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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  $\gamma_V$  for molten salts up to 400°C and 400 bars is described. The results, which are considered to be accurate to  $\pm 3\%$ , are compared with previous work.

## INTRODUCTION

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

$$\beta_T = \alpha_P / \gamma_V. \tag{1}$$

Values of  $\alpha_P$  may be obtained from density data which have been accurately determined in many cases and tabulated by Janz.<sup>4</sup>

 $\gamma_V$  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<sup>2</sup> have reported activation volumes for specific conductance,  $\Delta V_e$ , for molten alkali metal nitrates and a number of other salts have since been studied in this department.  $\gamma_V$  and  $\beta_T$  feature in the relationships

and

$$\Delta V_{\rm A} = \Delta V_{\rm s} + \beta_T R T \tag{2}$$

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$$(E_r)_V = (E_r)_P - \gamma_V T \Delta V_r, \tag{3}$$

where  $\Delta V_A$  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  $\gamma_V$  is used are<sup>3</sup>

$$C_V = C_P - T V \alpha_P \gamma_V \tag{4}$$

$$(U^E)_V = (H^E)_P - T\gamma_V V^E.$$
<sup>(5)</sup>

The determination of  $\gamma_V$  and  $\beta_T$  for molten salts has been the subject of few studies limited to alkali metal nitrates.<sup>4-6</sup> Owens<sup>4</sup> used a piston in cylinder method to 9000 bars pressure, but his results are subject to frictional errors in the low pressure range. Fray<sup>5</sup> used a pyknometric technique to measure  $\beta_T$ , but poor temperature control in the internally heated vessel and dissolution of the pressurizing gas (argon) probably introduced errors. Bannard, Barton, and Hills<sup>6</sup> used a pyknometric technique to measure  $\gamma_V$  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<sup>6</sup> are considered to be the most accurate ones available for comparison with the present work. Adiabatic compressibilities have been determined by an ultrasonic technique,<sup>7,8</sup> and  $\beta_T$  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  $\sim 2^{\circ}$ /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,  $\gamma_V$  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. The pressure vessel was made from Firth-Vickers 448 stainless steel and had a working volume of about 10 ml.

The transducer was an AS22 model (Coutant Transducers Limited, 47 Milford Road, Reading, RG1 8LN, England) rated up to 700 bars at diaphragm temperatures up to 300°C. The system was operated at 300-400°C without undue shortening of the working lifetime. Cooling water was circulated around the section of the transducer stem outside the furnace in order to prevent the strain gauge from overheating. The transducer was calibrated against a Bourdon gauge (Budenburg Gauge Company Limited), previously calibrated on a dead weight tester. The calibration was performed at various temperatures and 'the slope of graphs of transducer output voltage against pressure did not depend on temperature. Hysteresis was not important provided the pressure did not exceed 400 bars.

The transducer and thermocouple well were sealed into opposite ends of the vessel as shown in Fig. 1. A thrust nut B acted on a collar C threaded onto the transducer stem A forcing it against a copper washer D located on a step in the vessel bore. The thermocouple well H was fitted with a collar F and nut G forcing it into the conical seating E. An alternative arrangement for the thermocouple well, shown in Fig. 2, allowed the volume of the vessel (and hence the temperature at which  $\gamma_V$  was measured) to be varied without reloading the vessel. The thermocouple well was in two pieces which were slotted to fit together, similar to a nonrotating valve stem. A seal was made onto the inner section of the well E by means of the aluminium washer B. When the thrust nut A was slackened, the outer section of the well (C) could be turned in thread D, thus moving E in or out of the vessel.

In practice, the vessel was preheated, removed from the furnace, and clamped in a vise. The transducer was removed and the melt was pipetted in. The vessel was then sealed, replaced in the furnace, and the run performed.

#### RESULTS

The slope of the plot of pressure against temperature,  $\gamma_{obs}$ , must be corrected for thermal expansion of the vessel and for elastic expansion due to the internal pressure.







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FIG. 3.  $\gamma v$  for molten sodium nitrate plotted against temperature, with the best line through the data of Bannard, Barton, and Hills.<sup>6</sup>

It may be shown that

$$\gamma_{V} = \gamma_{obs} / [1 - (\alpha_{(V)} + 2\gamma_{obs} E_{r}) / \alpha_{(L)}], \qquad (6)$$

where  $\alpha_{(V)}$  and  $\alpha_{(L)}$  are the cubic expansion coefficients of the vessel and the liquid, respectively, and  $E_r$  is the fractional change in bore radius for unit increase in the internal pressure. The value of  $E_r$  is given by Bett and Newitt<sup>9</sup> as

$$E_{r} = [r_{i}^{2}/E(r_{0}^{2} - r_{i}^{2})][(1 - 2\nu) + (1 + \nu)r_{0}^{2}/r_{i}^{2}], \quad (7)$$

where  $r_i$  and  $r_0$  are the inner and outer radii of the vessel, E is the elastic modulus, and  $\nu$  Poisson's ratio for the vessel material.

