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A CONSTANT VOLUME - CONSTANT MASS SYSTEM FOR MEASURING THE P-V-T PROPERTIES OF HEAVY WATER AND MEASUREMENTS OF THE SATURATED VAPOUR PRESSURE OF HEAVY WATER

by

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ABSTRACT

A constant volume-constant mass system has been developed to measure the P-v-T properties of heavy water for pressures up to the critical values. Heat was added to a given mass of water and temperatures and pressures were measured at steady state, when the change of temperature was less than or equal to 0.01 degrees Celsius per hour. Changes in apparatus volume were functions only of temperature and were estimated from the coefficient of thermal expansion. New experimental data are given for the vapour pressure of light and heavy water, from 200 to 300 degrees Celsius. The data for the saturated vapour pressure of heavy water result from direct measurements and agree closely with the data of other studies, which report pressure measurements with respect to those of ordinary water. An average deviation of 0.02 percent exists between the direct measurements of this study and the indirect measurements of other studies.

An equation for the saturated vapour pressure of heavy water, as a function of temperature from 100 to 370 degrees Celsius, is presented in the form of a Chebyshev polynomial. This expression may be employed to derive other thermodynamic properties, without referring to the equivalent data for ordinary water.

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NOMENCLATURE

a	Van der Waal's constant
A	Helmholtz potential
b	Van der Waal's constant
c	Subscript, denoting the critical state
C	Constant
C_p	Constant pressure specific heat
d	Altitude with respect to sea level
D	Latitude in degrees
f	Subscript, denoting saturated liquid
F	Safety factor
g	Subscript, denoting saturated vapour
G	Gibbs potential
G_L	Local gravitational acceleration
h	Specific enthalpy
H	Enthalpy
k	Thermal conductivity
K	Compressibility
L	Length
M	Constant of integration
N	Constant of integration
o	Reference perfect gas state where P approaches zero
P	Pressure
P_b	Barometric pressure
pc	Pressure correction

P_n	Nominal pressure
q	Heat per unit volume
R	Gas constant, resistan[illegible], internal radius
R_o	Resistance at temperature 0 deg. C.
R_T	Resistance at temperature T deg. C.
S	Entropy, deviation
t	Wall thickness
T	Temperature
T_L	Temperature at $z = L$
T_o	Temperature at $z = o$
U	Internal energy
v	Specific volume
V	Volume
z	Axial distance
Z	Compressibility factor
α	Temperature coefficient
β	Reduced pressure
α', β', γ	Properties of saturated liquid and vapour defined by Osborne (2)
δ	Temperature coefficient
θ	Reduced temperature
σ	Design stress
τ	Reduced temperature
ϕ	Reduced volume

CHAPTER 1

INTRODUCTION

1-1. Approach

Heavy water is an important component of the Canadian CANDU nuclear reactor, hence a comprehensive and precise account of its thermodynamic behaviour is essential. Currently an internationally accepted table of thermodynamic properties for heavy water is not available.

Previous studies, at the University of Western Ontario by Chan (1), resulted in the development of a calorimeter apparatus for investigating the thermodynamic properties of saturated heavy water liquid and vapour. The investigation consisted of three fundamental experiments, based on the principles laid down by Osborne (2), in his studies of ordinary water. The three experiments may be described as:-

i) Non-isothermal energy addition at a constant rate to a constant mass homogeneous fluid system at two phase conditions.

ii) Isothermal energy addition at a constant rate and saturated liquid withdrawal process.

iii) Isothermal energy addition at a constant rate and saturated vapour withdrawal process.

A detailed account of the theory and method of each experiment is provided in reference (1). The thermodynamic expressions describing this method are:

$$\alpha' = h_f - Tv_f \frac{dp}{dT} \quad \text{-----------} \quad (1.1)$$

$$\beta' = v_f\ T \frac{dp}{dT} \quad \text{-----------} \quad (1.2)$$

$$\gamma = v_g\ T \frac{dp}{dT} \quad \text{-----------} \quad (1.3)$$

where α', β', γ are quantities determined from energy and mass measurements conducted during the three governing experiments. Values for v_f and v_g may be obtained from equations (1.1), (1.2) and (1.3), if an expression for the saturated vapour pressure as a function of temperature is available or determined. At present, a suitable expression is not available.

The main purpose of the author's research was to design and develop a system, for measuring accurately the P-v-T properties of heavy water and light water at states below the critical point pressure and temperature, with particular emphasis on the superheated vapour region. With experimental data for P, v and T, values for entropy and specific heat may be calculated from the following expressions:-

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \quad \text{---------------} \quad (1.4)$$

$$S = -\int_{P_0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dP + S_0 \quad \text{-----------} \quad (1.5)$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \quad \text{-----------} \quad (1.6)$$

However, with the introduction of a second derivative in equation (1.6) a loss of precision is experienced. To avoid the second derivative, the Helmholtz and Gibbs potentials are introduced as outlined by Kirillin et al (3).

$$\left(\frac{\partial A}{\partial v}\right)_T = -P \quad \text{-----------------} \quad (1.7)$$

$$A = \int_{P_O}^{P} P dv + A_O \quad \text{-----------------} \quad (1.8)$$

$$\left(\frac{\partial G}{\partial P}\right)_T - v \quad \text{-----------------} \quad (1.9)$$

$$G = \int_{P_O}^{P} v dP + G_O \quad \text{-----------------} \quad (1.10)$$

$$U = A + TS \quad \text{-----------------} \quad (1.11)$$

$$H = G + TS \quad \text{-----------------} \quad (1.12)$$

To apply this method P-v-T data should be collected along isotherms. Mass would be withdrawn and weighed while the temperature is held constant. This technique requires weighing at each datum point and each mass determination depends on the previous measurement. Since accumulative errors may result, unless extreme care and a refined technique are developed, this method will not be employed initially to collect P-v-T data.

To assist in the reduction of calorimetric data employing equations 1.1, 1.2 and 1.3, the P-v-T system developed was employed, to compile pressure versus temperature data from 200 to 300 degrees Celsius for saturated heavy water. Preliminary P-v-T data for superheated heavy water were also obtained.

1-2. Literature Review of Related Measurement Techniques

The following is a brief account of related systems used by other investigators, to determine the thermodynamic properties of heavy water and light water. The methods and procedures employed in these studies, have influenced the design of the P-v-T apparatus developed in this study.

Measurements of the P-v-T properties of heavy water were conducted at the Moscow Power Institute by Kirillin et al (4), using a modified version of their method (3) for ordinary water studies. The original apparatus was of cylindrical geometry, with a thin wall piezometer (sample vessel) located inside a thickwalled pressure vessel. Stainless steel was used for both vessels due to its weldability, anticorrosive properties and insignificant vapour adsorption. The pressure difference across the piezometer walls was in general less than 4 bars. A pressure equalization system, incorporating a deadweight gauge and bourdon tube movement, provided a reading of reference pressure. Both the piezometer, and the space between the piezometer and the pressure vessel were charged with water. A heavy walled copper casting enclosed the pressure vessel. Heating elements, installed on the copper vessel, and surrounding insulation combined to provide an isothermal enclosure.

Small heat exchangers were installed on the tubing from the vessels, to maintain the vapour-liquid meniscus within a controlled region. Temperature was determined with a platinum resistance thermometer placed between the pressure vessel and the copper vessel. P-v-T measurements were estimated accurate to 0.2 percent.

Their modified system employed for heavy water measurements lacks the thin walled piezometer, and the pressure vessel serves as the sample vessel. Other aspects of the system appear similar. The single vessel system simplified the experimental procedure. The amount of water in the system at any time was deduced from the weight of water removed during test and the weight of water remaining after test. During the experiment water was discharged into a vessel containing oil for weighing purposes. Volume changes of 2% resulted from thermal expansion and isothermal deformation. Corrections were applied using available data for stainless steel. Measurements of temperature and pressure were considered accurate to 0.05°C. and 0.05 percent, respectively. The experimental P-v-T results were estimated accurate to within 0.3 percent. Their subcritical P-v-T data for superheated heavy water vapour is shown in Table 1, Page 7.

TABLE 1

EXPERIMENTAL VALUES FOR THE SPECIFIC VOLUME OF SUPERHEATED HEAVY WATER (4)

300°C.		350°C.		360°C.		369°C.		371°C.	
P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g
84.96	19.21	87.65	24.02	72.85	31.11	76.36	30.14	118.50	17.42
		144.76	11.12	133.06	13.88	123.81	16.21	168.53	9.912
				164.42	9.392	181.19	8.306	205.33	5.869
				188.17	6.113	208.50	4.946		

For their measurements of the P-v-T properties of heavy water, Rivkin et al (5) employed a double walled spherically shaped vessel, immersed in a temperature controlled bath. This inner vessel, and the space between the two spheres contained liquid. With this arrangement the inner vessel experienced negligible pressure deformation. The temperature was determined from the bath temperature. Pressure was measured with a deadweight gauge. A mercury seal was located between the heavy water sample and the oil of the deadweight gauge. This system was used to obtain P v data under isothermal conditions by intermittent withdrawal of liquid. Trakhtengerts (6) estimated the accuracy, of their specific volume data, to be 0.1 to 0.2 percent. Their P-v-T data for subcritical superheated heavy water vapour is displayed in Table 2, pages 9 and 10.

The methods and procedures, used at the Massachusetts Institute of Technology in the 1920's and 1930's to investigate the P-v-T properties of ordinary water, are described in detail by Keyes (7). The change of volume of a fixed mass of water was measured by means of a calibrated piston or volumometer with change of temperature or pressure. A single walled sample vessel was utilized, hence pressure deformation of the vessel occurred. The sample vessel and

TABLE 2

EXPERIMENTAL VALUES FOR THE SPECIFIC VOLUME OF SUPERHEATED HEAVY WATER (5)

275.02°C.		300.03°C.		325.05°C.		340.02°C.	
P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g
61.16	1.1929	89.18	1.2739	125.00	1.3911	149.76	1.4989
64.11	1.1922	98.38	1.2700	137.30	1.3807	157.07	1.48692
69.11	1.1909	118.01	1.2621	176.21	1.3542	176.81	1.45953
98.33	1.1838	177.16	1.2411				
137.80	1.1748						
177.04	1.1665						

TABLE 2 (CONTINUED)

EXPERIMENTAL VALUES FOR THE SPECIFIC VOLUME OF SUPERHEATED HEAVY WATER (5)

350.05°C.		359.98°C.		360.03°C.		364.96°C.	
P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g	P bars	v cm^3/g
168.94	1.60326	191.59	1.7604	192.30	1.7566	204.62	1.8694
186.03	1.5576	193.54	1.7454	195.89	1.7296	206.19	1.8475
		196.88	1.7233				
		201.80	1.6962				

the volumometer were maintained in a temperature controlled bath. A deadweight gauge and a platinum resistance thermometer were employed to measure pressure and temperature respectively. A mercury U tube separated the oil of the deadweight gauge from the test fluid. A small heat exchanger on the tubing from the sample vessel insured the vapour-liquid meniscus remained in a certain region. Sample vessels employed were fabricated from nickel, chrome-vanadium steel, and 18/8 stainless steel. Both cylindrical and spherical containers were used. The isothermal deformations were calculated and the thermal expansion measured for the alloy materials. The 18/8 stainless steel displayed regular and reproducible thermal expansion behaviour. Chemical interactions with water, over a period of many months, at temperatures up to 460°C. appeared negligible. However, specific volumes greater than 150 cc per gram were not measured (Keyes et al (8)) due to the adsorptive property of water.

Although no specific estimate of the accuracy of their volumetric measurements was made (Nowak et al (9)), Smith et al (10) mentioned that temperatures were reproducible to about 0.01 deg. C. while pressures were accurate to 5 parts in 10,000.

The measurements by Kell et al (11), at the National Research Council, of the P-v-T properties of liquid ordinary water were performed on a similar system. Type 304 stainless steel was used for the sample vessel. This vessel was pressurized on the outside to provide equal pressure across its walls. The thermal expansion coefficient of the material was measured. Corrections were applied for the change in vessel volume due to compression. A value of 0.700×10^{-6} per bar was determined for the compressibility (K) of the stainless steel vessel. The effect of compression on the volume may be calculated from the following equation:-

$$V = V_o \ (1 - KP)$$

The more recent studies by Kell et al (12, 13), of the virial coefficients of ordinary, and heavy water, employed essentially the same system with modifications to the sample vessel. They have devised a procedure of isothermal liquid injection, employing their volumometer, which does not require direct measurement of the system volume. The second and third virial coefficients of ordinary and heavy water were determined with this new method.

A general review of the P-v-T measurement techniques is provided by Ellington et al (14). Of particular interest are their comments regarding constant volume-constant mass, and variable volume, and constant mass systems.

The former is considered the simplest in concept, and capable of providing results with errors of the order of 0.005 percent for gases and 0.001 percent for liquids. However, achieving errors of less than 0.1 percent is difficult and highly dependent on the accuracy of volume determination. A variation of this system is discussed with a constant volume and mass bled off periodically during test. Normal errors are of the order of 0.1 percent, however with extreme refinement errors may be reduced to approximately 0.01 percent. The variable volume constant mass system was in general used as far back as 1893. Errors of the order of 0.01 percent are mentioned. Some of the most accurate data currently available (e.g. (8), (11)) has been obtained with this method.

The saturated vapour pressure of heavy water was measured indirectly by Oliver et al (15), (16). Two heavy walled monel boiling point tubes contained ordinary and heavy water respectively. For insulation purposes a vacuum vessel surrounded each tube. The tubes were pressurized with a common helium supply. The temperatures of the two boiling-point tubes were adjusted until the pressures were equal. With a platinum resistance thermometer the temperature of each sample was measured. The pressure in each tube was determined from the saturated vapour pressure data for ordinary water (Osborne et al (17)). The helium supply was isolated from direct contact with the water samples, by using cold traps. The temperature measurements were estimated to be accurate to ± 0.01°C. Data for the vapour pressure of heavy water from approximately 208°C. to the critical point is shown in Table 3, page 15. The crossover temperature was evaluated as 220.68°C.

Rivkin et al (18) utilized their previously mentioned P-v-T apparatus to obtain data for the saturated vapour pressure of heavy water, from 275 to 365°C. Their data is presented in Table 4, page 16. Agreement with the values of Oliver et al to within 0.03 percent is displayed in Table 5, page 17.

Liu et al (18), in a recent study, investigated the vapour pressure of heavy water from 106 to 300°C. The ordinary and heavy water samples were placed in platinum cups in similar but separate pressure cells. The cells were symmetrically installed inside a large aluminum block and the assembly immersed in a temperature regulated oil bath. The temperature of the oil bath was determined with a resistance thermometer - Mueller bridge system. The pressure in each cell was balanced across individual bellows with an inert gas. Differences between the gas pressures was detected with a mercury-filled differential manometer.

VAPOUR PRESSURE OF D_2O AND BOILING POINT DIFFERENCE BETWEEN H_2O AND D_2O (15)

Pressure bars	Temperature °C.	$\Delta T,^{\alpha}$ °C.	Pressure bars	Temperature °C.	$\Delta T,^{\alpha}$ °C.
18.355	208.21	-0.141	69.961	285.05	0.708
21.687	216.55	- .047	83.047	296.77	.832
23.162	219.92	- .010	94.486	305.89	.927
23.442	220.55	- .007	98.940	309.23	.952
23.497	220.66	- .003	109.96	316.96	1.063
23.506	220.68	.000	123.58	325.74	1.150
23.599	220.89	.004	124.07	326.04	1.162
23.807	221.34	.008	139.45	335.04	1.268
24.181	222.15	.019	152.76	342.24	1.343
24.470	222.78	.023	171.84	351.67	1.468
24.833	223.55	.033	188.71	359.30	1.575
25.133	224.19	.035	204.39	365.85	1.68
25.580	225.11	.049	209.46	367.87	1.70
25.956	225.90	.051	212.79	369.12	1.75
26.547	227.09	.063	215.96	370.41	1.72
26.616	227.22	.065	216.38	370.51	1.78
28.268	230.45	.107	217.77	370.75	2.08
28.616	231.12	.115	219.01	370.9	2.39
42.119	253.05	.362	219.98	370.9	2.71
55.858	270.39	.544			

$^{\alpha}$Algebraically add ΔT values to b.p. of D_2O to obtain b.p. of H_2O.

TABLE 4

SATURATED VAPOUR PRESSURE OF HEAVY WATER FROM 275 TO 365 DEG. C. (RIVKIN ET AL (5))

Temperature Deg. C.	Pressure Bars	Temperature Deg. C.	Pressure Bars
275	60.06	350	168.33
300	86.98	360	190.34
325	122.36	365	202.25
340	148.53		

TABLE 5

COMPARISON OF THE VAPOUR PRESSURE DATA FOR HEAVY WATER OF RIVKIN ET AL (5) AND OLIVER ET AL (15)

Temperature Deg. C.	Pressure, Bars	
	Ref. (5)	Ref. (15)
275	60.05	60.04
300	86.98	86.97
325	122.36	122.39
340	148.53	148.53
350	168.33	168.33
360	190.34	190.36
365	202.25	202.27

Their data, which is the average of 5 to 20 observations at each temperature, is listed in Table 6, Page 19. Comparison of their values of P_{D_2O}/P_{H_2O} with those of Oliver et al (15) is shown in Table 7, Page 20. Agreement to within 0.01 percent is indicated except at 220°C. where they differ by approximately 0.02 percent. Liu et al (18) estimated their crossover temperature at 220.77°C. Although this value agrees well with the value of Oliver et al (15), there is substantial disagreement with the values of Riesenfeld et al (19) and Miles et al (20). Liu et al (18) conclude that the data, above 100°C., of the latter two investigators was of lower precision and of more questionable accuracy.

Jones (21) employed a differential tensimeter to measure the difference in vapour pressure between heavy and ordinary water from approximately 3 to 115°C. The samples of heavy and ordinary water were isolated by capillaries of mercury connected to a differential mercury manometer. The complete system was immersed in a temperature controlled bath. An observation port was provided in the bath to permit reading of the manometer. Although the data of Jones was outside the temperature range of this current investigation, it was recorded in Table 8, page 21. The data of Liu et al (18) demonstrated close agreement with the data of Jones, in the small temperature

TABLE 6

SATURATED VAPOUR PRESSURE OF HEAVY WATER FROM 100 TO 300 DEG. C. (LIU ET AL (18))

Temperature Deg. C.	Pressure Bars	Temperature Deg. C.	Pressure Bars
106.00	1.1934	220.00	23.197
125.00	2.2424	221.00	23.650
136.33	3.1629	225.00	25.525
150.00	4.6566	250.00	39.993
175.00	8.8162	275.00	60.028
200.00	15.476	300.00	86.955

TABLE 7

COMPARISON OF THE VAPOUR PRESSURE DATA FOR HEAVY WATER OF LIU ET AL (18) AND OLIVER ET AL (15)

Temperature Deg. C.	Vapour Pressure Ratio P_{D_2O}/P_{H_2O}	
	Ref. (18)	Ref. (15)
220	.9998	.9996
221	1.0001	1.0000
225	1.0008	1.0008
250	1.0055	1.0055
275	1.0092	1.0093
300	1.0122	1.0123

TABLE 8

SATURATED VAPOUR PRESSURE OF HEAVY WATER FROM 3 TO 115 DEG. C. (JONES (21))

Temperature Deg. C.	Vapour Pressure Difference $P_{H_2O} - P_{D_2O}$, Bars	Temperature Deg. C.	Vapour Pressure Difference $P_{H_2O} - P_{D_2O}$, Bars
3.80	.001293	50.25	.01216
4.50	.001573	55.51	.01484
4.96	.001493	55.69	.01491
8.90	.002066	61.30	.01799
10.05	.002040	64.19	.01980
14.68	.002520	68.03	.02242
20.25	.003386	68.92	.02305
22.04	.003733	71.85	.02506
29.20	.005026	74.93	.02750
29.59	.005173	77.87	.02996
37.94	.007493	80.74	.03232
38.54	.007613	83.38	.03461
38.86	.007826	83.77	.03510
39.47	.007986	86.78	.03768
44.60	.009706	88.78	.03941
44.96	.009986	89.02	.03970
46.38	.01045	92.00	.04273
49.75	.01199	92.88	.04349

TABLE 8 (CONTINUED)

Temperature Deg. C.	Vapour Pressure Difference $P_{H_2O} - P_{D_2O}$, Bars	Temperature Deg. C.	Vapour Pressure Difference $P_{H_2O} - P_{D_2O}$, Bars
93.00	.04376	105.32	.05641
93.17	.04352	106.12	.05728
93.15	.04569	106.29	.05741
97.36	.04782	107.50	.05829
97.37	.04781	107.16	.05898
97.72	.04845	107.78	.05913
97.77	.04846	108.22	.06019
100.53	.05127	109.63	.06125
100.84	.05164	110.37	.06217
100.89	.05216	111.92	.06425
100.94	.05222	112.29	.06439
101.52	.05222	112.38	.06469
102.13	.05297	113.93	.06633
103.04	.05432	114.31	.06661

range where the two studies overlapped. The measurements by Lewis et al (22) (10 points from 20° to 110°C.), and Combs et al (23) (10 points from 10° to 55°C.) appeared to support the data of Jones.

Pupezin et al (24) measured the vapour pressure of heavy water relative to ordinary water. The two separate samples were maintained at the same temperature in a thermostatically controlled bath. The reference pressure was measured with a Texas Instrument Company quartz Bourdon gauge, and the isotopic differential pressure, to several parts in 10^4, with a Datametrics Division, CGS Corporation, capacitance type differential manometer. The temperature is determined by resistance thermometry. Pupezin et al claim improved precision as a result of the extreme care in preparing samples. For example, five to six repeated melt-freeze-pump cycles were deemed necessary to thoroughly degas the samples. Their investigation covered the range -64° to 100°C. Agreement within 1 percent existed with Jones (21) from 60 to 90°C., with Lewis et al (22) from 40 to 90°C. and with Miles et al (20) from 30 to 80°C.

Besley et al (25) measured the vapour pressure of heavy and ordinary water from 0 to 25°C. In their system the equilibrium vapour pressure of the sample is exerted on the base of a mercury column. The mercury manometer was constructed so that viewing occurred through plane glass surfaces, rather than the conventional optically imperfect cylindrical tubing. In the temperature range 0 to 25°C. they have found considerable scatter between the data of Miles et al (20), Combs et al (23), Jones (21), Pupezin et al (24) and their data. Agreement is much poorer than for ordinary water over the same temperature range. The studies of Bartholomé et al (26), Lewis et al (22) and Riesenfeld et al (19) were considered to be in poor agreement with the other studies.

The constant volume constant mass system developed during this study was somewhat influenced by the techniques used at the University of Western Ontario for calorimetric investigations (1). The calorimetric apparatus consisted of concentric spherical vessels. The calorimeter or innermost pressure vessel is machined from inconel, and contains electric heating elements attached to a silver heat diffusion system, which ensures uniform distribution of energy input. A thin walled copper shell (adiabatic shield), with attached heating element, surrounds the calorimeter. The outermost vessel is a heavy walled copper vacuum vessel with an integral heating element. By maintaining the adiabatic shield at the same temperature as the vacuum vessel, the radial heat loss from the calorimeter may be considered negligible. Hence, the energy input may be assumed to be absorbed by the water and the calorimeter only. Both the energy input, and the calorimeter temperature are measured very accurately. Similarities in constructional details, and thermometry techniques assisted in the development of the P-v-T system.

In the preceding discussion, of P-v-T systems, it was noted that some investigators chose a double walled vessel, to eliminate pressure deformations. The maximum operating temperature and pressure, in the current study, were 300 deg. C. and 85 bars, respectively. For these conditions, the thermal expansion and isothermal pressure deformation, of the spherical sample vessel (to be described later), resulted in a change in system volume of the order of 1.4 percent and 0.2 percent, respectively. At the maximum recommended operating pressure of 220 bars, the isothermal pressure deformation could have increased to approximately 0.4 percent. Kell et al (11), in their study of ordinary water at high pressures, corrected for the compression of the inner vessel, of their double vessel system. At pressures of 85 bars the change in volume due to compressibility was approximately 0.006 percent. No correction was applied for this small change in volume. A double walled spherical vessel was designed and employed in this study.

1-3. Literature Review of Related Theory or Correlations

The Steam Table by Vukalovitch (27) for ordinary water contains a section for superheated vapour, developed from an equation of state based on the theory of association. The concept of association, as applied to imperfect gases, refers to the combination of single gas molecules into groups or complexes of two, three, four or more molecules. These complexes may be treated as perfect gases or as in this case Van der Waal's gases.

$$(P + a/V^2)(V-b) = RT \left\{1 - \frac{A_1(T)}{V-b} - \frac{A_2(T)}{(V-b)^2}\right\} \tag{1.12}$$

$$\text{where } A_1(T) = \frac{C_1Ne^{T_cT^{-1}}}{T^w} \tag{1.13}$$

$$A_2(T) = \frac{C_2N^2e^{2T_cT^{-1}}}{T^x} - \frac{4C_1^2N^2e^{2T_cT^{-1}}}{T^y} \tag{1.14}$$

$$a = \frac{27}{8} RT_cb \tag{1.15}$$

$$b = \frac{RT_c}{8P_c} \tag{1.16}$$

$$w = (3 + 2m_1)/2 \tag{1.17}$$

$$x = (6 + 3m_2)/2 \tag{1.18}$$

$$y = (6 + 4m_1)/2 \tag{1.19}$$

R - gas constant

V - any volume containing N particles

m - 1, 2, 3 depending on the type of molecule

C_1, C_2, - calculated from the critical point information or from available P-v-T data.

The quantity m is chosen equal to 0 for monatomic gases, 1 for diatomic gases, 3 for gases with highly symmetrical molecules, and 2 for all other gases.

Vukalovitch applied equation 1.12 to available data for imperfect gases, air oxygen, nitrogen and carbon monoxide, with resulting agreement of the order of 1 to 2 percent, except near the critical point regions. Since both superheated heavy, and light water vapour are considered similar imperfect gases, it would seem reasonable to attempt to employ equation 1.12 to describe superheated heavy water vapour, in a manner similar to the method employed by Vukalovitch for light water.

Another possible method, of obtaining the P-v-T properties of superheated heavy water, involves invoking the principle of thermodynamic similarity, in the form of the theorem of corresponding states. Whalley (28) discussed the great similarity, in molecular structure, between heavy water and ordinary water. This close similarity indicates that the theorem of corresponding states may be applied.

If the properties are quoted as fractions of their critical values, i.e. as $\beta = P/P_C$, $\tau = T/T_C$, and $\phi = v/v_C$ β, τ, and ϕ are referred to as reduced properties. Any two gases at the same reduced pressure and reduced temperature have the same reduced volume. This statement is known as the theorem of corresponding states. It may also be expressed as a functional relation.

$$\phi = f(\beta, \tau) \text{ - - - - - - - - - - - - - } (1.20)$$

A quantity termed the compressibility factor $Z = \frac{Pv}{RT}$ may be evaluated at the critical point to determine the critical compressibility factor. The compressibility factor indicates how far a gas deviates for a perfect gas.

