scatter and deviate considerably from more recent data on purer material. Ramsay and Travers determined the critical temperature by measuring the temperature at which the meniscus between the saturated vapor and liquid phase disappeared. However, they were unable to measure the critical pressure directly, and relied upon an extrapolation of their vapor pressure curve to obtain their reported critical pressure. Since the vapor pressure data of Ramsay and Travers are in rather poor agreement with more recent data, it is likely that their critical temperature and pressure are in error.

Crommelin's measurements of the critical pressure and temperature involved direct observation of the disappearance of the meniscus. Crommelin (*2*) stated that he did not attempt a very exact determination of these critical parameters since he suspected that the argon he used contained some impurity and that the constancy of temperature of the cryostat left something to be desired. The critical constants reported by Michels, Levelt, and De Graff (*7*) were not obtained by direct observation. Their critical temperature was obtained by extrapolation of T-P-density data involving the saturated vapor-liquid envelope. The critical pressure was obtained by extrapolation of their vapor pressure curve to this temperature.

The authors believe that the only direct visual observation of the critical point for argon which has been carefully made using highly pure argon is that reported in the present research, which gave T_c = 150.65 ± 0.02° K., P_c = 47.92 ± 0.05 atm. The earlier critical data of Crommelin agree very closely with these values. The pressure computed from Equation 1 for this critical temperature is 47.90 atm. Equation 3 of Van Itterbeek *et al.* (*10*) and the vapor pressure equation of Lurii and Rabinovich (*5*) yield 47.79 atm. and 47.95 atm., respectively, for T = 150.65° K.

ACKNOWLEDGMENT

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Heat Capacities of Sea Water Solutions at Salinities of 1 to 12% and Temperatures of 2° to 80° C.

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The heat capacity of sea water solutions to 12% salinity and up to 80° C. have been measured and correlated to within ±0.001 cal. per gram ° C. Tabular values are given for each 10° C. and 1% salinity. The sea water used is typical of ocean water throughout the world.

RELIABLE data on physical properties of sea water and its concentrates and dilutions are of immediate importance in desalination studies and in research investigations into the nature of sea water. Realistic predictions of equipment and energy requirements of conversion processes depend upon accurate information as to the variation of physical properties with temperature, composition, and pressure.

Heat capacity measurements have now been made at 1 atm. pressure for sea water solutions, ranging in concentration from ⅓ to 3½ times that of natural sea water—i.e., solutions of about 1 to 12% salinity. The temperature range covered is 2° to 80° C. The composition of sea water of 3.43% salinity is given by Severdrup, Johnson, and Fleming (*6*) in Table I. Previously, heat capacity data on sea water solutions have been available only up to 4% salinity and over a temperature range of −2° to +30° C.

Table I. Major Constituents of Sea Water from Reference (*6*) for Water of 3.43% Salinity (19 ‰ Chlorinity)[a]

Ion	Wt. %
Cl^-	1.898
SO_4^{-2}	0.265
HCO_3^-	0.014
Br^-	0.006
Na^-	1.056
Mg^{-2}	0.127
Ca^{-2}	0.040
K^-	0.038
Sr^{-2}	0.001
Total	3.445

[a] Typical La Jolla sea water ranges from 3.30 to 3.39% salinity. (1% Salinity = 1.0046% total dissolved solids.) Density = 1.0243 grams per ml. at 20° C.

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(2). Equations have been developed for heat capacities as a combined function of temperature and concentration. A nomograph has been constructed from which the heat capacities can be readily estimated.

EXPERIMENTAL

Apparatus and Procedure. The method for determining heat capacities at constant pressure of 1 atm. is that of classic calorimetry. A cross-sectional diagram of the calorimeter is shown in Figure 1. An accurately weighed liquid sample (about 4300 grams) is placed in a 5-liter spherical Dewar flask (1), the narrow neck of which is fitted with a Teflon stopper (2) equipped with holes for stirrer, heater, and two thermometers. The jacket (3) is a 20-liter pressure cooker adapted with inlet and outlet for circulation of water from a constant temperature bath (4). The cover (5) of the cooker supports a pair of concentric, 2-foot glass columns (6), between which the water is circulated to maintain a constant temperature above the calorimeter. The bath temperature is controlled by a Hallikainen Thermomtrol unit comprising a sensing probe and a regulator with a controlling sensitivity of 0.001° C. The bath temperature is adjusted to about 1½° C. above the temperature within the calorimeter. The system is allowed to stabilize thermally. This requires about two to three hours after assembly of the apparatus.

