Subatmospheric Vapor Pressures Evaluated from Internal Energy Measurements

H.A. Duarte-Garza* and J.W. Magee
Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, CO 80303-3328 USA

A novel method was developed to calculate vapor pressures at temperatures below the normal boiling point, where traditional methods yield results which are often less than satisfactory, especially at pressures below about 1 kPa. This method was applied to substances for which published sources of vapor pressures were inconsistent at temperatures between their triple and normal boiling point temperatures. Vapor pressures were calculated from measured internal energy increments in the vapor + liquid two-phase region, $\Delta U^{(2)}$. The method employed a thermodynamic relationship between the derivative quantity $(\partial U^{(2)}/\partial V)_T$ and the vapor pressure (p ?) and its temperature derivative $(\partial p/\partial T)_\sigma$. This method was applied to three substances: 1,1,1,2-tetrafluoroethane (R134a), pentafluoroethane (R125), and difluoromethane (R32). Agreement with experimentally measured vapor pressures near the normal boiling point (101.325 kPa) was within the experimental uncertainty of approximately ±0.04 kPa (±0.04%). Very good agreement (±0.005 to ±0.045 kPa) was found with a published method at the triple point temperatures. By comparison of calculated internal energies of vaporization $\Delta_{vap}U$, a test was made of the thermodynamic consistency of a published p-ρ-T equation of state with p_σ data obtained with this method. The method was also applied to evaluate published p_σ data which are in disagreement by more than their claimed uncertainty in order to ascertain the most reliable vapor pressures.

Permanent address: Department of Chemical and Natural Gas Engineering
Campus Box 193
Texas A&M University
Kingsville, TX 78363 USA