Calculations of the critical compressibility factors, by Juza et al (29) indicate that the compressibility factors for ordinary and heavy water differ by only 0.058 percent. The compressibility factors for ordinary water and heavy water were tabulated as 0.241494 (T_C = 374.15°C, P_C = 221.29 bars, v_C = 3.26 cm^3/g) and 0.241635 (T_C = 371.50°C, P_C = 218.83 bars, v_C = 2.955 cm /g), respectively. If equation 1.20 is evaluated for ordinary water, it is assumed that, the equivalent equation for heavy water will be similar. Kesselman (30) compared P-v-T data for superheated heavy water vapour, derived by the theorem of corresponding states, to the experimental P-v-T data for superheated heavy water of Kirillin et al (31), and obtained agreement to 0.2 percent. The following critical values were employed by Kesselman for heavy water:

P_C = 218.31 bars; T_C = 371.5°C; v = 2.955 cm^3/g.

Based on the study of Kesselman for heavy water, and employing available experimental data, Kirillin (32) constructed a steam table for heavy water. Since the experimental data of Kirillin et al (4) have an estimated accuracy of 0.3 percent the data for superheated heavy water contained in the table (31) will be less accurate than the equivalent experimental data for light water employed, in the development of the internationally accepted steam tables for light water.

The theorem of corresponding states is useful in evaluating the P-v-T properties of superheated heavy water vapour, however to possibly establish tables to the accuracy of light water tables, more experiment data are necessary. For example, more experimental data at the critical point, and in the superheated vapour region are required to establish that an equation of state, independent of previous studies of light water, is not necessary to obtain the accuracy of data presently available for light water. As an example, Rivkin et al (32), in 1963, evaluated the critical specific volume of heavy water, at the critical point and differed by approximately 7 percent with the earlier value of Eck (33).

Recently, Trakhtengerts (6) developed an equation of state for superheated heavy water employing the theorem of corresponding states, the experimental data of references (4, 5), the new critical point data of reference

(32), and the virial equation of state for ordinary water of Vukalovitch et al (34) in reduced form. Initially the constants in the Vukalovitch equation for ordinary water were left unaltered. On the average, deviations amounted to 0.4 percent. The critical parameters (32) employed were:

$v_C = 2.956$ cm³/g, $T_C = 370.9$°C. and $P_C = 217.23$ bars.

To establish agreement with experimental data, the coefficients were adjusted by a temperature dependent factor. In addition, the critical specific volume was arbitrarily set at 2.92 cm³/g. The resulting average deviation from experimental data (4) was of the order of 0.2 percent. Precise experimental P-v-T data for superheated heavy water would be useful for further possible application of the theorem of corresponding states, or for the development of an equation of state independent of existing light water data.

An equation of state for superheated heavy water was expressed in virial form by Whalley et al (13).

$$PV/RT = 1 + B/V + C/V^2 + \cdots \qquad (1.21)$$

Since the second and third virial coefficients are functions of temperature, they presented expressions $B = f_1(T)$ and $C = f_2(T)$ in their study (12) of superheated ordinary water. Values (13) of virial coefficients for superheated heavy water were determined in the range 150 to 500 deg. C. The coefficients were tabulated and the difference between B_{D_2O}

and B_{H_2O} determined. Vodar et al (35) compared the virial equation of state, with the coefficients of Kell et al (13), to the experimental data of Rivkin et al (36). Agreement existed to within an accuracy of 0.1 percent.

Table 9, page 32, displays the critical parameters of heavy water (40) evaluated by classical analysis. Stanley (41) described the emergence of a new description of the critical region as embodied in the twin phrases "static scaling laws" and "dynamic scaling laws". The "classical" (e.g. Van der Waals) thermodynamic theories were shown to be in disagreement with experimental evidence. Fisher (42) demonstrated the disagreement of the classical theories with both experimental and theoretical values, in his statistical mechanics treatment of the critical phenomena. Stanley (41) stated that we still know neither whether the scaling laws are fully supported experimentally nor, if they are ultimately justified theoretically. Kell (40) tabulated the critical parameters of ordinary water, including the scaling law values of Sengers (43). The critical parameters were: $T_C = 374.35°C$; $v_C = 3.08 \text{ cm}^3/g$; P_C -. A later paper by Sengers et al (44) evaluated the critical temperature as 373.9 deg. C., however the critical specific volume remained unchanged.

The rapid change in the area of critical point phenomena was evident, from the fact that, one hundred and seventy five of Stanley's references were published in the five years

TABLE 9

CRITICAL PARAMETERS OF HEAVY WATER

BY CLASSICAL ANALYSIS (40)

	T_C	P_C	V_C
	°C, IPTS-48	bars	cm^3/g
Riesenfeld et al (37)	371.5	221.2	3.07 (E)
Eck (33)	371.5	217.2	2.77 (E)
Oliver et al (15)	370.9	218.6	-
Whalley (28)	371.1	218.8	3.05 (C)
Elliot (38)	371.1	221.36	2.96 (C)
Blank (39)	370.66	216.59	- (E)

(E) Experimental

(C) Correlator

prior to 1971.

The present study has not dealt with assessment of critical point data but has arbitrarily employed the critical point data of Whalley (28). A classical approach to the critical point was adopted in this study.

For saturated heavy water a pressure-temperature relationship may be developed in the form of a Chebyshev polynomial. Gibson et al (45) succeeded in fitting this type of polynomial to the pressure and temperature values for saturated ordinary water given in the 1963 International Skeleton Tables, to within approximately one tenth of the specified tolerance of these tables. The equation was of the following form:

$$\ln \beta = \sum_{r=o}^{11} a_r T_r(x) \quad \text{- - - - - - - - - - - - -} \quad (1.22)$$

$$x = \{2(\tfrac{1}{\theta} - 0.95)^{0.4} - A\}/_B \quad \text{- - - - - - - -} \quad (1.23)$$

a_o - a_{11}, A and B evaluated to fit the available data.

T - temperature, (°C + 273.15)

β - reduced pressure

θ - reduced temperature

Ambrose et al (46) also employed an eleventh-order Chebyshev polynomial to define the vapour pressure of ordinary water. They presented a detailed account of the goodness of fit with the latest available vapour pressure data. The maximum deviation from the fitted data was approximately 0.01 percent. The equation for vapour pressure in KPa was expressed as follows:-

$$T \log_{10}P = a_0/2 + \sum_{r=1}^{11} a_r E_r(y) \qquad (1.24)$$

$$y = \{2T - (T\,max + T\,min)\}/(Tmax - T\,min) \qquad (1.25)$$

a_0----a_{11} are evaluated to fit the available data. T max and T min are two temperatures respectively just above and just below the range of measured values. Temperatures were expressed in degrees Kelvin (IPTS-68).

CHAPTER 2

APPARATUS

2-1. General Description

To provide an apparatus for the experimental determination of the P-v-T properties of heavy water for pressures up to the critical values, a system of the constant volume-constant mass type was developed by the author. The inherent simplicity and great accuracy potential of the constant volume-constant mass system was described by Ellington et al (14), in his review of P-v-T measurement techniques.

For this system the author selected spherical geometry to minimize surface area and to provide a symetrical temperature distribution. Hence radial heat transfer losses are minimal and essentially uniform. A double walled vessel, consisting of two component vessels, namely, the sample and pressure vessel, contains a constant mass of fluid. Temperature was determined with a platinum resistance thermometer. Pressures were balanced across a diaphragm and measured with a deadweight gauge. Changes in volume were estimated from temperature measurements and the coefficient of thermal expansion. Figure 1, page 37, displays schematically the essential components.

FIGURE 1 P-V-T APPARATUS

Item	Description
1	Sample Vessel
2	Pressure Vessel
3	Thermowell
4	Isothermal Enclosure
5	Diatomaceous earth
6	Enclosure
7	Supports
8	Unions
9	Thermocouple junction
10	Evacuated space
11	Capillary tubing to Sample Vessel
12	Capillary tubing to space between Items 1 and 2
13	Vacuum-support tubing
14	Junction Box
15	Resistance Thermometer
16	Bolted Joint
17	Welded Joint

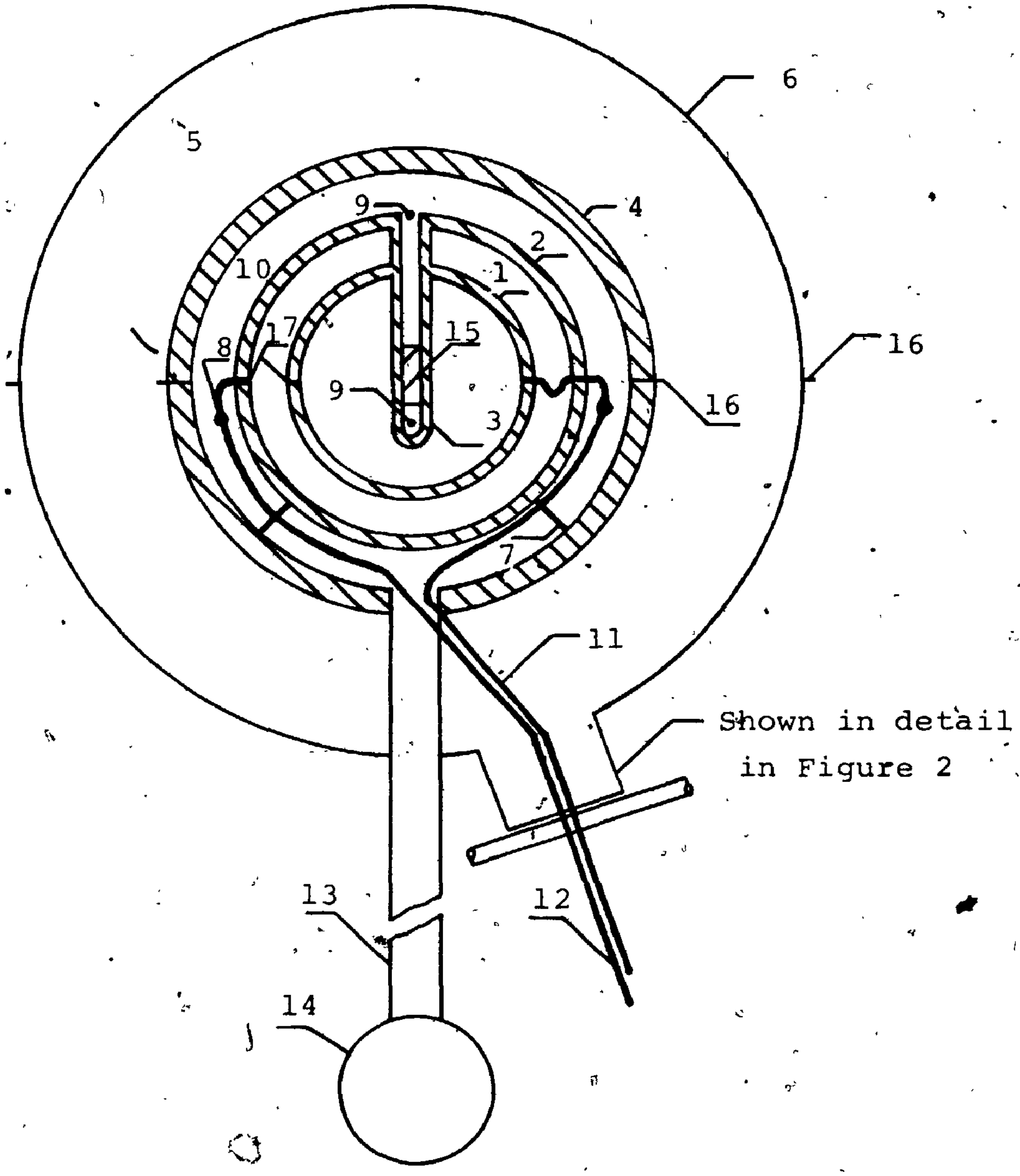


FIGURE 1 P-V-T APPARATUS

The sample vessel has an inside diameter of five (± 0.004) inches and a wall thickness of a quarter of an inch $(^{+\,0.004}_{-\,0.000})$. The pressure vessel and the sample vessel were machined as hemispheres from type 304 stainless steel and welded by the "TIG" method. A thermowell supports the sample vessel from the pressure vessel and extends beyond the centre, placing the contained capsule platinum resistance thermometer at the centre of the system. This arrangement permits the sample vessel to expand or contract with temperature change. The resulting space between the two spheres is 0.75 inches.

A copper sphere (Isothermal Enclosure) with a ten inch inside diameter and a half inch wall thickness encompasses and supports the pressure vessel. A spherical spun aluminum vessel encloses a five inch thick concentric layer of diatomaceous earth insulation around the isothermal enclosure.

Resistance wire, cemented in concentric grooves, on the outer surfaces of both the pressure vessel and the isothermal enclosure, supplies heat to elevate or maintain system temperature. Differential thermocouples were located on the inner surface of the thermowell at the top and bottom extremities. Other locations include the outer surface of the pressure vessel, the inner surface of the isothermal enclosure, between these surfaces and on either side of the small guard heaters, on filler tubes, and on vacuum-support tubing. From these readings, the extent of radial and circumferential temperature gradients could be ascertained. Differential thermocouples straddling heaters provided an emf output which may be minimized by careful control of the voltage supply to these heaters.

Fluid access to the sample vessel-pressure vessel assembly is provided at the equator, by 0.125 inch outer diameter type 304 stainless steel capillary tubing with 0.20 inch bore. This arrangement, as shown in Figure 1, page 37, with unions on each tubing, permits easy installation or removal of the sample vessel-pressure vessel assembly. The tubing from the sample vessel, and the tubing from the cavity between the sample vessel and pressure vessel pass through a vacuum-support tubing just beneath the isothermal enclosure. To minimize the mass of fluid in these tubes, they are heated to maintain vapour conditions. Outside the spun aluminum sphere a small heat exchanger ensures that condensation will take place in a controlled region. A junction box on the lower end of the vacuum-support tube permits wiring for heaters, thermocouples, and the resistance thermometer to pass through vacuum seals.

A mass of heavy water was degassed and weighed prior to charging into the evacuated sample vessel. The charging process employed the vapour pressure of the sample fluid under boiling conditions. Similarly an equivalent mass, compensating for the relative volumes, was charged into the space between the sample and pressure vessels. Consequently, the two cavities contained samples of the same specific volume, which resulted in approximately the same pressure at the same temperature. This situation existed at steady state conditions and was approximated during extremely low heating rates.

When steady state conditions existed at the desired temperature level, the vapour pressure in the sample vessel was balanced by an equal pressure applied at the diaphragm. This pressure was determined from the deadweight gauge and combined with the barometric pressure to provide an absolute pressure reading.

The capsule platinum resistance thermometer connected in a Mueller type resistance bridge circuit provided a reading of system temperature. The output of the differential thermocouples was measured with a microvolt meter. Figures 2 to 9, Appendix A, show the overall system and related equipment.

2-2. Design and Development

(A) Sample Vessel

Of prime concern in selecting the metal for vessel fabrication was its anticorrosive and thermal expansion properties. Initially, nickel was viewed favourably, however, the thermal expansion coefficient as measured by Nix et al (47) displays an unusual peak in the temperature range of this study. Platinum seemed to be the ideal choice with exceptional anticorrosive properties and well defined thermal expansion coefficient, Nix et al (48). However, available funding did not permit investment in this rather expensive material. Type 304 stainless steel was the final choice. Measurements of the coefficient of thermal expansion for type 304 stainless steel are available from the literature (49, 7). Since the material is an alloy, to obtain the maximum potential accuracy of the system, the thermal expansion of the actual material should be measured. Dr. Kirby (50), at the National Research Council, was developing a system to determine with great accuracy the thermal expansion of metals used in gas thermometry. He expressed interest in measuring the properties of type 304 stainless steel and was sent samples machined to his specification near the end of 1969. The measurements are still pending as a result of developmental problems. The linear expansion coefficient was to be defined to 0.01 percent from room temperature to the critical point temperature.

For safety sake, the sample vessel was designed to withstand 220 bars at 371°C. in the event of loss of pressure in the pressure vessel. The formulae of Roark (51), for stress in a thin walled vessel, were applied with the details shown in Appendix B.

Considerable time and effort was spent attempting to find a welder with the skill and experience required for this fabrication. Sample pieces were welded by four local welding concerns, and in each case, sectioning displayed visible imperfections. The selection of welding rod material and preliminary weldment design was facilitated by references (52) and (53). The vessel is shown in Figure 10, Appendix A.

(B) Pressure Vessel

In an attempt to reduce expenditures, the pressure vessel was to be fabricated from type 304 stainless steel hemisphere castings. The castings were to satisfy close dimensional tolerance. To assure quality X-Rays accompanied by radiographic report were required. After a first effort and a great loss of time, the hemispheres were machined from round bar at the University of Western

Ontario. The vessel was designed to withstand 220 bars at 371°C. Design calculations may be found in Appendix B.

The pressure vessel was welded to the sample vessel at the thermowell. A stabilized 18-8 alloy (ER347) filler rod was used, while an inert atmosphere (Argon) existed inside the vessels. It was found necessary to rotate the hemispheres during welding at a very slow even speed. Prior to making the first circumferential weld pass, the hemispheres were tacked to preserve the desired root spacing. With all precautions, it was difficult to preserve uniform root spacing and penetration as the weld pass progressed. The filler tubing, from the sample vessel to the pressure vessel, was bent into a flexible u shape and constructed from .0625 inch outer diameter by .020 inch wall thickness stainless steel tubing. Capillary tubing was welded to the pressure vessel to complete the filler tube access to both the sample vessel and the space between the two vessels. The sample vessel and the completed assembly were hydraulically pressurized to 275 bars at room temperature.

Concentric grooves were cut in the surface of the vessel at one half inch intervals. Fiberglass coated nichrome heating wire of approximately 5.5 ohm per foot electrical resistance was cemented in the grooves with Thermostix* cement. Constructional details are shown in Figures 11 to 15, Appendix A.

(C) Isothermal Enclosure

This vessel is similar to the type used in calorimetric studies at the University of Western Ontario. Great difficulty was experienced in securing non porous copper castings for their system. To alleviate this problem the hemispheres were spun from half inch plate. This proved unsatisfactory. The resulting shapes fell somewhere between conical and hemispherical. Wall thickness variation was severe from less than three eights of an inch to five eights of an inch. Surface defects lead to doubt concerning the vacuum holding capabilities of a spun vessel. Eventually, hydroformed hemispheres of C.D.A.110 copper of excellent quality were obtained from Van Bussel Metalcraft, Detriot, Michigan.

The two mating surfaces of the hemispheres were machined very accurately to provide sealing surfaces for a metal V-seal. Compact contoured clamping brackets were bolted to the outside of the hemispheres to preload the seal and permit evacuation to a pressure of less than 6×10^{-5} bars. Heating wire of approximately 1.1 ohm per foot was

*Thermostix, Adhesive Products Corporation, Bronx, New York.

installed on the surface of the vessel, in a manner similar to the method described for the pressure vessel. Grooves were however placed at one quarter inch intervals. The isothermal enclosure is supported by a .840 in. outer diameter by .710 in. inner diameter stainless steel tubing (vacuum-support tube). Silver soldered to the top end of the tube was a stainless steel hex with threaded projection and machined shoulder. A hole was drilled in the bottom of the enclosure and threaded for the hex fitting. A vacuum seal was created, as the machined shoulder of the hex pressed against a concentric knife edge machined on the enclosure, during the tightening process. The isothermal enclosure is shown in Figures 2 and 16, Appendix A.

(D) Thermometry

At the geometric centre of the concentric vessels and at the heart of the temperature measurement system was a capsule platinum resistance thermometer. The thermometer was installed at the bottom of the thermowell and packed with magnesium oxide powder, to ensure that thermal contact existed. Pure platinum leads were spotwelded to the thermometer and extended for two and a half feet. Connections to pure copper leads were made in the vacuum support tubing.

Thirty four thermocouple junctions were formed from premium grade 30 gauge iron and constantan wire by spotwelding in an argon gas atmosphere. Each junction was placed between two mica strips and the whole assembly crimped inside a silver tab. The tabs ranged in size from $\frac{1}{4}$ in. to $\frac{3}{8}$in wide by $\frac{1}{2}$ in. long. The narrower tabs were installed where space limitations existed (e.g. between the concentric grooves on the pressure vessel surface). Threaded rod (3/64 in. diameter) was spot welded to the pressure vessel surface and the inner surface of the copper vessel was drilled and tapped for 3/64 in. diameter screws. In this manner the tabs were affixed to the vessel surfaces. Although the tabs were contoured to match the surface curvature, Thermostix cement was placed around the tab perimeter. For the differential thermocouples the constantan wire was employed between the two junctions. All thermocouple, thermometer and power leads were fiberglass insulated.

Two absolute thermocouples were installed one on the surface of the pressure vessel in close proximity to the thermowell and the other on the inner surface of the bottom hemisphere of the isothermal enclosure. To indicate the extent of radial temperature variation in the sample-pressure vessel assembly, a differential thermocouple was placed in the thermowell. One tab was bound to the resistance thermometer with thermocouple wire and the other tab was placed in packed magnesium oxide near the top of the thermowell. Other differential thermocouples were located as indicated in Table 10, Page 48, and Figures 16 to 19, Appendix A. All the thermometer, thermocouple, and power leads extend down the vacuum-support tube and exit through vacuum (Conax) seals at the junction box. The brass junction box, Figure 20, Appendix A, is soldered to the lower end of the vacuum support tube. Vacuum pump connections are made at the junction box for evacuation of the space between the pressure vessel and the isothermal enclosure.

TABLE 3

LOCATION OF DIFFERENTIAL THERMOCOUPLES

Pressure Vessel (Outer Surface)

Designation

c* - between the vicinity of the thermowell at the top of the vessel and the equator of the sphere adjacent to the capillary tube from the sample vessel.

d - between the area immediately adjacent to the capillary tube from the pressure vessel and the bottom of the pressure vessel.

e - between two points spanning one third of the circumference at the equator.

Isothermal Enclosure (Inner Surface)

g - from the equator to the bottom of the vessel.
l - from the equator to half way up the opposite side but at 90° with respect to the differential thermocouple g.

i - between two points spanning one third of the circumference at the equator.

*Other differential thermocouples are located in the thermowell, across the hex fitting and on the capillary tubing at the heat exchanger.

TABLE 3 (CONTINUED)

LOCATION OF DIFFERENTIAL THERMOCOUPLES

Pressure Vessel - Isothermal Enclosure

h and j - from the outer surface of the pressure vessel to the inner surface of the isothermal enclosure at the equator.

Capillary Tubing

f - on the tubing from the sample vessel between the pressure vessel and the hex fitting on the vacuum support tubing.

(E) Pressure System

The pressure system is shown in Figure 21, Page 51. The two filler tubes exit together from the isothermal enclosure through a projection in the hex fitting. Union connections are made in each capillary tube, inside the isothermal enclosure near the mid height or parting line of the enclosure. To minimize heat loss along the vacuum support tube, the hex and tube projection are wound with a heating element. Heating wire was wound around the capillary tubes, in three separate circuits, outside the isothermal enclosure. A cylindrical container filled with diatomaceous earth insulation was fastened to the outside of the spun aluminum vessel. The two capillary tubes were silver soldered together and passed through the centre of the container. (Figure 24, Page 53.)

A $\frac{1}{2}$ in. inner diameter stainless steel tube heat exchanger was soldered, at right angles to the capillary tubes, adjacent to the end of the cylindrical container. By adjusting the energy input to the heaters and the water flow rate in the heat exchanger, the position of the vapour to liquid meniscus was localized within a controlled region. The determination of the location of the meniscus is described in detail in Chapter 5.

To assist in measuring the pressure in the sample vessel without altering the volume or contaminating the test fluid, a differential pressure transducer was selected. In

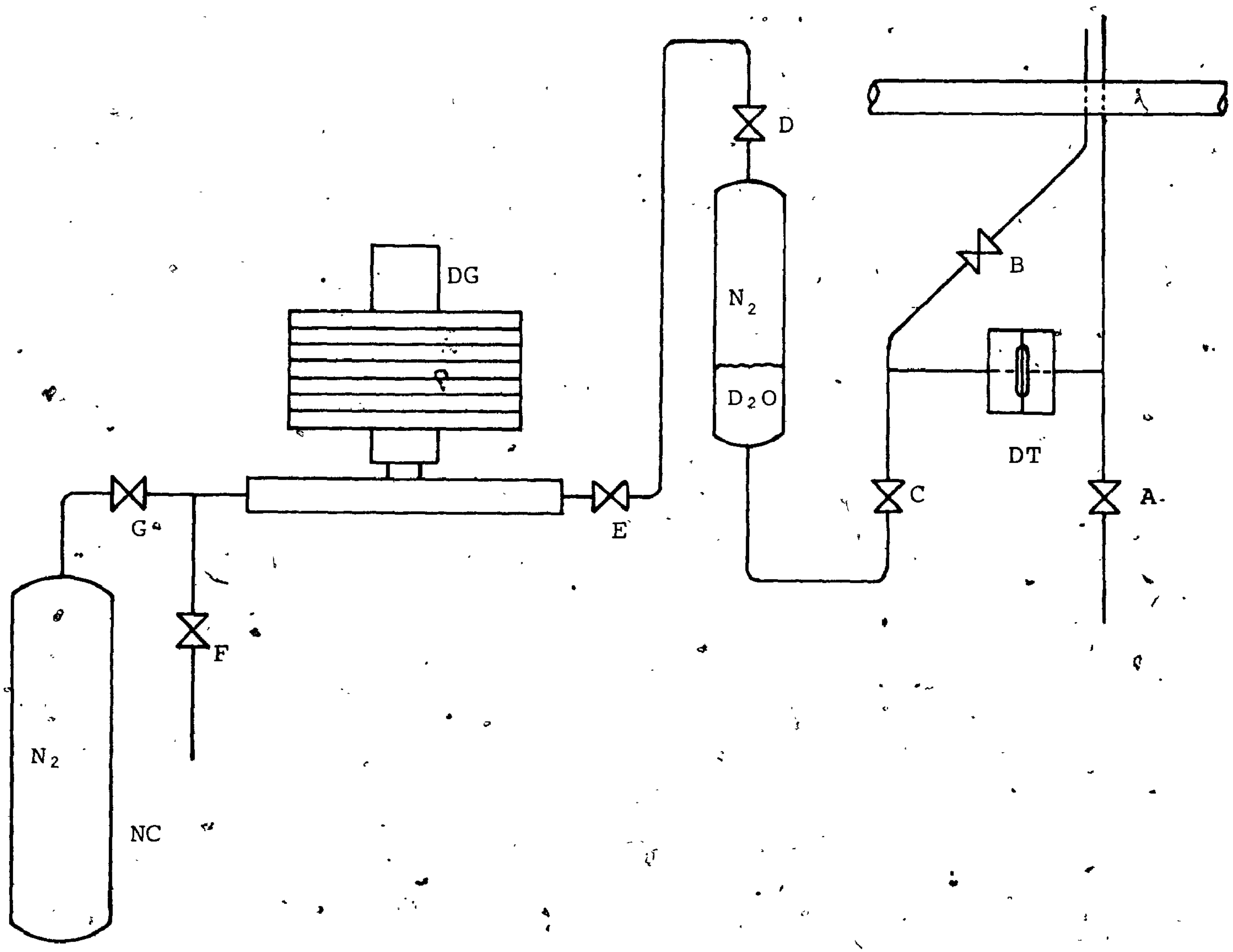


FIGURE 21 PRESSURE MEASUREMENT CIRCUIT

FIGURE 2a VAPOUR LIQUID HEAT EXCHANGER

Item	Description
A	Filler tube to sample vessel
B	Filler tube to space between the sample vessel and the pressure vessel.
C	Heater
D	Differential Thermocouple
E	Enclosure
F	Cylindrical enclosure projecting from and attached to Item E.
G	Tubing to direct coolant over Items A and B
H	Silver solder
I	Vacuum-support tubing
J	Diatomaceous earth
K	Thermocouple