The heating cycle consists of introducing electrical energy by means of a 1000-watt heater enclosed in a Vycor sheath (7). The heating time, calculated to yield a temperature rise of about 3° C., is preset with an automatic timer. The energy introduced in this way is recorded as watt-hour meter revolutions (about 25 revolutions) to the nearest 0.002 revolution by a Sangamo J-5 rotating standard watt-hour meter. This was checked against a standard meter of the San Diego Gas & Electric Co., San Diego, Calif., and had a maximum deviation of 0.03%. Firing (heating) time is also recorded, although the time does not enter into the calculations. An auxiliary heater is introduced into the circuit ahead of the main heater to absorb the initial power surge when the switch is first opened to the line voltage, which is controlled by a Sola voltage regulator.

Thermal equilibrium is reached in 20 to 30 minutes after firing, after which the temperature change closely approximates a linear function with time. Temperature readings are obtained with a combination of a platinum resistance thermometer (8), which has been calibrated and certified by The Leeds & Northrup Co., a Mueller bridge, and a Leeds & Northrup null-detector. By interpolating the null-detector needle deflection, resistances can be estimated to within $\pm 1 \times 10^{-5}$ ohm, corresponding to about $\pm 1 \times 10^{-4}$ ° C. A calibrated mercury thermometer (9) serves as a secondary check on temperature whenever quick, approximate readings are desired. The stirrer (10) is operated at 300 r.p.m., a rate determined to yield adequate stirring without excessive heat input.

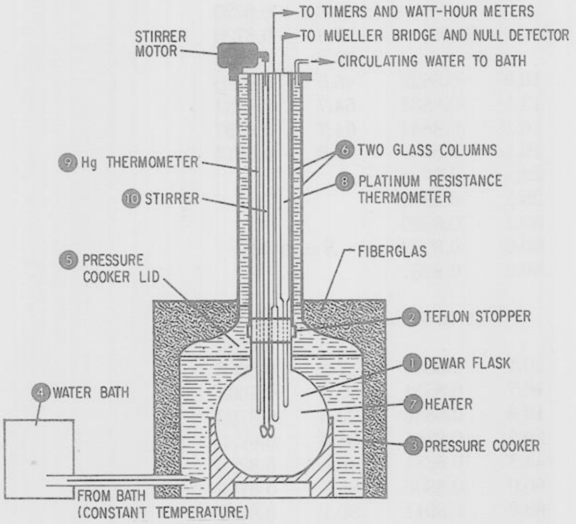

Figure 1. Cross section of calorimeter

Because the temperature rise is not instantaneous after firing, it is necessary to obtain T_0, the temperature at a hypothetical zero time t_0, by an indirect method. The authors have used the extrapolation method described by Challoner, Gundry, and Meetham (*1*). Using a time-temperature plot as shown in Figure 2, a time, t_0, is located for which area 1 is equal to area 2. Temperatures T_1 and T_2 are those temperatures reached by extrapolating the lines before and after firing to time t_0. The required temperature rise, ΔT, is the difference between these two extrapolated temperatures. For the authors' experiments, t_0 is of the order of 1¾ to 2 minutes.

The heat capacity of the sample is then calculated from the equation:

$$C_p \text{ (sample), cal./g. °C.} = \frac{\dfrac{\text{(energy input, cal.)}}{\Delta T} - wC_p}{\text{grams of sample}}$$

Calories are defined thermochemical calories equal to 4.1840 absolute joules; T is in ° C., and wC_p is the "effective heat capacity" of the calorimeter determined from measure-

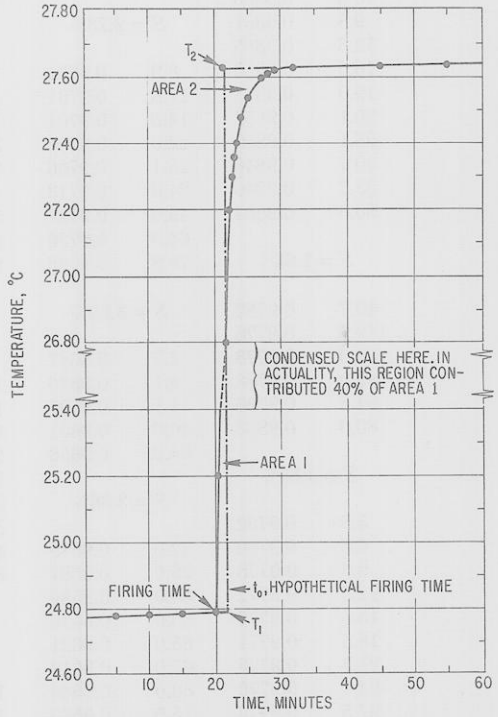

Figure 2. Typical method of determining t_0 by extrapolation of time-temperature curves

