



RICE UNIVERSITY

Investigation of Critical Points
Using a Dynatrol Detector

by

Gerald L. Brody

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H. Deans
Riki Kobayashi
Matu Sumner

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* Registered Trademark, patents pending

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ABSTRACT

The critical parameters for propane were determined using an Automation Products Dynatrol Detector. The Dynatrol is a system of coupled vibrating masses, whose resonant frequencies are functions of the density of the fluid surrounding one of the masses, namely the paddle which can be immersed in a test fluid. If the paddle is partly surrounded by liquid and partially by vapor, the resonant frequencies are measures of liquid level.

An experimental cell was filled at room temperature with propane such that two phases existed. The paddle of the Dynatrol was located in the cell such that, as the cell was rotated, the paddle was immersed first in the vapor phase, next in the liquid phase, and finally partially in both phases.

The temperature of the cell was raised and the amount of propane in the cell adjusted so that the Dynatrol frequencies indicated that the cell was half-full of liquid. If the interface of the two phases disappeared at the half full point, the point of interface disappearance was the critical point. By determining the amount of propane in the cell and the cell volume, all critical parameters were determined. The values obtained are shown below.

	Brody	A.P.I. 44
T_c ($^{\circ}\text{C}$)	96.5	96.8
P_c (atm)	42.0	42.01
ρ_c (g/cc)	0.220	0.228
z_c	0.268	0.278

INTRODUCTION

The critical point of a fluid is that point on its PVT surface where the distinction between the liquid and vapor phases ceases to exist, i.e., all of the intensive properties of the two phases are equal. The intensive property which is most often used experimentally is specific volume. The normal method of critical point determination relies on the optical observation of equal liquid and vapor volumes as the interface between them disappears.

This method suffers from two main disadvantages. The first is the necessity of using a window cell or a periscope to observe the interface. Both of these have inherent structural and sealing problems. Also, the light required to make optical observations can disturb thermal equilibrium.

The second disadvantage is that around the critical point of a fluid, density fluctuations manifest themselves as critical opalescence, a clouding of both phases. This makes the optical determination of the exact point of interface disappearance uncertain.

The main advantage of the Dynatrol method lies in the fact that no window or other optic device is necessary. Thus, a simply designed cell suffices. Another great advantage is the fact that critical opalescence or density

fluctuation does not effect Dynatrol readings, since the output of the Dynatrol is a function of the average density of the fluid, and the scale of the density fluctuations is much smaller than the size of the Dynatrol paddle.

The criteria for the critical point using the Dynatrol are shown in Fig. I. Here,

$$\rho_T = \frac{M_T}{V} = \frac{\text{Mass of Liquid and Vapor}}{\text{Volume of Cell}}$$

FIG. I

Dynatrol Trajectories

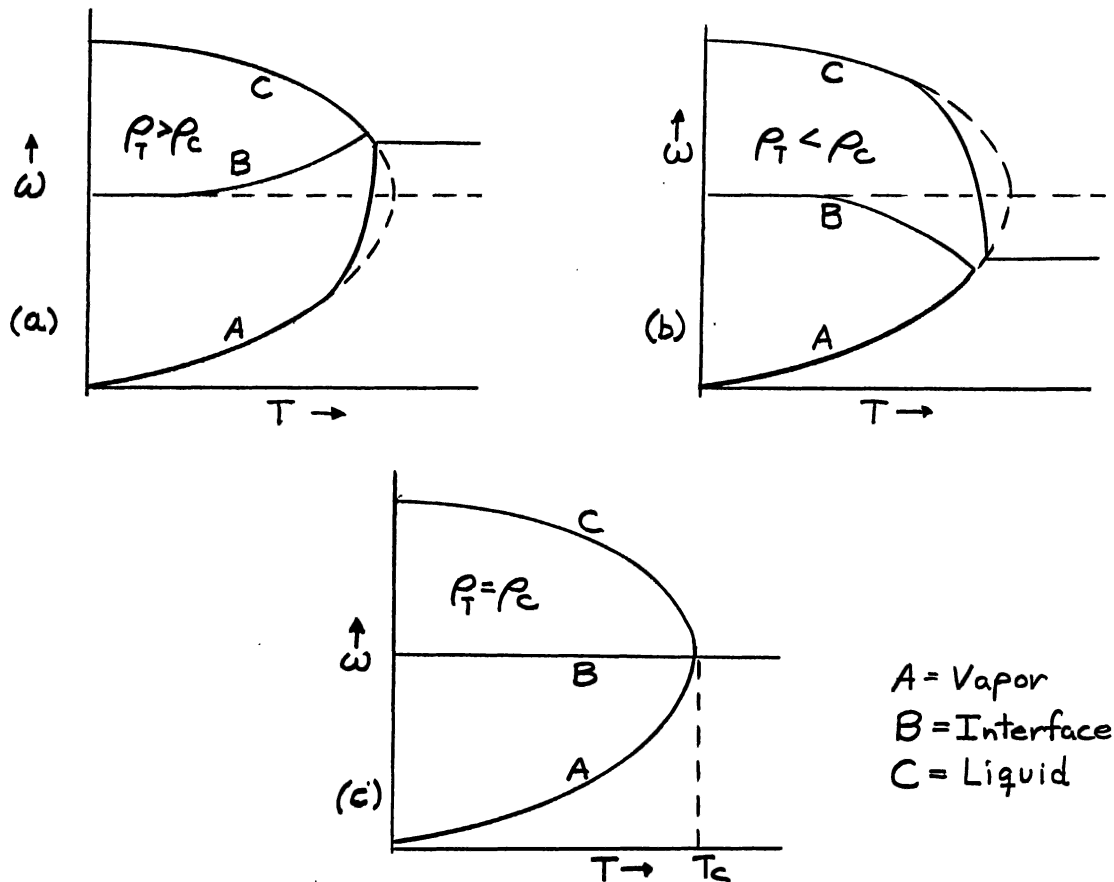
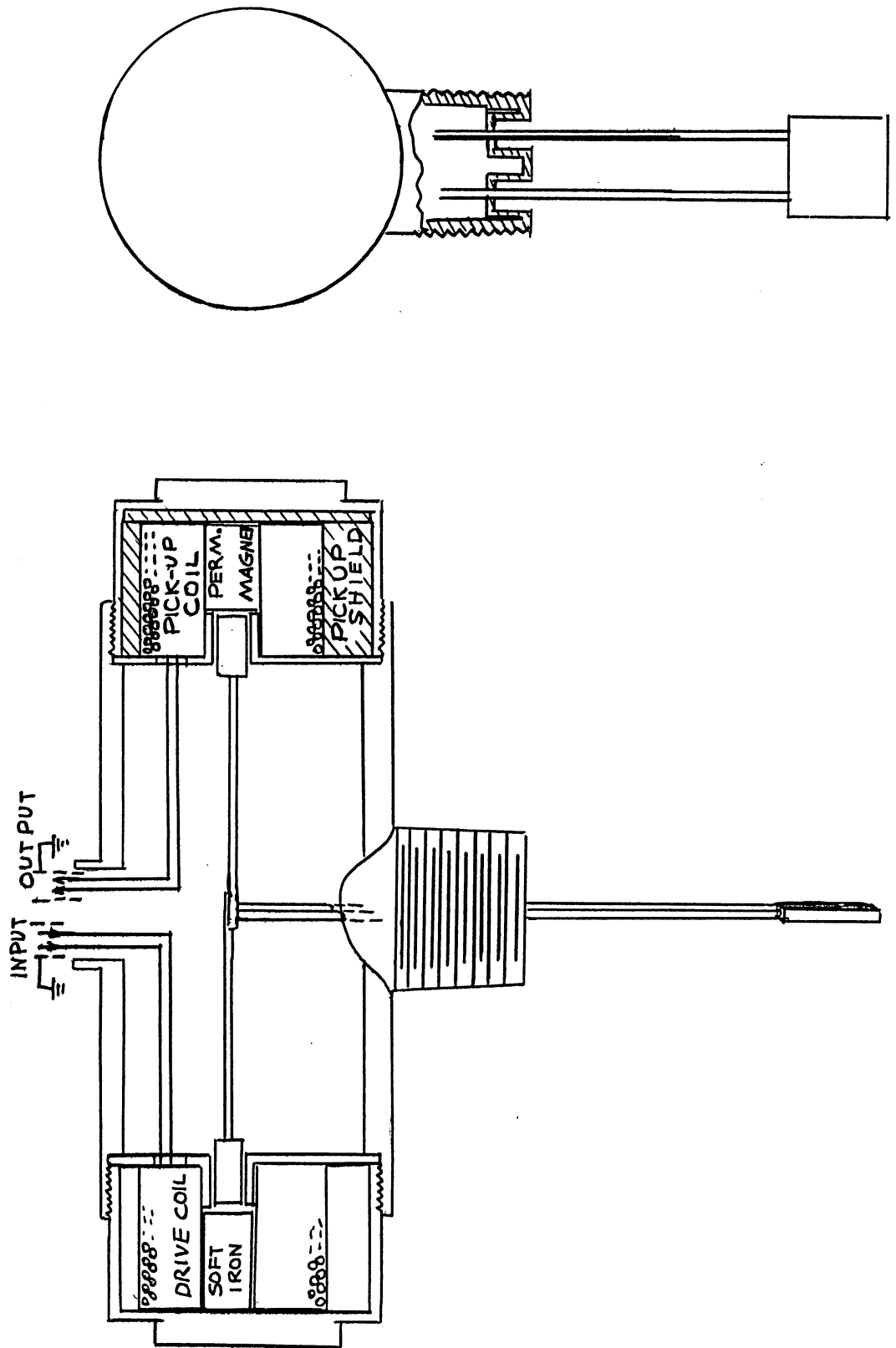


FIG. II

The Dynatrol



I. The Dynatrol

A. Mode of Use

In its normal applications, the Dynatrol (Fig. II) is designed to be driven by line voltage and has resonant peaks near 120 cps, twice line frequency. The amplitude of the output voltage is a function of the density of the fluid surrounding the paddle (Fig. III).