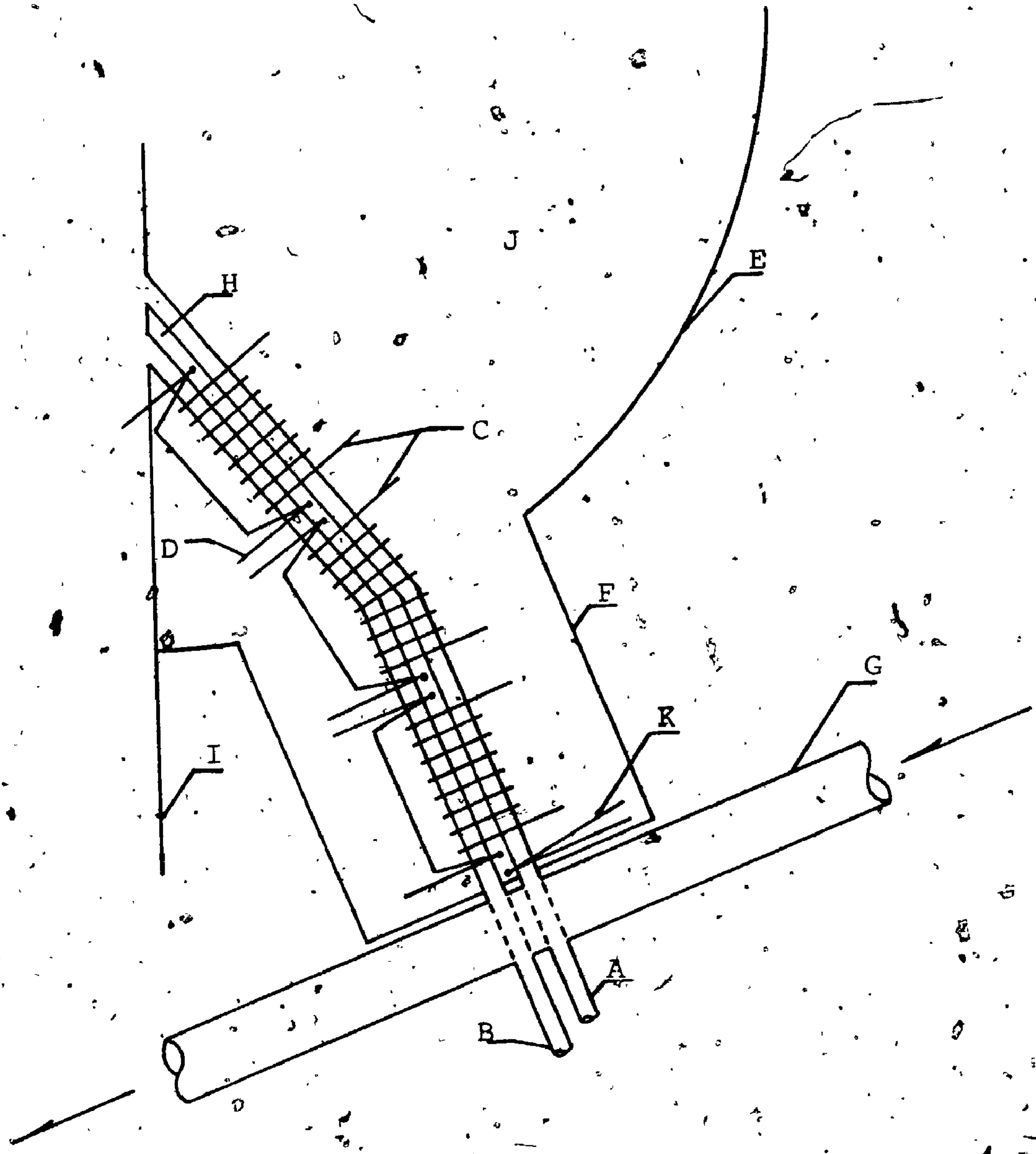


FIGURE 2.4 VAPOUR-LIQUID HEAT EXCHANGER

principle, all that is required to obtain a pressure reading is a high pressure gas, a deadweight gauge, a pressure transducer indicator and a barometer. This would permit a balancing pressure to be exerted across the 100 p.s.i. (6.89 bars) range diaphragm of the transducer, (maximum rated line pressure 345 bars) and this pressure determined at the deadweight gauge. However, the system is complicated by the fact that the capillary tubes are used for filling and discharging. During the greater part of the test, the pressure exerted by the fluid in the space between the sample and pressure vessel acts on the diaphragm, and the deadweight gauge system is shut off. The piston-cylinder assembly of the deadweight gauge operates in an oil bath, which is contained by a rubber membrane. If the pressure is altered rapidly the membrane will tear, and oil contaminates the gas regulator or the fluid sample surrounding the sample vessel. The water-nitrogen interface in the sample cylinder should be maintained close to the same height as the vapour liquid meniscus in the heat exchanger. The above mentioned constraints unfortunately add considerable complexity to the pressure system.

The capillary tube, from the sample vessel below the heat exchanger, extends directly to the tee with one side to the pressure transducer and the other to an angle pattern needle valve*. The transducer port and the tee are modified so that a .020 in. diameter bore extends to the transducer diaphragm cavity. The tee was fabricated from capillary tubing and welded, so that a .020 in. diameter bore existed in the tee, except on the end which entered the needle valve. Both the tee and the valve were modified, to permit the needle beyond its seat to extend into the capillary tube and minimize the entrapped volume on the capillary side of the valve seat. The needle valve was necessary for filling and discharging purposes.

The capillary tube from the space between the sample vessel and the pressure vessel, below the heat exchanger, is similar, except a globe pattern needle valve is placed between the heat exchanger and the tee. The angle pattern needle valve on the tee is necessary for filling and discharging, but also, for connection to the deadweight gauge pressure equalization system.

Rapid deterioration of needle valves in the system and on the deadweight gauge was experienced. This difficulty may be easily overcome by replacing the existing valves with similar valves now available with non rotating valve stems.

*All needle valves were Hoke Milli-mite forged needle valves of 316 stainless steel with 1° stems.

CHAPTER 3

INSTRUMENTATION

3-1. Temperature Measurement

A Mueller resistance bridge, a capsule platinum resistance thermometer, a spotlight galvanometer, two decade resistors, and a storage battery were incorporated to obtain the resistance of the thermometer during test conditions (Figure 25, Page 57,and 26 (Appendix A)). The decade resistor was adjusted, at different temperature levels, to insure that a current of approximately 2 milliamperes flowed through the resistance thermometer. Although the Mueller bridge was capable of measuring resistance changes of the order of 0.0001 ohms, it was not provided with a constant temperature enclosure. Since the windings are constructed of manganin wire, a suitable temperature correction (54) at temperature °C, with respect to 25°C. may be applied as follows:

$$R_T = R_{25^\circ} \{1 + .00001\,(T-25) - .0000004\,(T-25)^2\} \text{----}(3.1)$$

When an actual reading is made the approximate temperature is shown hence the resistance may be estimated. A current of 2 milliamperes was adjusted to flow through the resistance thermometer. The decade resistor, connected across the galvanometer, protected the galvanometer movement, by reducing the sensitivity during initial bridge adjustments.

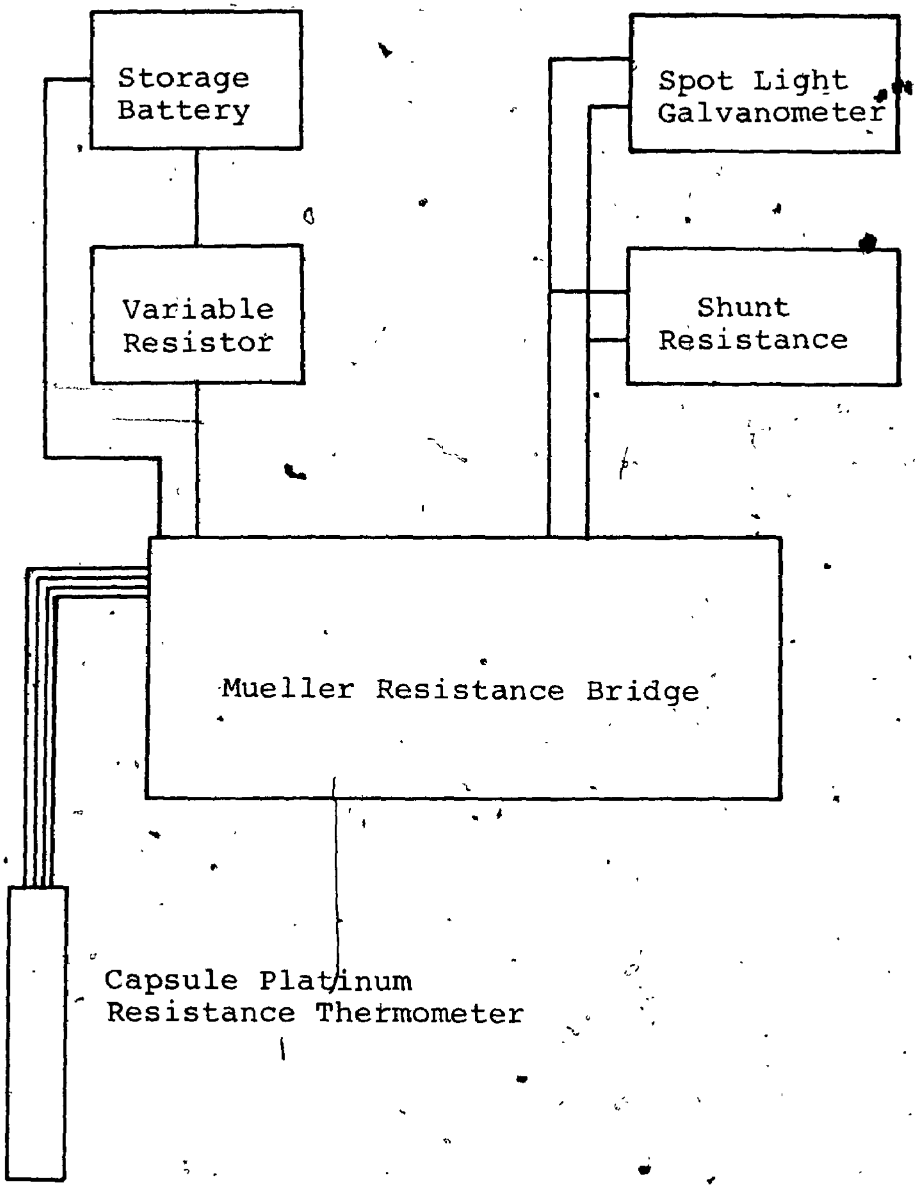


FIGURE 25 TEMPERATURE MEASUREMENT CIRCUIT
- RESISTANCE THERMOMETER

The bridge was adjusted until a balanced condition existed, as indicated by the null position on the galvanometer. To eliminate the effect of inequality in lead resistance, another reading was obtained with the commutator reversed. The two values for resistance R(T) were averaged and temperature T°C. determined from the following expression:

$$R(T) = R_O \{1 + \alpha[T^1 - \delta(T^1/100)(T^1/100 -1)]\} \text{ - - - } (3.2)$$

$$T^1 = T - .045\ (T/100)(T/100 -1)(T/419.58 -1)\ (T/630.74 -1). \text{ - - - - - - - - - - - } (3.3)$$

The absolute thermocouples measure temperature with reference to a constant temperature oil bath, maintained at approximately 200°C. (195.9225°C. ± .0038). Their output is determined with the aid of a potentiometer - galvanometer system, as shown in Figure 27 and 28, Appendix A. The emf. generated by the latter was measured directly with a microvoltmeter (Figure 29, (Page 59) and 30, (Appendix A)). At room temperature the differential thermocouples on the spherical vessels produced emfs. of .8 microvolts or less.

Absolute thermocouple readings were determined by balancing the thermocouple output with the output from the potentiometer. An emf. balance was indicated by a null position at the galvanometer. The emf. determined was relative to the temperature level of the constant temperature oil bath.

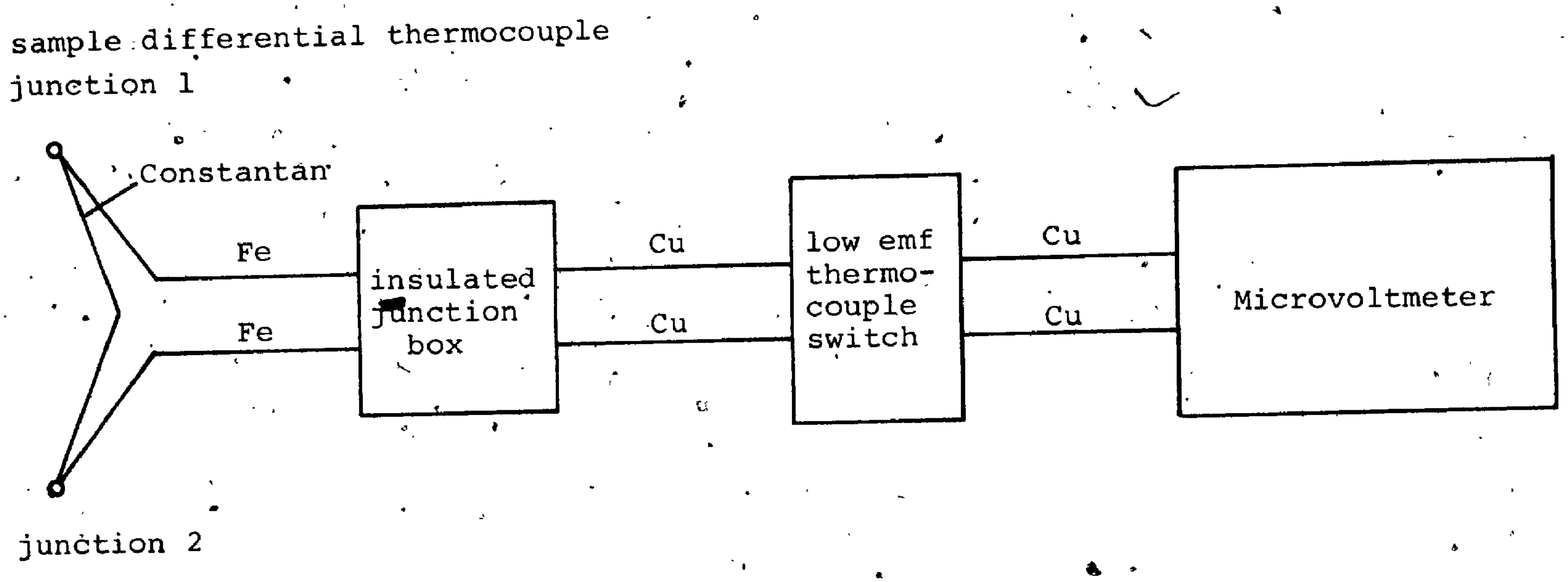


FIGURE 29 TEMPERATURE MEASUREMENT CIRCUIT - DIFFERENTIAL THERMOCOUPLE

3-2. Pressure Measurement

Pressure inside the sample vessel must be accurately determined, without upsetting steady state conditions, nor substantially increasing the liquid entrapped in the filler tubing. The pressure balance system of Figure 21, Page 51, approximated these requirements. During heat addition or removal from the system, valves A and C would be closed, while valve B remains open. When the desired temperature level is approached, valve B would be closed and valve C opened, to permit the pressure preset in the nitrogen cylinder-deadweight gauge system, to be imposed on the left hand side of the diaphragm type differential pressure transducer. With practice the pressure on the left side can be adjusted to equal the sample vessel pressure, without experiencing pressure differences of greater than 10 p.s.i. (.689 bars) across the 100 p.s.i. (6.89 bars) range diaphragm. Valves G and F permit increasing the pressure from the high pressure cylinder of nitrogen or decreasing the pressure, by bleeding nitrogen to the atmosphere. Valves D and E impose time lags in transmitting pressure changes to and from the pressure transducer. For further time delay and control, an additional needle valve H was placed between the sample vessel and valve C. To reduce the possibility of oil contamination from the deadweight gauge, a check valve was placed between the deadweight gauge and valve G, and an oil trap inserted between valves E and D.

When the correct balancing pressure is applied at the diaphragm, the transducer indicator will display a reading in agreement with the calibrated value for that pressure level. The deadweight gauge is loaded to the calibration reference height, as shown by the pointer in Figure 23, Appendix A. The weights applied together with the area of the piston give a nominal value for pressure. Corrections for local gravity, air buoyancy, and hydraulic head are applied to this value as suggested by the manufacturer* and described by Cross (55). The corrected value for pressure was added to the barometric pressure reading, obtained from a mercurial barometer.

The expression for pressure (bars) was applied as follows:- ------ (3.4)

$$P/.0689476 = (G_L/980.217)\, P_n(1 - .0012/8.4) + .1705 \pm pc + P_b$$

where: G_L is the local acceleration due to gravity (cm/sec^2);

980.217 cm/sec^2 is the acceleration due to gravity at the location where calibration occurred;

P_n is the nominal pressure (psi) determined by dividing the nominal value of the weights by the effective area of the piston;

---

*Mansfield and Green, Solon, Ohio.

$.0012\ \mathrm{gms/cm^3}$	is the density of air;
$8.4\ \mathrm{gms/cm^3}$	is the density of brass;
.1705 psi	is the hydraulic head correction due to the height of oil in the isolating membrane of the dead weight gauge;
pc	is the pressure correction (psi) due to the difference in height between the capillary meniscus and the nitrogen-water interface in the sample cylinder;
P_b	is the barometric pressure (psi);

The local acceleration due to gravity ($G_L = 980.359\ \mathrm{cm/sec^2}$) was calculated from:- - - - - (3.5)

$$G_L = 980.616 - 2.5862 \cos 2D + .0058 \cos^2 2D - .000094d$$

where: D is the latitude in degrees;

d is the altitude with respect to sea level in feet.

The deadweight gauge was calibrated by the manufacturer through intercomparison with an N.B.S. calibrated deadweight gauge. When the forementioned corrections are applied an accuracy of 0.03 percent or better will result.

3-3. Mass Measurement

A precise Mettler analytical balance, with a maximum capacity of 1000 grams and an accuracy of approximately 0.0001 grams, was used to determine the weight of water samples and containers. It was difficult to obtain a mass measurement of container plus sample to an accuracy of much greater than 0.001 grams. Since the flask plus fittings protrude beyond the balance enclosure, the sliding doors on the balance must be left open, resulting in slight continuous motion of the weighing pan.

Water samples studied in this research had a mass of approximately 50 grams. Figure 31, Page 64, shows the charging and discharging system employed. The balance is displayed in Figure 32, Appendix A.

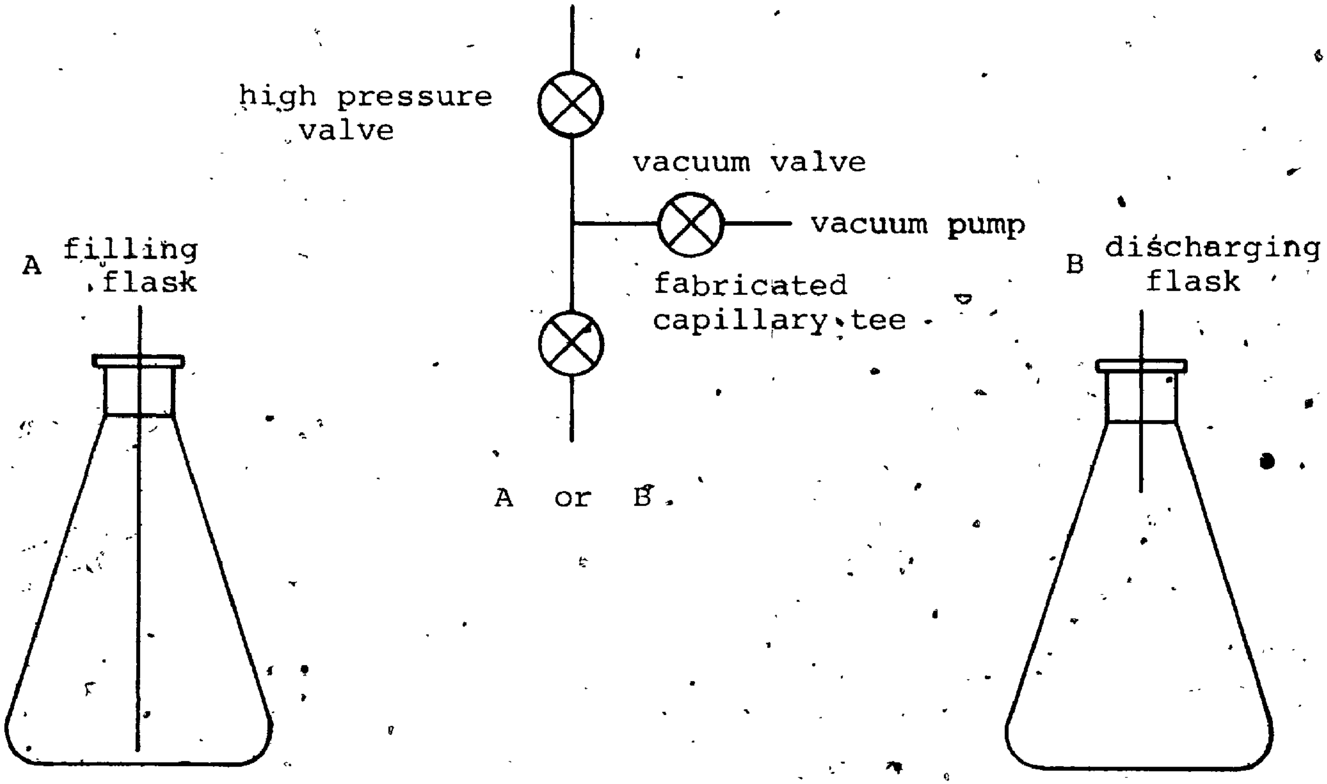


FIGURE 31 CHARGING AND DISCHARGING SYSTEM

CHAPTER 4

CALIBRATION

4-1. Resistance Thermometer

The platinum resistance thermometer was calibrated by the manufacturer* at −196°C., −183°C., 0°C., 100°C. and 250°C., by comparison to a platinum resistance temperature standard calibrated by the National Bureau of Standards. A measuring current of 2.0 milliamperes was employed. The following equations were used to calculate the resistance versus temperature relationship on the International Practical Temperature Scale of 1968 (Metrologia, Vol. 5, No. 2, April 1969). The resistance R(T) in the range 0° to 500°C. was calculated using equations (4-1) and (4-2).

$$R(T) = R_0 \{1 + \alpha[T^1 - \delta(T^1/100)(T^1/100 - 1)]\} \text{ - - - - } (4.1)$$

$$T^1 = T - .045(T/100)(T/100 - 1)(T/419.58 - 1)(T/630.74 - 1) \text{ - - - - - - - - - - - - - - - - } (4.2)$$

Temperature T is the value on the IPTS-68. The following values were found for the constants in the foregoing:-

Constant	Value
R_0 (ice point)	25.568680
α	0.003926275
δ	1.496529

---

* Rosemount Engineering Company, Minneapolis, Minnesota.

Constant	Value
A_4	3.0767
C_4	2.4195
A_3	-1.8309
B_3	4.2828
C_3	-2.6743

A triple point resistance of 25.5712 ohms was measured at University of Western Ontario using a triple (H_2O) cell. Rosemount estimated calibration accuracy is shown in Figure 33, Page 67. The thermometer has a stated stability .001 to .01°C.

For comparison with the data of other investigators, temperatures on the IPTS-68 were converted to the IPTS-48. This conversion is described by Kell (56) and Benedict et al (57). Between 0° and 630°C. the conversion is

$$T_{48} = T_{68} - W(T_{68}) - Z(T_{68}) \quad \text{- - - - - - - - - -} \quad (4.3)$$

where: $W(T) = 0.00045T(T/100 - 1) \times$

$$(T/419.58 - 1) \times (T/630.74 - 1) \quad \text{- - - - - - - - -} \quad (4.4)$$

and $Z(T) - (4.9035 \times 10^{-5}\, T(T/100 - 1))/$

$$(1 - 2.94855 \times 10^{-4}\, T) \quad \text{- - - - - - - - - - - - - -} \quad (4.5)$$

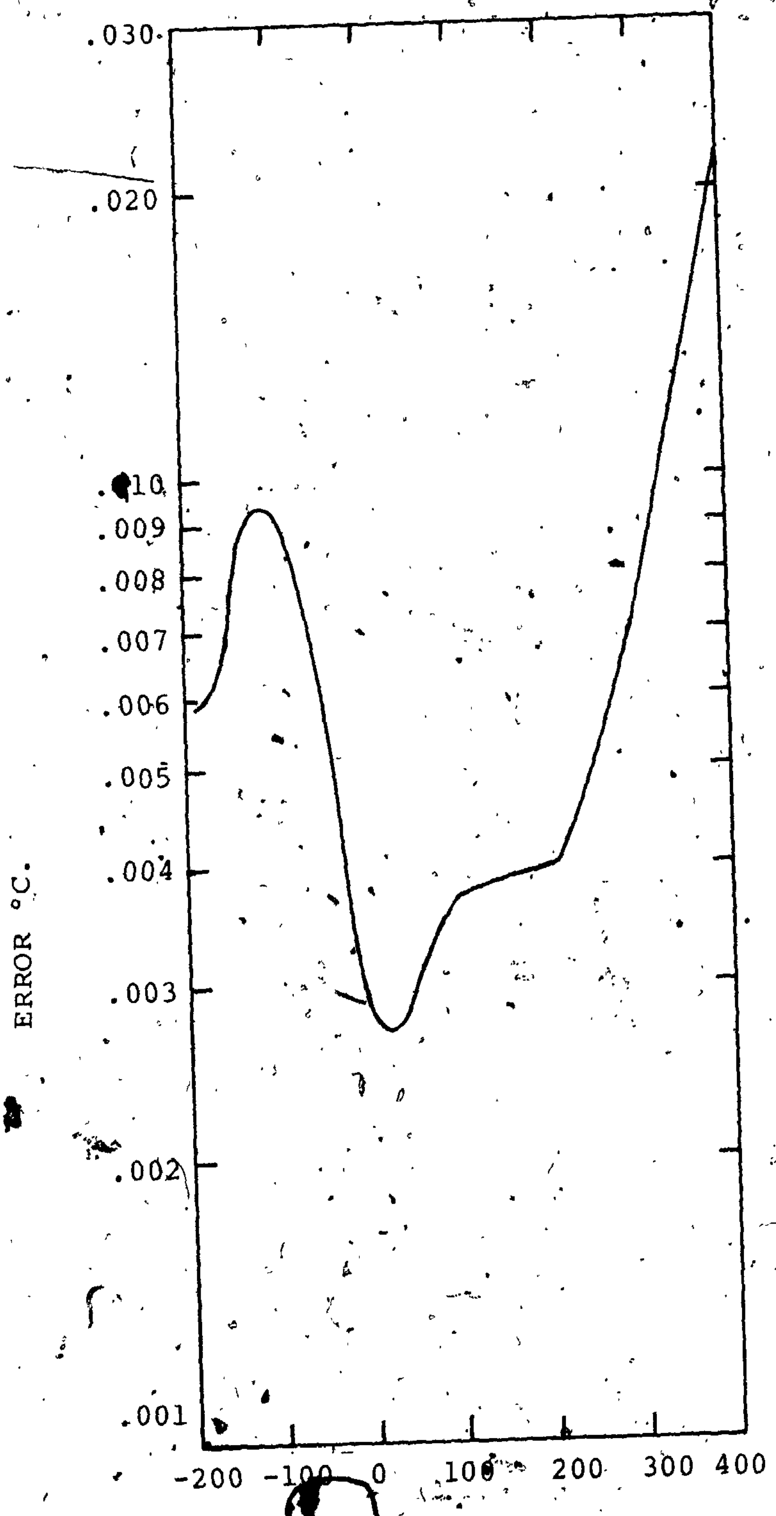


FIGURE 33 CALIBRATION ACCURACY

4-2. Resistance Bridge

The resistance of two primary standard resistors were determined with the Mueller resistance bridge. These standard resistors had calibrated resistances of 1.0000002 and 100.0030 ohms at 25°C. The calibration values were obtained at the National Bureau of Standards and the National Research Council respectively. Mueller bridge measurement for the two resistors corrected to 25°C. were as follows:

Mueller Bridge Measurement	Corrected Calibration Value
1.0002	.9999957
100.0015	100.0012

As a further check, an intercomparison of decade dial settings was made in the manner described by Mueller (58) and tabulated in Appendix C. This intercomparison was continued to a resistance of sixty one ohms. For values of resistance of 0.1000 ohms or greater, external variable decade resistors were used as reference. From 0.1000 to 0.0050 ohms manganin slide wire systems sufficied. For the lowest values the unbalance, as observed by the galvanometer deflection, provided a satisfactory reference.

