($P$ in atm., $t$ in ° C.). The standard deviation for an individual measurement is 0.06 atm. calculated from values extended one figure beyond those tabulated in Table II.

The deviation of the water vapor pressures determined in the calibration from the values found in Dorsey (*2*) for the corresponding temperatures introduces a systematic uncertainty into the nitromethane vapor pressure of about 0.06 atm. at 100° and 0.5 atm. at 200° C. apart from the much smaller random uncertainty represented by the standard deviation of 0.06 atm. However, the agreement between the vapor pressures determined and those extrapolated from the work of McCullough *et al.* is considerably closer.

At 131.8° C., the pressure calculated from Equation 3 is 0.023 atm. greater than that calculated from the Antoine equation of McCullough *et al.* (*4*). Extrapolation of their Cox equation gives pressures slightly greater (0.13 atm. at 187° C.) than those calculated from Equation 3. Toops (*5*) also gives constants for the Antoine equation, which are not very different from those given by McCullough *et al.*

The change in density with composition can be estimated from the differences between the densities of samples I and II, as represented by Equations 1 and 2. Since the difference in purity between samples I and II is about 3 mole %, the authors would expect the density measured by Toops to be about 0.1% higher than the density of sample I.

Detonation and combustion experiments, which require relatively large quantities of nitromethane, are usually made with samples having considerable amounts of impurities. An estimate of the density of a particular sample can be made by assuming the specific volumes of its components additive in proportion to the weight fraction of each component. The additivity method is only approximate and does not completely account for the difference between samples I and II but is helpful in indicating the trend. When the density and thermal expansion are involved in the analysis of detonation and combustion experiments, it seems worthwhile to make some allowance for the effect of impurities if the densities of these impurities are known.

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# The Critical Temperature, Critical Pressure, and Vapor Pressure of Argon

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**The vapor pressure of argon has been measured in a glass equilibrium cell over the range 114.40° to 150.65° K. The critical temperature and critical pressure, determined by observing the formation and the disappearance of the meniscus, were 150.65 ± 0.02° K. and 47.92 ± 0.05 atm., respectively. The results obtained have been compared with published data, and an empirical equation has been developed to represent what are believed to be the most reliable vapor pressure data over the range 90° to 150.65° K.**

ALTHOUGH several investigations of the vapor pressure and critical constants of argon have been made, the reported data are in considerable disagreement. In fact, the reported critical temperatures differ by as much as 5° K. and the critical pressures by several atmospheres. Therefore, as part of an extensive study of vapor-liquid equilibrium in the helium-argon system (*6*), the critical temperature, critical pressure, and the vapor pressure of argon were determined. The results are compared with corresponding data published in the literature. A correlation equation which describes the vapor pressure of argon from 90° K. to the critical point is given.

## EXPERIMENTAL

The cryostat and glass equilibrium cell used are shown in Figure 1. The equilibrium cell (capacity, 8 cc.) was very similar to one used by Eakin, Ellington, and Gami (*4*) for dew-point and bubble-point measurements except that no mechanism for stirring was provided. A constant temperature was maintained by removing heat from the propane cryostat through the copper cooling tube, T, which was cooled at its upper end by liquid nitrogen boiling at atmospheric pressure. The vapor pressure cell, G, and the power end of the cooling tube were immersed in liquid propane, which was rapidly circulated through the cooling tube and around the cell by the propellers, S3, located inside the cooling tube.

The temperature of the equilibrium cell was measured using a copper-constantan (Driver-Harris Advance brand) thermocouple, A, located on the outside wall of the cell as shown in Figure 1. E.m.f. measurements were made using a Leeds and Northrup Type K-3 potentiometer and Type 9834 DC electronic null detector. Readings could be made to ±0.1 $\mu$v. corresponding to ±0.005°. The thermocouple was calibrated in place against a platinum