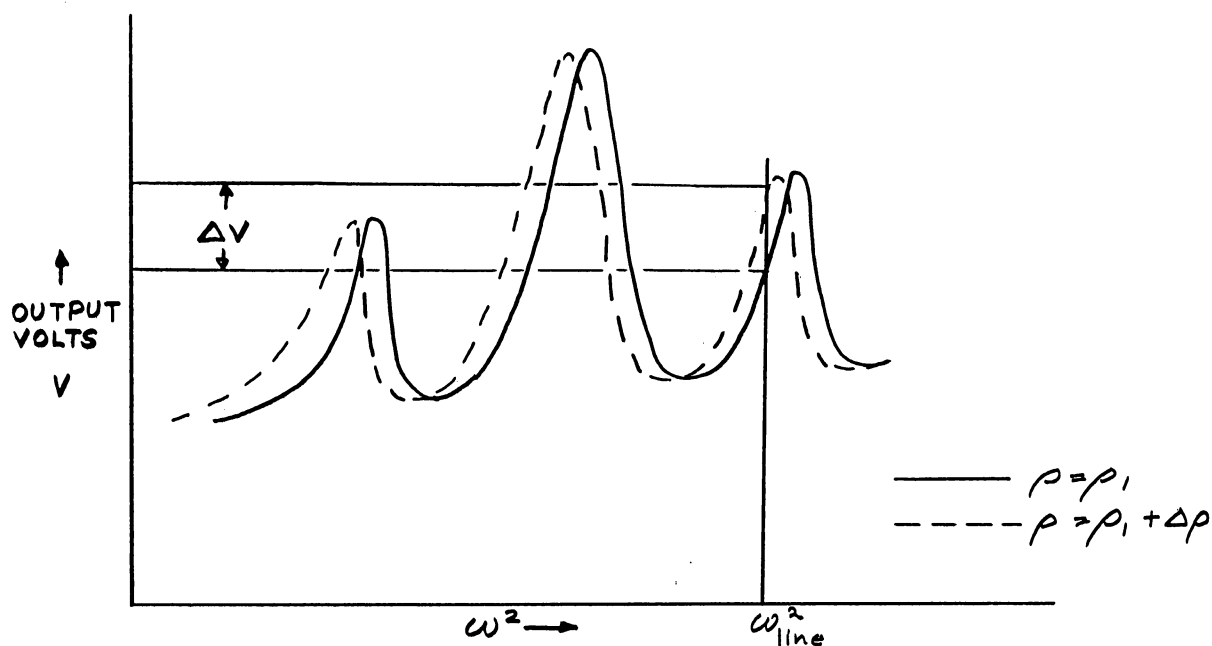


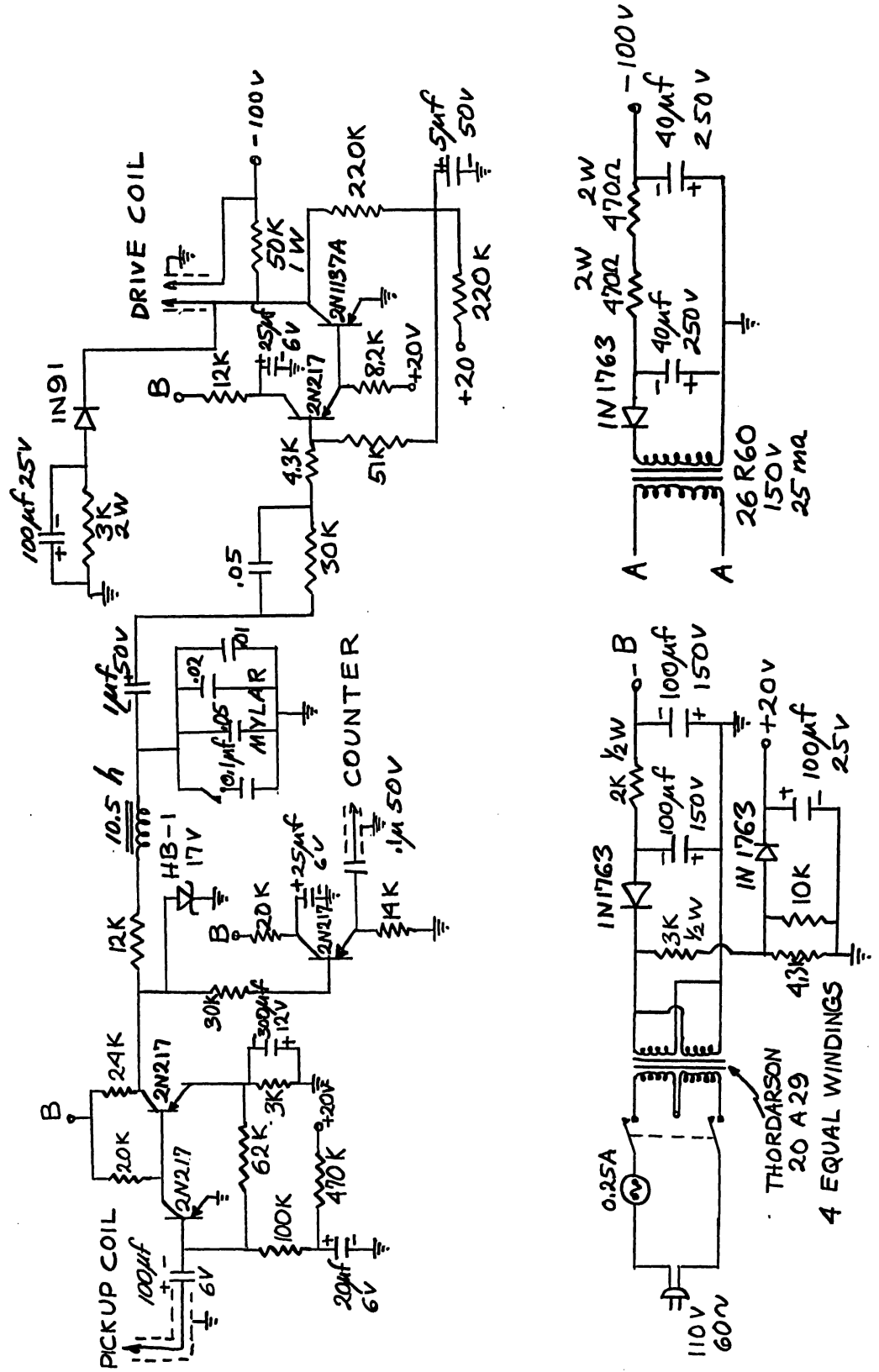
FIG. III

Typical Dynatrol Response

It was found, however, that by following the frequency shift of one of the maxima with density, a more sensitive and stable output was obtained. A special amplifier was constructed for this purpose (Fig. IV).

FIG. IV

Dynatrol Amplifier



The output signal of the Dynatrol is amplified and passed through a low pass filter which shifts it 90° . This filter also tends to stabilize the peak of lowest frequency. This signal is then amplified by a saturation stage, and the resulting square wave is used to drive the Dynatrol. Since, in the resonant frequency of interest, the phase shift through the Dynatrol is 90° , the amplifier-Dynatrol combination forms an oscillator whose resonant frequency is that of the Dynatrol itself.

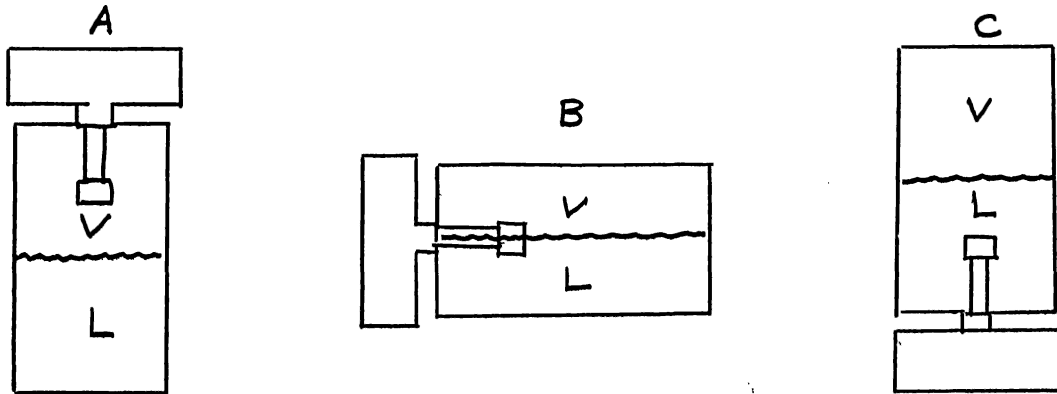
The Dynatrol amplifier also has an output for the measurement of frequency. This signal from the amplifier is sent to a frequency divider which produces a pulse for every n^{th} input cycle, where "n" is adjustable from 1 to 64. This pulse is transmitted to a counter* which indicates 10 times the period of the pulses. The counter thus provides a number proportional to the Dynatrol period.

B. Position in Cell

The position of the Dynatrol in the experimental cell is shown in Fig. V. This orientation was selected to give measures of both vapor and liquid densities and fluid level. When the cell is exactly half-full of liquid, the paddle is centered in its surrounding phase (Fig. V, A and C) or centered between the phases (Fig. V, B).

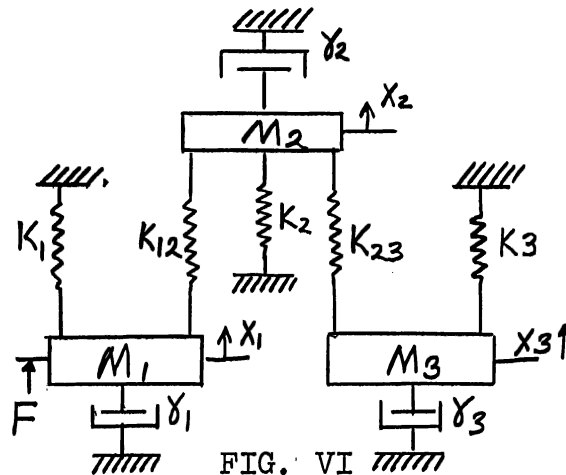
* Computer Measurements Co. Model 226B, 7 decades, frequency and period meter with a 1 megacycle generator.

FIG. V
Paddle Positions



C. Theory³

The Dynatrol may be represented by the approximate physical model shown below in Fig. VI.



Dynatrol Physical Model

Here, M_1 and M_3 are the masses of the drive and pickup rods respectively, and M_2 is the mass of the paddle. The $\gamma_i = (i=1,2,3)$ are the viscous damping factors of their respective masses.

The K_i ($i=1,2,3$) are the spring constants analogous to damping due to density. K_{12} and K_{23} are the spring constants for the pseudo springs which are the paddle supports.

