SPEED OF SOUND AS A SOURCE OF ACCURATE THERMODYNAMIC PROPERTIES OF GASES

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Abstract — **A procedure for deriving thermodynamic properties of gases (the compression factor, the specific heat capacity at constant volume, and the specific heat capacity at constant pressure) from the speed of sound is presented. It is based on numerical integration of differential equations connecting the speed of sound with other thermodynamic properties. The set of differential equations is solved as the initial-boundary-value problem. The initial values of the compression factor and the specific heat capacity at constant volume are specified along the isochore in the perfect-gas limit, while the boundary values of the compression factor are specified along two isotherms at the lowest temperatures of the range. The procedure is tested on methane, ethane, and carbon dioxide. The average absolute deviations of the compression factor, the specific heat capacity at constant volume, and the specific heat capacity at constant pressure, from respective reference values, are 0.0001%, 0.004%, and 0.008%, respectively.**

Keywords — **Speed of sound, compression factor, heat capacity, gases.**

I. INTRODUCTION

Knowledge of thermodynamic properties of fluids appearing in chemical industry is of crucial importance for analysis of processes and for design of process equipment. For some substances these properties are not available at all (e.g., newly synthesized compounds), for some they are available only in limited range of pressure and/or temperature (e.g., at atmospheric pressure and surrounding temperature), while for some reliability of these properties is questionable (e.g., high uncertainty of measurement). Traditionally, the engineers and scientists have been using tables and charts from various handbooks as the main source of such data. However, when one decides to make its own compilation, the discrepancies among different sources may become obvious. In such situation the decision may be difficult. Besides, tabulated data are rather inappropriate for big scale calculations involving digital computers (e.g., Computer Aided Design, Computational Fluid Dynamics). For this purpose the equations of state are more appropriate.

Van der Waals was the first who posed the equation of state which took into account influence of intermolecular forces in gases under elevated pressures (van der Waals, 1873). Since that, literally hundreds of various modifications of his equation have appeared. Although some of these equations of state have accuracy which satisfies majority of technical and scientific applications

(Span, 2000), a vast majority of them fail to represent thermodynamic properties of substances for which they are designed (not only thermal but caloric as well) with uncertainties not exceeding those of direct measurements. Only equations in reference quality (e.g., reference or fundamental equations of state) may represent thermodynamic surface (including critical region) as reliably as direct measurement. Unfortunately, only a few of such equations of state have been developed to date (e.g., for argon (Tegeler *et al.*, 1999), nitrogen (Span *et al.*, 2000), carbon dioxide (Span and Wagner, 1996), water (Wagner and Pruss, 2002), methane (Setzmann and Wagner, 1991) and ethylene (Smukala *et al.*, 2000)).

Generally, the caloric properties are measured with the uncertainties which are several orders of magnitude higher than those of the thermal properties. The situation is especially critical with the heat capacity (e.g., both isobaric and isochoric) (Younglove, 1974; Bier *et al.*, 1976; and Ernst *et al.*, 1989), since this property is very important when the full thermodynamic equation of state (e.g., both thermal and caloric) is designed. Fortunately, there is one exception to this rule – the speed of sound. Advances in measurement of this caloric property in the last several decades made this property very attractive source of other thermodynamic properties. These thermodynamic properties may be derived from the speed of sound with accuracy exceeding that of respective direct measurements. Nowadays, the speed of sound is measured with outstanding accuracy (Trusler and Zarari, 1992; Estrada-Alexanders and Trusler, 1997; and Estrada-Alexanders and Trusler, 1998), even exceeding that of the thermal properties (Pieperbeck *et al.*, 1991; Funke *et al.*, 2002; and Klimeck *et al.*, 2001). Thanking to this fact, this caloric property is used in the design of the reference equation of state in its final stage, that is, for fine adjustment of the equation parameters (Schmidt and Wagner, 1985; Setzmann and Wagner, 1989; and Span and Wagner, 2003). However, the thermodynamic properties may also be derived from the speed of sound directly. Unfortunately, the speed of sound is connected to other thermodynamic properties through the set of partial differential equations whose general solution has not been found yet. The only exception is a part of the thermodynamic surface comprising the region of dilute gases at low pressures where analytical solution may be obtained from the model of intermolecular potential energy (Maitland and Smith, 1973; Trusler *et al.*, 1997; and Estela-Uribe and Trusler, 2000). However, if higher pressures are considered the