Reports

Vapor Pressure of Water at Its Triple Point: Highly Accurate Value

Abstract. *The vapor pressure of water at its triple point was measured with greatly increased accuracy. The triple point was realized with newly designed equipment that enhanced the stability of the pressure and permitted any air released from solution to be removed by pumping. A diaphragm pressure transducer separated the water vapor from the helium used to transmit the pressure to the manometer. The pressure was measured with the National Bureau of Standards precision mercury manometer. The vapor pressure at the triple point was found to be 611.657 pascals with random uncertainties at the 99 percent confidence level of ± 0.010 pascal. The systematic errors are estimated to be relatively insignificant.*

Formulations of the vapor pressure of water are based upon data from several sources. The *Wärmetabellen* (*1*), an admirable achievement for its time, summarized thermodynamic work done at the Physikalisch-Technischen Reichsanstalt (PTR), and included tables of the vapor pressure of water that are still quoted in the most recent editions of some handbooks. In the more authoritative steam tables a later treatment of the PTR values, given in the tabulation of Osborne, Stimson, and Ginnings (*2*) (the Gerry equation), has been incorporated, combined with the experimental measurements reported by Osborne, Stimson, Fiock, and Ginnings (*3*) and correlated by Osborne and Meyers (*4*). Recently, very much more accurate values of the vapor pressure of water between 25° and 100°C have been reported by Stimson (*5*). However, no measurements of high accuracy have been made at the triple point, so that the measurements yielding the *Wärmetabellen* value, 610.92 pascals, constitute the principal experimental basis for the currently common values of 611.1 or 611.2 pascals.

In view of the high accuracy of the vapor pressures from 25° to 100°C reported by Stimson, and the accurate representation of them in the semitheoretical equation of Wexler and Greenspan (*6*), a more accurate value at the triple point would be very useful. By chance, we found ourselves with the experience and equipment in being that were especially suitable for making such an improved measurement.

A modified triple point cell was constructed and filled with very pure water during a commercial procedure for the production of triple point cells. The added glassware sections made it possible to transfer the water from the triple point section (after a mantle had been frozen on the inner well) by a percolator to a reservoir. The water was distilled from the reservoir through a trap and allowed to flow in a thin sheet over the otherwise exposed ice of the mantle. This permitted realization of triple point conditions or near-triple point conditions over a large area, and provided high stability to the observed pressure for both temperatures to 0.2°C. A reason for circulating and distilling the water was to drive off as much dissolved air as possible, so as to then pump off the contaminating gases. The arrangement also assured that the mantle was not in contact with water containing dissolved, involatile salts. The absence of a significant residue of contaminating gases during measurements was demonstrated in the experimental procedures, which showed that further pump-outs produced no detectable change in the measured pressure.

The vapor pressure apparatus was isolated from the manometer by a diaphragm pressure transducer. The gas used in the manometer lines for transmission of the pressure was helium. The diaphragm zero was determined to be a reproducible function of temperature, but it was also experimentally confirmed both before and after each group of pressure readings.

The National Bureau of Standards precision mercury manometer, built for gas thermometry (*7*), was used to measure the pressure. Because the pressure was small, the significant errors were different and somewhat larger than for the range contemplated for gas thermometry. In particular, the measurement of the manometer zero and the calibration of a 4.6-mm gage block were made with special care to reduce the errors. A method of balancing the manometer capacitance bridge by a precision variable capacitor was developed to allow a departure from the pressure for a 4.6-mm gage block. The characteristics of the manometer and measuring system were well enough known that this method of capacitance interpolation was not an important source of error (*8*).

The vapor pressure at the triple point was measured on three different occasions. The results from the first series of measurements were used to analyze the process to improve techniques and procedures. The results from the second series were reported to the 8th International Conference on the Properties of Steam (*9*) as 611.636 pascals with an estimated total uncertainty (3 σ limits, where σ is the standard deviation) of ± 0.061 pascal. The random error was much reduced by improvements in the procedures for the third series, so that the result, 611.657 pascals, has an estimated total uncertainty at the 99 percent confidence level of ± 0.010 pascal for random errors; the systematic errors are estimated to be relatively insignificant.

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References and Notes

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2. N. S. Osborne, H. F. Stimson, D. C. Ginnings, *J. Res. Nat. Bur. Stand.* **23**, 261 (1959).
3. N. S. Osborne, H. F. Stimson, E. F. Fiock, D. C. Ginnings, *ibid.* **10**, 155 (1933).
4. N. S. Osborne and C. H. Meyers, *ibid.* **13**, 1 (1934).
5. H. F. Stimson, *ibid.* **73A**, 493 (1969).
6. A. Wexler and L. Greenspan, *ibid.* **75A**, 213 (1971).
7. L. A. Guildner, H. F. Stimson, R. L. Anderson, R. E. Edsinger, *Metrologia* **6**, 1 (1970).
8. The same combination of apparatus is suitable for measurements of the vapor pressure of water up to 25° or 30°C. Our laboratory also has a good steam boiler, designed for fixed-point calibrations at 100°C; like the earlier equipment of Stimson, it can also be used over a range from 25° to 111°C. We plan to complete new vapor pressure measurements above the triple point up to 111°C in the reasonably near future, so that the information will be available for consideration in the adoptions of new formulations by the International Union of Pure and Applied Chemistry Commission 1.4, Physicochemical Measurements and Standards, and by the International Association for the Properties of Steam.
9. D. P. Johnson, L. A. Guildner, F. E. Jones, paper presented at the 8th International Conference on the Properties of Steam, Giens, France, September 1974.

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