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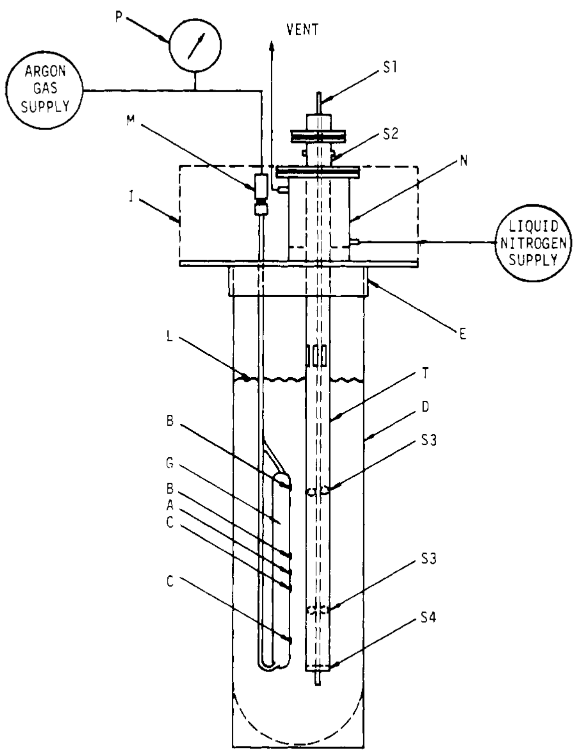

| | | | |
|---|---|---|---|
| A | THERMOCOUPLE | M | METAL TO GLASS TUBING CONNECTOR (STAINLESS STEEL) |
| B-B | TEMPERATURE DIFFERENCE THERMOCOUPLE | N | NITROGEN BOILER (MONEL) |
| C-C | TEMPERATURE DIFFERENCE THERMOCOUPLE | P | PRESSURE GAUGE |
| D | CRYOSTAT DEWAR (GLASS) | S1 | STIRRER SHAFT (STAINLESS STEEL) |
| E | DEWAR SEAL SLEEVE (BRASS) | S2 | SHAFT SEAL AND BEARING ASSEMBLY (BRASS) |
| G | EQUILIBRIUM CELL (GLASS) | S3 | PROPELLOR (STAINLESS STEEL) |
| I | INSULATION (POLYURETHANE FOAM) | S4 | SLEEVE BEARING (BRASS) |
| L | LIQUID PROPANE | T | COOLING TUBE (COPPER) |

Figure 1. The cryostat and equilibrium cell

Table I. Experimental Vapor Pressure of Liquid Argon

| Observed[a] Temperature, ° K. | Observed[a] Pressure, Atm. |
|---|---|
| 142.16 | 34.28 |
| 142.28 | 34.45 |
| 142.16 | 34.25 |
| 150.09 | 46.88 |
| 150.11 | 46.92 |
| 150.17 | 47.02 |
| 150.20 | 47.06 |
| 150.27 | 47.22 |
| 150.31 | 47.26 |
| 150.65 ± 0.02 crit. temp.[b] | 47.92 ± 0.05 crit. press.[b] |
| 150.65 ± 0.02 crit. temp.[b] | 47.92 ± 0.05 crit. press.[b] |
| 150.63 | 47.89 |
| 115.50 | 9.31 |
| 115.44 | 9.30 |
| 115.46 | 9.30 |
| 114.89 | 8.97 |
| 114.40 | 8.72 |
| 115.07 | 9.07 |
| 115.55 | 9.32 |
| 125.96 | 16.49 |
| 125.11 | 15.77 |

[a] Chronological order over a period of six days. [b] Each observation is the average of two independent measurements using a single charge of argon.

resistance thermometer which had been calibrated previously by the U.S. National Bureau of Standards on the International Temperature Scale. Conversion to the International Practical Kelvin Scale was made assuming the ice point to be 273.15° K. A statistical analysis of the calibration data indicated that the accuracy of the measurements was at least as good as ±0.02° K.

The equilibrium cell also was provided with two single-junction copper-constantan difference thermocouples, B-B and C-C, which permitted examination of temperature gradients along the cell. Several difference thermocouples were calibrated after installation in the cryostat. The ones selected for use produced less than 0.1 $\mu$v. when the two junctions were subjected to the same temperature. During vapor pressure measurements no temperature gradients larger than about ±0.005° K. were noted.

Equilibrium cell pressure was measured with an 8-inch diameter Martin Decker 1500-p.s.i.g. precision test gage which was stated by the manufacturer to be accurate to within 0.15 atm. The gage was calibrated against a dead-weight gage throughout the full range of pressures covered in the present studies and found to have an accuracy of ±0.05 atm.