If M_1 is force with a periodic function F , the equations of motion can be written,

$$\ddot{x}_1 + \frac{\gamma_1}{M_1} \dot{x}_1 + \frac{K_1}{M_1} x_1 + \frac{K_{12}}{M_1} (x_1 - x_2) = F e^{i\omega t}$$

$$\ddot{x}_2 + \frac{\gamma_2}{M_2} \dot{x}_2 + \frac{K_2}{M_2} x_2 + \frac{K_{12}}{M_2} (x_2 - x_1) + \frac{K_{23}}{M_2} (x_2 - x_3) = 0$$

$$\ddot{x}_3 + \frac{\gamma_3}{M_3} \dot{x}_3 + \frac{K_3}{M_3} x_3 + \frac{K_{23}}{M_3} (x_3 - x_2) = 0$$

Let $\frac{\gamma_i}{M_i} = \lambda_i$, $\frac{K_i}{M_i} = \alpha_i$, $\frac{K_{12}}{M_1} = \alpha_{12}$, $\frac{K_{23}}{M_2} = \alpha_{23}$,

$$\frac{K_{12}}{M_2} = \alpha_{21}, \quad \frac{K_{23}}{M_3} = \alpha_{32},$$

thus

$$\ddot{x}_1 + \lambda_1 \dot{x}_1 + \alpha_1 x_1 + \alpha_{12} (x_1 - x_2) = F e^{i\omega t}$$

$$\ddot{x}_2 + \lambda_2 \dot{x}_2 + \alpha_2 x_2 + \alpha_{21} (x_2 - x_1) + \alpha_{23} (x_2 - x_3) = 0$$

$$\ddot{x}_3 + \lambda_3 \dot{x}_3 + \alpha_3 x_3 + \alpha_{32} (x_3 - x_2) = 0$$

Let $x_i = A_i e^{i\omega t}$ where the A_i are complex,

then $x_i = A_i e^{i\omega t}$

$$\dot{x}_i = i\omega x_i = i\omega A_i e^{i\omega t}$$

$$\ddot{x}_i = -\omega^2 x_i = -\omega^2 A_i e^{i\omega t}$$

etc.

$$\text{let } \alpha_1 = \alpha_1^i + \alpha_{12}$$

$$\alpha_2 = \alpha_2^i + \alpha_{21} + \alpha_{23}$$

$$\alpha_3 = \alpha_3^i + \alpha_{32}$$

Substituting,

$$\begin{aligned}
 & [(\alpha_1 - \omega^2) + i\omega\lambda_1]A_1 - \alpha_{12}A_2 = F \\
 & -\alpha_{21}A_1 + [(\alpha_2 - \omega^2) + i\omega\lambda_2]A_2 - \alpha_{23}A_3 = 0 \\
 & -\alpha_{32}A_2 + [(\alpha_3 - \omega^2) + i\omega\lambda_3]A_3 = 0
 \end{aligned}$$

or,

$$\begin{bmatrix}
 [(\alpha_1 - \omega^2) + i\lambda_1\omega] & -\alpha_{12} & 0 \\
 -\alpha_{21} & [(\alpha_2 - \omega^2) + i\lambda_2\omega] & -\alpha_{23} \\
 0 & -\alpha_{32} & [(\alpha_3 - \omega^2) + i\lambda_3\omega]
 \end{bmatrix}
 \begin{bmatrix}
 A_1 \\
 A_2 \\
 A_3
 \end{bmatrix}
 =
 \begin{bmatrix}
 F \\
 0 \\
 0
 \end{bmatrix}$$

Since A_3 is the amplitude of the pickup slug, it is proportional to the output voltage of the unit. Solving for A_3 ,

$$A_3 = \frac{\alpha_{21} \alpha_{32} F}{[D_0]}$$

The determinate $[D_0]$ is too complicated for the interpretation of physical data. Therefore, several approximations shall be made. Since the drive and pickup slugs are surrounded by air, the viscous factors λ_1 and λ_3 should be negligible. For low viscosity fluids surrounding the paddle, λ_2 should also be very small. If we also assume that $K_{12} = K_{23}$, $K_1 = K_3$, and $M_1 = M_3$ then,

$$\begin{aligned}
 \alpha_{12} &= \alpha_{32} = a & \alpha_1 &= \alpha_3 = \alpha \\
 \alpha_{21} &= \alpha_{23} = b & \alpha_2 &= \beta
 \end{aligned}$$

This gives

$$[D] = \begin{bmatrix} \alpha - \omega^2 & -a & 0 \\ -b & \beta - \omega^2 & -b \\ 0 & -a & \alpha - \omega^2 \end{bmatrix}$$

The frequencies of peak amplitude are thus the poles of the equation

$$A_3 = \frac{abF}{[D]}$$

and thus the roots of the equation,

$$[D] = 0$$

or $(\alpha - \omega^2)[(\alpha - \omega^2)(\beta - \omega^2) - 2ab] = 0$

whose roots are

$$r_1 = \frac{\alpha + \beta}{2} - \sqrt{\left(\frac{\alpha - \beta}{2}\right)^2 + 2ab}$$

$$r_2 = \alpha$$

$$r_3 = \frac{\alpha + \beta}{2} + \sqrt{\left(\frac{\alpha - \beta}{2}\right)^2 + 2ab}$$

A qualitative analysis of these roots shows the following behavior.

	$\frac{1}{\beta} \rightarrow \text{large}$	$\frac{1}{\beta} = \frac{1}{\alpha}$	$\frac{1}{\beta} \rightarrow \text{small}$
$\frac{1}{r_1}$	large	$\frac{1}{\alpha - \sqrt{2ab}}$	$\frac{1}{\alpha}$
$\frac{1}{r_2}$	$\frac{1}{\alpha}$	$\frac{1}{\alpha}$	$\frac{1}{\alpha}$
$\frac{1}{r_3}$	$\frac{\alpha}{1 + 2ab}$	$\frac{1}{\alpha + \sqrt{2ab}}$	$\frac{1}{\beta}$

It is assumed that for a body vibrating in a fluid, the effective mass of the body is given by

$$M = M^0 + c\rho$$

where $(c\rho)$ is the induced mass and

where

M^0 = rest mass

c = proportionality constant

ρ = fluid density

Since
$$\beta = \frac{K_2}{M_2}$$

then
$$\beta = \frac{K_2}{M_2^0 + c\rho}$$

or
$$\frac{1}{\beta} = c_1 \rho + c_2$$

Thus, a plot of $(\frac{1}{r_i})(i=1,2,3)$ versus $(\frac{1}{\beta})$ should be similar to a plot of $(\frac{1}{\omega^2})$ versus (ρ) which was determined experimentally. These plots are shown in Fig. VII.

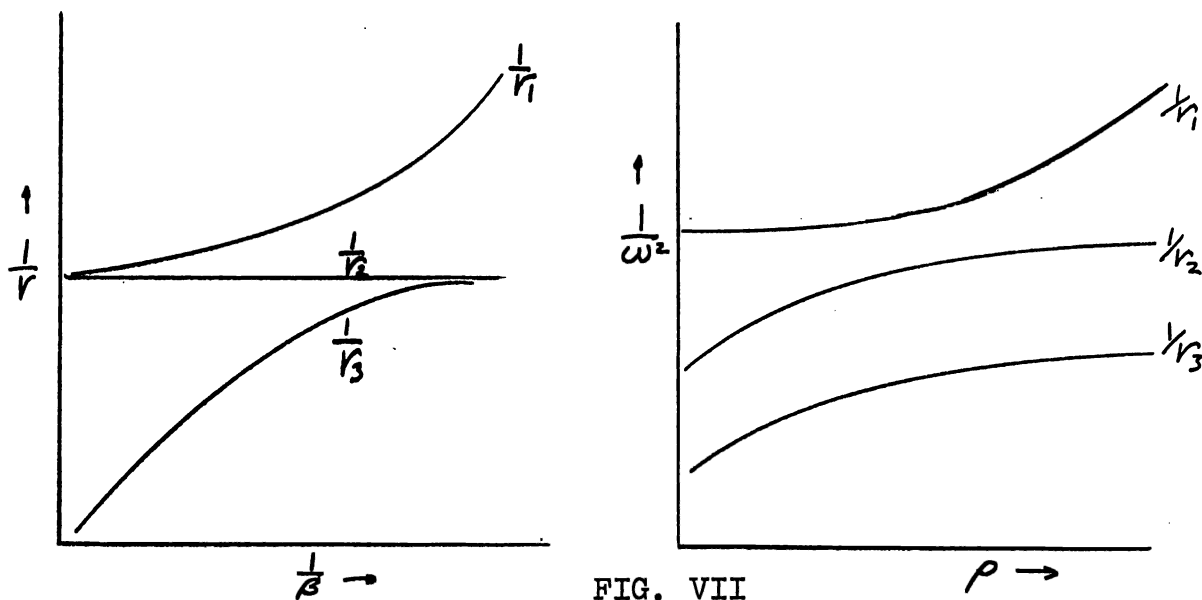


FIG. VII

Comparison of Theoretical and Experimental
Dynatrol Behavior

In reality, M_1 and M_3 are not exactly equal. Thus, a

more realistic model is formed if the substitution is made,

$$M_1 = M_0 (1 + \epsilon)$$

$$M_3 = M_0 (1 - \epsilon)$$

This produces the following determinate equation.

$$\begin{bmatrix} \frac{\alpha}{1+\epsilon} - \omega^2 & \frac{a}{1+\epsilon} & 0 \\ b & \beta - \omega^2 & b \\ 0 & \frac{a}{1-\epsilon} & \frac{\alpha}{1-\epsilon} - \omega^2 \end{bmatrix} = 0$$

If $\omega^2 = r$, and $\epsilon \ll 1$,

$$(\alpha - r) [(\alpha - r)(\beta - r) - 2ab] - (\epsilon r)^2 (\beta - r) = 0$$

The experimental roots for two liquids of different density and approximately equal viscosity suffice to determine the six unknowns, α , ϵ , β_1 , β_2 , $(2ab)_1$, and $(2ab)_2$, where 1 and 2 refer to the two fluids.

The six simultaneous equations to be solved are,

$$(\alpha - r_i^j) [(\alpha - r_i^j)(\beta_i - r_i^j) - (2ab)_i] - (\epsilon r_i^j)^2 (\beta_i - r_i^j) = 0$$

where

$i = 1, 2$ refers to the two fluids

$j = 1, 2, 3$ refers to the three values of ω^2 at peak amplitudes

$r_i^j =$ experimental values of ω^2

This first degree approximate model developed for the Dynatrol is useful in fitting data. However, for the purposes of this experiment, it was sufficient to show that the Dynatrol resonant frequencies were monotonic functions

of density. This has been shown, both theoretically and experimentally.

D. Calibrations

The Dynatrol output was found to be a function of temperature, pressure, and position, as well as density. In order to take these factors into account, several calibrations were made.

The first of these was for dependance of the frequency on density, at room temperature and pressure (Fig. VIII). The cell was placed in position B (horizontal). It was filled first with one fluid, then with another, and so on, until the density range from 0 to 1.6 g/cc was covered. The upper curve ($\frac{1}{r_1}$) was the one followed in this experiment. The value shown for propane was taken at the critical and corrected to 25°C and 1 atm. Clearly, the Dynatrol frequency is a monotonic decreasing function of density.

The second calibration was for temperature dependance (Fig. IX). The horizontal cell contained air and was open to the atmosphere. The frequency change due to the change in density of air was negligible.