Table II. Estimates of Experimental Errors

Possible Error	Magnitude	Effect on C_p, %
Calibration uncertainty	2 cal. maximum	0.05[a]
Watt-hour meter reproducibility		0.03[a]
Extrapolation of T_1, T_2	0.0002°/reading	0.02
Reading T_1, T_2	0.0001°/reading	0.02
Weight of water	0.2 gram/reading	0.02
	Total	0.14%

[a] Maximum.

Table III. Sea Water Solutions Used in Heat Capacity Measurements

Sample	Salinity[a], Wt. %
La Jolla sea water	
Natural concentration	3.34 – 3.36
Dilution to ⅓ natural	1.12
Dilution to ½ natural	1.65, 1.69, 1.70
Dilution to ⅔ natural	2.23
Concentration to 2 times natural	6.67
Concentration to 2½ times natural	8.32
Concentration to 3 times natural	10.10
Concentration to 3½ times natural	11.40, 11.74
Equatorial Pacific sea water	3.40
Atlantic sea water	3.36

[a] Salinity as defined in text.

ments using pure water. Accurate values are known for pure water from the work of Osborne, Stimson, and Ginnings (*3*).

Systematic errors in the measurements are avoided by the calibration of the system. Those errors which remain, and an estimate of their magnitude, are listed in Table II. An accuracy of about 1 part per 1000 may be expected.

Sea Water. With two exceptions, all samples of sea water used in this study have been obtained directly from the end of the Scripps Institution of Oceanography pier at La Jolla, Calif., at a depth of 1 to 10 feet from the bottom of the ocean. Sea water here is relatively free from contaminants and maintains a fairly constant salinity. Salinity of this sea water varies from about 3.30 to 3.39% over a typical 1-year period (*7*). Other oceanic waters in the