The argon gas used was certified by the supplier to have a purity of 99.999% except for the presence of some water. The gas was dried by passing through a bed of Linde 5-A molecular sieve before use in the measurements. The gas was analyzed by means of a gas chromatograph with a Linde 5-A molecular sieve column at room temperature using helium as the carrier gas. No impurities were detected. A complete description of the equipment and experimental procedure can be found elsewhere (*6*).

## EXPERIMENTAL RESULTS

Twenty determinations of the vapor pressure were made with the results shown in Table I. The temperature and corresponding pressure were measured while visual observation of the argon showed that both liquid and vapor were present in the cell. The quantity of liquid in the cell was varied so that these data actually represent conditions of dew-point, bubble-point, and a variety of liquid levels in the cell. Observations of pressure and temperature were made only after the temperature of the cell had remained constant to within ±0.005° for at least ten minutes.

The critical point was visually observed on two occasions, resulting in a critical temperature of 150.65 ± 0.02° K. and critical pressure of 47.92 ± 0.05 atm. These observations were made by filling the cell approximately one-half full of liquid argon at approximately 150° K. The temperature was increased slowly until the meniscus disappeared. This disappearance of the meniscus upon increasing the temperature was not sharp, since diffusion from the bottom of the cell (the dense phase) into the upper end of the cell was relatively slow. This resulted in persistent density gradients which dissipated slowly.

However, in every case there was a sharp and distinct indication of the critical point upon slowly lowering the cell temperature from above the critical temperature at the rate of less than 0.01° per minute. A period of critical opalescence, which had a faint purple cast, occurred and lasted for approximately 30 seconds. This opalescence was dissipated throughout the cell by the formation of many droplets of liquid which immediately fell to the bottom forming two phases. The temperature and pressure were noted just as drop formation began.

On each of the two occasions the cell was charged with argon and the temperature was varied such that the critical point was achieved four times, twice during increasing temperature and twice during decreasing temperature. The temperatures and pressures were observed only when the temperature was decreasing and were in every case identical to within 0.005° K. and 0.01 atm.

## COMPARISON WITH PUBLISHED RESULTS

**Vapor Pressure.** Measurements of the vapor pressure of argon above the normal boiling point have been reported by Olszewski (*8*), Ramsay and Travers (*9*), Crommelin (*2*, *3*), Clark *et al.* (*1*), Michels, Levelt, and De Graff (*7*), Van Itterbeek, Verbeke, and Staes (*11*), and Van Itterbeek *et al.* (*10*). Consideration of these data shows considerable disagreement. However, the earlier data of Clark *et al.* (*1*) (the Amsterdam data), the later data of Van Itterbeek and coworkers (*10*), and the data of this research (Table I) appeared to agree within the stated experimental error of these investigations. Therefore, these three sets of vapor pressure data were fitted by a least squares technique to an equation having the form used by Van Itterbeek *et al.* (*10*) (their Equation 3)

$$\log_{10} P = A/T + B + CT + DT^2 + ET^3 + FT^4 + GT^5 \qquad (1)$$

where $P$ represents pressure in atmospheres and $T$ represents temperature in degrees Kelvin.

The resulting values of the constants are as follows:

$A = -2725.8945$
$B = 125.94099$
$C = -2.5880991$
$D = 2.9104260 \times 10^{-2}$
$E = -1.8288605 \times 10^{-4}$
$F = 6.0839925 \times 10^{-7}$
$G = -8.3610062 \times 10^{-10}$

The pressure differences between vapor pressures computed from Equation 1 and the various sets of experimental data are given in Figure 2. Also shown are lines which correspond to the pressure differences which would arise from errors in temperature of 0.02° and 0.05°. The vapor pressure data of Olszewski (*8*) and of Ramsay and Travers (*9*) are not shown, as they lie outside the scale of the graph in both the negative and positive directions.

Consideration of Figure 2 shows that, except for the neighborhood of the normal boiling point, Equation 1 fits the experimental data of Clark *et al.* (*1*), Van Itterbeek *et al.* (*10*), and the present work within the estimated experimental error of these investigations. A careful study of the temperature scales used in these three investigations suggests that the scales probably do not deviate from one another by more than 0.02° K. over the range 90° to 150° K. Over this range, both Equation 1 of the present paper and Equation 3 of Van Itterbeek *et al.* (*10*), which was fitted by them to their own experimental data, agree to within 0.005 atm. However, these equations both predict a normal boiling point for argon of 87.19° K., whereas the true value probably lies nearer to 87.25° to 87.29° K. (*1*).