The third calibration was for pressure dependance (Fig. X). With the cell in the horizontal position, air at 25°C was brought up to several pressures from 100 to

FIG. VIII

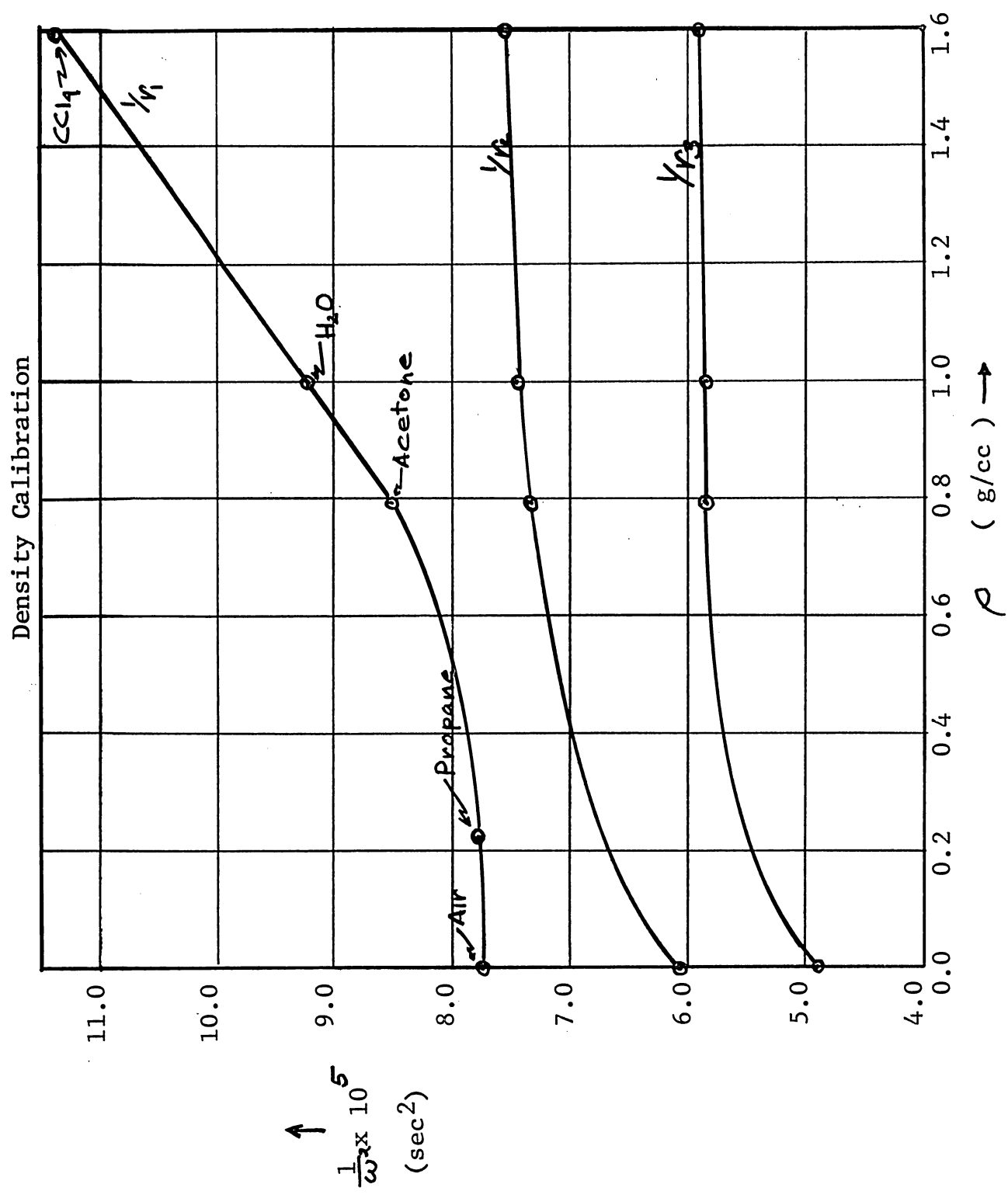


FIG. IX

Temperature Calibration

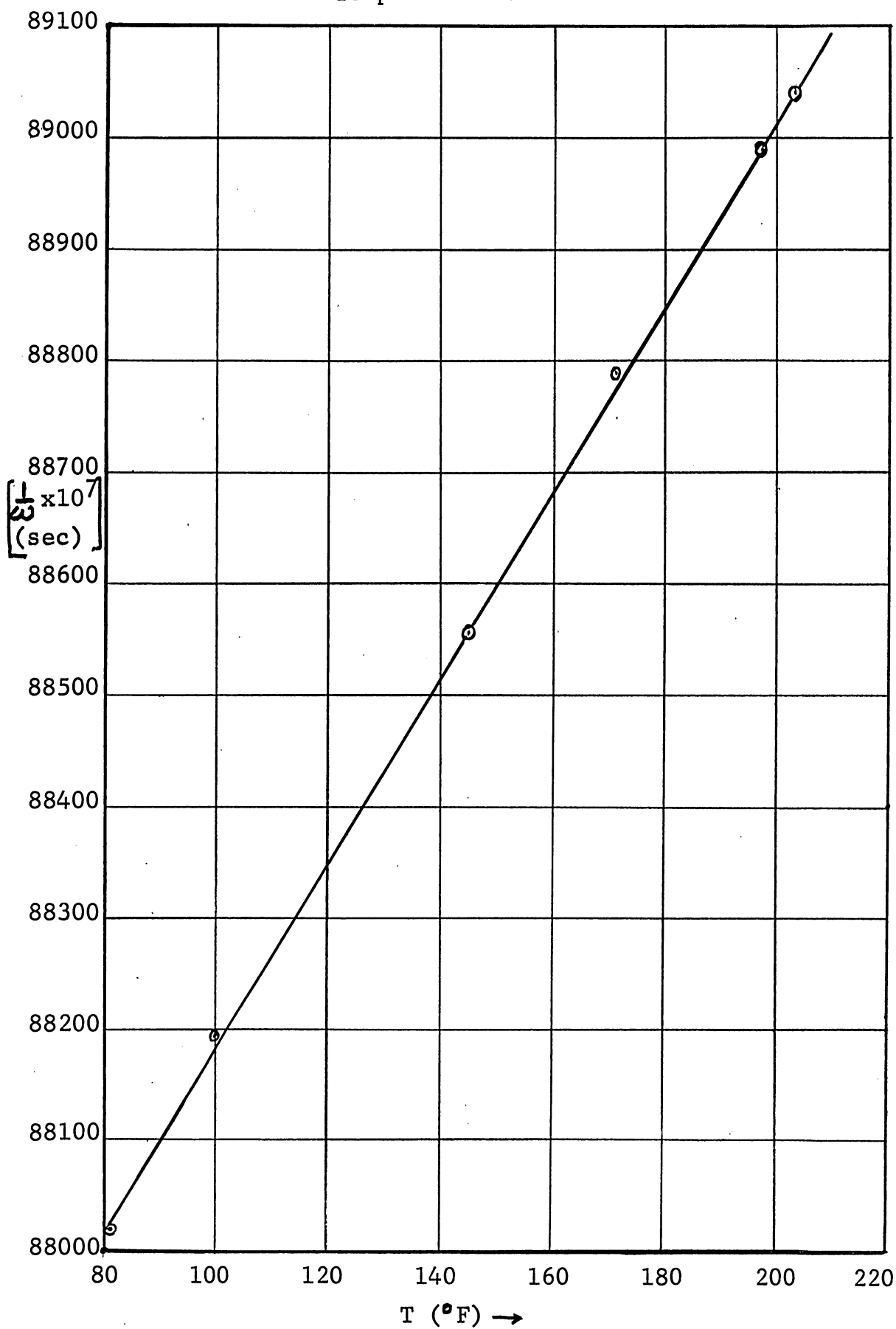


FIG. X

Pressure Calibration

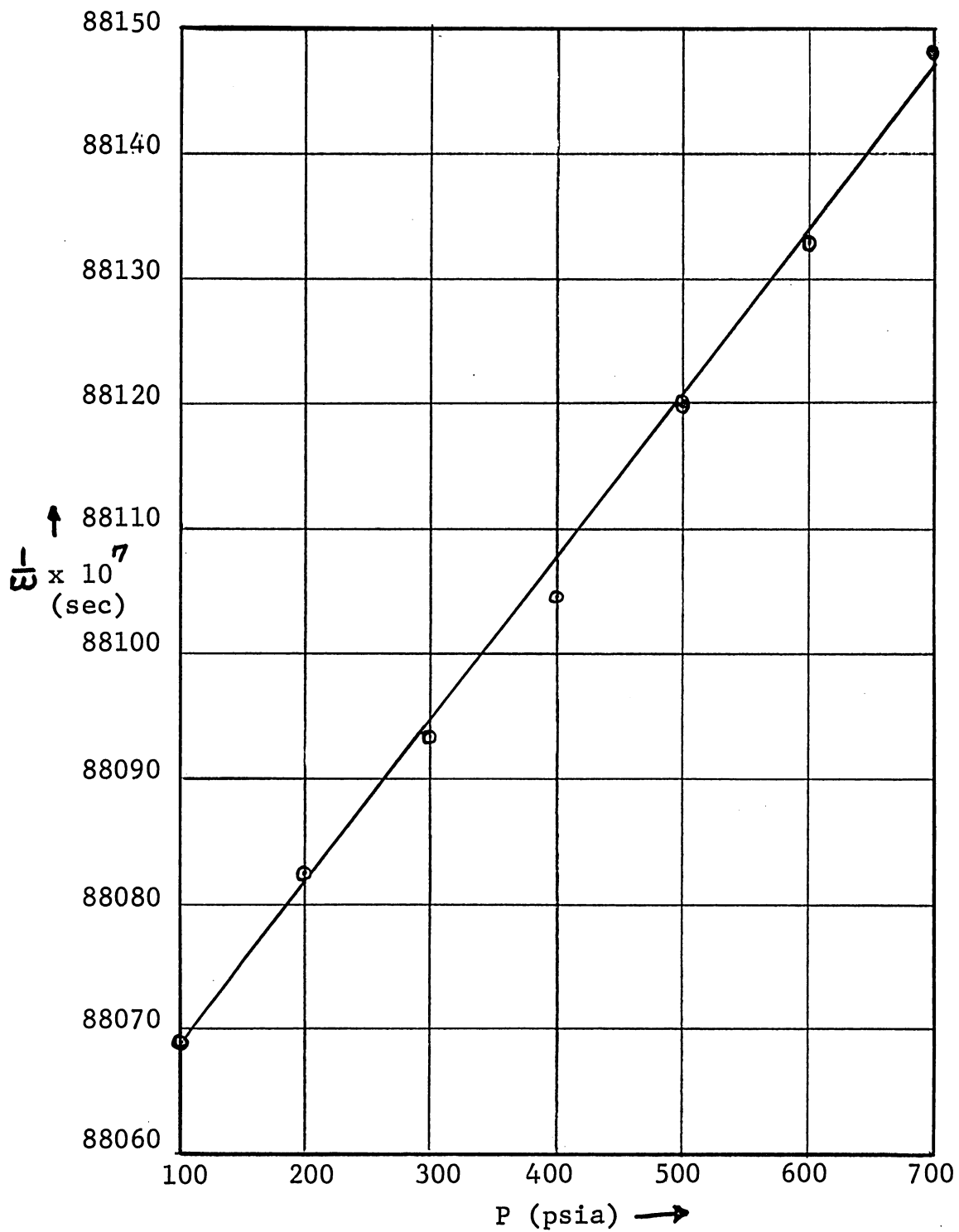
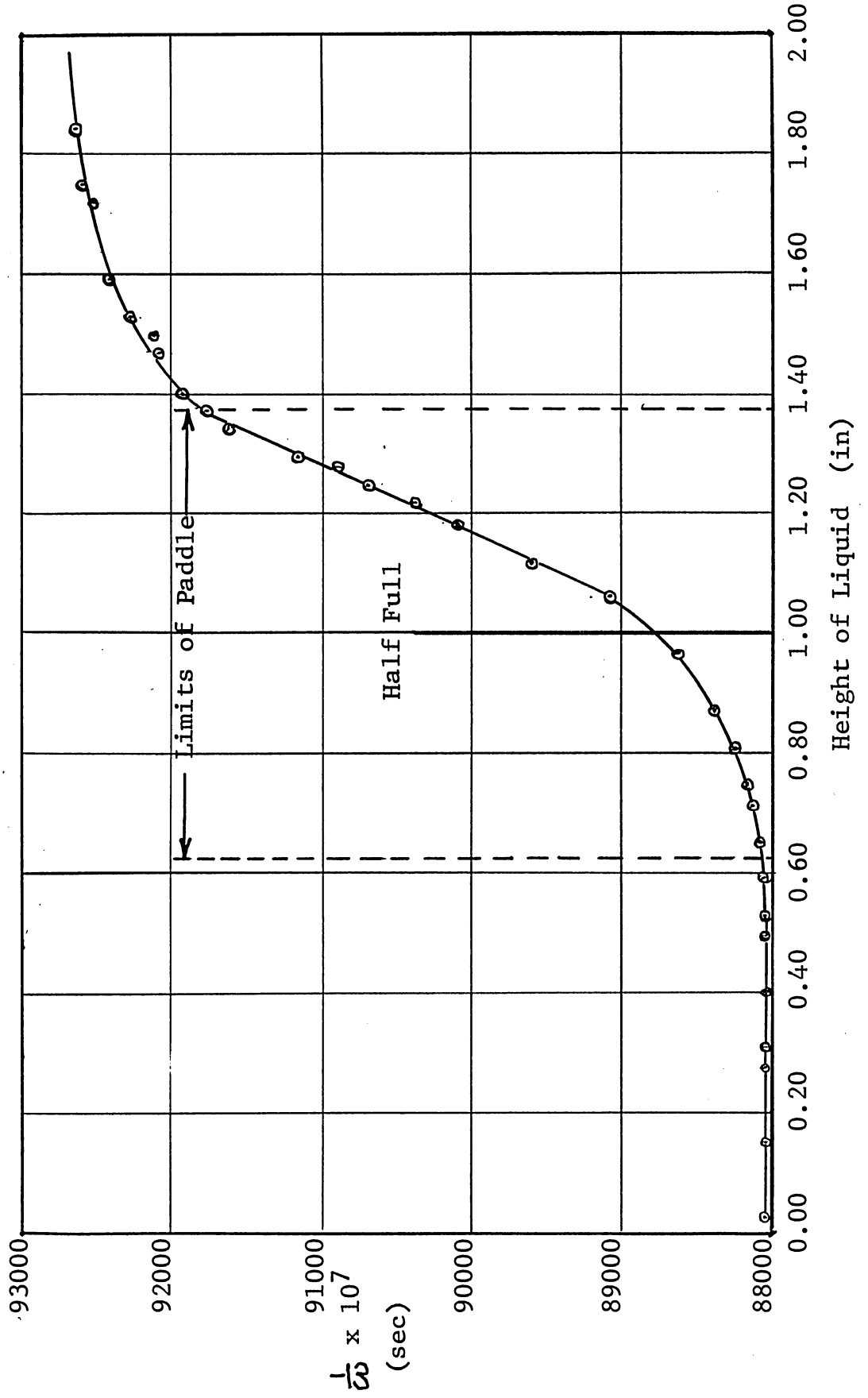