Table IV. Experimental Values of Heat Capacities of Sea Water Solutions

T, °C.	C_p^a	T, °C.	C_p^a	T, °C.	C_p^a	T, °C.	C_p^a	T, °C.	C_p^a
$S = 1.12\%$		$S = 1.70\%$ cont.		$S = 3.36\%$ cont.		$S = 5.01\%$ cont.		$S = 10.10\%$ cont.	
9.0	0.9866	11.2	0.9771	65.0	0.9613	64.9	0.9437	80.0	0.8929
12.3	0.9854	14.5	0.9763	65.0	0.9620	79.7	0.9453	2.1	0.8777
15.3	0.9854	17.6	0.9762	80.0	0.9643			5.3	0.8793
18.4	0.9853	20.7	0.9766	16.0	0.9568	$S = 6.67\%$		8.1	0.8808
35.1	0.9848	32.5	0.9772	19.0	0.9574			11.3	0.8814
49.9	0.9857	44.4	0.9772	55.0	0.9611	8.7	0.9156	14.3	0.8827
60.0	0.9864	59.9	0.9785	58.0	0.9613	12.2	0.9158	17.4	0.8835
75.5	0.9896	70.0	0.9805	65.0	0.9621	18.9	0.9176	20.4	0.8851
78.6	0.9893			75.0	0.9634	29.7	0.9203	22.4	0.8851
9.8	0.9861	$S = 2.23\%$		3.5	0.9553	40.1	0.9227	25.5	0.8853
12.8	0.9855			6.5	0.9558	49.9	0.9240	28.1	0.8867
16.0	0.9850	8.9	0.9701	11.1	0.9556	60.3	0.9264	31.0	0.8872
19.0	0.9848	11.8	0.9701	14.2	0.9559	69.4	0.9266	34.1	0.8890
25.1	0.9852	14.8	0.9701	17.4	0.9562	80.4	0.9279	40.1	0.8893
28.1	0.9850	22.0	0.9703	20.4	0.9570	15.0	0.9167	52.0	0.8907
30.7	0.9846	25.1	0.9706	30.2	0.9579	18.5	0.9192	60.0	0.8913
33.7	0.9846	34.8	0.9713	40.1	0.9590	34.5	0.9227	70.0	0.8921
50.0	0.9854	49.9	0.9727	50.0	0.9597	36.0	0.9226	10.0	0.8814
		64.9	0.9736	64.9	0.9614	55.0	0.9254	24.9	0.8867
$S = 1.65\%$		79.8	0.9766	80.1	0.9635	68.0	0.9267	50.7	0.8891
						71.0	0.9272	80.0	0.8924
10.7	0.9782	$S = 3.00\%$		$S = 3.36\%$[b]				12.8	0.8833
19.8	0.9776					$S = 8.32\%$		79.0	0.8955
35.0	0.9778	2.7	0.9587	7.9	0.9560				
49.9	0.9788	8.1	0.9586	10.8	0.9559	8.0	0.8971	$S = 11.40\%$	
64.5	0.9796	11.1	0.9591	11.0	0.9556	11.0	0.8984		
80.0	0.9833	40.0	0.9621	17.0	0.9567	14.0	0.8997	2.1	0.8649
		64.9	0.9656	20.0	0.9566	20.1	0.9015	5.3	0.8666
$S = 1.69\%$				21.1	0.9575	34.9	0.9053	8.5	0.8684
		$S = 3.36\%$		26.2	0.9571	48.9	0.9080	11.5	0.8694
3.3	0.9782			35.7	0.9588	64.7	0.9099	14.7	0.8701
6.3	0.9780	22.0	0.9579	45.5	0.9599	79.8	0.9123	17.8	0.8716
9.3	0.9778	25.0	0.9587	65.7	0.9627			20.8	0.8720
12.5	0.9772	35.0	0.9586			$S = 9.96\%$		23.9	0.8730
15.5	0.9772	55.0	0.9616	$S = 3.40\%$[c]				29.5	0.8749
18.5	0.9771	65.0	0.9621			10.0	0.8820	45.5	0.8780
21.5	0.9773	65.0	0.9619	7.6	0.9536	13.1	0.8833	54.7	0.8781
24.4	0.9770	80.0	0.9646	10.7	0.9546	16.1	0.8844	64.7	0.8797
27.5	0.9773	15.5	0.9560	19.4	0.9551	19.1	0.8850	79.8	0.8813
29.9	0.9775	16.9	0.9562	34.3	0.9573	22.1	0.8858		
33.0	0.9778	19.9	0.9574	50.1	0.9586	25.3	0.8868		
40.1	0.9776	59.0	0.9613	61.8	0.9610	39.1	0.8896		
60.1	0.9797	55.0	0.9601	70.2	0.9616	60.0	0.8923	$S = 11.74\%$	
13.1	0.9776	75.0	0.9634	79.1	0.9641	80.0	0.8957		
16.3	0.9768	80.0	0.9643						
19.3	0.9770	80.0	0.9636			$S = 10.10\%$		11.8	0.8658
22.2	0.9767	22.5	0.9568	$S = 5.01\%$				14.8	0.8677
40.1	0.9779	23.5	0.9578			10.1	0.8801	17.8	0.8688
55.1	0.9790	50.0	0.9603	8.9	0.9345	16.7	0.8831	20.9	0.8695
80.0	0.9828	70.0	0.9623	11.9	0.9350	19.8	0.8836	23.8	0.8703
		25.0	0.9567	15.2	0.9355	29.2	0.8864	35.8	0.8735
$S = 1.70\%$		35.0	0.9582	18.2	0.9368	44.8	0.8881	49.8	0.8755
		45.0	0.9578	33.5	0.9398	60.0	0.8905	65.0	0.8762
8.1	0.9772	47.0	0.9575	49.6	0.9418	69.8	0.8911	80.1	0.8788

[a] Calories per gram °C. [b] Atlantic (Wrightsville Beach, N. C.) sea water. [c] Equatorial Pacific sea water.

