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 γ_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, γ_{obs}, must be corrected for thermal expansion of the vessel and for elastic expansion due to the internal pressure.

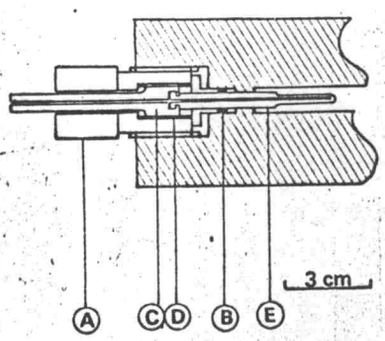

FIG. 2. Adjustable thermocouple well. A—Thrust nut; B—aluminium washer; C—outer section of the thermocouple well; D—thread to move the well in or out of the vessel; and E—inner section of the thermocouple well.

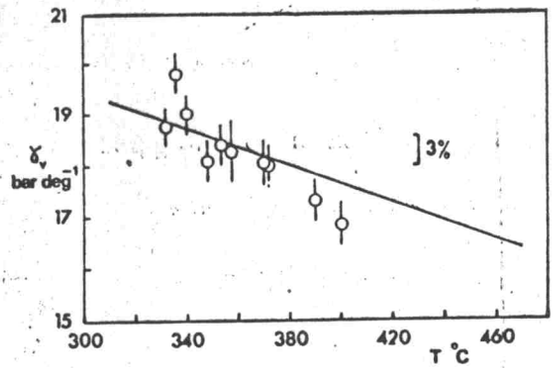

FIG. 3. γ_V for molten sodium nitrate plotted against temperature, with the best line through the data of Bannard, Barton, and Hills.[6]

It may be shown that

$$\gamma_V=\gamma_{obs}/[1-(\alpha_{(V)}+2\gamma_{obs}E_r)/\alpha_{(L)}], \quad (6)$$

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[9] 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 ν Poisson's ratio for the vessel material.

For molten sodium nitrate in the temperature range 310–400°C, γ_V was higher than γ_{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[6] for molten sodium nitrate over the temperature range 310–480°C are fitted by the line

$$\gamma_V=24.85-(1.80\times10^{-2})T, \quad (8)$$

where T is in degrees Celsius and γ_V in bars·deg^{-1}. 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

$$\gamma_V=30.35-(3.36\times10^{-2})T, \quad (9)$$

and values of γ_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 $LiClO_4$, $NaClO_3$, $NaNO_2$, $(n\text{-hex})_4NBF_4$, KSCN, and Na_2S_4, which is spontaneously flammable in air and has a substantial vapor