FIG. XI

Height of Liquid Calibration



700 psia. Again, the frequency shift due to the change in air density was negligible.

The fourth calibration was for frequency as a function of liquid level (Fig. XI). The cell was placed in the horizontal position and filled to various levels with acetone. The asymmetry of the curve is due primarily to the curvature of $\frac{1}{n}$ (Fig. VIII). At the half-way mark, the frequency of the Dynatrol was 112.7 cps. The frequency predicted by Fig. VIII for a fluid whose density is the average of the densities of acetone and air is 112.6 cps. Thus, the detection of the "half-full" point, even for fluids of widely different densities, is excellent. In the neighborhood of the critical, where the densities of the phases tend toward a common value, the detection of the "half-full" point should be even more precise.

II. The Experimental Apparatus

A. The Cell

The experimental cell (Fig. XII) was made of 416 stainless steel. The cell was designed for 2000 psia at 250°F with a safety factor of 4. The closure gasket was made of annealed copper. Closure bolts and nuts were case hardened steel.

FIG. XII
Experimental Cell

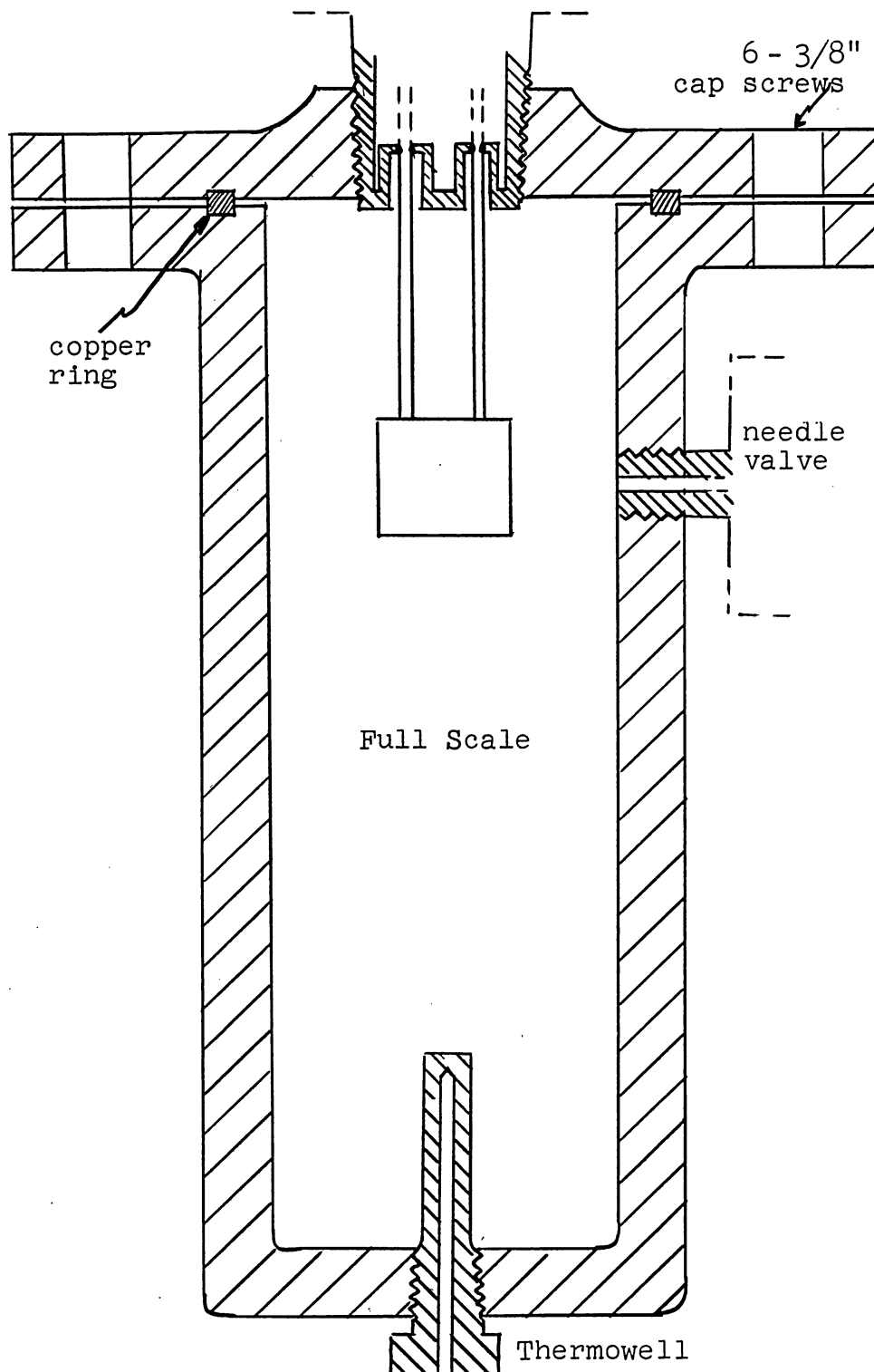


FIG. XIII
Experimental Apparatus

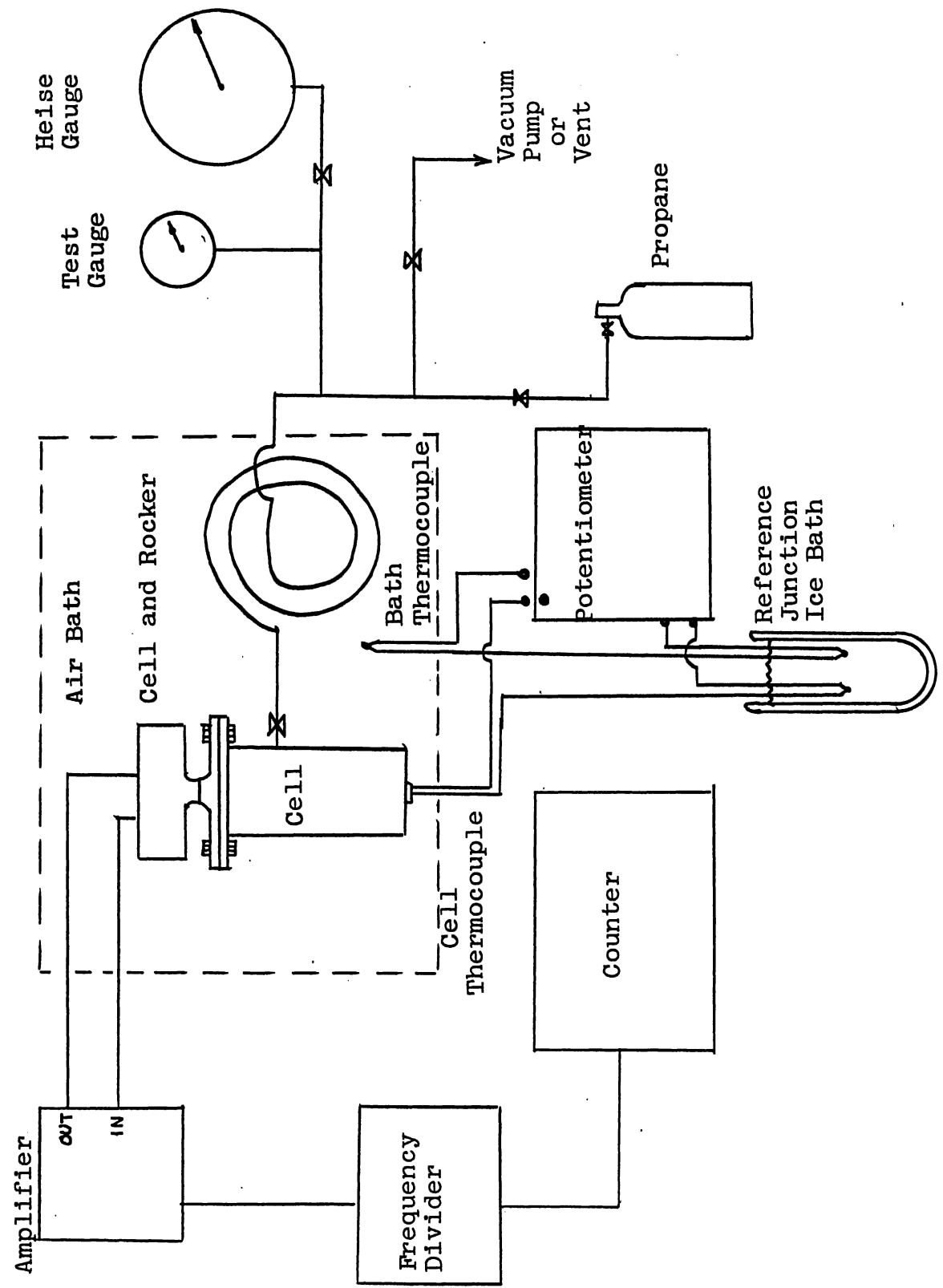
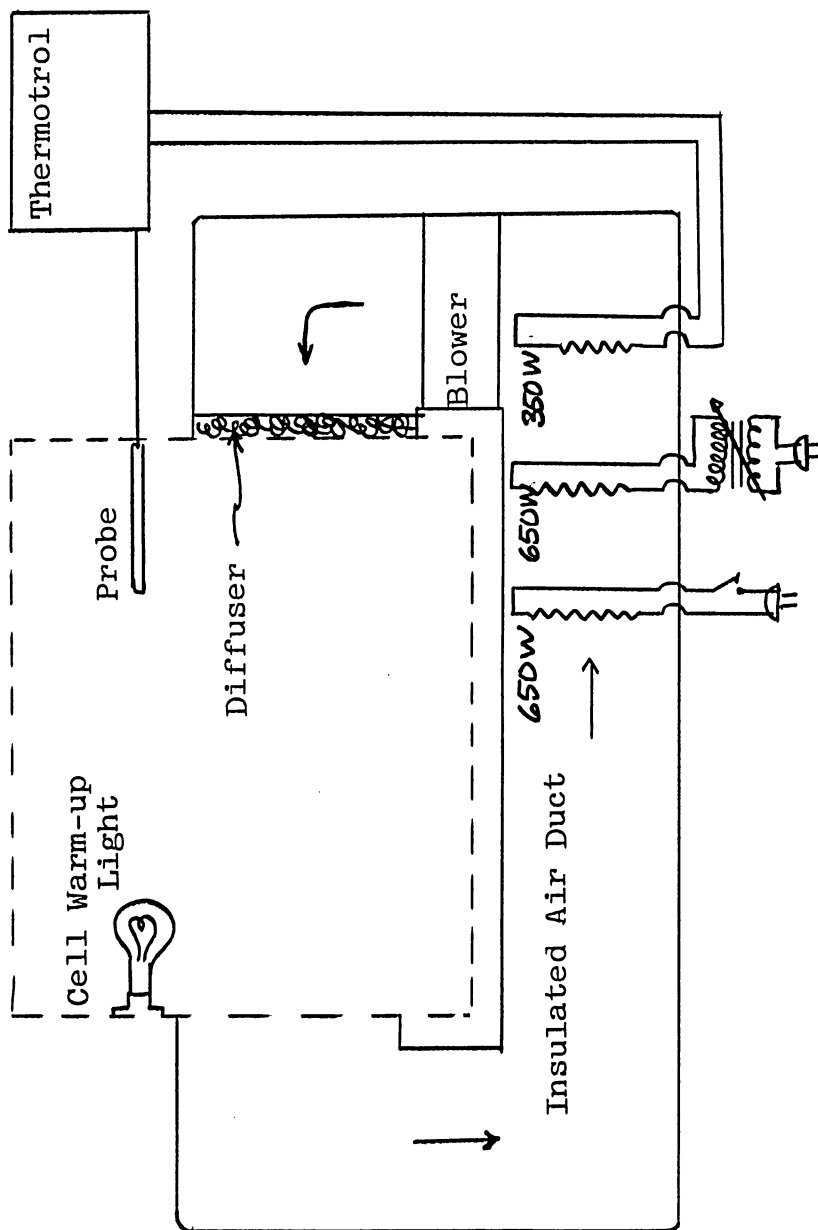


FIG. XIV
Air Bath



B. The Air Bath

The air bath used (Figs. XIII, XIV) employed a blower which circulated air through the cell chamber and back through a heavily insulated duct. Three separate nichrome heaters (two 650 watt heaters and one 350 watt heater) were mounted in the duct. One of the large heaters was connected to a powerstat to give coarse control. The 350 watt heater was controlled by a Thermotrol* temperature controller. The remaining 650 watt heater was used for quick bath warm-ups. A large lamp in the cell chamber was used to bring the cell temperature up quickly. The bath was heavily insulated and gave better than ± 0.01 F^o control over short time periods. However, due to severe line voltage fluctuations at various times during a day, temperature offsets of ± 0.1 F^o were observed.

C. Thermocouples

Two thermocouples were employed in this experiment. One was placed in the cell thermowell. The other was placed in the air-space immediately over the cell. The cell thermocouple was calibrated against a platinum resistance thermometer in a well-stirred mineral oil bath.

D. Pressure Gauge

Pressure measurements were made with a 0 to 1000 psi Heise pressure gauge. The accuracy of the gauge was ± 1 psi over the entire range of pressures.

*Hallikainen Instruments Thermotrol Model 1053 A

III. The Run