Lurii and Rabinovich (*5*) have fitted an equation of the form of Equation 1 (with $F, G = 0$) to the experimental data of Clark *et al.* (*1*), Michels, Levelt, and De Graff (*7*), Crommelin (*2*, *3*), and to the data of other investigators below the normal boiling point. Vapor pressures computed from this equation are shown in Figure 2. This equation gives a normal boiling point of 87.28° K.

**Critical Constants.** The critical temperature and pressure of argon have been reported by Olszewski (*8*), Ramsay and Travers (*9*), Crommelin (*2*), and Michels, Levelt, and De Graff (*7*). The results are summarized in Table II. Olszewski's values are the average of several determinations which showed considerable scatter. Olszewski commented that the argon he used contained a trace of nitrogen. The argon vapor pressure data of Olszewski show considerable

Table II. Critical Temperature and Pressure of Argon

| Temperature, ° K. | Pressure, Atm. | Investigator |
|---|---|---|
| −121.0° C. (152.15° K.)[a] | 50.6 | Olszewski (*8*) |
| 155.5, 155.7 | 52.9 | Ramsay and Travers (*9*) |
| −122.44° C. (150.71° K.)[a] | 47.996 | Crommelin (*2*) |
| −122.29° C. (150.86° K.)[a] | 48.34 | Michels, Levelt, and De Graff (*7*) |
| 150.65 ± 0.02 | 47.92 ± 0.05 | This research |

[a] ° K. = ° C. + 273.15

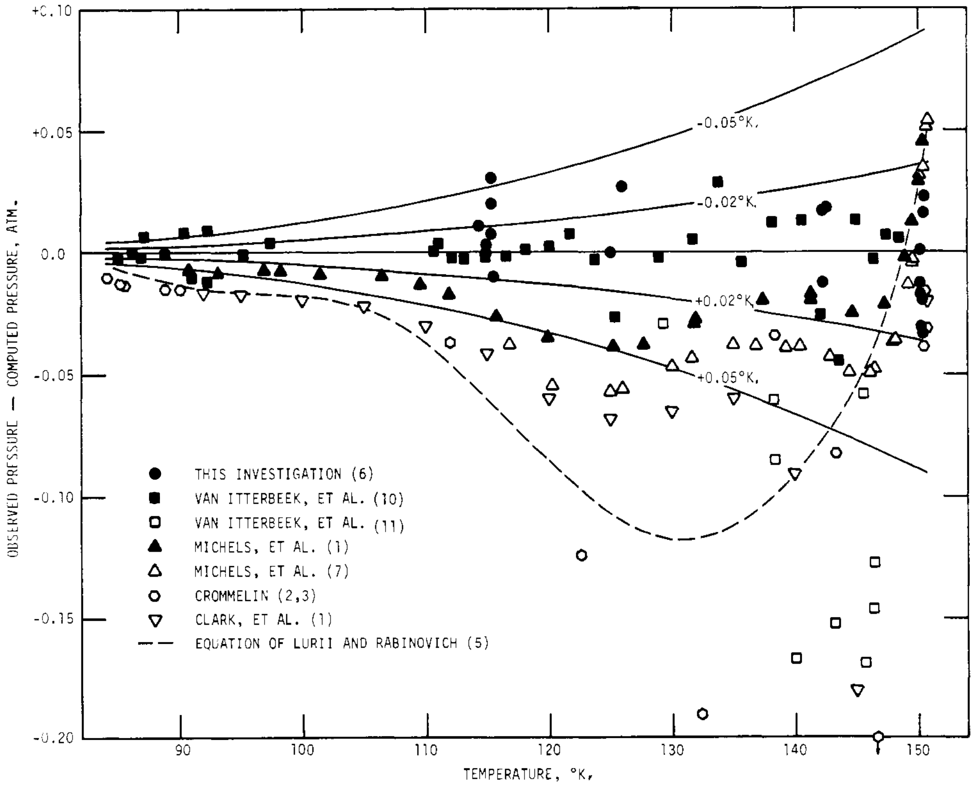

Figure 2. Comparison of correlation equation with published data

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.

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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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