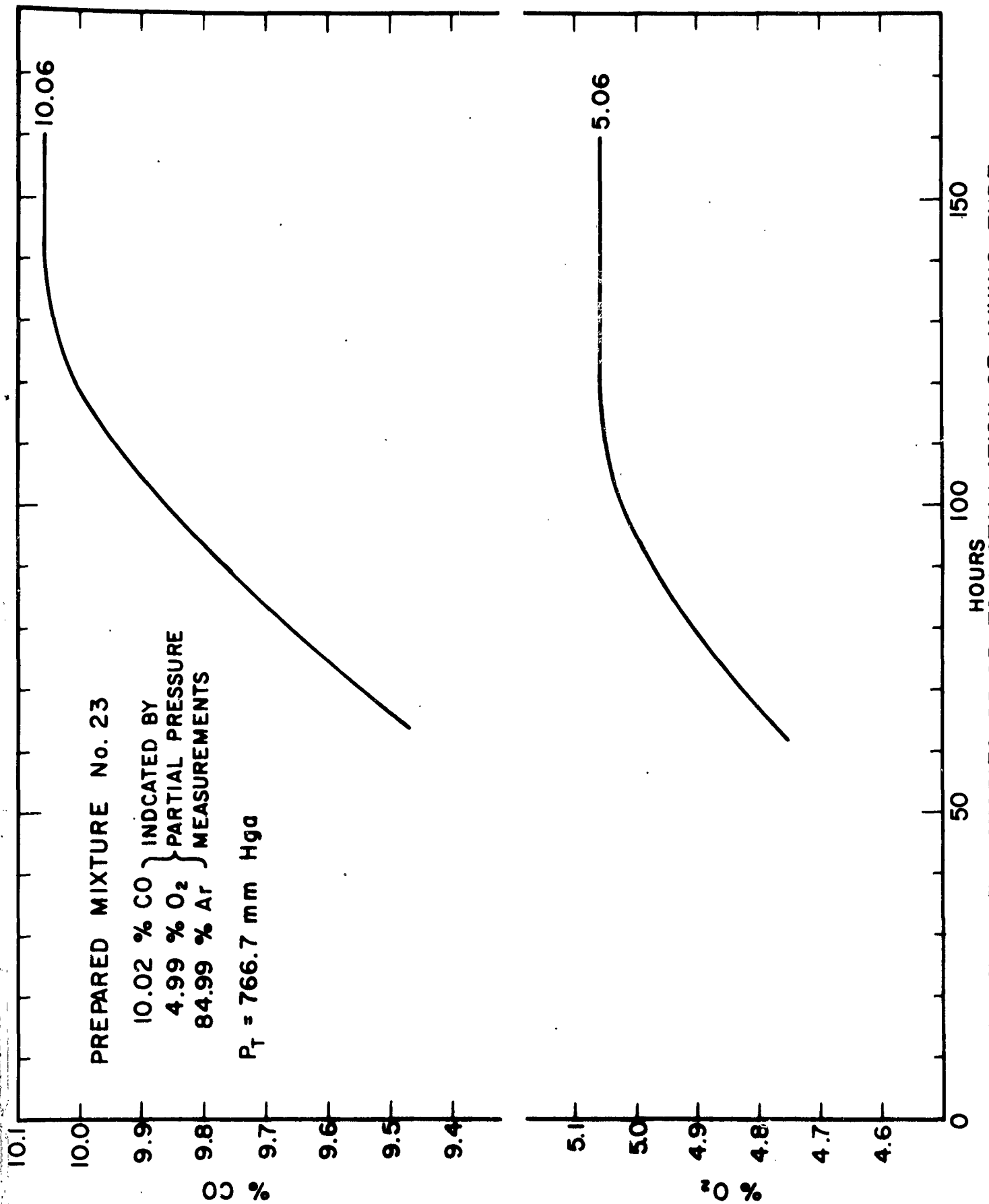


FIG. 6 : MIXTURE TIME HISTORIES PRIOR TO INSTALLATION OF MIXING TUBE.