The cell was first cleaned with hot soap and water, next rinsed with water, and then rinsed with acetone. The cell was then evacuated at room temperature for ten hours by a vacuum pump. The cell was next filled with propane to a pressure of 50 psia and evacuated with a vacuum pump. This procedure of propane elution was repeated seven times to remove essentially all inert gases.

The cell was then placed in a horizontal position in an ice bath and opened to the cylinder of propane. As propane was condensed into the cell, readings of the Dynatrol period were noted. When a reading was taken indicating that the liquid surface had almost cleared the paddle, the propane supply was cut off and the ice bath removed. This procedure insured an excess of propane.

Since an excess mass of propane was present, as the temperature was increased, the liquid level rose. Propane was bled out of the cell to keep the interface level covering about 60% of the paddle. Control of the amount of propane bled was accomplished with a needle valve, and the level drop was indicated by the Dynatrol period (Figs. XV, XVI, XVII).

To insure thermal and vapor-liquid equilibrium during readings, the cell had to be rocked while the bath blower

was operating. A motorized rocker could not be used, since this would provide a mechanical linkage with the bath vibrations set up by the blower and rocker motors. The cell rocker was mounted on slabs of RTV Silastic 502 to decouple it from the bath floor. A "T" bar was fashioned with a key which mated a slot in the rocker bearing. This bar was then slipped through a brass bushing in the bath door and fitted into the rocker bearing. Thus the cell was rocked manually with the "T" bar. The positions of the "T" bar with the cell in its one horizontal and two vertical positions respectively were marked on the bath door, and the friction of the brass bushing served to hold the cell in the required positions. It was observed that, in this manner, vibrational pickup was held to an acceptable level.

The cell was rocked through an angle of about 70° at a rate of about one cycle per second for a period of two minutes before each reading. The readings were taken in the order, (1) vapor, (2) liquid, (3) interface, and then were repeated. An average of the two sets was recorded. In no case was a reading accepted if the deviation from the average was more than one (1) in the fifth place.

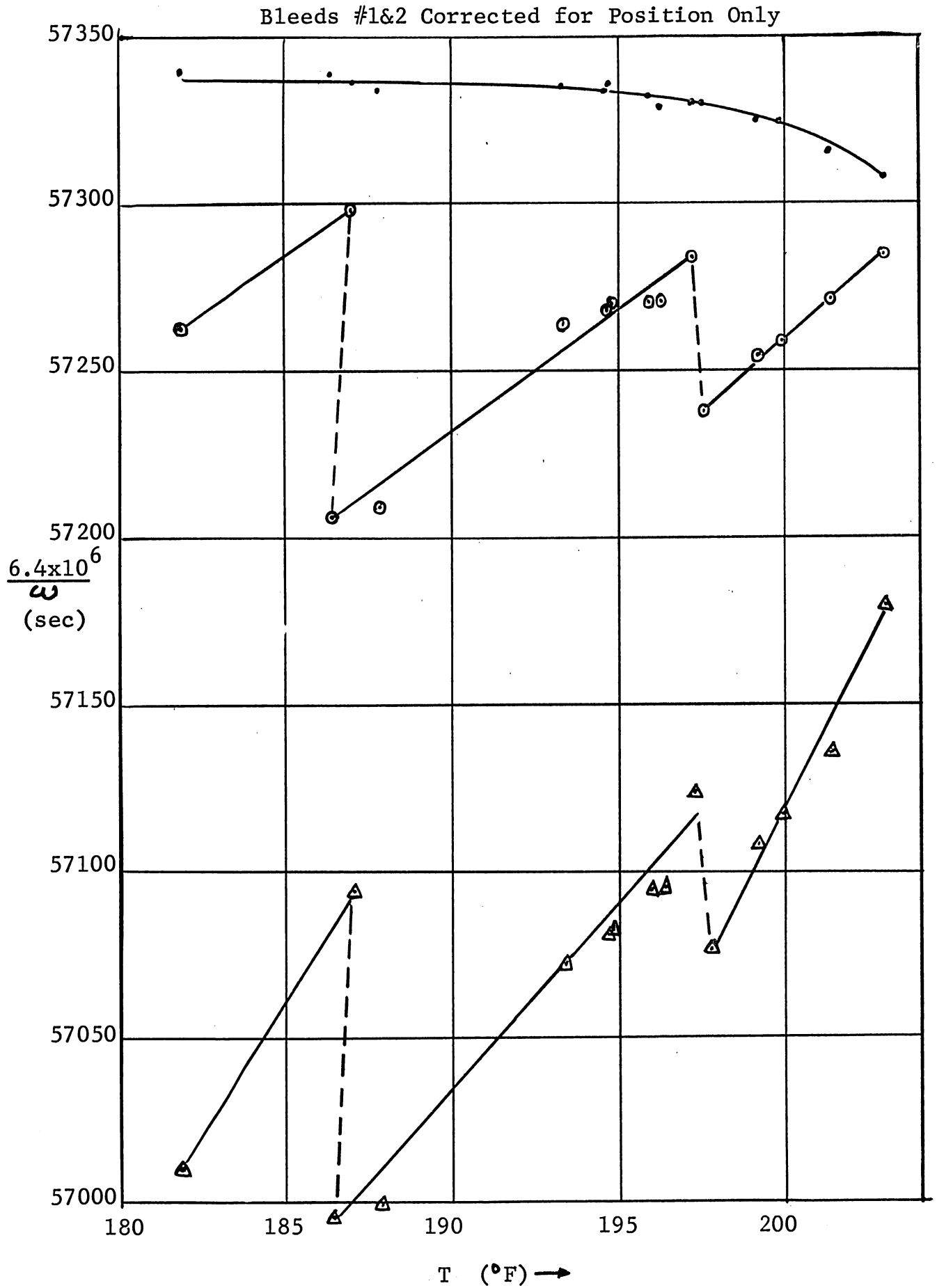
Since the criteria for assuring a critical point are that as $P \rightarrow P_c$ and $T \rightarrow T_c$, $\rho_L \rightarrow \rho_V$, and the liquid and vapor phases must occupy equal volumes, it follows that the

trajectories of the liquid, vapor, and interface Dynatrol periods must meet in a single point and that all three must be equal upon emergence from the two phase envelope.