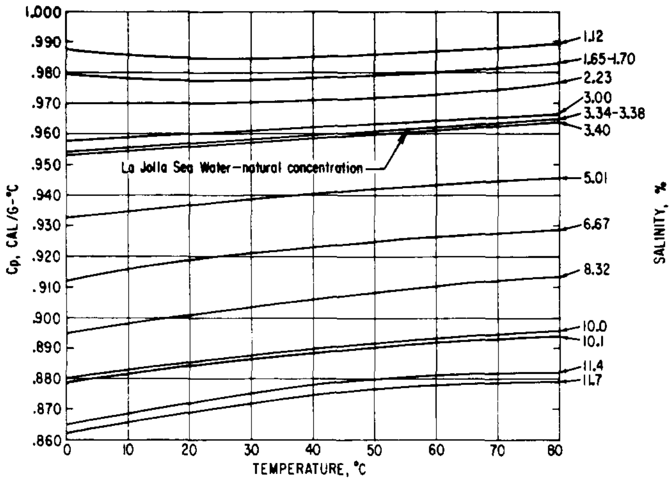

Figure 3. Heat capacity of sea water solutions at salinities of 1.12 to 11.7%

Table V. Equations of Heat Capacity as a Combined Function of Temperature and Salinity

No.	Equation	Deviation from Exptl. Values at 90% Confidence Limit
1	$C_p = 0.9948 - 0.011412S + [(0.42997 + 0.15192S) \times 10^{-4}T]^a$	> 0.004
2	$C_p = 1.0007 - 0.014880S + (2.8618 \times 10^{-4}S^2) + [(0.42997 + 0.15192S) \times 10^{-4}T]$	0.003
3	$C_p = 1.0007 - 0.014880S + (2.8618 \times 10^{-4}S^2) - [(0.14054 - 0.48497S + 0.027454S^2) \times 10^{-4}T]$	0.003
4	$C_p = 1.0049 - 0.016210S + (3.5261 \times 10^{-4}S^2) - [(3.2506 - 1.4795S + 0.07765S^2) \times 10^{-4}T] +$ $[(3.8013 - 1.2084S + 0.06121S^2) \times 10^{-6}T^2]$	0.001

[a] C_p = cal./gram ° C.; S = per cent salinity; T = ° C.

Table VI. Smoothed Values of Heat Capacities of Sea Water Solutions[a]

	Salinity, Wt. %												
T, ° C.	0	1	2	3	4	5	6	7	8	9	10	11	12
0	1.005[b]	0.989	0.974	0.959	0.946	0.933	0.920	0.909	0.898	0.888	0.878	0.869	0.861
10	1.002	0.987	0.973	0.960	0.947	0.935	0.923	0.912	0.901	0.891	0.882	0.873	0.864
20	1.000	0.986	0.973	0.961	0.949	0.937	0.926	0.915	0.904	0.894	0.885	0.876	0.867
30	0.999	0.986	0.974	0.962	0.950	0.939	0.928	0.917	0.907	0.897	0.887	0.878	0.869
40	0.998	0.986	0.974	0.963	0.951	0.940	0.930	0.919	0.909	0.899	0.890	0.880	0.871
50	0.998	0.986	0.975	0.964	0.953	0.942	0.931	0.921	0.911	0.901	0.892	0.882	0.873
60	0.999	0.988	0.976	0.965	0.954	0.943	0.933	0.923	0.912	0.903	0.893	0.884	0.874
70	1.001	0.989	0.978	0.966	0.955	0.945	0.934	0.924	0.914	0.904	0.894	0.884	0.875
80	1.003	0.991	0.980	0.968	0.957	0.946	0.935	0.925	0.914	0.904	0.894	0.885	0.876

[a] Based on Equation 4 of Table V. [b] All values are within 0.001 of the experimental value except pure water at 0° C., for which the smoothed value is 0.003 cal./gram ° C. lower than that shown in (*3*).

vicinity have approximately the same salinities (*4*, *5*). The two additional samples were obtained by a Scripps research vessel from the equatorial Pacific and by the Wrightsville Beach, N.C., laboratory of the Office of Saline Water, U.S. Dept. of the Interior, from the Atlantic Ocean. Heat capacities of these samples agreed well within experimental error with La Jolla sea water solutions of the same salinity.

For this study, sea water at its normal concentration was treated by one of two methods: filtering through coarse filter paper, or filtering through diatomaceous earth, acidifying to a pH of about 4.5 with concentrated sulfuric acid, and then degassing. This second procedure is typical of that followed in evaporation desalination units, where acidification near a pH of about 4.5 assures that $CaCO_3$ or $Mg(OH)_2$ precipitation will not occur even in sea water concentrated to more than three times its normal concentration.

Sea water concentrates are obtained by a careful evaporation of water until the desired concentrate is reached, as calculated by weight loss. Dilutions of sea water were prepared by addition of the appropriate amounts of distilled water. Salinities for the experimental samples are shown in Table III.

