

experimental error. The slopes of these lines correspond to the condition of constant meniscus position, and require correction to allow for the change in the volume of the pyknometer with pressure. If $(\partial P/\partial T)^{\text{obs}}$ is the observed slope, $(\partial P/\partial T)_V$ for the melt can be found using the equation

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)^{\text{obs}} \left(1 - \frac{\beta_c}{\beta_m}\right) = \left(\frac{\partial P}{\partial T}\right)^{\text{obs}} \left[1 + \frac{\beta_c}{\alpha_m} \left(\frac{\partial P}{\partial T}\right)^{\text{obs}}\right], \quad (4)$$

where subscripts m and c refer to the melt and the container material respectively. β_c has been measured between room temperature and 400°C for Pyrex and silica.⁸ For use in eqn

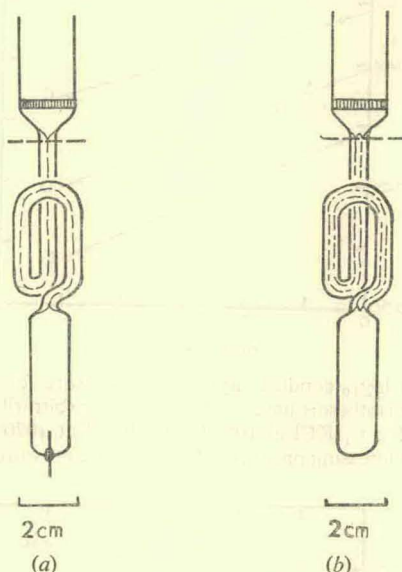


FIG. 2.—Pyknometers used to measure $(\partial P/\partial T)_V$. (a) Pyrex cell; (b) silica cell, with twin-bore capillary.

(4), these results were extrapolated to higher temperatures (500°C for Pyrex, 800°C for silica). Uncertainty in β_c represents the greatest source of error in the experiments; the total uncertainty in $(\partial P/\partial T)_V$ is estimated to be $\pm 4\%$.

RESULTS

CONDUCTANCE MEASUREMENTS

Following established practice,⁹ we describe the experimental temperature and pressure coefficients of conductivity using the Arrhenius equation and the terminology of the transition state theory. We restrict our use of the terms "activation volume" and "activation energy" to refer simply to the quantities defined operationally by eqn (1), (5) and (7). We do not believe that the transition state theory is applicable to ion migration in fused salts, and do not intend to imply that ΔV , E_P and E_V relate to the formation of a transition state.

Isothermal plots of $\ln \kappa$ against pressure for the alkali halides and silver halides were linear within experimental error. A selection of these plots is presented in fig. 3-5. Straight lines were fitted by least squares, and the "activation volume" ΔV_κ was found using the equation

$$\Delta V_\kappa = -RT(\partial \ln \kappa / \partial P)_T. \quad (5)$$

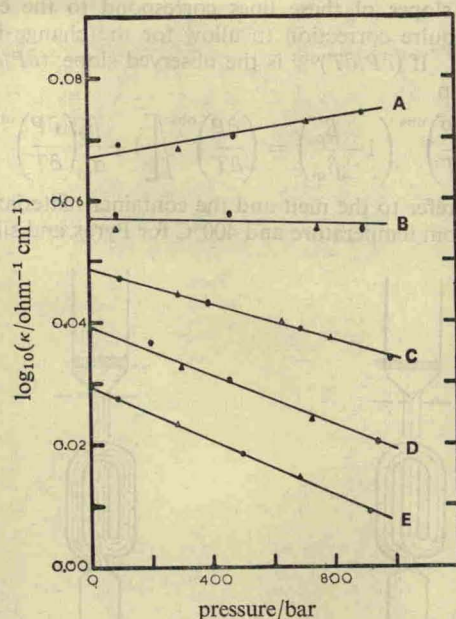


FIG. 3.—Isothermal plots of $\log_{10}(\text{conductivity})$ against pressure for fused alkali metal chlorides. For ease of presentation, the isotherms have been positioned arbitrarily on the $\log \kappa$ axis. A, LiCl at 968 K; B, NaCl at 1098 K; C, KCl at 1065 K; D, RbCl at 1070 K; E, CsCl at 1074 K. \bullet , increasing pressure; \blacktriangle , decreasing pressure.

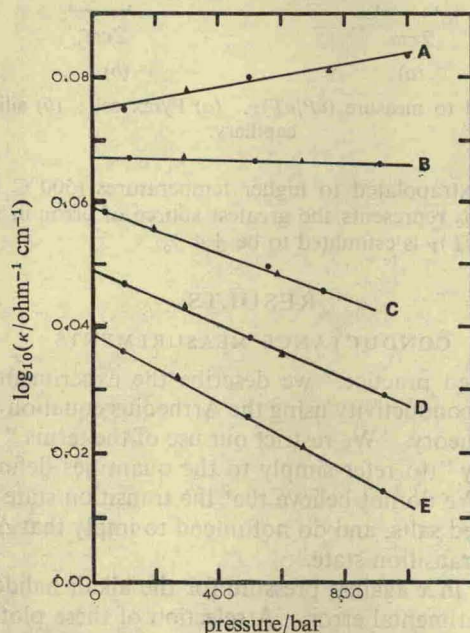


FIG. 4.—Isothermal plots of $\log_{10}(\text{conductivity})$ against pressure for fused alkali metal bromides. The isotherms have been positioned arbitrarily on the $\log \kappa$ axis. A, LiBr at 870 K; B, NaBr at 1062 K; C, KBr at 1050 K; D, RbBr at 1075 K; E, CsBr at 1069 K. \bullet , increasing pressure; \blacktriangle , decreasing pressure.