4-3. Potentiometer

The potentiometer system used for absolute thermocouple measurements was spot checked, by taking readings with two essentially similar potentiometer systems.

Readings were obtained at equilibrium and in immediate sequence. Agreement to better than 0.02 percent was observed.

4-4. Thermocouple

Although initial design proposals included a system with easy access to the platinum resistance thermometer, this was abandoned to simplify the system and reduce cost. In the event of resistance thermometer deterioration, partial disassembly of the system is required. If this occurred, the two absolute thermocouples would be useful to assist in completion of a test run. Data obtained in this manner, although approximate, would be a useful guide in further investigations with a new resistance thermometer.

Emf. readings for the thermocouples are tabulated in Table 11, Page 70, together with resistance values for the platinum resistance thermometer, at the same temperature levels. Since no difficulties were experienced with the resistance thermometer, in this study, the tabulated values are provided for possible future reference.

4-5. Differential Pressure Transducer

Although the diaphragm type differential pressure transducer is employed in essentially a null displacement manner, a calibration procedure is required. If equal

TABLE 4

THERMOCOUPLE CALIBRATION

Temperature °C. (Platinum Resistance Thermometer)		Thermocouple Emf. Output* (mv)	
Location	Thermowell	A Pressure Vessel	B Isothermal Enclosure
Readings	IPTS68		
1	202.612	.3663	.3835
2	202.747	.3730	.3880
3	202.763	.3735	.3890
4	202.765	.3740	.3898
5	202.838	.3785	.3949
6	247.945	2.8691	2.8834
7	247.932	2.8683	2.8831
8	247.930	2.8680	2.8830
9	247.927	2.8678	2.8829
10	294.672	5.4384	5.4588
11	294.698	5.4401	5.4611

TABLE 4 (CONTINUED)

Temperature °C. (Platinum Resistance Thermometer).		Thermocouple Emf. Output* (mV)	
Location Readings	Thermowell IPTS68	A Pressure Vessel	B Isothermal Enclosure
12	294.716	5.4411	5.4626
13	294.757	5.4433	5.4652
14	294.924	5.4531	5.4748
15	294.937	5.4539	5.4754
16	294.949	5.4549	5.4762
17	331.099	7.4392	7.4571
18	331.101	7.4392	7.4577
19	331.107	7.4395	7.4582
20	331.115	7.4403	7.4590
21	330.921	7.4303	7.4464
22	330.913	7.4294	7.4460
23	330.757	7.4210	7.4371

*Reference Bath Temperature 195.922°C. ± .0038 (IPTS-48) pressures are applied to both sides of the diaphragm, a zero shift of the order of 5 psi (.345 bars) is experienced at a pressure level of 3000 psig (206.8 bars). When the pressure was removed, the zero returned to the original value to within 0.1 psi (6.9 x 10^{-3} bars). Measurements of zero shift versus line pressure are recorded in Appendix D. Figure 34, Page 73, shows the system employed for calibration of the 100 psi (6.89 bars) differential pressure transducer. The valves in this system are necessary to permit a differential pressure to be applied across the diaphragm. This is required to obtain a span setting on the transducer indicator. If for example, a full scale deflection is adjusted for a pressure differential of 100 psi (6.89 bars) then pressure differentials of 0.1 psi (6.9 x 10^{-3}) bars and greater may be noted from the indicator needle deflection. Since the smallest weights supplied with the deadweight gauge were equivalent to 0.5 psi, (3.4 x 10^{-2} bars) it was difficult to obtain a perfect balance across the diaphragm. The unbalance could be determined from the meter deflection, however smaller weights were constructed from brass washers, hence minimizing the unbalance.

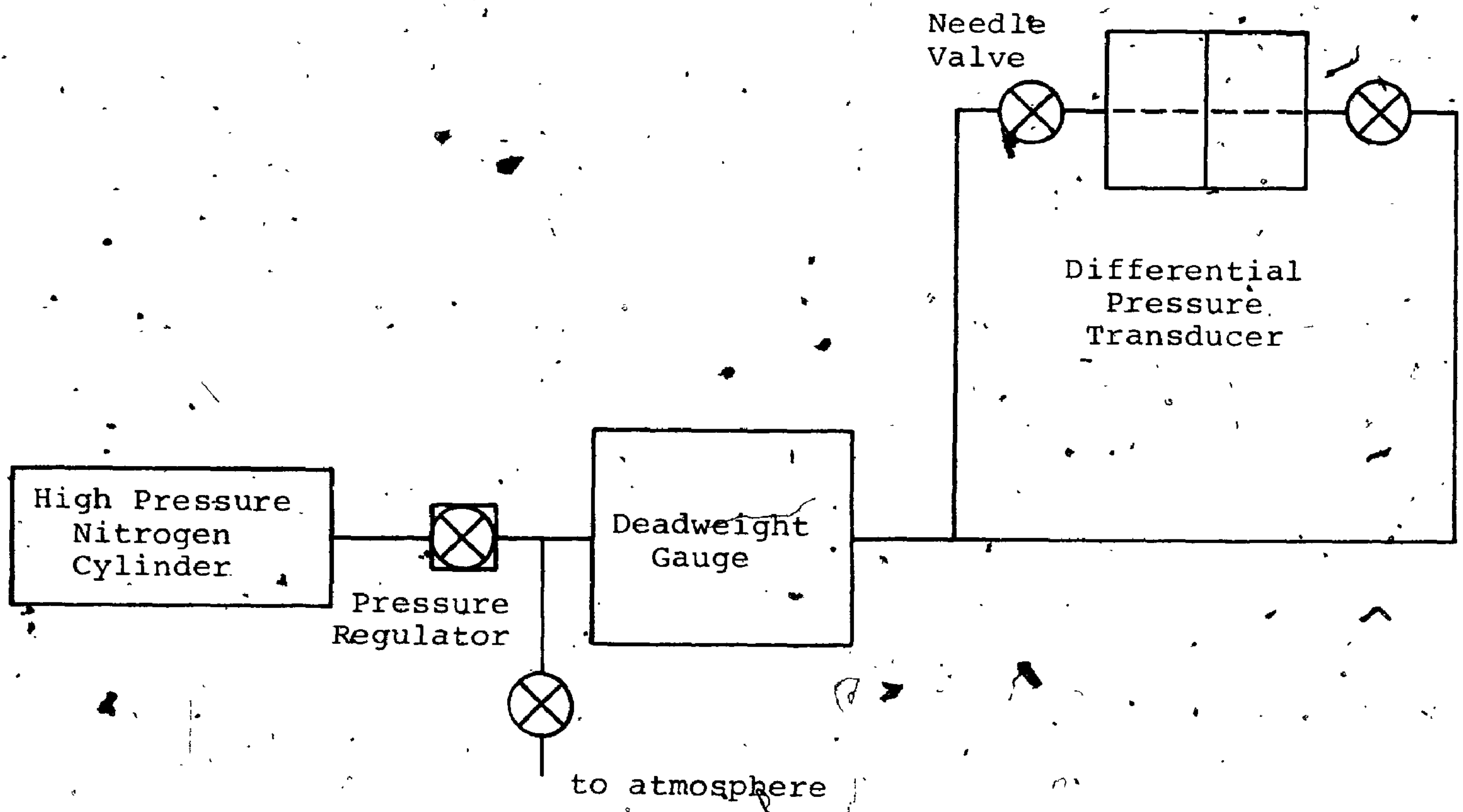


FIGURE 34 SYSTEM FOR TRANSDUCER CALIBRATION

4-6. System Volume Measurement

To determine the precise specified volume of the fluid under study, it is important to know the volume of the system at any temperature, with respect to a reference temperature. Measurements of system volume at room temperature are tabulated in Appendix E. Included in Appendix E are the data and expression determined experimentally by Furman (49) and Keyes (7) for the thermal expansion behaviour of stainless steel.

The sample vessel was evacuated with a diffusion type vacuum pump to a pressure of less than 6 x 10^{-6} bars. Double distilled, deionized, and degassed ordinary water of 1.8 Megohm - cm resistivity was charged into the system. The charging process was continued, until the vapour pressure of the heated liquid charge caused sufficient water to enter the vessel. As the sample vessel approached the filled condition, the sound of boiling from within decreased and then ceased. The temperature of the charge was allowed to reach room temperature. The pressure in the sample vessel could be determined from the pressure transducer. The vessel was heated and the water discharged into an evacuated flask. Since the balance had a capacity of 1000 grams, a 750 ml. flask was employed twice in the discharge procedure.

During charging and discharging the heat exchanger on the capillary tubing was used to cool the liquid sample. The space between the sample vessel and the pressure vessel was evacuated, while filling of the sample vessel proceeded. No pressure differences greater than 0.7 bars occurred across the differential pressure transducer, during this procedure. When discharging was required, both vessels, at approximately 100 deg. C. were discharged simultaneously into two separate evacuated flasks. As discharging neared completion, the temperature of the system was increased to 200 deg. C. to complete the process. The heat exchanger was again utilized. Evacuation of the two vessels, after discharging, continued at 200 deg. C. for seven days. In other aspects, the methods of sample preparation, charging and discharging were essentially similar to those employed by Chan (1). Volume measurements were also obtained for the tee, the needle valve and the pressure transducer. A hypodermic syringe was employed to fill the tee and valve. Physical measurements of the transducer permitted determination of its internal volume.

The value of system volume tabulated in Table 16, page 87, was based on one measurement. An additional measurement was available, however this value applied to the sample vessel prior to assembly, with the pressure vessel. The sample vessel filler tubing was approximately one quarter of an inch longer and was fitted with a globe pattern needle valve. The latter measurement was 1048.2 cm^3 and agrees to within 0.1 percent with the former measurement, of Table 16, page 87.

The system volume was determined at elevated temperature, utilizing the volume measured at room temperature (VV), and the linear expansion coefficients (LEC) of Furman (49). The following expression was employed.

$$V = VV + 3\ (LEC)\,(VV)\ \Delta T \text{ - - - - - - - - - - - - } (4.6).$$

CHAPTER 5

EXPERIMENTAL METHOD

5-1. Saturated Vapour Pressure of Light and Heavy Water

A mass of light or heavy water was degassed and weighed prior to charging into the sample vessel, which was evacuated to a pressure of less than 6×10^{-6} bars. Since the saturated vapour pressure is required, the mass of charge was selected, to produce two phase conditions, throughout the temperature range of the study. The charging process employed the vapour pressure of the sample fluid, under boiling conditions. The charging and discharging system is displayed in Figure 31, Page 64, showing the flask, the tee and the two additional valves required in this procedure. The flask was evacuated, prior to filling with water, then the tee was evacuated. Heat was applied to the flask and the appropriate valves opened, to initiate filling. The system was weighed again after filling, to determine the mass of liquid charged into the sample vessel. In a like manner, the space between the sample and pressure vessels was charged with a mass, to provide a similar specific volume, which resulted in approximately the same pressure, at the same temperature.

The ordinary water sample was double distilled, deionized and the resistivity was measured at 1.8 Megohm-cm.

Heavy water, with a purity of 99.79 percent by weight, was supplied by Atomic Energy of Canada Limited.

Heat was added to the system, primarily by the heating element on the isothermal enclosure. The power input to the smaller heaters on the filler tubing and the hex fitting were also manually controlled, to raise or to maintain the temperature at the desired value. Voltage settings for the D.C. Power supplies controlling the heating elements were approximated, from settings employed during familiarization with the uncharged system. Table 12, Page 79, provides a voltage versus temperature information, for the heating element on the isothermal enclosure. Differential thermocouple output indicates the degree of control and isothermality attained. Steady state conditions were considered to exist, when the change of temperature as indicated by the resistance thermometer was less than or equal to 0.01 degrees Celsius per hour.

The pressure system, as shown in Figure 22, and 23, Appendix A, was operated as described previously, however, the method of balancing the pressure was modified slightly. During tests with ordinary water the appropriate valves were adjusted, to permit the balancing pressure to be imposed on the diaphragm and the deadweight gauge read as soon as possible. With later tests on heavy water the balancing pressure was imposed on the diaphragm as before,

TABLE 5

VOLTAGE SUPPLIED TO THE HEATING ELEMENTS ON THE ISOTHERMAL ENCLOSURE AT THE INDICATED TEMPERATURES (EVACUATED SYSTEM)

Voltage (Volts)	Temperature (Deg. C.)
72.31	202.7
82.52	247.9
92.78	294.9
101.15	331.1

Heating element resistance = 136 ohms

except one half to one hour passed before a deadweight gauge reading was obtained. During this time a minimum of pressure adjustments were made, prior to the actual pressure reading. By referring to Table 13 of Appendix D compensation for zero shift is possible, while balancing pressure at the diaphragm.

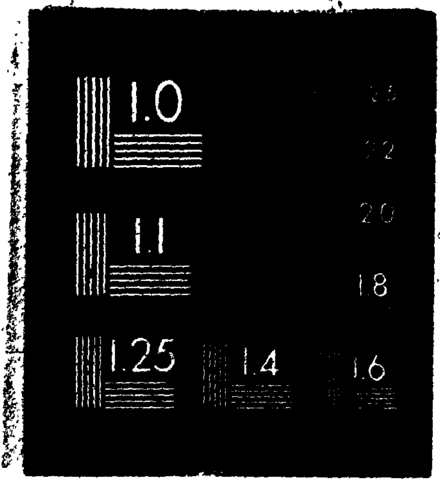
5-2. P-v-T Properties of Superheated Heavy Water

The experimental method used is similar, in most aspects, to the method employed for measuring the saturated vapour pressure. The criteria for selection of the mass is based on the specific volume required for the investigation. Once superheated vapour conditions are established, by elevating the temperature above the temperature at which two phase conditions exist, the complete volume must be maintained at that temperature. Since external filler tubing remains essentially at room temperature, this is impossible. The heat transfer situation at the heat exchanger must be considered, to estimate the location of the vapour-liquid interface, within the filler tubing. Assuming this approximates the case of uniderectional heat flow in a medium, with a uniformly distributed heat source. Considering cylindrical geometry, the differential equation may be expressed as:-

$$\frac{\partial^2 T}{\partial Z^2} = \frac{q}{k} \qquad (5.1)$$

$$\text{or} \quad T' = qz^2/2k + Mz + N \qquad (5.2)$$

2 OF/DE 2



after integration. Constants M and N may be evaluated from the boundary conditions:

$T = T_O$ at $z = o$ and $T = T_L$ at $z = L$ to give $N = T_O$

$$\text{and } M = \frac{T_L - T_O}{L} + \frac{q}{k}\frac{L}{2} \text{ - - - - - - - - - - - - - - } (5.3)$$

The temperature in terms of z may be expressed as follows:

$$T = T_O - \left(\frac{T_O - T_L}{L}\right) z + \frac{q}{k}\,\frac{(L - z)}{2}\, z \text{ - - - - - - - - - - } (5.4)$$

Since the position where the saturation temperature for the known pressure exists is required, the equation is placed in the following form:

$$\left(\frac{q}{2k}\right) z^2 + \left[\left(\frac{T_O - T_L}{L}\right) - \frac{qL}{2k}\right] z + (T - T_O) = 0 \text{ - - } (5.5)$$

Values for the saturation temperature and the specific volume of saturated liquid of heavy water were obtained from reference (28). The heat generated per unit volume (q) may be calculated, from the power input to the heating elements on the filler tubing inside the heat exchanger and the dimensions of the capillary tubing. Quantities T_O, T_L and L are determined from the thermocouples and their placement as shown in Figure 24, Page 53. The distances (L), between the two junctions of each differential thermocouple in Figure 24, page 53, moving from top to bottom, were 2.44, 2.38, and 2.63 inches, respectively. From the thermocouples, the temperatures, between each heater and at the extremities, (i.e. T_O and T_L) were determined. Hence, the heated section with axial temperature range, encompassing the saturation temperature (T) of the liquid was isolated. Applying equation 5.5 with the correct value for L, T_O, T_L and T resulted in a value of z, the location where the temperature was the saturation temperature for the measured pressure. The system mass and volume is then reduced, by the amount between the interface and the transducer diaphragm, to calculate the specific volume of the superheated heavy water sample. The distance along the capillary tubing from junction K in Figure 24, page 53, to the capillary tee below (not shown in Figure 24) was measured as 3.16 inches. This distance plus the distance from K to the liquid-vapour interface, together with the component volumes listed in Appendix E, were utilized in this volume calculation.

To decrease the time required for P-v-T data acquisition, the existing constant volume-constant mass system could be converted to a constant volume-variable mass system. This modification would require inserting an additional needle valve in the discharge line from the sample vessel. Liquid would be withdrawn from the sample vessel, and weighed, while the system remained essentially at constant temperature. The time required to obtain steady state conditions would be reduced, since readings are obtained under isothermal conditions, rather than at different temperatures in the manner described for the constant volume-constant mass system. The inherent disadvantage however would be the possibility of accumulative errors in mass determination, since each successive reading would depend on the preceding reading.

CHAPTER 6

EXPERIMENTAL RESULTS

Experimental data for the saturated vapour pressure of ordinary and heavy water plus P-v-T data for superheated heavy water are contained in Tables 14, 15 and 16 (Pages 85, 86, and 87) respectively. Unprocessed data is tabulated in Appendix H. The values for the saturated vapour pressure were obtained over the temperature range of approximately 200° to 300°C. Since the deadweight gauge manufacturer stated that a loss of sensitivity of the instrument may occur, at pressures below 17 bars, this study investigated properties above 200°C., where the saturated vapour pressure is in excess of 17 bars. The P-v-T data of Table 16 is preliminary in nature and very close to saturated vapour conditions.

The degree of isothermality attained on the isothermal enclosure and within the enclosed system may be ascertained from differential thermocouples. Table 17, Page 88, provides the emf. outputs of the appropriate thermocouples at room temperature together with their respective locations. At a temperature level of approximately 300°C. with superheated heavy water vapour contained in the sample vessel the emf. outputs shown in Table 18, Page 89 were measured.

TABLE 14

SATURATED VAPOUR PRESSURE OF ORDINARY WATER (THIS STUDY)

Temperature (Deg. C.)		Saturated Vapour Pressure (Bars)
IPTS-48	IPTS-68	
205.957	206.002	17.553
205.960	206.005	17.556
205.966	206.011	17.564
251.541	251.602	40.755
251.570	251.631	40.782
251.603	251.664	40.823
286.493	286.564	70.649
286.520	286.591	70.670
286.539	286.610	70.684

TABLE 15

SATURATED VAPOUR PRESSURE OF HEAVY WATER (THIS STUDY)

Temperature (Deg. C.)		Saturated Vapour Pressure (Bars)
IPTS-48	IPTS-68	
205.995	206.040	17.538
205.999	206.044	17.541
206.003	206.048	17.548
251.057	251.118	40.712
251.068	251.129	40.715
251.080	251.141	40.729
286.464	286.535	71.454
286.465	286.536	71.454
286.468	286.539	71.454
294.577	294.649	80.516
294.610	294.682	80.554
294.654	294.726	80.609

TABLE 16

P-V-T DATA FOR SUPERHEATED HEAVY WATER (THIS STUDY)

Temperature (Deg. C.)		Pressure (Bars)	Specific Volume (cm^3/gm)
IPTS-48	IPTS-68		
299.367	299.439	84.670	19.721
299.385	299.457	84.677	19.721

System Volume = 1049.3 cm^3 (21°C.)

Mass of Heavy Water = 54.090 gms

TABLE 17

EMF OUTPUT OF DIFFERENTIAL THERMOCOUPLES AT ROOM TEMPERATURE

Designation	Location	Emf. Output (Microvolts)
b	Thermowell	0.67
c	Pressure Vessel	0.50
d	Pressure Vessel	0.50
e	Pressure Vessel	0.75
g	Isothermal Enclosure	0.75
l	Isothermal Enclosure	0.50
i	Isothermal Enclosure	0.75
h	Pressure Vessel to Isothermal Enclosure	0.50
j	Pressure Vessel to Isothermal Enclosure	0.67
f	Capillary Tubing - Pressure Vessel to Isothermal Enclosure	0.67

TABLE 18

EMF OUTPUT OF DIFFERENTIAL THERMOCOUPLES AT APPROXIMATELY 300 DEG. C.

Designation	Location	Emf. Output (Microvolts)
b	Thermowell	+ 6.0
c	Pressure Vessel	- 1.5
d	Pressure Vessel	- 4.6
e	Pressure Vessel	-13.0
g	Isothermal Enclosure	+13.0
l	Isothermal Enclosure	+ 8.0
i	Isothermal Enclosure	- 7.0
h	Pressure Vessel to Isothermal Enclosure	+22.0
j	Pressure Vessel to Isothermal Enclosure	-10.0
f	Capillary Tubing - Pressure Vessel to Isothermal Enclosure	+18.0

The maximum radial temperature gradient along the thermowell was approximately 0.1°C. Between the pressure vessel and the isothermal enclosure a radial temperature gradient of the order of 0.3°C. existed. Circumferentially around the outer surface of the pressure vessel and the inner surface of the isothermal enclosure temperature variations were found of the order of 0.1°C. and 0.2°C. respectively.

Table 19, page 91, lists possible errors to be found in the data reported in this study. These are estimates, based on assumptions regarding the accuracy of measurement of pressure, temperature, volume and mass. The deadweight gauge was calibrated, by the manufacturer, to an accuracy of 0.03 percent. It was assumed that other sources of error, in pressure measurement, were less than 0.01 percent and deemed insignificant in this analysis. Temperature measurements were assumed in error by one half the maximum radial temperature gradient along the thermowell (0.05°C). Errors in volume determination were attributed to a 1 percent assumed error in the linear expansion data of Furman (49) and to mass measurements with possible errors of the order of 0.1 grams. The mass of test samples were determined to to within 0.01 grams. This analysis estimated the overall error in the P-v-T and P-T data as 0.05 and 0.04 percent, respectively.

TABLE 19

ESTIMATE OF ERRORS (59, 28) IN DATA FOR HEAVY WATER (THIS STUDY)

Quantity	Error (percent)
Pressure	0.03
Temperature	0.03
Volume	0.02
Mass	0.02

Total error = $(.03^2 + .03^2 + .02^2 + .02^2)^{.5}$

(P-v-T data) = 0.05 percent

Total error = $(.03^2 + .03^2)^{.5}$

(PT data) = 0.04 percent

CHAPTER 7

CORRELATION OF EXPERIMENTAL DATA

7-1. Saturated Vapour Pressure of Heavy Water

Close agreement exists between the measurements of this study (60), for the saturated vapour pressures of heavy water displayed in Table 20, Page 93, and the equivalent values calculated from the correlations of Oliver et al (15). Whalley (28) provided a table of the saturated vapour pressure of heavy water from 3.8 to 370 deg. C., employing the correlations of Oliver et al (15), and other experimental investigations, with reference to the saturated vapour pressure data, of Osborne et al (17), for ordinary water.

The Chebyshev polynomial of Gibson et al (45) was fitted to the twenty eight values of saturated vapour pressure, tabulated by Whalley from 100 to 370 deg. C. Pertinent information regarding Chebyshev polynomials, and their fitting to equally spaced data by the method of least squares, is available from Kuo (61). A more extensive account of this procedure is contained in Appendix F. The resulting correlation, for the saturated vapour pressure of heavy water from 100 to 370 deg. C., may be expressed as follows:

$$\ln \beta = \sum_{r=o}^{n} a_r T_r(x) \text{ - - - - - - - - - - - - } (7.1)$$

TABLE 20

COMPARISON OF THE VAPOUR PRESSURE DATA FOR HEAVY WATER OF THIS STUDY WITH THE EQUIVALENT VALUES OF OLIVER ET AL (15)

Temperature (Deg. C.)		Saturated Vapour Pressure (Bars)	
IPTS-48	IPTS-68	This Study	Ref. 15
205.995	206.040	17.538	17.542
205.999	206.044	17.541	17.543
206.003	206.048	17.548	17.544
251.057	251.118	40.712	40.718
251.068	251.129	40.715	40.725
251.080	251.141	40.729	40.734
286.464	286.535	71.454	71.448
286.465	286.536	71.454	71.449
286.468	286.539	71.454	71.452
294.577	294.649	80.516	80.471
294.610	294.682	80.554	80.508
294.654	294.726	80.609	80.559

Average deviation 0.02 percent.

Maximum deviation 0.06 percent.

where $x = 2\left(\frac{1}{\theta} - 0.95\right)^{0.4} - A/B$ - - - - - - - (7.2)

$n = 11$

$\beta = P/P_C$

$\theta = T/T_C$

c = critical point

p = pressure, bar

T = temperature, (°C. + 273.15)

$A = 1.45220717$, $B = -0.84878953$

$a_0 = 0.33622085 \times 10^{-8}$

$a_1 = -0.26789253 \times 10^{1}$

$a_2 = 0.56912925 \times 10^{1}$

$a_3 = -0.53678761 \times 10^{1}$

$a_4 = 0.39465989 \times 10^{1}$

$a_5 = -0.25569752 \times 10^{1}$

$a_6 = 0.14684357 \times 10^{1}$

$a_7 = -0.73636325$

$a_8 = 0.31398240$

$a_9 = -0.10916159$

$a_{10} = 0.28491683 \times 10^{-1}$

$a_{11} = -0.46126663 \times 10^{-2}$

The average deviation from the tabulated values is 0.02 percent. Over the temperature range of 170 to 370 degrees Celsius, the average deviation is reduced to 0.01 percent.

7.2. P-v-T Properties of Superheated Heavy Water

During the development of the system, an equation of state, based on the association theory for real gases, was applied to the experimental data of Kirillin et al (4) for the P-v-T properties of superheated heavy water. Vukalovitch (27) developed this equation of state, for application to superheated ordinary water vapour. The equation of

Vukalovitch with two constants was fitted (62) to the critical point data of Whalley (28), and the experimental P-v-T data of Kirillin et al (4) for heavy water.

