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Measurement of the Thermal Pressure Coefficient $(\partial P/\partial T)_V$ of Molten Salts

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A method for the determination of the thermal pressure coefficient $(\partial P/\partial T)_V$ or γ_V for molten salts up to 400°C and 400 bars is described. The results, which are considered to be accurate to ±3%, are compared with previous work.

INTRODUCTION

THE thermal pressure coefficient $(\partial P/\partial T)_V$ or γ_V of molten salts is of interest since, in conjunction with a value for the expansivity $(1/V)(\partial V/\partial T)_P$ or α_P, a value of the isothermal compressibility $-(1/V)(\partial V/\partial P)_T$ or β_T may be obtained by using the relation

$$\beta_T = \alpha_P/\gamma_V. \quad (1)$$

Values of α_P may be obtained from density data which have been accurately determined in many cases and tabulated by Janz.[1]

γ_V is generally needed if thermodynamic parameters relating to constant volume conditions are to be derived from corresponding quantities at constant pressure. Barton, Cleaver, and Hills[2] have reported activation volumes for specific conductance, ΔV_κ, for molten alkali metal nitrates and a number of other salts have since been studied in this department. γ_V and β_T feature in the relationships

$$\Delta V_\Lambda = \Delta V_\kappa + \beta_T RT \quad (2)$$

and

$$(E_\kappa)_V = (E_\kappa)_P - \gamma_V T \Delta V_\kappa, \quad (3)$$

where ΔV_Λ is an activation volume for equivalent conductance, and E_V and E_P are activation energies for conductance at constant volume and at constant pressure, respectively.

Further examples of equations in which γ_V is used are[3]

$$C_V = C_P - TV\alpha_P\gamma_V \quad (4)$$

$$(U^E)_V = (H^E)_P - T\gamma_V V^E. \quad (5)$$

The determination of γ_V and β_T for molten salts has been the subject of few studies limited to alkali metal nitrates.[4-6] Owens[4] used a piston in cylinder method to 9000 bars pressure, but his results are subject to frictional errors in the low pressure range. Fray[5] used a pyknometric technique to measure β_T, but poor temperature control in the internally heated vessel and dissolution of the pressurizing gas (argon) probably introduced errors. Bannard, Barton, and Hills[6] used a pyknometric technique to measure γ_V in an externally heated vessel with good temperature control. Care was taken to prevent dissolution of the pressurizing gas (argon) by providing a long capillary between the gas–liquid interface and the main body of the melt. Therefore these results[6] are considered to be the most accurate ones available for comparison with the present work. Adiabatic compressibilities have been determined by an ultrasonic technique,[7,8] and β_T may be derived only if the specific heat of the melt is known.

In order to collect data for molten salts other than alkali metal nitrates, the following relatively quick and easy method has been developed and tested with molten sodium nitrate.

METHOD

A pressure vessel was completely filled with melt and was sealed. It was then placed in a horizontal furnace and was heated at a steady rate of ~2°/min. The temperature was measured with a Chromel–Alumel thermocouple located in a reentrant well. The pressure generated was measured with a strain gauge transducer which had a diaphragm in contact with the melt. The outputs of the thermocouple and transducer were fed either to an X–Y recorder or to a data logging system and, after making corrections for thermal expansion and dilation of the vessel, γ_V was obtained.

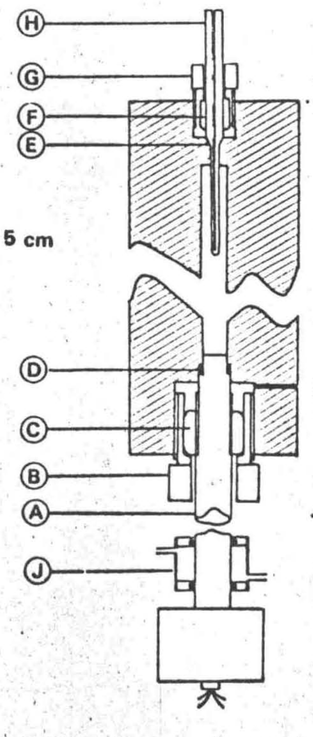

Fig. 1. Pressure vessel, showing the transducer seal and simple thermocouple well. A—Transducer; B—thrust nut; C—collar on the transducer stem; D—copper washer; E—conical seating of the thermocouple well; F—collar on the thermocouple well; G—thrust nut; H—thermocouple well; and J—water jacket.