Since, however, the period of the Dynatrol is, to a small extent, dependent upon position, the emergent trajectory was a pencil of three lines. The critical temperature was purposely overshoot to determine the necessary corrections. It was found that the vapor and interface readings were off by a constant amount with reference to the liquid readings. By employing these additive constants, the emergent trajectories coincided. The density at which the three trajectories were in the configuration of Fig. I,c was thus the critical density (Fig. XVIII). The cell was closed off with a needle valve at the critical point and allowed to cool.

The cell was then removed from its rocker and the thermocouple removed from its well. The cell was weighed, vented, evacuated with a vacuum, and weighed again. The cell was then filled with distilled water by removing the thermowell. Bubbles were eliminated by rocking the cell and allowing any trapped air to escape through the thermowell hole. The well was then replaced to its original depth with the needle valve cracked open to allow the excess water to escape. The needle valve was then closed, and the water remaining in the outer part of the valve was removed

with a pipe cleaner. The cell was weighed and the filling and weighing procedures repeated. From these weighings, cell volume and mass of propane were calculated.



Bleed #3 Corrected for Position Only

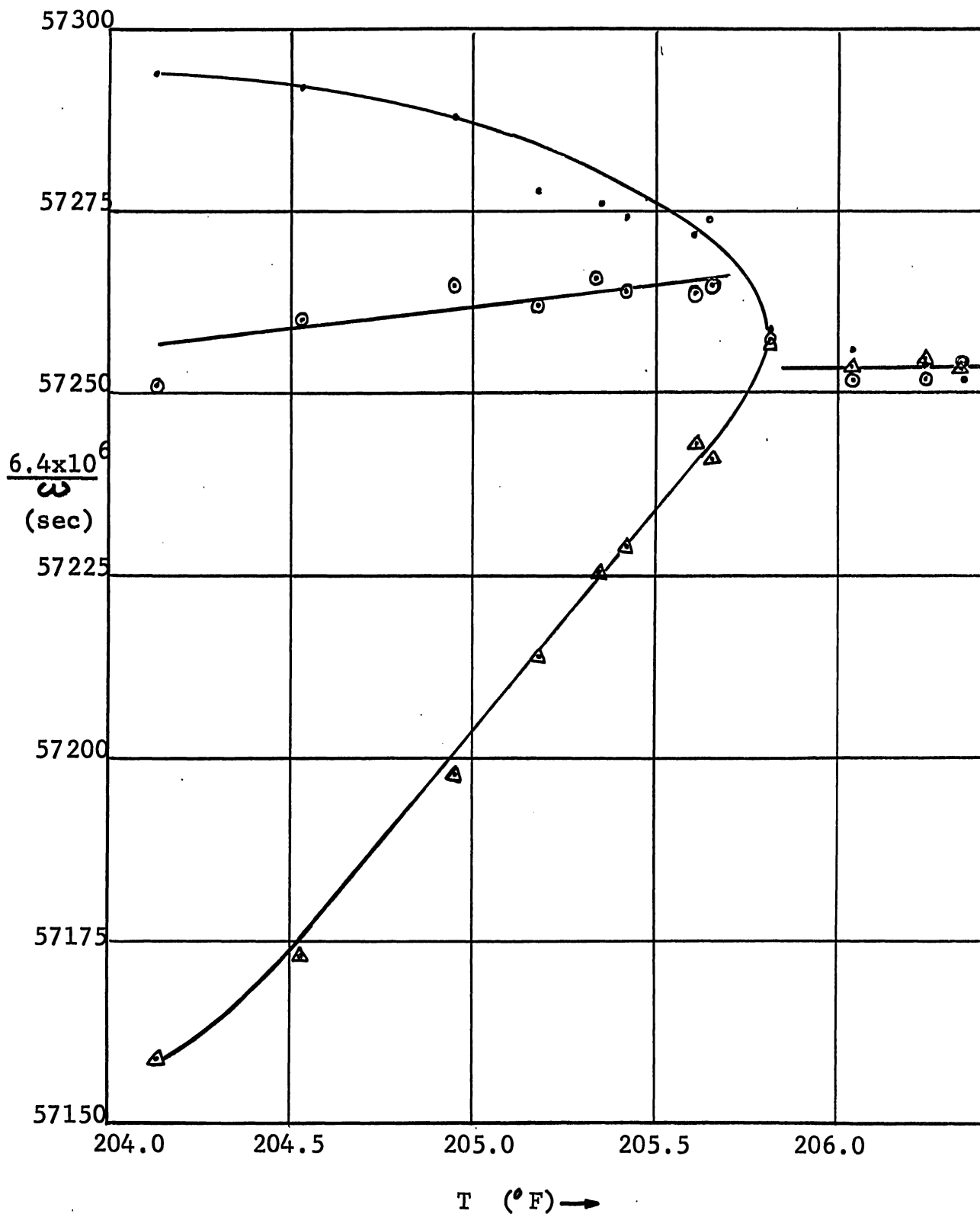


FIG. XVII

Bleed #4 Corrected for Position Only

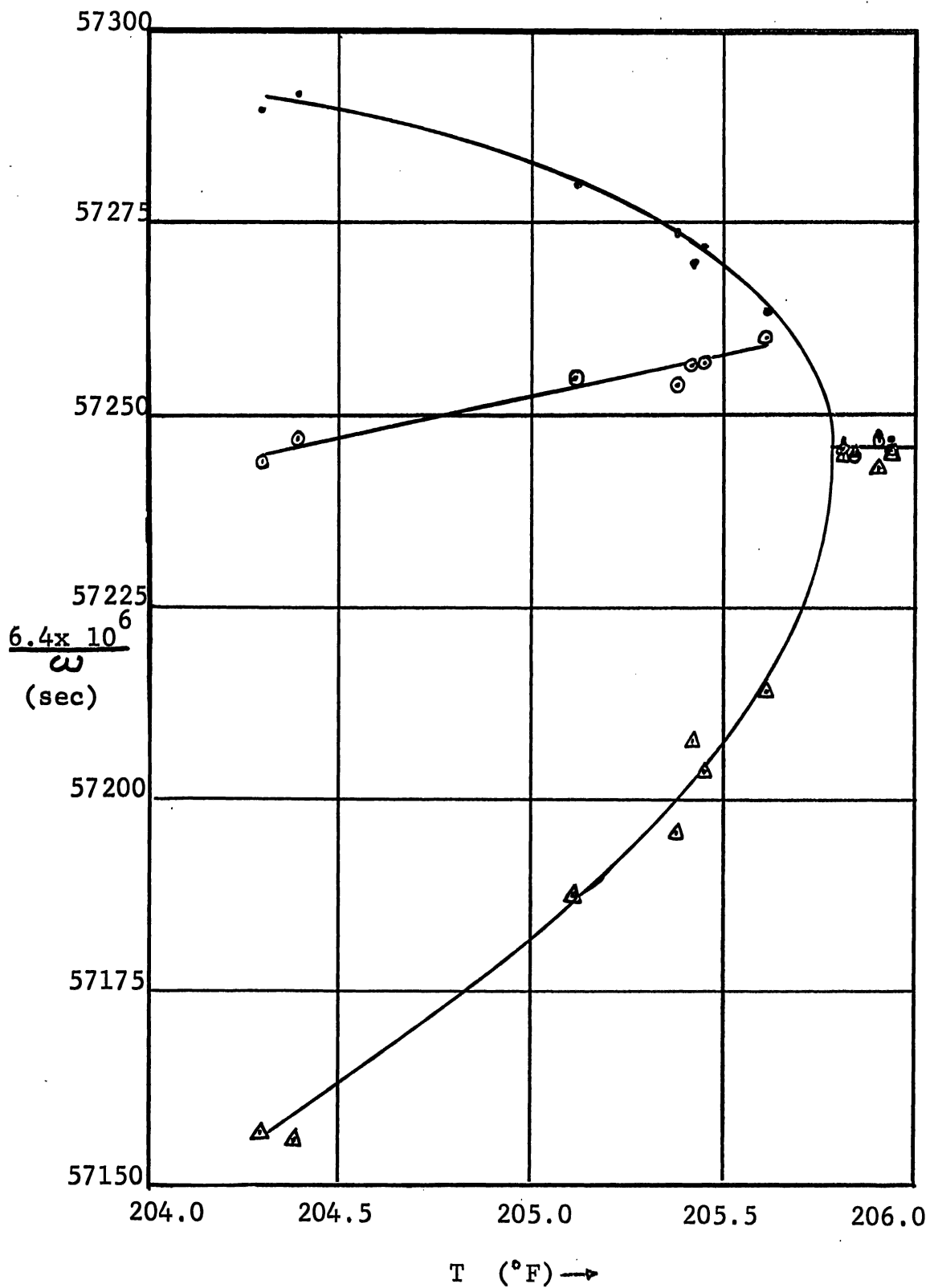
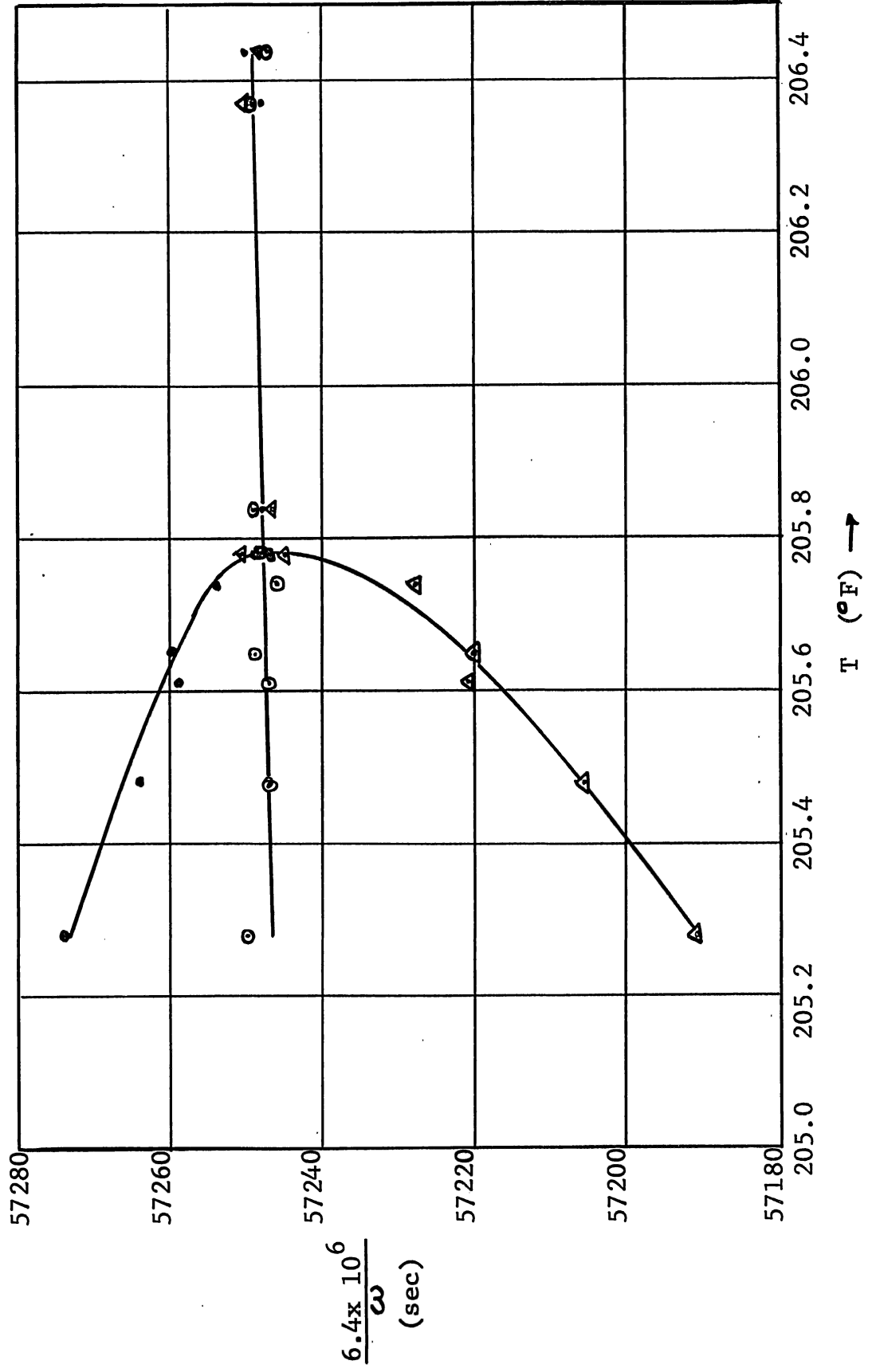