Although Vukalovitch suggested that the constants might be evaluated at the critical point, a more successful fit (63), was obtained, by employing only the experimental data of Kirillin et al. The equation, explicit in terms of pressure for the region 315 to 405 deg. C. and 71 to 147 bars, follows:

$$P = \frac{1}{144v^2}\left[\frac{v^2RT}{v-b}\left\{1-\frac{A_1(T)}{v-b} - \frac{A_2(T)}{(v-b)^2}\right\}- a\right] \quad - - - - (7.3)$$

$$A_1(T) = \frac{C_1 N}{T^{3.5}} e^{T_C T^{-1}} \quad - - - - - - - - - - - - - (7.4)$$

$$A_2(T) = \frac{N}{T^7}^2 (C_2T - 4C_1^2)\, e^{2T_C T^{-1}} \quad - - - - - - - (7.5)$$

where: $a = \frac{27}{8} RT_C b$

$$b = \frac{RT_C}{8P_C}$$

C_1 = $0.933747967 \times 10^{-17}$

C_2 = $0.333387092 \times 10^{-36}$

P = pressure (bars x 14.5038)

P_C = critical pressure, (bars x 14.5038)

T_C = critical temperature, 1.8 (°C + 273.15)

v = specific volume, $cm^3\ mole^{-1} \times 3.53146 \times 10^{-5}$

N = Avogadro's number

R = gas constant

T = temperature, 1.8 (°C + 273.15)

The following values were suggested by Whalley (28):

$$P_C = 218.8 \text{ bar}$$

$$T_C = 371.1 \text{ deg. C.}$$

The equation agrees with the data points selected to approximately one percent. Further details regarding this development are found in Appendix G.

Since the equation of state is in the form $P = f(v,T)$, the Maxwell relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$ - - - - - - - - (7.6)

may be integrated to give an expression for entropy.

$$s_{v,T} = \left(\int_{v_o}^{v} \left(\frac{\partial P}{\partial T}\right)_v\right)_T dv + S_{o,T} \text{ - - - - - - - - - (7.7)}$$

From the equation of state and setting:

$$SS = \ln (v-b) - \left(\frac{5}{2} + \frac{T_C}{T}\right) \frac{A_1(T)}{v-b} - \frac{T_C A_2(T)}{T(v-b)^2}$$

$$- \frac{5}{2} \frac{N^2}{T^7} \left(C_2 T - \frac{24}{5} C_1^2\right) e \frac{2T_C/T}{(v-b)^2} \text{ - - - - - (7.8)}$$

the expression for entropy follows:

$$s_{v,T} = {}^R/778.26 \; \{(SS)_T\}_{v_o}^{v} + s_{o,T} \text{ - - - - - - (7.9)}$$

Similarly an equation for enthalpy may be obtained

since $dh = T\,ds + v\,dP$ - - - - - - - - - - - - - (7.10)

and $\left(\frac{\partial h}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T$ - - - - - - - - - - (7.11)

or $h_{v,T} = \left(\int_{v_o}^{v} T\left(\frac{\partial P}{\partial T}\right)_v dv\right)_T$

$$+ \left(\int_{v_o}^{v} v\left(\frac{\partial P}{\partial v}\right)_T dv\right)_T + h_{o,T} \text{ - - - - - - (7.12)}$$

i.e. $h_{v,T} = \frac{RT}{778.26}\left(\{(SS)_T\}_{v_o}^{v} + \{(HH)_T\}_{v_o}^{v}\right) + h_{o,T}$ - (7.13) where:

$$HH = \frac{b}{(v-b)} - \ln (v-b) - 2[\frac{1}{(v-b)} \quad \frac{b}{2(v-b)^2}] A_1(T)$$

$$-3 [\frac{1}{2(v-b)^2} + \frac{b}{3(v-b)^3}] A (T) - \frac{2a}{vRT} \quad - - - (7.14)$$

The subscript o signifies the reference perfect gas state, which would be approached by superheated heavy water vapour, as the pressure decreased to zero. Values for h_o, T may be calculated by the following relation of Juza et al (29):

$$h_o, T = 0.43 \, (1703.83 + (2.02804) \, (T/1.8) + 4.2726$$

$$(\frac{T/1.8 - 705}{100})^2 - 1.1105 \times 10^{-2} (\frac{T/1.8 - 705}{100})^4) \quad - - - (7.15)$$

Values for s_o, T were obtained from the work of Friedman et al (64).

CHAPTER 8

DISCUSSION

The saturated vapour pressure of ordinary water, obtained in this study, was shown in Table 21, page 99, For comparison, these values are displayed together with the equivalent values of Bridgeman et al (65) in Table 21 Page 99, Keenan et al (66) also employed the vapour pressure equation of Bridgeman et al (65) as a reference, in the development of their 1969 steam tables. An average deviation of 0.13 percent exists, between these values of saturated vapour pressure, over the range of measurement from 200 to 300 deg. C. This deviation was higher than anticipated, and was due to lack of experience in operating the pressure measurement circuit. During subsequent tests with heavy water, the balancing of pressure across the diaphragm employing the deadweight gauge system was instituted, and maintained when the required temperature level was reached. In this manner, less unbalance occurred across the diaphragm, prior to pressure measurements. In the case of ordinary water, a complete balancing procedure was attempted for each datum point.

TABLE 21

COMPARISON OF THE VAPOUR PRESSURE DATA FOR ORDINARY WATER OF THIS STUDY WITH THE EQUIVALENT VALUES OF BRIDGEMAN ET AL (65)

Temperature (Deg. C.)		Saturated Vapour Pressure (Bars)	
IPTS-48	IPTS-68	This Study	Ref. (65)
205.957	206.002	17.553	17.585
205.960	206.005	17.556	17.586
205.966	206.011	17.564	17.588
251.541	251.602	40.755	40.820
251.570	251.631	40.782	40.840
251.603	251.664	40.823	40.862
286.493	286.564	70.649	70.717
286.520	286.591	70.670	70.746
286.539	286.610	70.684	70.765

Average deviation 0.13 percent.

The saturated vapour pressure of heavy water measured in this study (60) was recorded in Table 20, page 93, together with the equivalent values calculated from the correlation of Oliver et al (15), and with reference to the saturated vapour pressure of ordinary water correlated by Bridgeman et al (65). Since the average deviation and maximum deviation were 0.02 and 0.06 percent respectively, the values are considered to be in close agreement. Table 7, page 20, displayed both the data of Oliver et al (15) and that of Liu et al (18). Agreement to within 0.03 percent was demonstrated, over the temperature range of this study (200 to 300°C.). In Table 5, page 17, the vapour pressure of Oliver et al (15) and those of Rivkin et al (5) agreed to within 0.02 percent, for values in the 200 to 300 deg.C temperature range. Hence, substantial agreement exists between the data of this study (60) and those of other investigators (15, 18, 5). The saturated vapour pressure table of Whalley (28) was developed, primarily, from the correlations of Oliver et al (15) and was employed to develop the Chebyshev polynomial for the saturated vapour pressure of heavy water, described in Chapter 7 and Appendix F.

A study of the saturated vapour pressure by Issaresu (67) is compared in Table 22, page 101, with the similar

TABLE 22

COMPARISON OF THE VAPOUR PRESSURE DATA FOR HEAVY WATER OF WHALLEY (28) AND ISSARESCU (67)

Temperature (Deg.C.)	Pressure (bars)	
	Whalley	Issarescu
100	0.9647	0.96461
120	1.9135	1.9134
140	3.5176	3.5175
160	6.066	6.0660
180	9.911	9.9104
200	15.462	15.461
220	23.194	23.188
240	33.605	33.611
260	47.275	47.242
280	64.83	64.929
300	86.98	87.180
320	114.52	114.883
340	148.54	149.029

values by Whalley (28), over the range utilized in fitting the Chebyshev polynomial. Discrepancies of the order of 0.3 percent and greater, exist between these values of saturated vapour pressure. Unfortunately, Issarescu, in his isentropic checking of data, referred primarily to the studies in the 1930's by Miles et al (20) Bartholomé et al (26) and Riesenfeld et al (19).

This author has indicated, in Chapter 1, that variance between the latter and more recent investigations exists. In the paper by Issarescu, no reference has been made to the measurements by Oliver et al (15), which extend from approximately 200 to 370 deg. C.

Although the readings for superheated heavy water vapour, as shown in Table 16, Page 87, are preliminary, they were analysed (60) by the principle of thermodynamic similarity. To calculate the similar properties of superheated ordinary water, the equation of state of Keenan et al (68) was utilized, together with the critical values of Whalley (28) for both ordinary and heavy water. The thermodynamic similarity between ordinary and heavy water permits the use of the law of corresponding states (Kesselman (30)). The corresponding state for ordinary water should have the same values for reduced temperature, pressure, and specific volume. The equivalence of the corresponding state was checked by selecting an equivalent reduced temperature and pressure, then comparing the reduced specific volumes. This comparison is shown in Table 23, Page 104. Agreement to within 0.05 percent was noted.

The data of Table 16, page 87, for superheated heavy water vapour, were also compared with the corresponding values, for pressure, calculated from the virial equation of state (equation 1.21). Values for the second (B) and third (C) virial coefficients were obtained, from the results of Kell et al (13). For the two data points of Table 16 the values of pressure, as calculated from equation 1.21, were 84.592 and 84.594 bars. This indicated agreement with the measured values for pressure, to within 0.1 percent.

TABLE

THE THERMODYNAMIC SIMILARITY BETWEEN THE P-V-T DATA FOR HEAVY WATER AND THE CORRESPONDING VALUES FOR ORDINARY WATER

	Heavy Water				Ordinary Water		
State	Pressure (Bars)	Temperatures (Deg. C.)	Specific Volume (cm^3/g)	Reduced Volume	Pressure	Temperature	Reduced Volume
1	84.670	299.367	19.721	7.1815	85.598	301.843	7.1779
2	84.677	299.385	19.721	7.1815	85.606	301.861	7.1777

CHAPTER 9

CONCLUSIONS

A system has been developed capable of measuring the P-v-T properties of D_2O, to an accuracy of better than 0.1 percent (1000 ppm). Ellington et al (14), in reviewing P-v-T measurement techniques, considered the constant volume-constant mass system capable of achieving results accurate to 0.005 percent for gases. However, unless an extremely accurate volume determination is obtained, errors of less than 0.1 percent will be difficult to attain. It appears that, with further volume measurements and further experience with the pressure measurement system, the error may be reduced to the order of instrument error. Since the dead-weight gauge has a calibration accuracy of 0.03 percent, this limits the minimum expected error to this value.

The preliminary P-v-T data, of this study, for superheated heavy water vapour shown in Table 15, Page indicate agreement of 0.05 percent, with data obtained by considering thermodynamic similarity between heavy and ordinary water, as embodied in the law of corresponding states. However, more experimental data for the P-v-T properties of superheated heavy water vapour are required, to establish that the concept of thermodynamic similarity between heavy water and light water may be employed over the superheated vapour region, to define the properties of heavy water to the accuracy of the existing International Skeleton Tables for light water. The additional data would also permit further direct development of an equation of state for superheated D_2O.

The measurements of the saturated vapour pressure of heavy water, of this study, lead to the application of a Chebyshev polynomial, which describes these data and the data of Oliver et al (15) from 100 to 370 deg. C. to within 0.08 percent. Additional precise measurements would permit further development of the polynomial, possibly describing the saturated vapour pressure data for heavy water to the accuracy available in the International Skeleton Tables for ordinary water. This would be valuable not only for reducing existing calorimetric data, but also to resolve existing discrepancies between reported values for the saturated vapour pressure of heavy water.

