

Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres

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Tabular values of density, internal energy, enthalpy, and entropy of liquid and gaseous argon are presented for temperatures from 83.8 to 300 K at pressures of 0.01 to 1000 atmospheres. Diagrams of specific heats, compressibility factor, and entropy are included. The properties presented are calculated from an equation of state which was fitted to experimental P - ρ - T data from the world literature. Extensive comparisons were made between the equation of state and the experimental data, and deviation plots are presented. The second virial coefficient and Joule-Thomson inversion curve were also calculated and comparisons made with values from other sources. A vapor pressure equation which covers the range from the triple point to the critical point is also given.

Key Words: Argon; compressibility factor; enthalpy; entropy; equation of state; internal energy; Joule-Thomson coefficient; P - V - T ; specific heat; vapor pressure; virial coefficient.

1. Introduction

In recent years technical interest in pure argon has greatly accelerated. This accelerated interest has been evidenced by a demand which has more than sextupled in 12 years. United States production has continued to increase from less than 200,000,000 cubic feet per year in 1953 to almost 1,300,000,000 cubic feet in 1965, with about 80 percent being shipped in liquid form [3].¹

In addition, scientific interest in argon has arisen because of its characteristically "ideal" structural makeup. That is, argon is monatomic, with the relatively uncomplicated interatomic forces being approximated by spherically symmetric, nonpolar models. In addition, the quantum effects on argon are relatively small. Although helium and neon might be considered to be more "ideal" fluids from the standpoint of simple models, the quantum effects are relatively large for these two fluids as compared to argon. For these reasons argon might be expected to permit a more direct classical investigation and experimental verification of the theoretical model predictions.

In view of the increased activity in cryogenic engineering and physics, it was apparent that a set of consistent thermodynamic properties, over a relatively large region of the thermodynamic surface, was needed. Although many investigators had published data for the thermodynamic properties of argon, each tabulation was, in general, limited to the property range of interest of the specific investigator, and large gaps in the data existed. In addition, where the ranges of data did

overlap, there was a substantial degree of inconsistency in some instances. For these reasons, this laboratory undertook the program of making a critical analysis of the thermodynamic properties of argon in the cryogenic temperature range, including the low temperature-high density region.

In recent years, much of the technical design and synthesis has been done with the aid of high speed digital computers. Thus the need for an analytical equation of state has become quite significant when compared with the use of tables and charts of thermodynamic properties. Many equations of state have been proposed in the literature, each with its own peculiar strengths and weaknesses. Some of these equations represented the data in certain regions of the thermodynamic surface, but were quite inadequate in other regions of the surface. Therefore, the need was established for a single equation of state which could accurately and consistently represent the data for both the liquid and vapor phases with a consistent transition from the low temperature-high density region to the low density region.

In the case of argon, it is difficult to assess the general overall adequacy of an equation of state in terms of deviations from the experimental P - V - T surface. That is, due to the inconsistency of some of the overlapping experimental data sources, there is no single experimental P - V - T surface which can be used as a reference. Also, the significance of the deviations is wholly dependent upon the variable chosen for the comparison and the specific region of the thermodynamic surface which is being studied. In certain regions of the surface,

¹ Figures in brackets indicate the literature references (sec. 17).

large pressure deviations are caused by insignificant density errors, while in other regions the reverse is true. In general, the equation of state presented in section 7 represents the different sources of experimental data to within the accuracy of the data, except at the higher temperatures on the coexistence boundary and the critical region where the deviations are, in a few cases, greater than the accuracy of the data. Numerous deviation plots are presented (sec. 8) in a manner which permits the comparison of the equation of state with each of the experimental data sources over the various regions of the thermodynamic surface.

2. Survey of the Literature

A comprehensive search of the literature resulted in a bibliography of about 425 references. The temperatures which were included in this search covered the range from 0 to 300 K. In addition to manual-reviewing techniques, the data retrieval personnel and the computerized search techniques of the Cryogenic Data Center of the National Bureau of Standards at Boulder, Colo. were utilized. As a result, a bibliography on the thermophysical properties of argon [4] was prepared and published in 1964. The literature search was continually updated so that current data were rapidly assimilated.

From this literature search, the most appropriate P - V - T data, vapor pressure data, coexistence density data, and fixed point data were selected for consideration and evaluation. In addition, virial coefficient data, Joule-Thomson data, specific heat data, and information on equations of state were acquired and considered.

Although many equations of state were presented in the literature, none of these equations appeared to have been developed to adequately represent the data for argon for temperatures from below the normal boiling point to twice the critical temperature for the gaseous, dense gas, and liquid regions. Hirschfelder et al. [5] developed a generalized equation of state which arbitrarily divided the P - V - T surface into three regions, namely, gas, dense gas, and liquid regions. For these three regions, Hirschfelder et al. [5] developed three equations in such a manner that discontinuities at the junction of these regions were avoided.

Appearing in the literature were other techniques for representing the P - V - T data. For some fluids, where perhaps one source of highly precise

As a part of the critical analysis, it was deemed necessary to develop a vapor pressure equation which would accurately represent the experimental vapor pressure data from the triple point to the critical point. This vapor pressure equation could then be used, in conjunction with the equation of state, to calculate some of the derived thermodynamic properties such as enthalpy, entropy, etc.

Thus it was concluded that a critical analysis of thermodynamic properties of argon was to be made for temperatures to about 300 K and for pressures to about 1000 atm wherever the experimental data permitted this pressure range.

data were available, the P - V - T data could be represented by polynomials along isotherms or polynomials along isochores. One such isothermal representation is the virial equation of state.

The virial equation of state is based on fundamental grounds in that it can be derived from fundamental statistical mechanics. Furthermore, in principle, this equation of state depends upon a very small number of parameters in that once one characterizes the potential function (by assigning values to its parameters) all virial coefficients can be calculated. In practice, however, only the second virial coefficient has been calculated properly. The third virial has been calculated in the approximation where nonadditivity is neglected for a small number of functions. All higher virials have really not been calculated except for the fourth and fifth virials for the hard sphere and (12-6) potentials. Thus, in actual practice, a virial equation of state is, in effect, an equation of state with a number of parameters equal to the number of virials times the number of isotherms (perhaps minus the second virials). Thus, Michels et al. [1, 6] equation of state remains a 100 parameter representation of his 19 isotherms until higher virials can be properly calculated from potential functions.

In addition, where multiple sets of data exist (as with argon) at odd temperature and density spacings, a complete correlation at all points of the P - V - T surface becomes very difficult with these polynomials. That is, if isothermal polynomials are used, then each set of coefficients is valid only for the one specific isotherm which was fitted. If a point on the P - V - T surface lies between two of the fitted isotherms, then other interpolative techniques must be used to obtain the P - V - T coordinates of this point.

3. Summary of P - V - T Data

Published experimental P - V - T data were reviewed and examined. As a result, the P - V - T data which were considered for use in this compilation were distributed as shown in table 1.

Evaluation of the experimental P - V - T data of van Itterbeek, Verbeke, and Staes [9] revealed

slight inconsistencies. Private communication from Verbeke [12] indicated that there were typographical errors in the original paper [9]. The new values given by Verbeke [12] were then used in this work.