For molten sodium nitrate in the temperature range 310-400 °C,  $\gamma_{V}$  was higher than  $\gamma_{obs}$  by 15%, of which approximately 10% was due to thermal expansion and 5% to dilation of the vessel.

The results of Bannard, Barton, and Hills<sup>6</sup> for molten sodium nitrate over the temperature range 310-480°C are fitted by the line

$$\gamma_{v} = 24.85 - (1.80 \times 10^{-2})T, \qquad (8)$$

where T is in degrees Celsius and  $\gamma_V$  in bars deg<sup>-1</sup>. The results of the present work are compared with this line in Fig. 3. Each point is the mean of four runs and the error bars show twice the standard deviation from the mean. The points are fitted by the line

$$\gamma_V = 30.35 - (3.36 \times 10^{-2})T, \qquad (9)$$

and values of  $\gamma_{\rm V}$  calculated from Eq. (9) deviate by a maximum of 4% from Eq. (8) over the temperature range 310-400°C. This satisfactory agreement demonstrates the soundness of the present method. It is relatively quick and easy to perform and lends itself to rapid acquisition of data for many volatile or flammable liquids up to 400°C, without the necessity of purchasing separate pressure generating equipment. The new method has been applied in this laboratory to melts such as LiClO<sub>4</sub>, NaClO<sub>3</sub>, NaNO<sub>2</sub>, (n-hex)<sub>4</sub>NBF<sub>4</sub>, KSCN, and Na<sub>2</sub>S<sub>4</sub>, which is spontaneously flammable in air and has a substantial vapor

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pressure of sulfur at 400°C.  $\gamma_{V}$  for this compound would be very difficult to measure by conventional pyknometric methods.

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# Refrigerating Vapor Bath

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A simple and inexpensive refrigerating vapor bath has been developed for the purpose of cooling gas line traps. The cooling medium in the bath is the cold vapor from liquid nitrogen. The temperature regulation range is from -196 to  $\sim 0^{\circ}$ C. For a glass-isolated stainless steel gas trap the liquid nitrogen consumption rate was less than  $\frac{1}{2}$  liter/24 h at temperatures between -130 and  $-196^{\circ}$ C.

## INTRODUCTION

MANY techniques have been developed to meet the varied refrigeration requirements that arise in the laboratory; the specific requirement addressed in this paper is that of refrigerating a gas line trap.

Most laboratories which employ gases for research purposes arrange to have the gas flow through one or more cold traps which serve to reduce impurities in the gas. By far, the most common refrigerant in use for cold traps is that made in the form of a chemical slurry. The simplicity and economy of this refrigerant make it popular in spite of its deficiencies, which are, to name a couple, discrete temperatures and tedious time consuming maintenance.

Several elaborate variable-temperature devices have been developed for more sophisticated refrigeration requirements, e.g., liquid H<sub>2</sub> and He cooling of samples to be used in studies on liquid hydrogen targets,<sup>1</sup> EPR,<sup>2</sup> electron bombardment,<sup>3-5</sup> and cathodoluminescence.<sup>6</sup> However, the refrigerating vapor bath (RVB), described herein, is designed to fill a greater, more broad based need than those references above<sup>1-6</sup>; i.e., it is intended to provide a simple, inexpensive, and convenient means of achieving dialable temperatures for a gas line cold trap. The features of the RVB make it an attractive and effective replacement for the chemical slurries so widely used for this purpose. Accordingly, this paper is written as a "how-to" paper, indicating principles of operation, construction, assembly, and liquid nitrogen consumption rate for typical operating conditions.

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#### APPARATUS DESCRIPTION

The RVB utilizes cold vapor from a reservoir of liquid nitrogen as the heat transfer medium. By varying the vapor density and temperature, the rate of heat loss from the gas trap can be controlled. Figure 1 is a schematic diagram of the apparatus. The charge of liquid nitrogen  $(LN_2)$  (1) is placed in Dewar (2). The stainless steel gas trap (3) is suspended above the refrigerant surface. The Dewar is closed with a seal (4) and the trap temperature is sensed by a Cu/Cn thermocouple (5).

The trap temperature will equilibrate at a point determined by the balance of heat transfer into and out of the Dewar. The heat transfer into the Dewar is primarily determined by thermal conduction of the signal and power leads passing through the seal (4), conduction down the walls of the Dewar, and the gas load on the trap. The molecules in the cold vapor serve to remove heat from the trap and transfer it to the liquid reservoir. Heat loss from the bath is regulated through evaporative cooling of the LN<sub>2</sub> reservoir—the vapor being released through a valve (6) in the seal of the Dewar.

There are two ways in which the RVB may be operated, depending upon whether the equilibrium temperature of

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