APPENDIX A

PHOTOGRAPHS

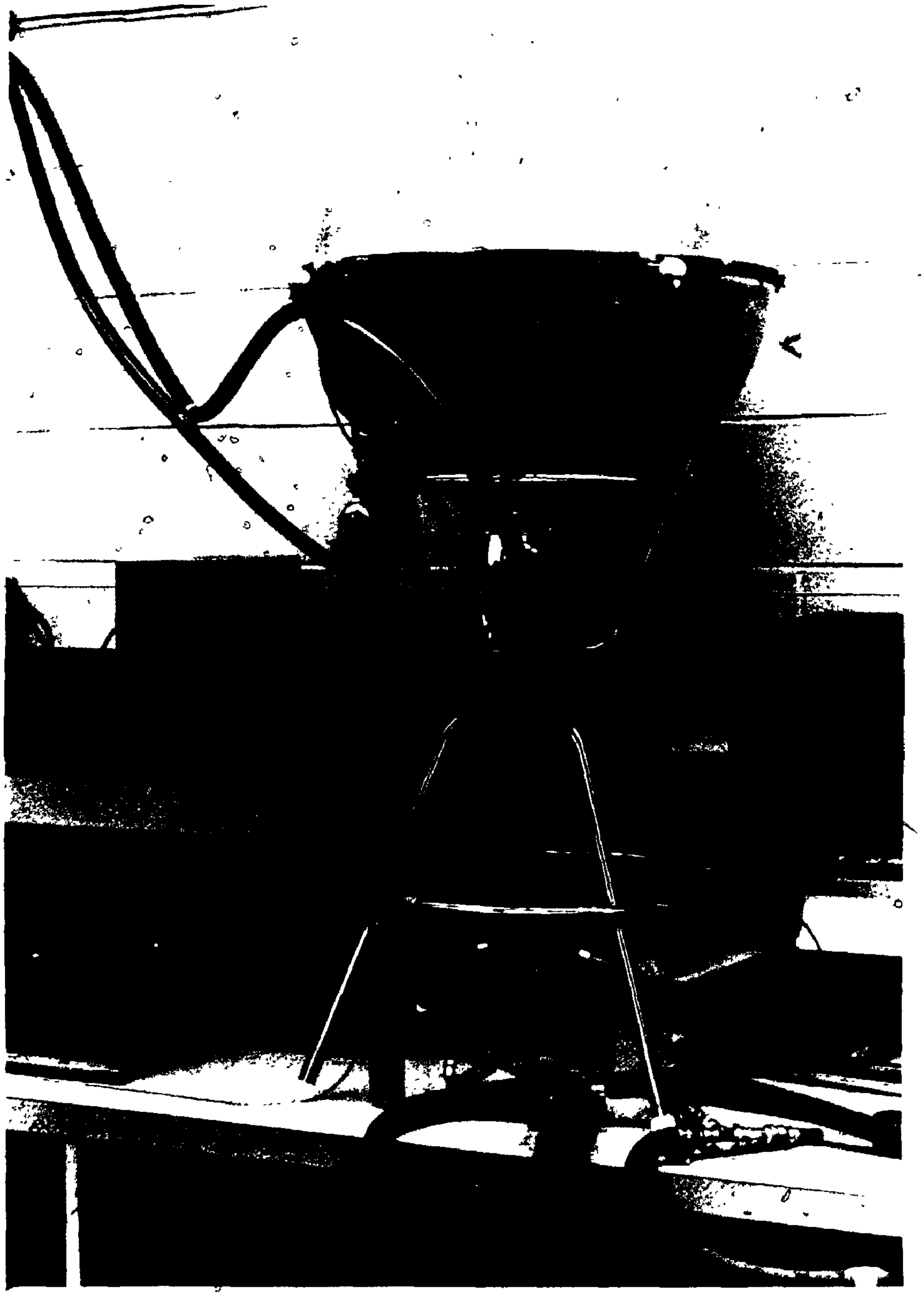


FIGURE 2 FRONT VIEW OF APPARATUS

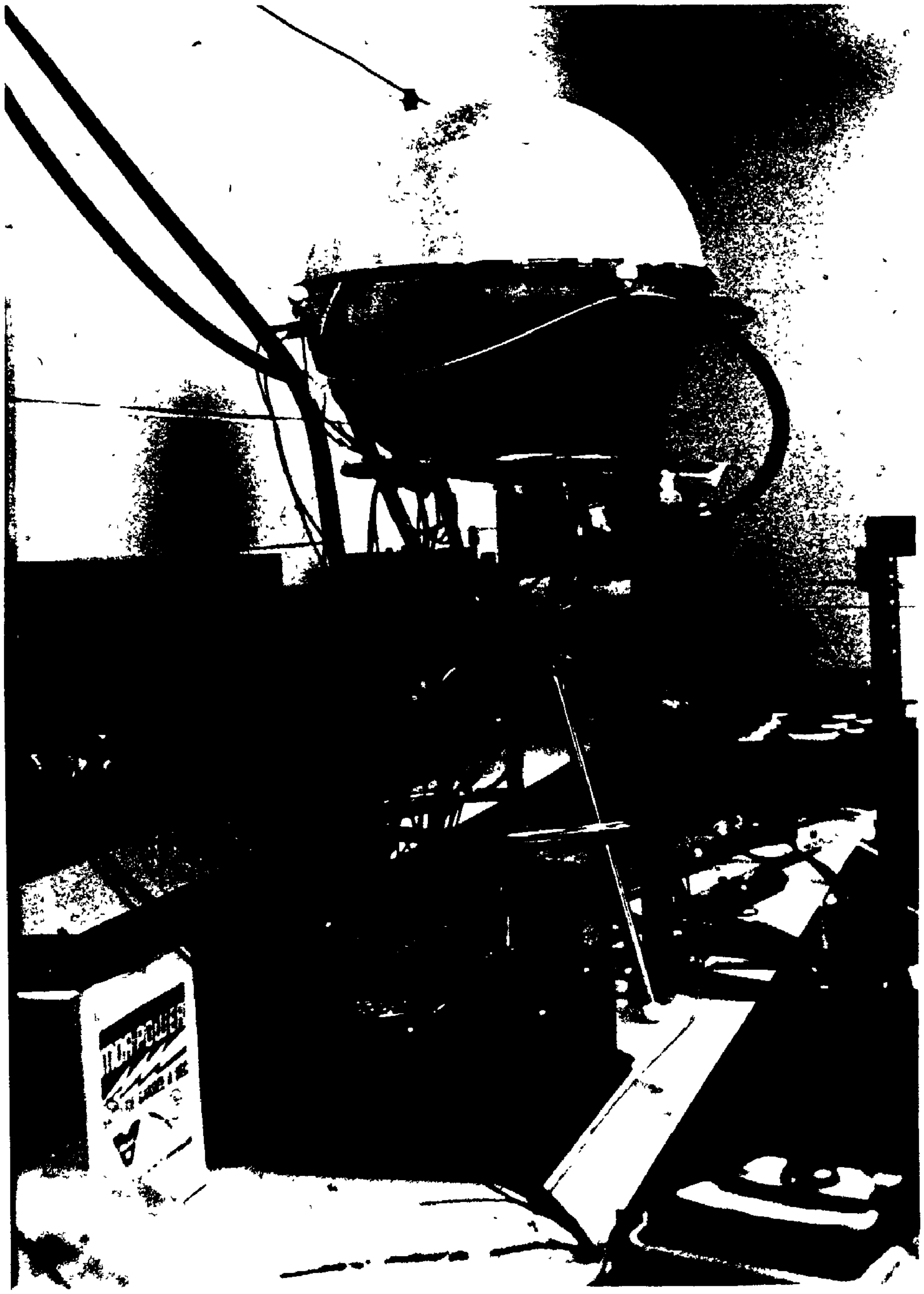


FIGURE 3 SIDE VIEW OF APPARATUS

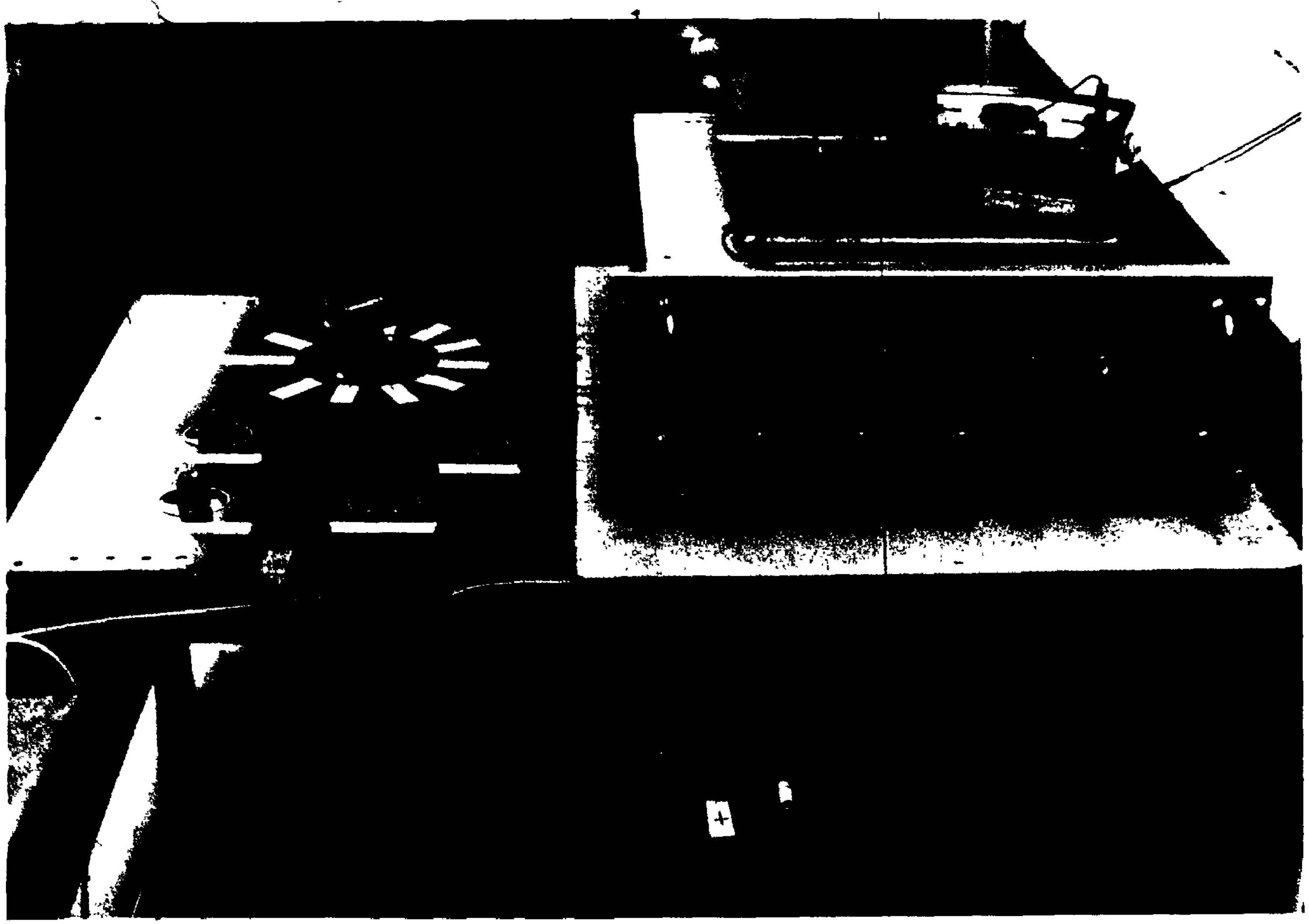


FIGURE 4 VIEW OF D.C. POWER SUPPLIES

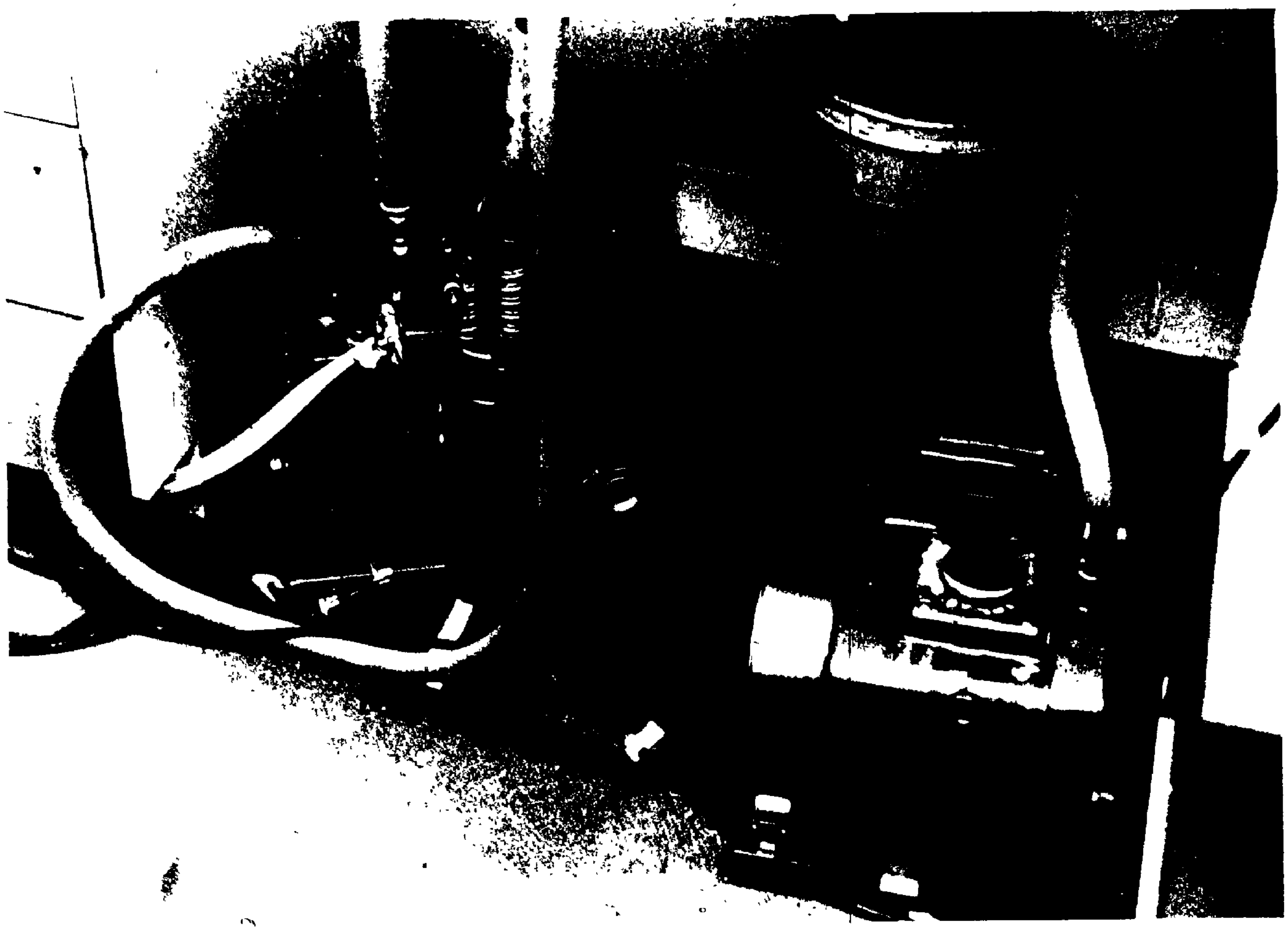


FIGURE 5 VIEW OF VACUUM PUMPS

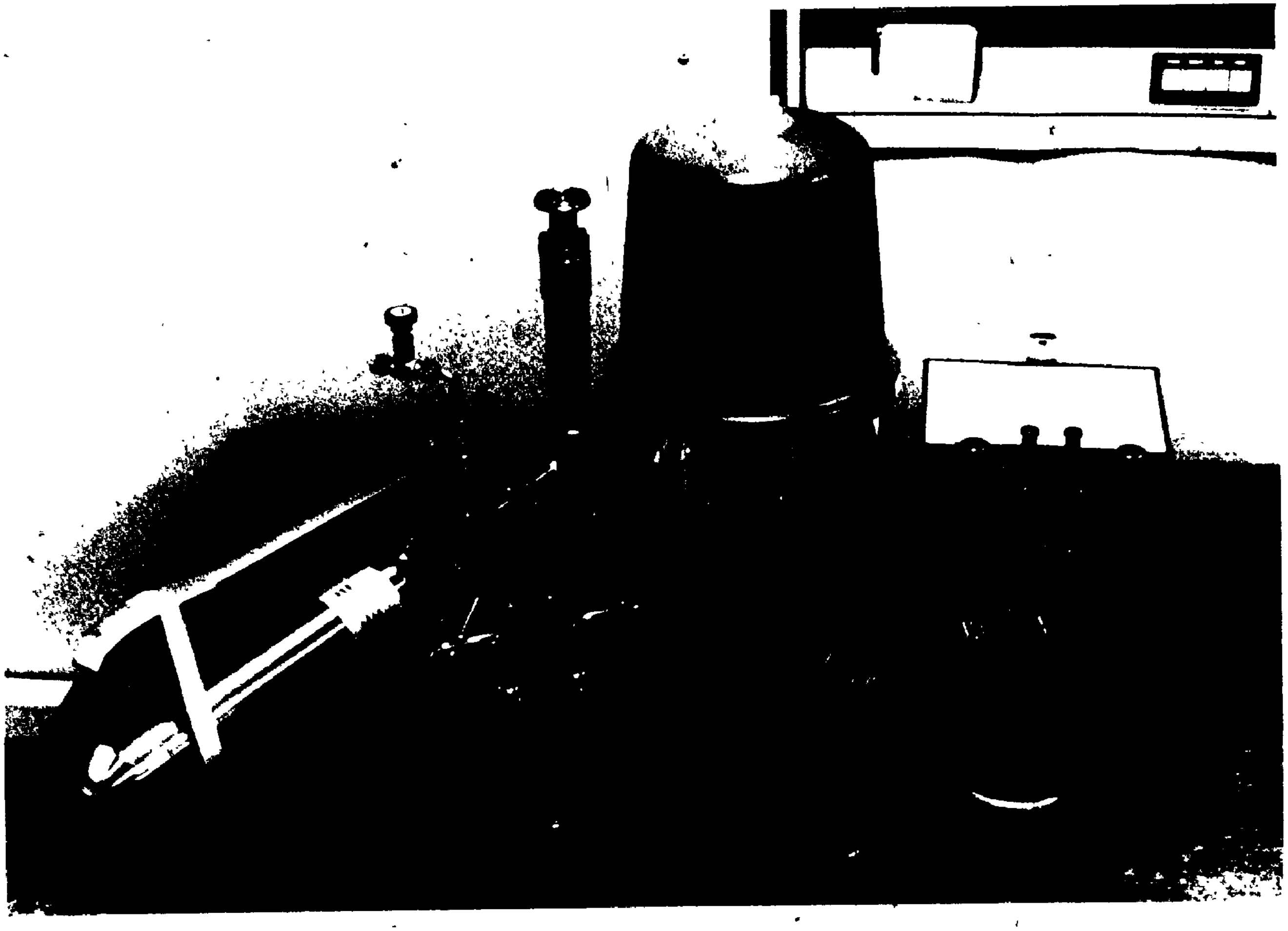


FIGURE 6 VIEW OF TRIPLE POINT CELL, STANDARD RESISTORS AND DEADWEIGHT GAUGE

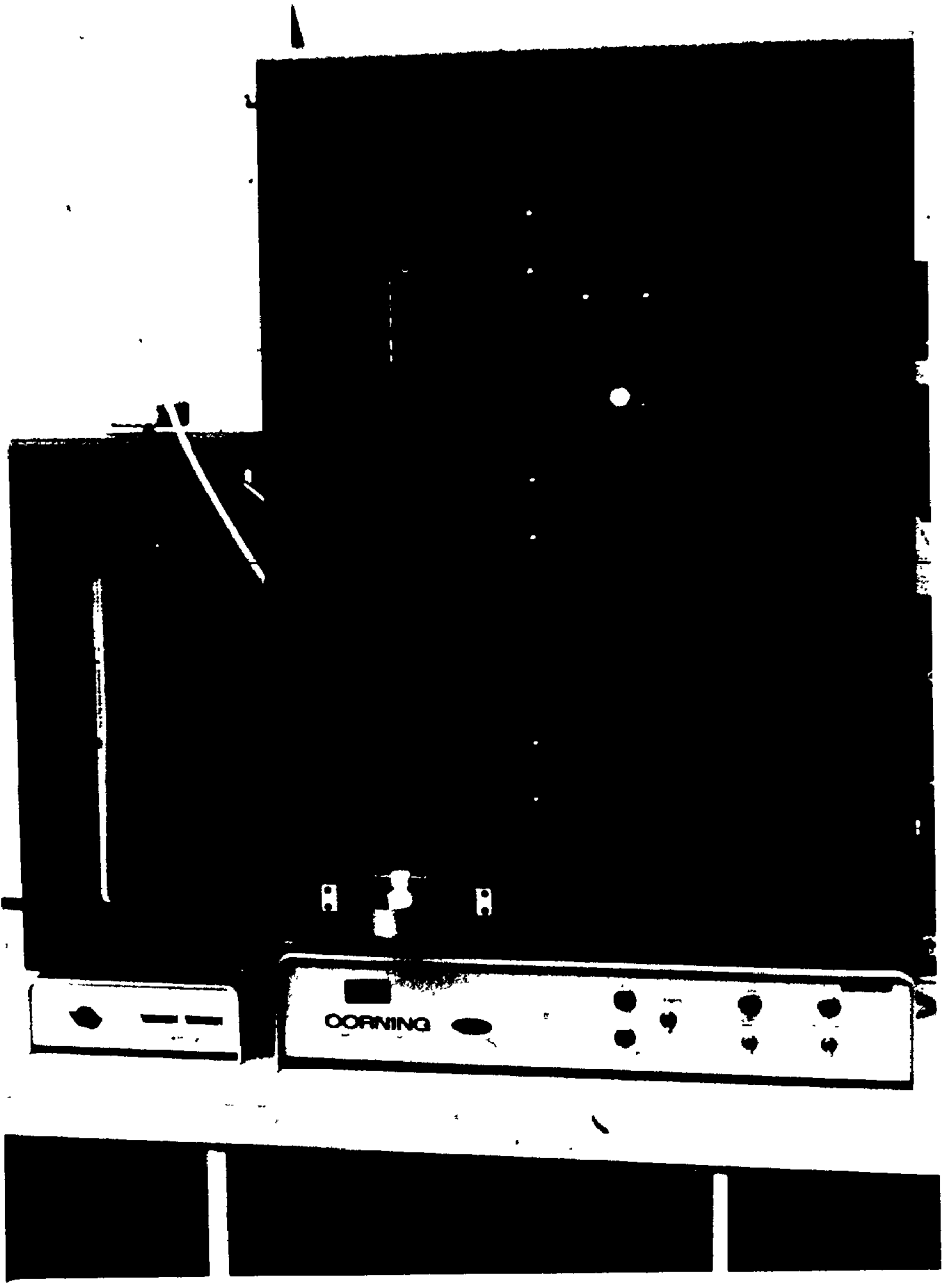


FIGURE 7 VIEW OF CORNING DISTILLER AND DEIONIZING UNIT

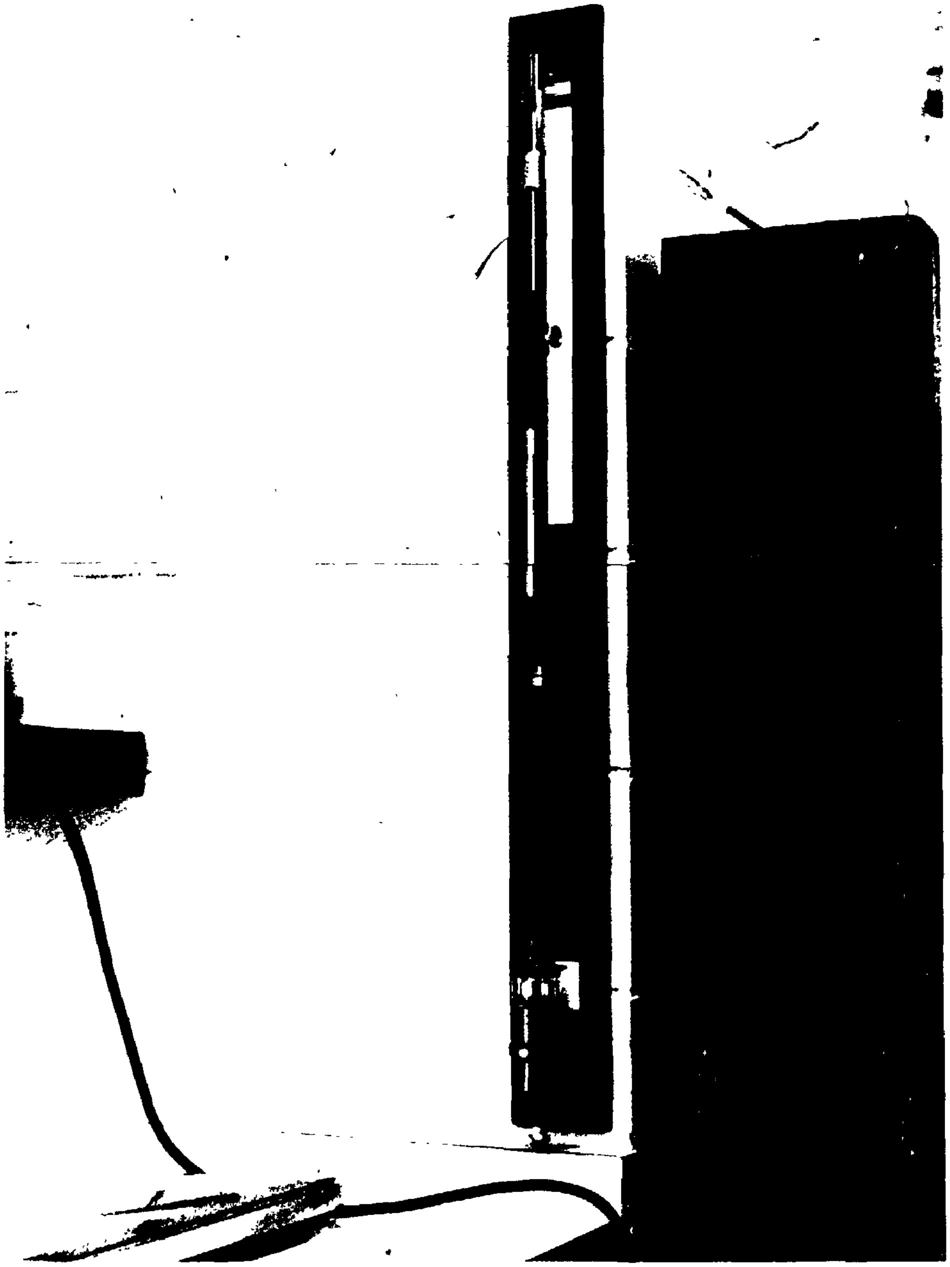


FIGURE 8 MERCURIAL BAROMETER

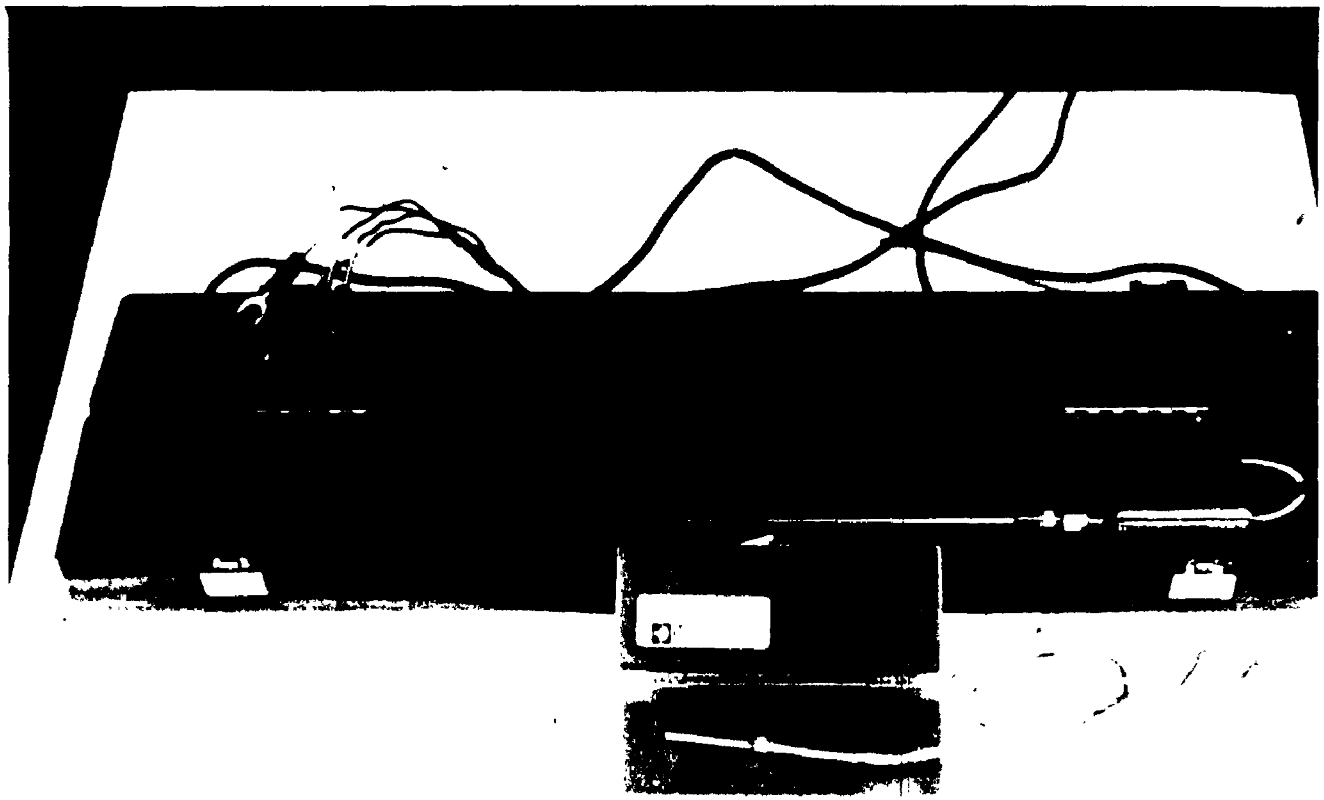


FIGURE 9 VIEW OF CAPSULE AND FULL SIZE PLATINUM RESISTANCE STANDARD

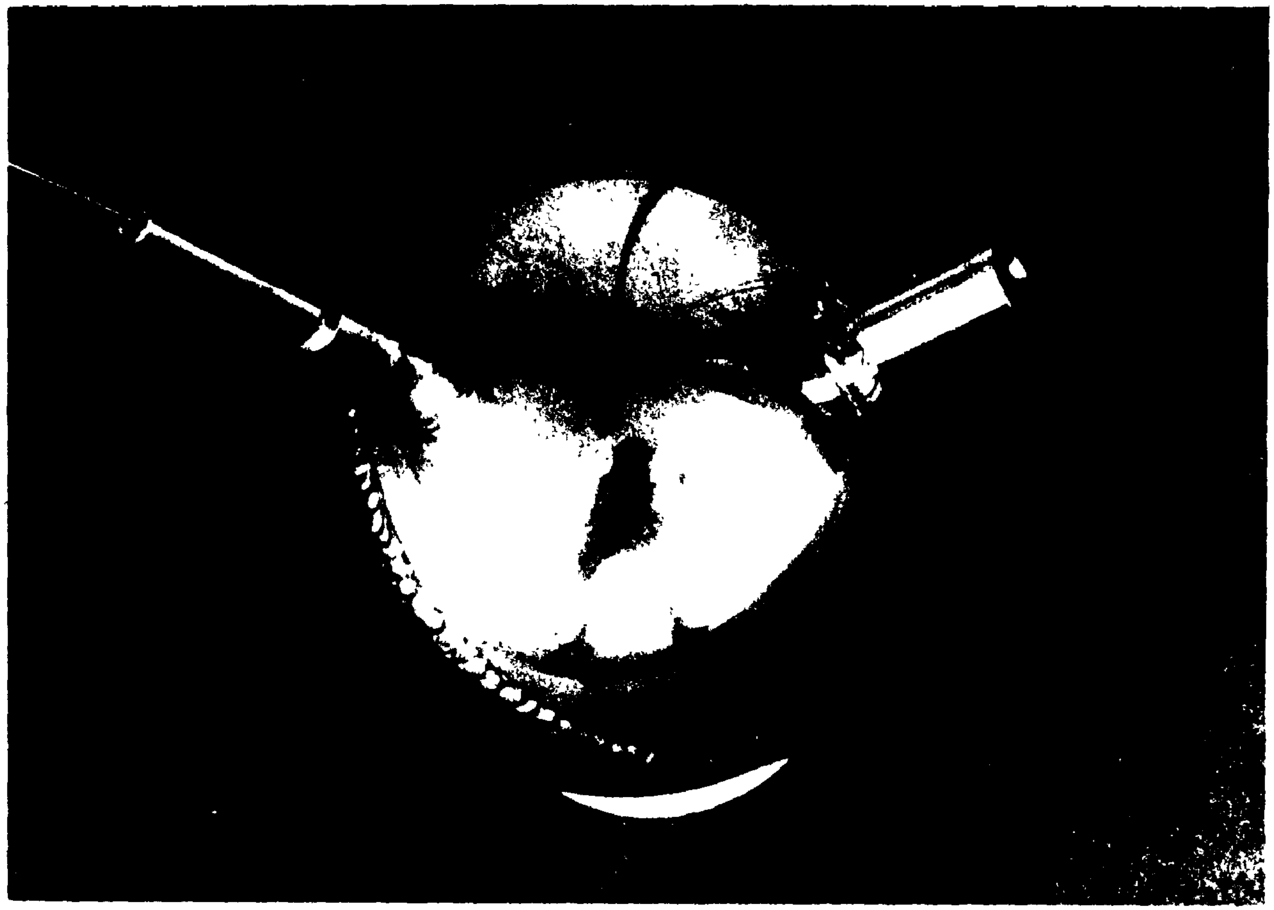


FIGURE 10 VIEW OF SAMPLE VESSEL

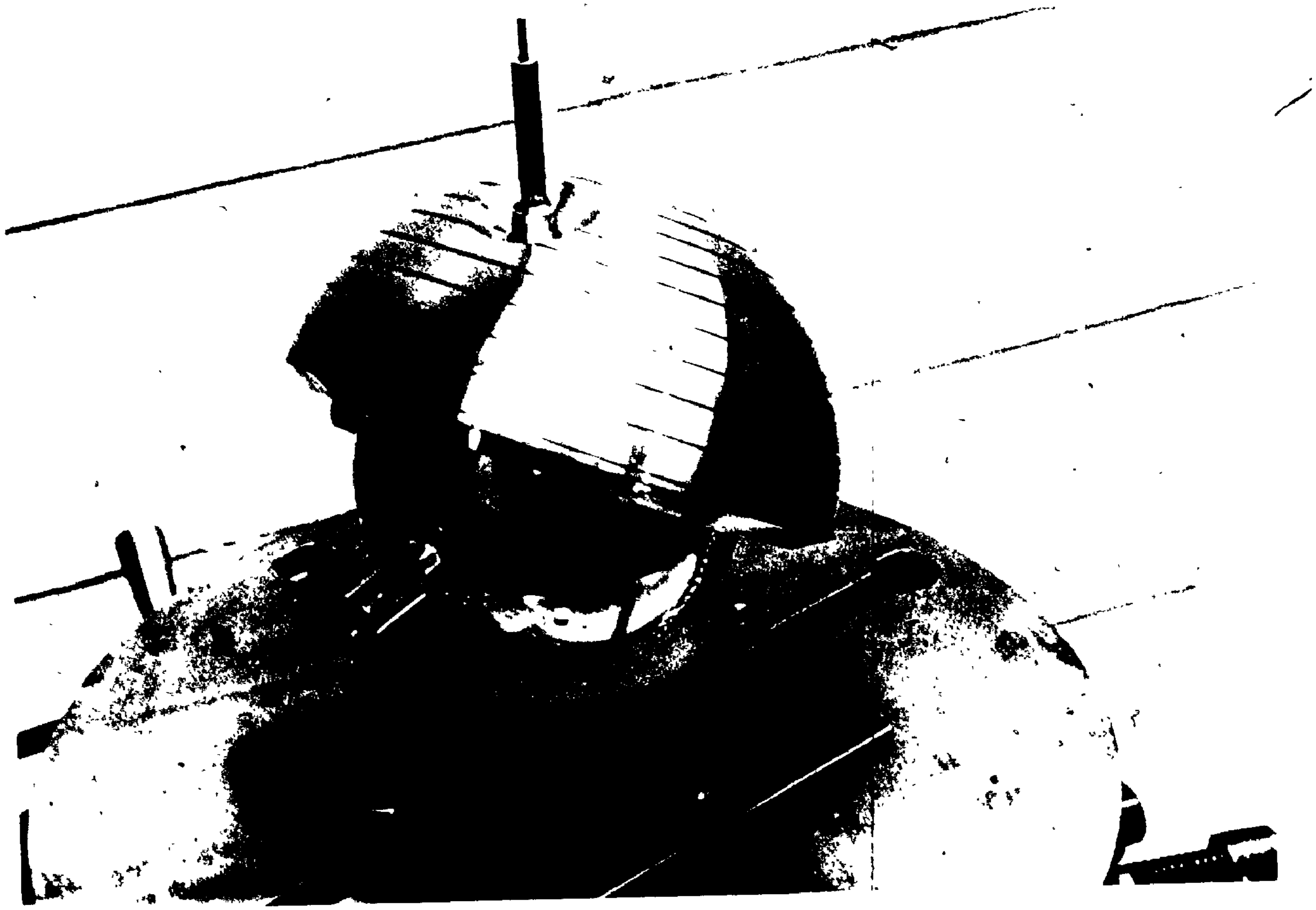


FIGURE 11 . VIEW OF SAMPLE VESSEL - PRESSURE VESSEL ASSEMBLY

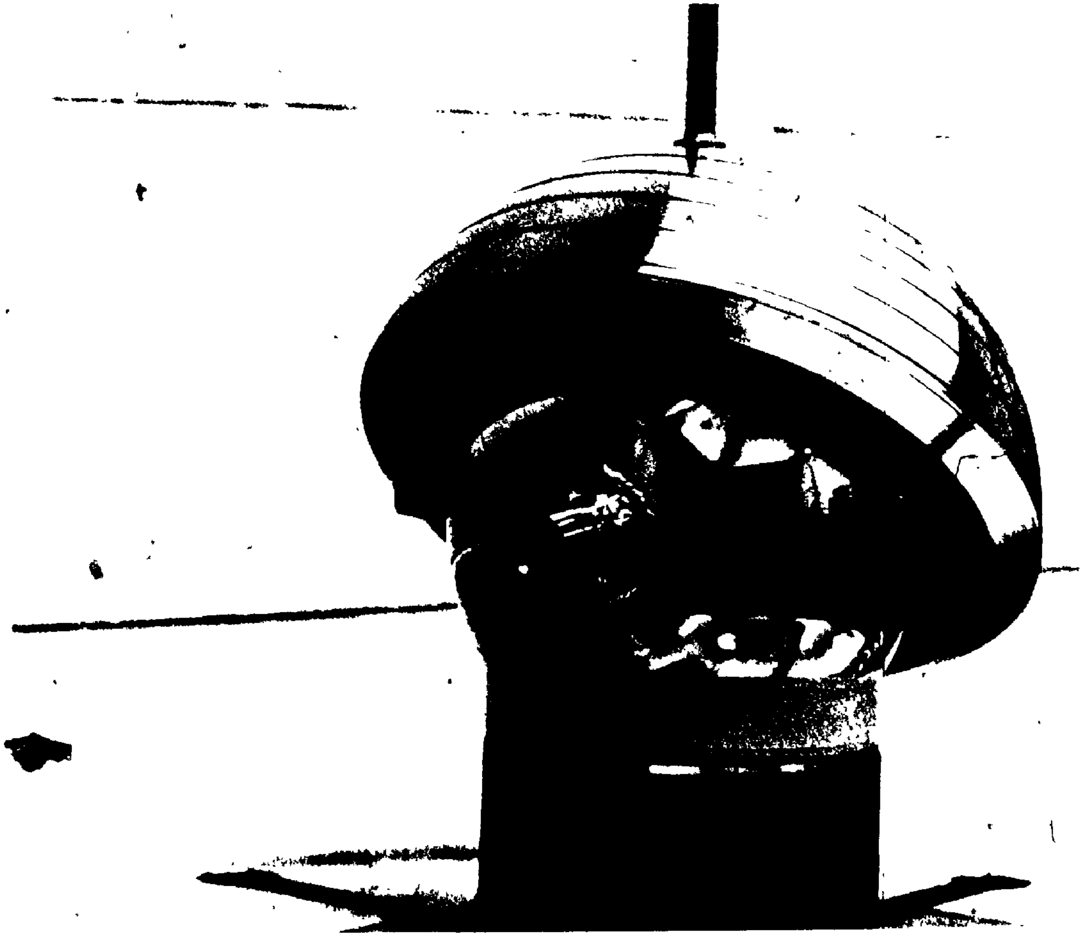


FIGURE 12 VIEW OF SAMPLE VESSEL - PRESSURE VESSEL ASSEMBLY

FIGURE 13 VIEW OF PRESSURE VESSEL SHOWING HEATING ELEMENT AND THERMOCOUPLE INSTALLATION

FIGURE 14 CLOSE-UP OF PRESSURE VESSEL
WITH INSTRUMENTATION

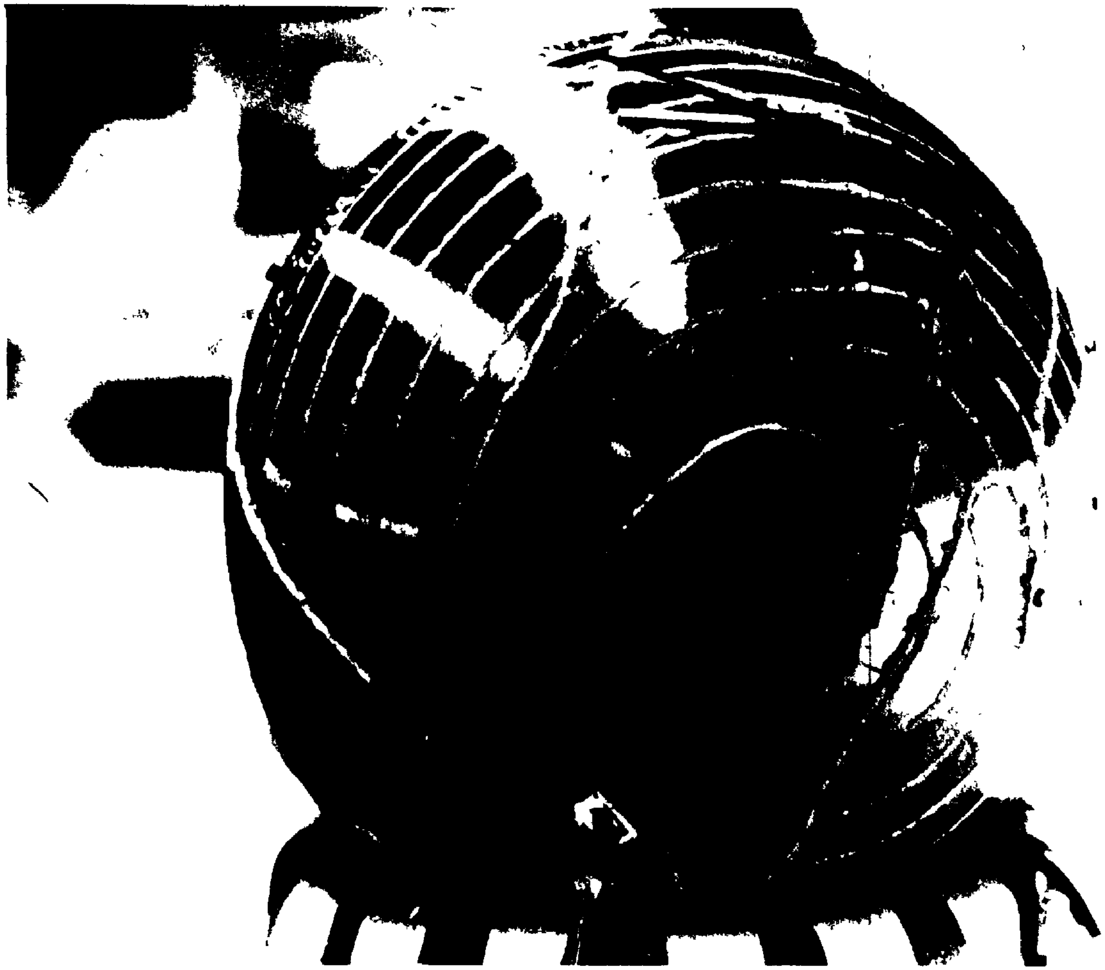


FIGURE 15 VIEW SHOWING PRESSURE VESSEL DETAILS

FIGURE 16 VIEW OF BOTTOM HALF OF THE ISOTHERMAL ENCLOSURE SHOWING THERMOCOUPLE INSTALLATION

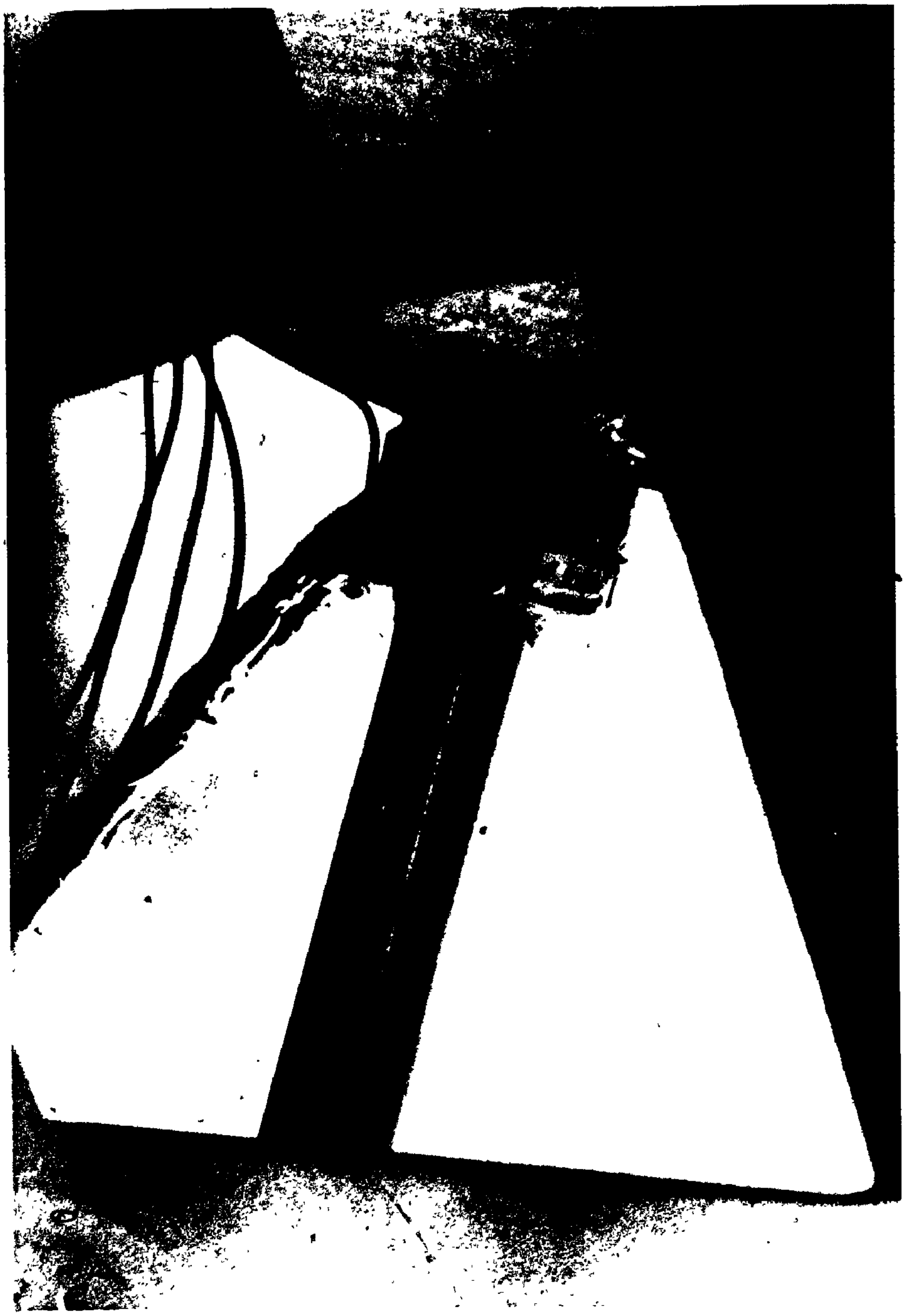


FIGURE 17 VIEW OF HEX FITTING AND VACUUM-SUPPORT TUBE WITH INSTRUMENTATION

FIGURE 18 VIEW OF THE ISOTHERMAL ENCLOSURE WITH THE PRESSURE VESSEL IN POSITION SHOWING THERMOCOUPLE PLACEMENT

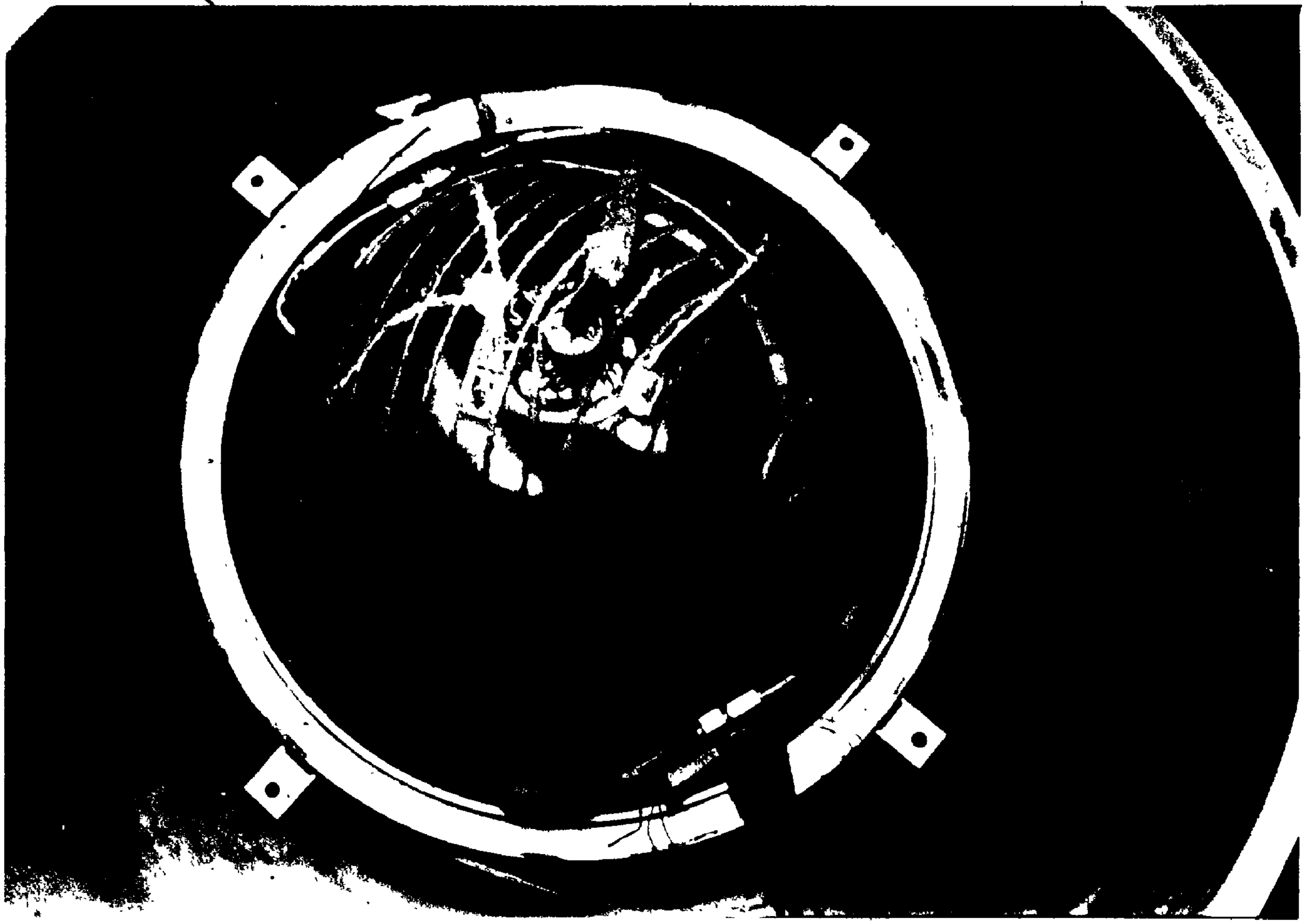


FIGURE 19 TOP VIEW OF PRESSURE VESSEL DISPLAYING INSTRUMENTATION ADJACENT TO THE THERMOWELL

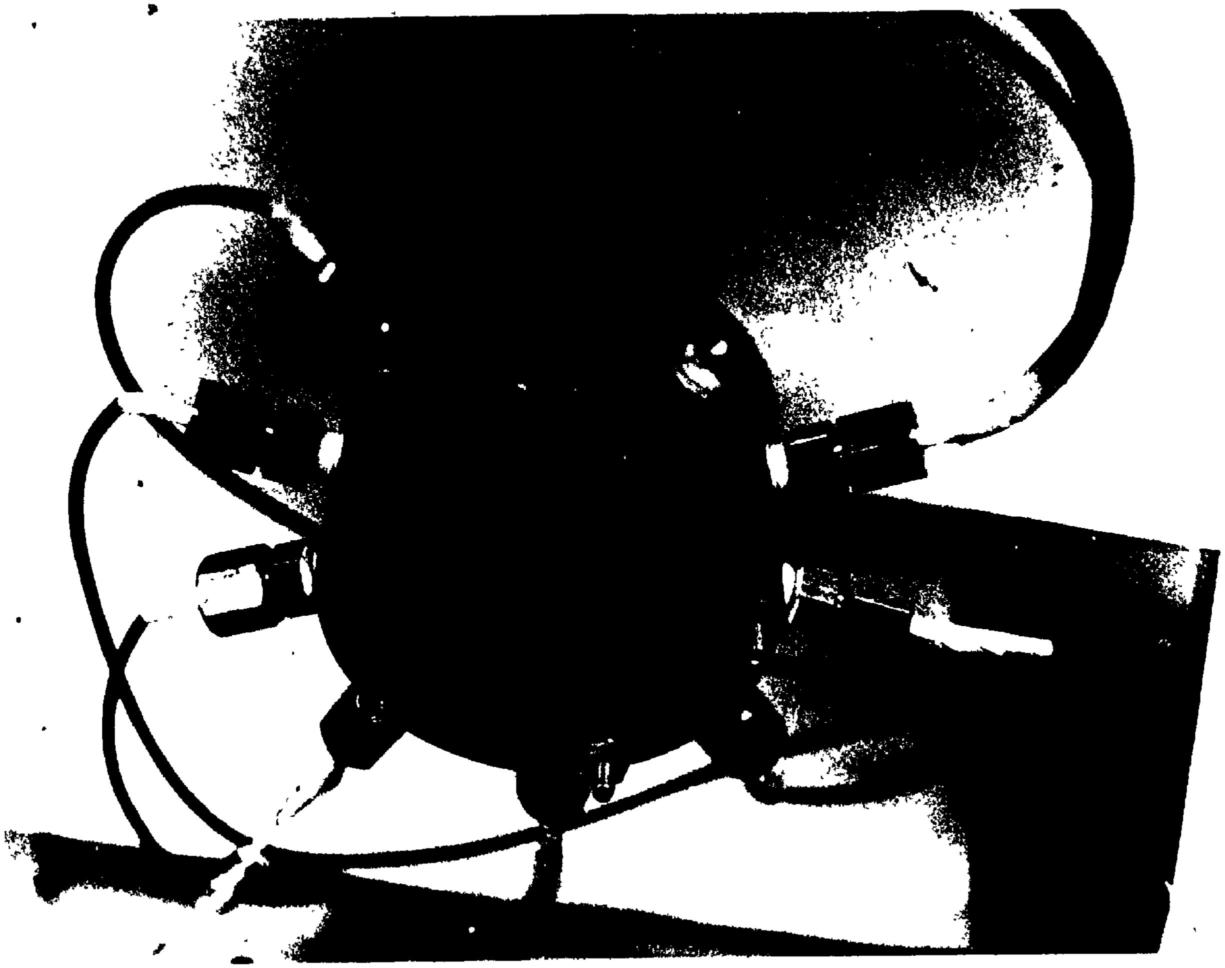


FIGURE 20 VIEW OF JUNCTION BOX

FIGURE 22 VIEW SHOWING THE FILLER TUBING, HEAT EXCHANGER AND DIFFERENTIAL PRESSURE TRANSDUCER

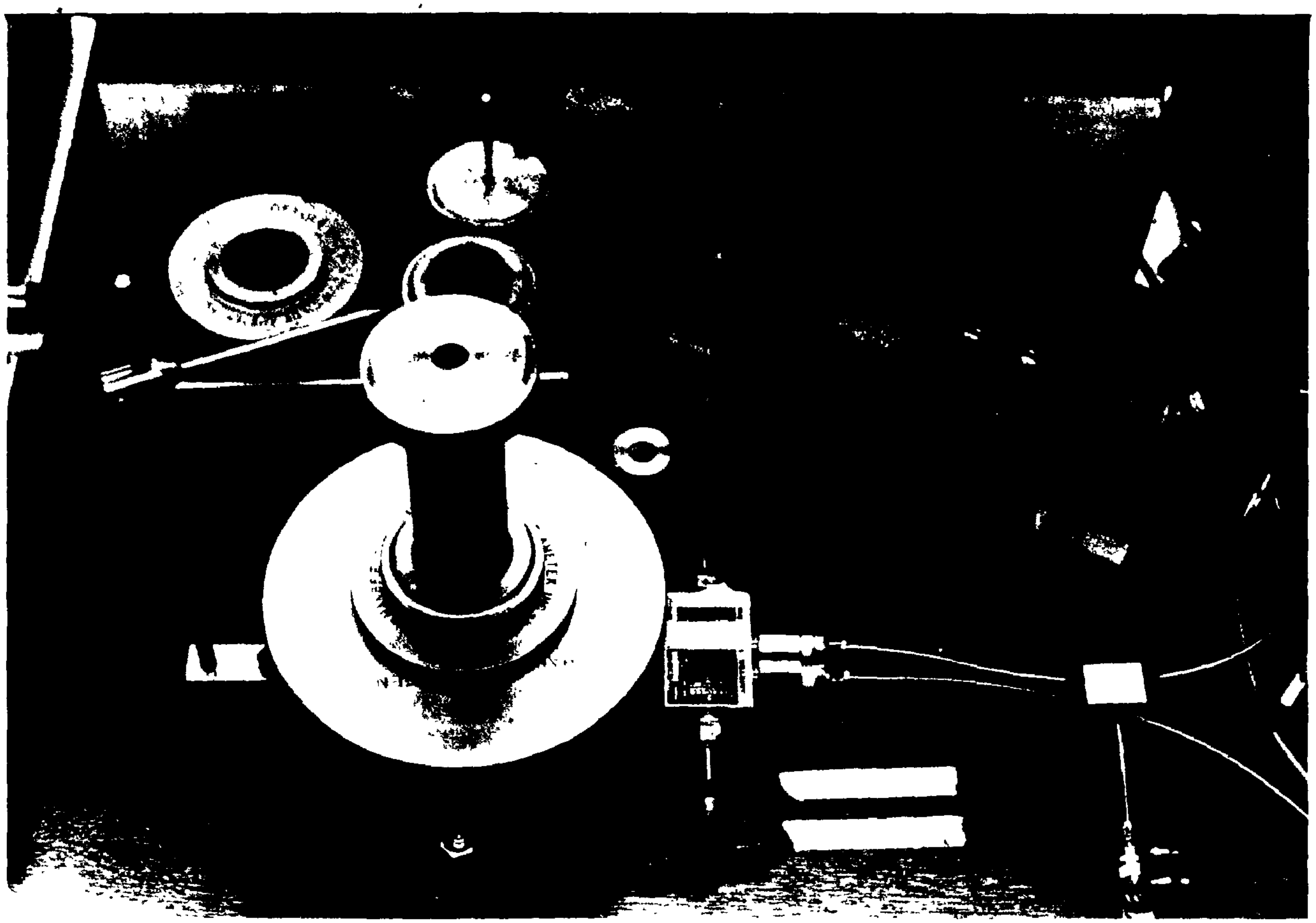


FIGURE 23 VIEW OF DEADWEIGHT GAUGE AND PRESSURE TRANSDUCER INDICATOR

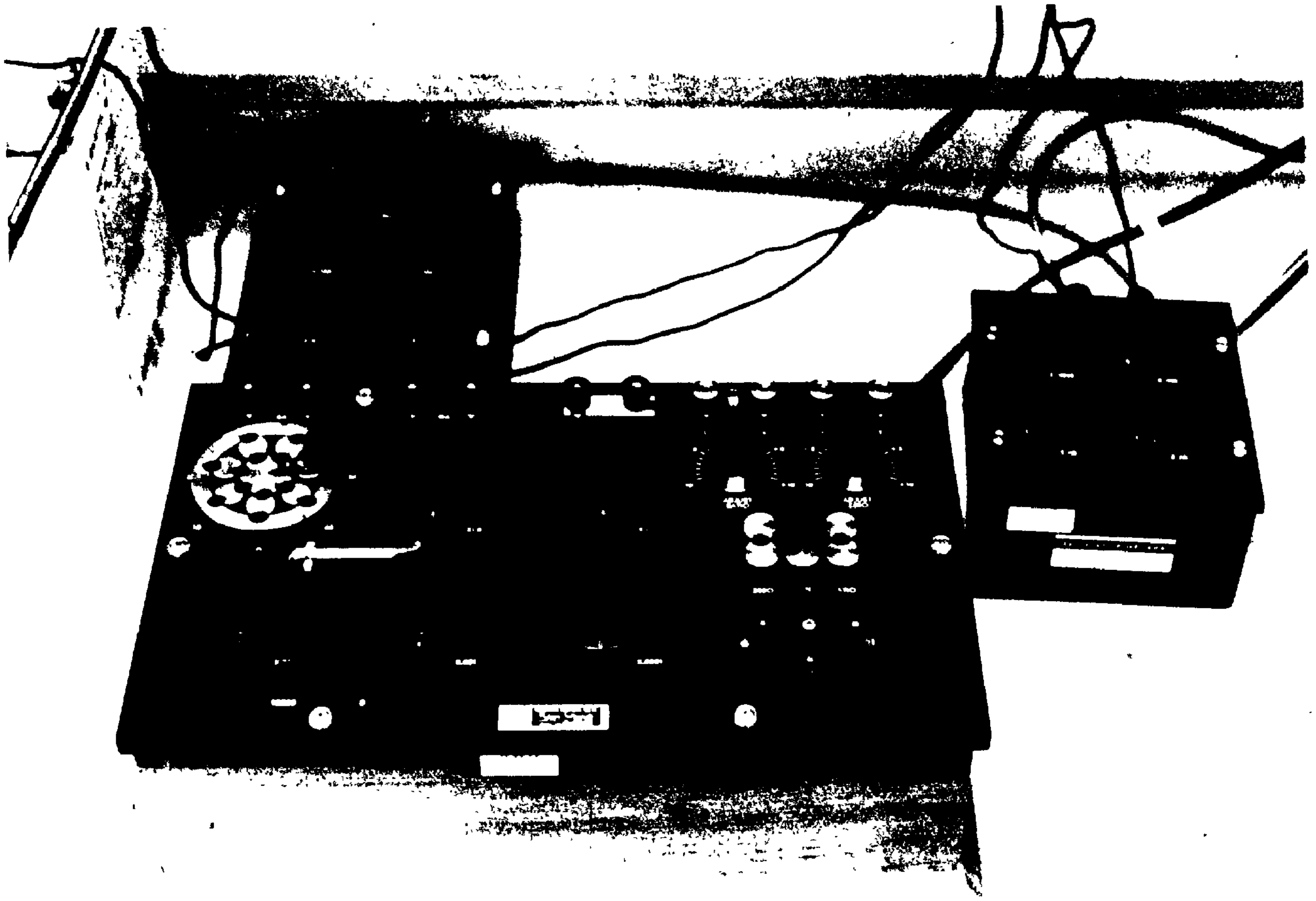


FIGURE 26 VIEW OF MUELLER RESISTANCE BRIDGE

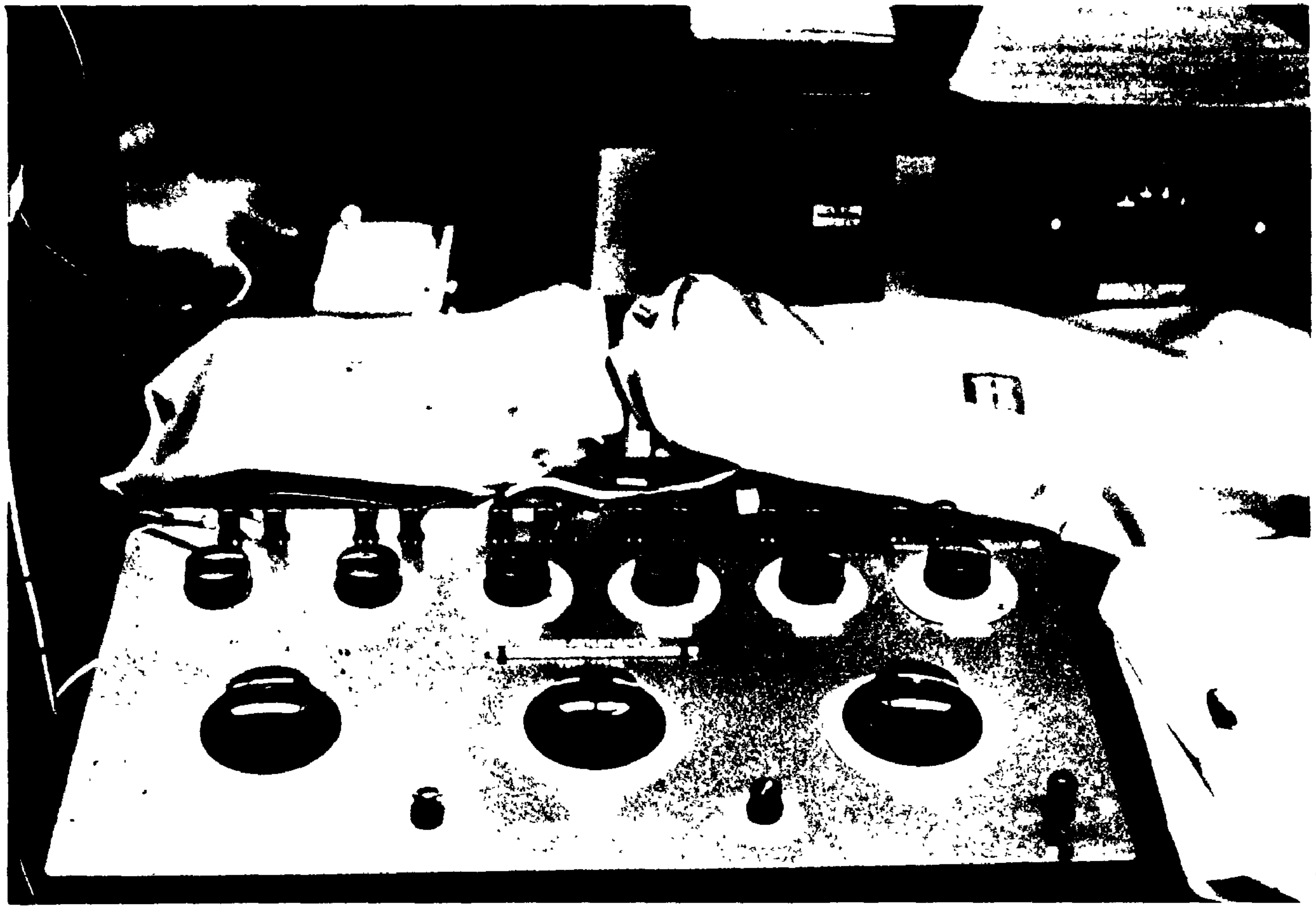


FIGURE 27 VIEW OF POTENTIOMETER - GALVANOMETER SYSTEM

FIGURE 28 VIEW OF CONSTANT TEMPERATURE BATH

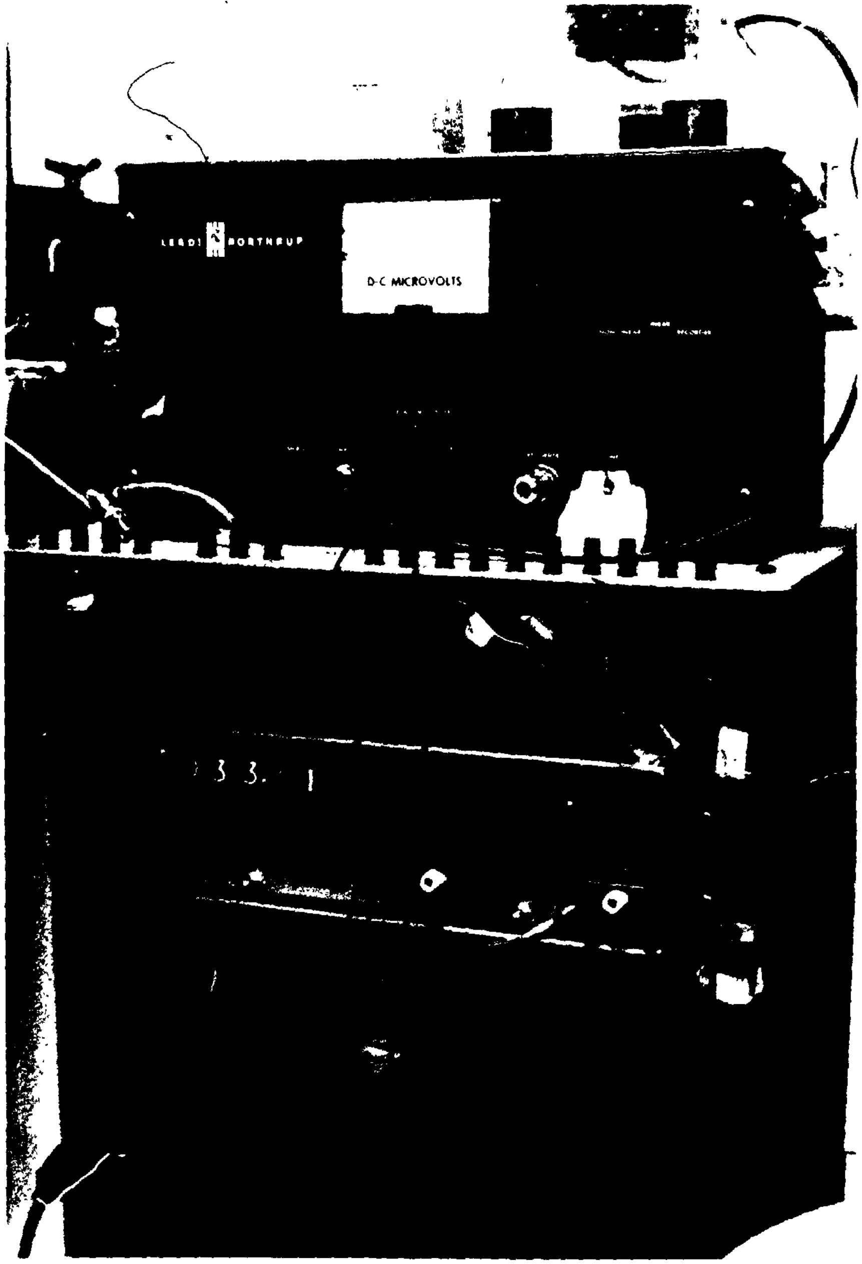


FIGURE 30 VIEW OF MICROVOLTMETER

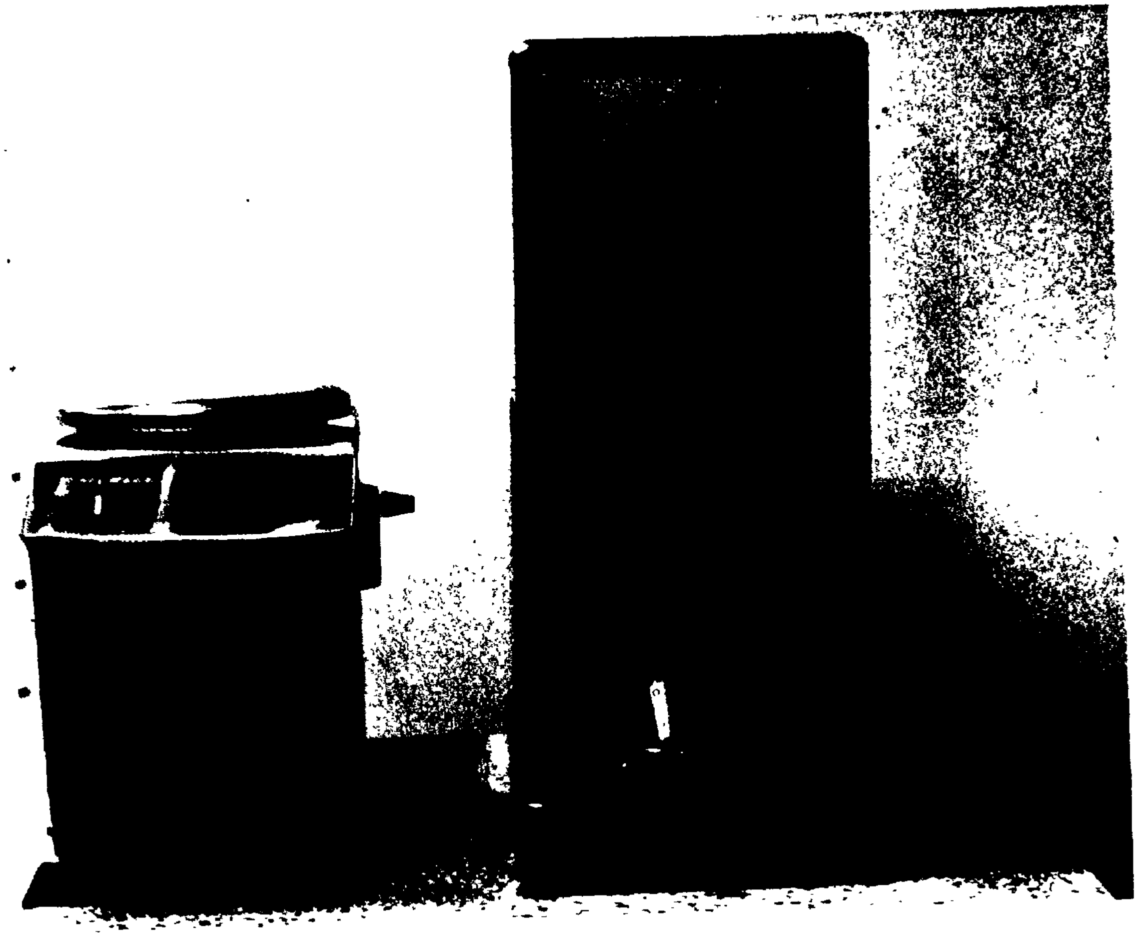


FIGURE 32 VIEW OF PRECISE METTLER ANALYTICAL BALANCE

APPENDIX B

DESIGN CALCULATIONS FOR THE SAMPLE AND PRESSURE VESSELS

The design calculations are based on maximum operating pressures and temperatures, equivalent to the critical point pressure and temperature for heavy water (approximately 3200 psi (221 bars) and 700°F. (371°C.)). The following equation may be employed to calculate the wall thickness of a thin walled ($t/R < 0.1$) spherical vessel (51):

$$t = \frac{PRF}{2\sigma} \qquad \text{- - - - - - - - - - - -} \qquad (B.1)$$

where t is the wall thickness,

P is the internal pressure,

R is the internal radius,

σ is the design stress,

F is the safety factor.

The design stress for type 304 stainless steel at these conditions is approximately 27,000 psi. If the internal radius of the sample vessel and the pressure vessel are 2.5 and 3.5 inches respectively, with safety factors of 1.7 and 1.8, the resulting wall thicknesses are as follows:

$t = 0.25$ inches (sample vessel)

$t = 0.375$ inches (pressure vessel)

Since the outer surface of the pressure vessel is grooved to accommodate the heating element, the wall thickness was increased to a half an inch.

APPENDIX C

TESTING OF RESISTANCE BRIDGE

An intercomparison of decade dial settings was made from 0.0001 to 61.0000 ohms, in the manner described by Mueller (58). This method involves balancing the resistance of an external decade resistance, with a combination of bridge decade settings. From 0.0050 to 0.1000 ohms a manganin slide wire served as a reference, and below 0.0050 ohms galvanometer deflections sufficed.

TABLE 24

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination A
61	60.	50.
	0.	10.
	.9	.9
	.10	.09
	.000	.009
	.0001	.0008
	61.0001	60.9998

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
51	50.	40.
	0.	10.
	.9	.9
	.09	.09
	.010	.010
	.0007	.0005
	51.0007	51.0005
41	40.	30.
	0.	10.
	.9	.9
	.10	.10
	.002	.002
	.0006	.0004
	41.0026	41.0024
31	30.	20.
	0.	10.
	.9	.9
	.10	.10
	.005	.005
	.0008	.0005
	31.0058	31.0055

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
21	20.	10.
	0.	10.
	.9	.9
	.10	.10
	.006	.006
	.0006	.0004
	21.0066	21.0064
11	10.	0.
	0.	10.
	.10	.10
	.01	.01
	.001	.001
	.0006	.0005
	10.1116	10.1115
10	10.	9.
	.0	1.0
	.01	.01
	.000	.000
	.0001	.0001
	10.0101	10.0101

TABLE 16 (CONTINUED

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination N
9	9.	8.
	.0	1.0
	.00	.00
	.009	.009
	.0005	.0005
	9.0095	9.0095
8	8.	7.
	.0	1.0
	.01	.01
	.001	.001
	.0004	.0005
	8.0114	8.0115
7	7.	6.
	.0	1.0
	.01	.01
	.001	.001
	.0003	.0003
	7.0113	7.0113

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
6	6.	5.
	.0	1.0
	.01	.01
	.002	.002
	.0003	.0002
	6.0123	6.0122
5	5.	4.
	.0	1.0
	.01	.01
	.007	.007
	.0006	.0007
	5.0176	5.0177
4	4.	3.
	.0	1.0
	.01	.01
	.000	.000
	.0005	.0006
	4.0105	4.0106

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
3	3.	2.
	.0	1.0
	.00	.00
	.009	.009
	.0006	.0007
	3.0096	3.0097
2	2.	1.
	.0	1.0
	.01	.01
	.000	.000
	.0004	.0005
	2.0104	2.0105
1	1.	0.
	.0	1.0
	.01	.01
	.000	.000
	.0009	.0010
	1.0109	1.0110

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
1	1.0	.9
	.00	.10
	.008	.008
	.0004	.0003
	1.0084	1.0083
.9	.9	.8
	.00	.10
	.009	.009
	.0008	.0007
	.9098	.9097
.8	.8	.7
	.00	.10
	.007	.007
	.0008	.0008
	.8078	.8078
.7	.7	.6
	.00	.10
	.008	.008
	.0002	.0002
	.7082	.7082

TABLE 16 (CONTINUED

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
.6	.6	.5
	.00	.10
	.008	.008
	.0002	.0001
	.6082	.6081
.5	.5	.4
	.00	.10
	.008	.008
	.0003	.0003
	.5083	.5083
.4	.4	.3
	.00	.10
	.009	.008
	.0000	.0009
	.4090	.4089
.3	.3	.2
	.00	.10
	.008	.008
	.0006	.0006
	.3086	.3086

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference External Decade	Combination A	Combination B
.2	.2	.1
	.00	.10
	.008	.008
	.0005	.0005
	.2085	.2085
.1	.1	.0
	.00	.10
	.008	.008
	.0006	.0006
	.1086	.1086
By slide wire		
.1	.10	.09
	.000	.010
	.0001	.0001
	.1001	.1001
.09	.09	.08
	.000	.010
	.0001	.0001
	.0901	.0901

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference By slide wire	Combination A	Combination B
.08	.08	.07
	.000	.010
	.0000	.0000
	.0800	.0800
.07	.07	.06