FIG. XVIII
Bleed #5 Corrected for Position Only



IV. Results and Error Analysis

A. Comparison of Results

	Beattie, ¹ Poffenberger, & Hadlock	Daschner ¹ & Brown	A.P.I. 44 ²	Brody
P_c (atm)	42.01	42.1	42.01	42.0
T_c (C)	96.81	96.85	96.81	96.54
ρ_c (g/cc)	0.2259	0.224	0.220	0.228
z_c	0.270	0.73	0.278	0.268

B. Error Analysis

The experimentally determined T_c is some 0.3°C lower than the accepted value. Some possible sources of error are discussed below.

1. Purity

The purity of the propane used was determined by a vapor phase chromatographic unit. The analysis showed a propane purity of 99.7%, with the primary impurities being ethane, propylene, and isobutane. Since an exact analysis was not made, the effect of impurities is not known.

2. The Thermocouple

The potentiometer was readable to ± 0.001 millivolts, which corresponds to $\pm 0.033^\circ\text{F}$. Thus, the

maximum possible thermocouple error was 0.07°F .

3. Thermal Gradients of the Cell

The power input to the Dynatrol unit was approximately 5 watts. Of this, about 4.5 watts were accounted for through heating of the Dynatrol coils. Conduction of heat from the Dynatrol case to the cell set up a slight thermal gradient over the length of the cell. This could cause the value determined for T_c to be low. The very small heating effect due to the paddle vibrations could also tend to make T_c low. Both of these effects should, however, be very small, since the cell was thoroughly rocked before each reading, and no discernible Dynatrol drift was encountered during readings.

V. Calculations

A. Calculation of Cell Volume

- (a) wt. of cell full of H₂O @ 25.2(°C) = tare + 179.116 (g)
 (b) wt. of cell (vacuum) = tare - 131.880 (g)
 (c) wt. of H₂O @ 25.2(°C) = (a)-(b) = 310.996 (g)
 (d) density (ρ) of H₂O @ 25.2(°C) = 0.99702 (g/cc)
 (e) volume of cell @ 25.2(°C) = $\frac{(c)}{(d)}$ = 311.926 (cm³)

B. Volume Correction for Cell Expansion

- (f) coefficient of expansion (α) for 416 stainless steel
 (0 to 100°C) = 5.5×10^{-6} (°F⁻¹)
 (g) $\Delta T = T_c - 25.2(°C) = 206(°F) - 78(°F) = 128(°F)$
 (h) $\Delta V = V(3\alpha)\Delta T$ (3)(e)(f)(g) = 0.66 (cm³)
 (i) volume of cell @ 206 (°F) = (e) + (h) = 312.58 (cm³)

C. Calculation of ρ_c

- (j) wt. of cell full of propane = tare - 60.676 (g)
 (k) wt. of propane (j)-(b) = 71.204 (g)
 (l) $\rho_c = \frac{(k)}{(i)}$ = 0.228 (g/cc)

D. Calculation of z_c

$$z_c = \frac{P_c M}{\rho_c T_c R} = \frac{(42.0)(\text{atm})(44.09)(\text{g/g mole})}{(228)(\text{g/l})(369.5)(°K)(0.08205)(1 \text{ atm/g mole } °K)}$$

$$= 0.268$$

E. Thermocouple Calibration

3.710 (mv) corresponds to 160.00 ($^{\circ}\text{F}$).

5.532 (mv) corresponds to 220.00 ($^{\circ}\text{F}$).

Over this range of temperatures,

$$T (^{\circ}\text{F}) = (37.83) + (32.931) \times (\text{mv}).$$

VI. Recommendations for Further Use of the Dynatrol

In this experiment, the critical point of a pure substance was studied. The critical points of mixtures may also be investigated with the same experimental apparatus. The only modification of technique would be the necessity of bleeding off the mixture above the critical temperature in order to insure a constant composition.

For the investigation of the thermal gradient of the cell, several thermowells could be located along the length of the cell.

The power input (and thus, the heating effects) of the Dynatrol could be reduced by redesigning the instrument and amplifier. A compromise between heating and sensitivity would have to be effected.

The Dynatrol could also be modified for greater sensitivity to density in the range of 0.1 to 0.5 g/cc, where most critical point investigations are carried out.

VII. Data

Approach to Critical Point

Uncorrected for Pressure, Temperature, and Position

$$\frac{6.4 \times 10^6}{\omega}$$

Remarks	<u>T (°F)</u>	<u>mv</u>	<u>P (psia)</u>	<u>Vapor</u>	<u>Liquid</u>	<u>Interface</u>
	160.00	3.710	388.0	56845	57318	57121
	170.96	4.043	435.0	56930	57328	57200
	181.80	4.372	484.5	57033	57340	57271
	187.00	4.530	511.0	57116	57337	57306
Bleed #1	186.35	4.510	510.0	57017	57339	57214
	187.83	4.555	514.0	57022	57334	57217
	193.26	4.720	547.0	57094	57335	57272
	194.58	4.760	551.0	57102	57334	57276
	195.90	4.800	558.0	57117	57332	57278
	194.71	4.764	553.0	57105	57336	57278
	196.23	4.810	559.5	57117	57329	57279
	197.22	4.840	567.0	57145	57330	57292
Bleed #2	197.54	4.850	568.0	57098	57330	57246
	199.06	4.896	579.0	57129	57325	57263
	199.85	4.920	581.5	57139	57324	57267
	201.33	4.965	588.5	57157	57316	57280
	202.88	5.012	598.0	57202	57308	57292
Bleed #3	204.13	5.050	606.0	57181	57294	57259
	204.95	5.075	612.0	57219	57288	57273
	205.18	5.082	613.0	57236	57278	57270
	205.35	5.087	614.0	57247	57276	57274
	205.42	5.089	614.0	57251	57274	57272
	206.34	5.117	620.0	57276	57252	57262
	206.70	5.128	622.0	57278	57257	57266
	206.77	5.130	623.0	57277	57256	57263
	206.77	5.130	623.0	57277	57255	57263
	206.04	5.108	618.0	57276	57256	57260
	206.24	5.114	619.0	57277	57255	57260
	205.81	5.101	617.0	57279	57259	57266
	205.61	5.095	615.0	57265	57272	57272
	205.65	5.096	616.0	57263	57274	57273
	204.53	5.062	608.5	57195	57292	57268

Approach to Critical Point (Continued)

Uncorrected for Pressure, Temperature, and Position

$$\frac{6.4 \times 10^6}{\omega}$$

Remarks	T (°F)	mv	P (psia)	Vapor	Liquid	Interface
Bleed #4	204.30	5.055	608.0	57179	57290	57252
	204.39	5.058	608.0	57178	57292	57255
	205.38	5.088	614.5	57218	57274	57262
	205.61	5.095	616.0	57236	57264	57263
	205.81	5.101	617.0	57267	57247	57258
	205.84	5.102	618.0	57267	57245	57253
	205.91	5.104	618.5	57265	57243	57255
	205.94	5.105	619.0	57268	57247	57254
	205.45	5.090	616.0	57226	57272	57265
	205.12	5.080	614.5	57210	57280	57263
	205.42	5.089	616.0	57230	57270	57265

Critical Density Run

Corrected for Position Only

$$\frac{6.4 \times 10^6}{\omega}$$

Remarks	T (°F)	mv	P (psia)	Vapor	Liquid	Interface
Bleed #5	205.48	5.091	616.0	57206	57264	57247
	205.61	5.095	617.0	57221	57259	57247
	205.65	5.096	617.0	57220	57260	57249
	205.74	5.099	618.0	57228	57254	57246
	205.78	5.100	618.0	57245	57248	57248
	205.28	5.085	615.0	57191	57274	57250
	205.78	5.100	618.0	57251	57250	57249
	206.37	5.118	623.0	57250	57248	57249
	206.44	5.120	623.0	57248	57250	57247
	205.84	5.102	618.0	57247	57248	57249

BIBLIOGRAPHY

1. Brown, George Granger, and Deschner, Walter W., Industrial and Engineering Chemistry, 32, 836-840 Table III, (1940).
2. Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. M., and Pimentel. G. C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa. Table 20i, p. 326. (1953).
3. Cardner, D., and Deans, H.A., Unpublished report for Automation Products, Incorporated.