"Salinity" is a defined term accepted throughout all fields of oceanography. For sea water, salinity is lower than the total dissolved solids by about 4 parts per 1000. The definition of salinity was established by an International Commission for the Production of Standard Sea Water in 1902 (*6*). Briefly, salinity is determined by titrating halides with a standard solution of silver nitrate, which yields a value for "chlorinity." This in turn is converted to salinity by the relationship:

$$S = 0.03 + 1.805\ Cl$$

where salinity, S, and chlorinity, Cl, are in parts per thousand (‰). Weight per cent salinity is 0.1 times this value.

RESULTS

The experimental heat capacities as a function of temperature are presented for all salinities in Table IV. The least squares quadratic curves fitted to the data are shown in Figure 3. For all cases, these curves show a standard deviation from the experimental points of well below 0.001 cal. per gram per ° C.

From these data, equations have been derived for heat capacities of sea water solutions as a combined function of temperature and salinity. Equations of varying complexity, together with an indication of their accuracy, are presented in Table V.

A nomograph has been constructed and is available from the authors.

Using the nine-term equation shown in Table V, the smoothed values for heat capacities of sea water solutions as a function of temperature and concentration are presented in Table VI. Agreement with experimental values is within 0.001 cal. per gram per ° C.

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Vapor Pressures of Liquid Nitrogen Between the Triple and Critical Points

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Vapor pressure measurements available in the literature for liquid nitrogen between the triple point (T_t = 63.14° K., P_t = 94.01 mm.) and the critical point (T_c = 126.15° K., P_c = 33.52 atm.) have been comprehensively analyzed and used to evaluate the constants of the Frost-Kalkwarf equation. This equation for nitrogen was as follows:

$$\log P = 13.84475 - \frac{401.055}{T} - 3.06762 \log T + 0.11443\, P/T^2$$

where P is the vapor pressure in millimeters of Hg and T is the corresponding temperature in degrees Kelvin. This equation reproduced 180 experimental vapor pressure measurements over the complete liquid range with an over-all average deviation of 0.82%. This relationship has also been used to evaluate vapor pressures at convenient temperatures ranging from the triple point to the critical point of nitrogen.

A NUMBER of vapor pressure measurements of nitrogen have been presented in the literature since the turn of the century and extend over the range included between the triple and the critical points. The early vapor pressure measurements of Olzewski (*17*) in 1884 and those of Wroblewski (*24*) in 1886 represent an initial attempt to establish this property for liquid nitrogen at a time when cryogenic experimental techniques were not as well advanced to permit the establishment of reliable values. Despite these limitations, Olzewski (*17*) and Wroblewski (24) reported critical values for nitrogen. In addition, Sarrau (*20*) in 1882, and Dewar (*6*) in 1884 also presented critical values for this substance. The critical values reported by these investigators are as follows:

Year	t_c, ° C.	P_c, Atm.	
1882	−123.8	42.1	Sarrau (*20*)
1884	−146.0	35.0	Olzewski (*17*)
1884	−146.0	35.0	Dewar (*6*)
1885	−146.0	33.0	Wroblewski (*24*)

Although improved vapor pressure determinations continued to be made (*1, 8, 21*), it was not until 1914 when Kamerlingh Onnes, Dorsman, and Holst (*14*) carried out exacting measurements for nitrogen which included the critical point. They reported t_c = −147.13° C. or T_c = 125.96° K. based on a temperature scale of 273.09° K. and a critical pressure, P_c = 33.49 atm. Their critical temperature, adjusted to the present temperature scale of 273.16° K. based on the triple point of water, becomes T_c = 126.03° K. In 1915 Cardoso (*3*) reported for nitrogen t_c = −144.7° C. and P_c = 33.65 atm. Further attempts to establish these critical constants were not made until 1951 when White, Friedman, and Johnston (*23*) reported the results of their studies as T_c = 126.26±0.04° K. and P_c = 33.54±0.02 atm. The critical values reported recently by White, Friedman, and Johnston (*23*) and those reported earlier by Kamerlingh Onnes, Dorsman, and Holst (*14*) are in good agreement, and consequently, their average values, T_c = 126.15° K. and P_c = 33.52 atm., have been accepted in this study to represent the critical values of nitrogen. These values, along with the critical density, d_c = 0.3110 grams per cc. reported by Mathias, Kamerlingh Onnes, and Crommelin (*16*) produce for nitrogen a critical compressibility factor, $z_c = 0.2918$.