	.000	.010
	.0003	.0003
	.0703	.0703
.06	.06	.05
	.000	.010
	.0001	.0001
	.0601	.0601
.05	.05	.04
	.000	.010
	.0008	.0009
	.0508	.0509
.04	.04	.03
	.000	.010
	.0000	.0000
	.0400	.0400

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference By slide wire	Combination A	Combination B
.03	.03	.02
	.000	.010
	.0010	.0010
	.0310	.0310
.02	.02	.01
	.000	.010
	.0001	.0001
	.0201	.0201
.01	.01	.00
	.000	.010
	.0002	.0002
	.0102	.0102
.01	.010	.009
	.0000	.0010
	.0100	.0100
.009	.009	.008
	.0000	.0010
	.0090	.0090
.008	.008	.007
	.0000	.0010
	.0080	.0080

TABLE 16 (CONTINUED)

RESISTANCE BRIDGE TEST RESULTS (IN OHMS)

Reference By slide wire	Combination A	Combination B
.007	.007	.006
	.0000	.0010
	.0070	.0070
.006	.006	.005
	.0000	.0010
	.0060	.0060
.005	.005	.004
	.0000	.0010
	.0050	.0050
By galvanometer deflection		
.004	.004	.003
	.0000	.0010
	.0040	.0040
.003	.003	.002
	.0000	.0010
	.0030	.0030
.002	.002	.001
	.0000	.0010
	.0020	.0020
.001	.001	.000
	.0000	.0010
	.0010	.0010

To obtain readings at settings of .0010 ohms and smaller the galvanometer zero was shifted to an offset of 18.6 units. As the bridge setting was altered in increments or decrements of .0001 ohms the galvanometer increment or decrement should be approximately constant.

Bridge Decade Setting	Galvanometer Offset (Units)
.0010	5.8
.0009	7.0
.0008	8.3
.0007	9.6
.0006	10.9
.0005	12.3
.0004	13.7
.0003	14.9
.0002	16.2
.0001	17.4
.0000	18.6

APPENDIX D

CALIBRATION DETAILS

FOR THE DIFFERENTIAL PRESSURE TRANSDUCER

The differential pressure transducer output is displayed on a transducer indicator. This display is influenced by two adjustments on the indicator, which control zero and span. To provide a full scale deflection for a pressure differential of ± 100 psi, (6.89 bars), a span of 560 was necessary. The calibration system shown in Figure 34, Page 73, was assembled to establish the span setting, and to study the zero shift with line pressure. Table 13, Pages 149 and 150, show the resultant zero shift for line pressures, varying from 0 to 3000 psig, (206.84 bars).

This information is required to balance the pressure across the diaphragm, to the zero position which is applicable for the existing line pressures. No adjustment is applied to the zero setting of the transducer indicator which is established initially, with atmospheric pressure applied across the diaphragm.

TABLE 13

DIFFERENTIAL PRESSURE TRANSDUCER

ZERO SHIFT WITH LINE PRESSURE

Line Pressure		Zero Shift	
(psig.)	(bars)	(psi)	(bars x 10)
500	34.474	+ 0.9	0.62
600	41.368	1.1	0.76
700	48.263	1.3	0.90
800	55.158	1.5	1.03
900	62.053	1.6 - 1.7	1.14
1000	68.947	1.8	1.24
1100	75.842	2.0	1.38
1200	82.737	2.2	1.52
1300	89.632	2.4	1.65
1400	96.526	2.6	1.79
1500	103.42	2.7 - 2.8	1.90
1600	110.32	2.9 - 3.0	2.03
1700	117.21	3.1	2.14
1800	124.11	3.3	2.28
1900	131.00	3.4 - 3.5	2.38
2000	137.89	3.6 - 3.7	2.52
2100	144.79	3.8	2.62
2200	151.68	4.0	2.76
2300	158.58	4.2	2.90

TABLE 13 (CONTINUED)

Line Pressure		Zero Shift	
(psig.)	(bars)	(psi)	(bars x 10)
2400	165.47	4.3	2.96
2500	172.37	4.4 - 4.5	3.07
2600	179.26	4.6	3.17
2700	186.16	4.8	3.31
2800	193.05	4.9 - 5.0	3.41
2900	199.95	5.1	3.52
3000	206.84	5.2	3.59

Atmospheric pressure = 1.0003bars

Temperature = 22.5°C.

APPENDIX E

DETAILS OF SYSTEM VOLUME MEASUREMENT

With the charging and discharging system of Figure 31, Page 64, the system may be filled with ordinary water, and the amount required weighed. In this manner, volume measurements, of the sample vessel plus filling tube assembly, may be obtained. As a result of these measurements, a volume of 1049.3 cm^3 at 21 deg. C. was established. The volume may be determined, at elevated temperatures, with the aid of thermal expansion information of type 304 stainless steel. The thermal expansion data of Furman (49) appears in Table 25, Page 152 and the correlation by Keyes (7) follows:

$$V_T = V_O(1.0000 + 4.815 \times 10^{-5} T + 1.818 \times 10^{-8} T^2 - 1.335 \times 10^{-11} T^3) \quad \text{------ (E.1)}$$

Specific volumes, reported in this study, are based on the data of Furman (49).

To define the specific volume, during the studies of the superheated vapour region, the volume of liquid contained between the vapour liquid interface and the diaphragm must be known. Figure 22, Appendix A, shows the capillary tubing, tee, angle pattern needle valve, and the transducer which will contain liquid.

TABLE 25

COEFFICIENT OF LINEAR EXPANSION OF TYPE 304 STAINLESS STEEL BY FURMAN (49)

Temperature (Deg. C.)	-17.778	93.333	148.89	204.44	260.00	315.56	371.11
Mean Coefficient (10^6 per Deg. C.)	15.66	15.84	16.20	16.56	16.92	17.10	17.46

Reference Temperature 21.1 Deg. C.

Component	Volume
Capillary tubing	.000314 in.^{3}/in.
	.00203 cm^3/cm
Tee plus valve	.00217 in.^{3}
	.0355 cm^3
Transducer	.00463 in.^{3}
	.0759 cm^3

The length of capillary tubing, to be considered, is estimated by solving the heat transfer equation described in Chapter 5. The volume calculated is subtracted from the volume of the sample vessel system for that temperature. By using the compressed liquid tables for ordinary water, the mass of liquid contained in this volume at the given pressure may be approximated, and subtracted from the weight of liquid charged.

APPENDIX F

CORRELATION FOR THE SATURATED VAPOUR PRESSURE OF HEAVY WATER

In general a Chebyshev polynomial (61) may be represented as:

$$Y_m(x) = C_oT_o(x) + C_1T_1(x) + \ldots + C_mT_m(x) \quad \text{------ (F.1)}$$

where $T_o(x) = 1$ -------------- (F.2)

$T_1(x) = x$ -------------- (F.3)

$T_2(x) = 2x^2 - 1$ -------------- (F.4)

$T_3(x) = 4x^3 - 3x$ -------------- (F.5)

$T_4(x) = 8x^4 - 8x^2 + 1$ -------------- (F.6)

$T_5(x) = 16x^5 - 20x^3 + 5x$ -------------- (F.7)

$T_6(x) = 32x^6 - 48x^4 + 18x^2 - 1$ ------------ (F.8)

By the recurrence relation:

$$T_{r+1}(x) - 2xT(x) + T_{r-1}(x) = 0 \quad \text{---- (F.9)}$$

other polynomials may be obtained.

If the Chebyshev polynomial were fitted to n data points (x_1, y_1), (x_2, y_2) ... (x_n, y_n), the method of least squares may be employed to determine the coefficients C_o, C_1, C_2 ..C_m. Least squares criteria require the following expressions to be a minimum $S = \sum_{i=1}^{n} [y_1 - \sum_{j=o}^{m} C_jT_j(x_i)]^2$ -------- (F.10)

or $\frac{\partial S}{\partial C_i} = 0 \quad j = 0, 1 \ldots m$ ------------ (F.11) representing a system of simultaneous equations that may be described in matrix form.

$$\begin{bmatrix} \Sigma T_0^2(x_i) & \Sigma T_0(x_i)T_1(x_i) & \ldots \Sigma T_0(x_i)T_m(x_i) \\ \Sigma T_1(x_i)T_0(x_i) & \Sigma T_1^2(x_i) & \ldots \Sigma T_1(x_i)T_m(x_i) \\ \vdots & & \vdots \\ \Sigma T_m(x_i)T_0(x_i) & \Sigma T_m(x_i)T_1(x_i) & \ldots \Sigma T_m^2(x_i) \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ \vdots \\ c_m \end{bmatrix} = \begin{bmatrix} \Sigma y_i T_0(x_i) \\ \Sigma y_i T_1(x_i) \\ \vdots \\ \Sigma y_i T_m(x_i) \end{bmatrix}$$

The matrix expression [T] [C] = [E] must be solved to obtain [C].

Gibson et al (22) fit with great accuracy the Chebyshev series: $\ln \beta = \sum_{r=0}^{11} a_r T_r(x)$ - - - - - - - - - - - - - - (F.13)

where $x = \{2(\frac{1}{\theta} - 0.95)^{0.4} - A\}/B$ - - - - - - (F.14)

β = reduced pressure

θ = reduced temperature

and $A = 1.45220717$

$B = -0.84878953$

to available data for the saturated vapour pressure of ordinary water.

The matrix expression [T] [C] = [E] was evaluated in this study (40), using a similar Chebyshev series with A and B unchanged, and employing the data for the saturated vapour pressure of heavy water by Whalley (28). The coefficients were determined, by solving the twelve simultaneous equations, by the method of elimination embodied in IBM subroutine SIMQ. Computations in double precision were achieved on an IBM 360 computer.

APPENDIX G

EQUATION OF STATE FOR SUPERHEATED HEAVY WATER

Vukalovitch (27) developed an equation of state for an imperfect gas, based on association theory. This equation with two constants may be written as follows:-

$$(P + a/V^2)(V-b) = RT\{1 - \frac{A_1(T)}{V-b} - \frac{A_2(T)}{(V-b)^2}\} \quad ---- \text{(G.1)}$$

$$\text{where } A_1(T) = \frac{C_1 N e^{T_C T^{-1}}}{T^w} \quad ---------------- \text{(G.2)}$$

$$A_2(T) = \frac{C_2 N^2 e^{2T_C T^{-1}}}{T^x} - \frac{4C_1^2 N^2 e^{2T_C T^{-1}}}{T^y} \quad -------- \text{(G.3)}$$

$$a = \frac{27}{8} RT_C b \quad ---------------- \text{(G.4)}$$

$$b = \frac{RT_C}{8P_C} \quad ---------------- \text{(G.5)}$$

$$w = (3 + 2m_1)/2 \quad ------------------ \text{(G.6)}$$

$$x = (6 + 3m_2)/2 \quad ------------------ \text{(G.7)}$$

$$y = (6 + 4m_1)/2 \quad ------------------ \text{(G.8)}$$

m - 1, 2, 3 depending on the type of molecule

C_1, C_2, - calculated from the critical point information or from available P-v-T data.

m_1 and m_2 are related to molecular structure.

If m_1 and m_2 are arbitrarily set equal to two, and the equation is rearranged to be explicit in terms of pressure, the following form evolves:

$$P = \frac{1}{144v^2}\left[\frac{v^2RT}{v-b}\left\{1-\frac{A_1(T)}{v-b}-\frac{A_2(T)}{(v-b)^2}\right\}-a\right] \quad --- \quad (G.9)$$

where $A_1(T) = \frac{C_1N}{T^{3.5}}e^{T_cT^{-1}}$ ------------(G.10)

$$A_2(T) = \frac{N^2}{T^7}(C_2T - 4C_1^2)e^{2T_cT^{-1}} \quad ---- \quad (G.11)$$

$$a = \frac{27}{8}RT_cb \quad -------------- \quad (G.12)$$

$$b = \frac{RT_c}{8P_c} \quad ------------- \quad (G.13)$$

C_1 = $0.933747967 \times 10^{-17}$

C_2 = $0.333387092 \times 10^{-36}$

P = pressure, (bars x 14.5038)

P_c = critical pressure, (bars x 14.5038)

T = temperature, 1.8 (°C + 273.15)

T_c = critical temperature, 1.8 (°C + 273.15)

v = specific volume, (cm^3 mole^{-1} x 3.53146×10^{-5})

N = Avogardro's number

R = gas constant.

The critical values for D_2O, suggested by Whalley (28), were used to calculate a and b. Constants C_1 and C_2 were evaluated, by applying the method of least squares with respect to the experimental P-v-T data of Kirillin et al (4) shown in Table 1, Page 7.

In the range 315 to 405°C, and 71 to 147 bars, the maximum deviation of the calculated values of pressure from the experimental values were approximately one percent, and the average deviation less than one half of a percent.

APPENDIX H

EXPERIMENTAL DATA (UNPROCESSED)

Saturated Vapour Pressure of Heavy Water

1. P (deadweight gauge) = 239.90 psig.*
   P (barometer) = 29.32 in Hg.
   T (barometer) = 72°F.
   R (resistance thermometer) = 45.9253 ohms.
   T (Mueller bridge) = 22.8°C.

*All pressure readings were corrected for zero shift prior to recording.

2. P dwg. = 239.8 psig.
   P ba = 29.32 in Hg.
   T ba = 73°F.
   R = 45.9255 ohms
   Tb = 23.1°C.

3. P dwg. = 239.76
   P ba = 29.365 in Hg.
   T ba = 73°F.
   R = 45.9259 ohms
   Tb = 23.2 °C.

4. P dwg. = 576.2 psig.
   P ba = 29.35 in Hg.
   T ba = 72°F.
   R = 50.2108 ohms
   Tb = 22.6°C.

5. P dwg. = 576.0 psig.
   P ba = 29.36 in Hg.
   T ba = 72°F.
   R = 50.2097 ohms
   Tb = 22.6°C.

6. P dwg. = 575.95 psig.
P ba = 29.36 in Hg.
T ba = 72°F.
R = 50.2086 ohms
Tb = 22.7°C.

7. P dwg = 1022.0 psig
P ba = 29.28 in Hg.
T ba = 67°F.
R = 53.5334 ohms
Tb = 20.0°C.

8. P dwg. = 1022.0 psig.
P ba = 29.29 in Hg.
T ba = 67°F.
R = 53.5332 ohms
Tb = 20.2°C.

9. Pdwg. = 1022.0 psig.
P ba = 29.29 in Hg.
T ba = 68°F.
R = 53.5335 ohms
Tb = 20.3°C.

10. P dwg = 1153.55 Psig
P ba = 29.16 in Hg.
T ba = 75°F.
R = 54.2868 ohms
Tb = 23.9°C,

11. P dwg. = 1154.1 psig.
Pba = 29.15 in Hg.
T ba = 76°F.
R = 54.2896 ohms
Tb = 24.3°C.

12. P dwg = 1154.9 psig
P ba = 29.15 in Hg.
T ba = 76°F.
R = 54.2936 ohms
Tb = 24.6°C.

Saturated Vapour Pressure of Ordinary Water

1. Pdwg = 240.05 psig
   P ba = 29.25 in Hg.
   T ba = 72°F.
   R = 45.9227 ohms
   Tb = 22.5°C.

2. P dwg = 239.94 psig.
   P ba = 29.25 in Hg
   T ba = 72°F.
   R = 45.9221 ohms.
   Tb = 22.5°C.

3. P dwg = 239.89 psig
   P ba = 29.25 in Hg.
   T ba = 72°F.
   R = 45.9218 ohms
   Tb = 22.5°C.

4. P dwg = 576.57 psig
   Pba = 29.385 in Hg.
   T ba = 72°F.
   R = 50.2545 ohms
   Tb = 22.3°C.

5. P dwg = 576.97 psig.
   P ba = 29.365 in Hg.
   T ba = 72°F.
   R = 50.2571 ohms
   Tb = 22.6°C.

6. Pdwg = 577.47 psig.
   P ba = 29.345 in Hg.
   T ba = 71°F.
   R = 50.2602 ohms
   Tb = 22.5°C.

7. P dwg = 1011.0 psig
   P ba = 29.03 in Hg.
   T ba = 71°F.
   R = 53.5342 ohms
   Tb = 22.6°C.

8. P dwg = 1010.5 psig
   P ba = 29.03 in Hg.
   T ba = 71°F.
   R = 53.5368 ohms
   Tb = 22.6°C.

9. P dwg. = 1010.5 psig
   P ba = 29.04 in Hg.
   T ba = 71°F.
   R = 53.5385 ohms
   Tb = 22.6°C.

P-v-T Data for Superheated Heavy Water

1. P dwg = 1213.72 psig
   P ba = 29.33 in Hg.
   T ba = 72°F.
   R = 54.7329 ohms
   Tb = 22.8°C.

2. P dwg = 1213.83 psig
   P ba = 29.33 in Hg.
   T ba = 72°F.
   R = 54.7345 ohms
   Tb = 22.95°C.

The following data was required for application of equation 5.5:

T_O = 155°F.
T_L = 580°F.
L = 2.63 inches

Voltage to the capillary heater = 12.780 volts. In the data reduction of pressure employing equation 3.4 the pressure correction pc was .169 psi.

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