

FIG. 5.—Isothermal plots of  $\log_{10}(\text{conductivity})$  against pressure for fused alkali metal iodides. The isotherms have been positioned arbitrarily on the  $\log \kappa$  axis. A, LiI at 798 K; B, NaI at 1053 K; C, KI at 1069 K; D, RbI at 1071 K; E, CsI at 1075 K. ●, increasing pressure; ▲, decreasing pressure.

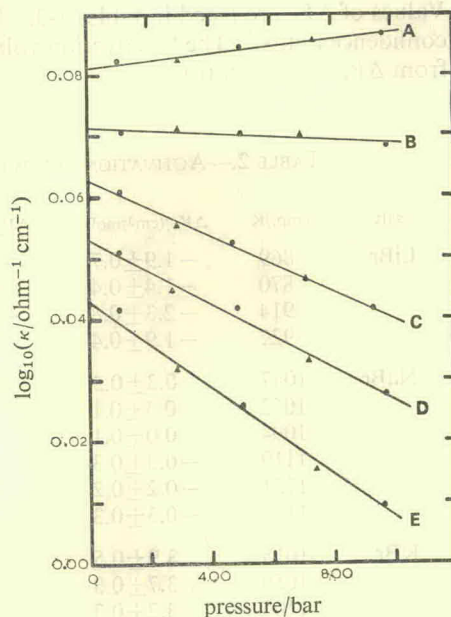


TABLE 1.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED CHLORIDES

| salt | temp./K | $\Delta V_{\kappa}/(\text{cm}^3/\text{mol})$ | $\Delta V_A/(\text{cm}^3/\text{mol})$ | $(E_A)_P/(\text{J/mol})$        | $(E_A)_V/(\text{J/mol})$ | $(E_A)_P/(\text{J/mol})$ |
|------|---------|----------------------------------------------|---------------------------------------|---------------------------------|--------------------------|--------------------------|
| LiCl | 916     | $-2.4 \pm 0.6$                               | $-0.8 \pm 0.6$                        | 8440 <sup>a</sup>               | 8560                     | 1.01                     |
|      | 921     | $-1.5 \pm 0.3$                               | $0.1 \pm 0.3$                         |                                 |                          |                          |
|      | 921     | $-2.2 \pm 0.4$                               | $-0.6 \pm 0.4$                        |                                 |                          |                          |
|      | 968     | $-1.2 \pm 0.7$                               | $0.5 \pm 0.7$                         |                                 |                          |                          |
|      | 973     | $-1.4 \pm 0.7$                               | $0.4 \pm 0.7$                         |                                 |                          |                          |
| NaCl | 1098    | $0.3 \pm 1.2$                                | $3.0 \pm 1.2$                         | 10 590 <sup>b</sup>             | 5960                     | 0.56                     |
|      | 1133    | $1.1 \pm 2.9$                                | $4.1 \pm 2.9$                         | $9\,300 \pm 800$ <sup>c</sup>   |                          |                          |
| KCl  | 1065    | $2.9 \pm 0.2$                                | $6.3 \pm 0.2$                         | 14 110 <sup>b</sup>             | 7310                     | 0.52                     |
|      | 1093    | $2.7 \pm 0.1$                                | $6.2 \pm 0.1$                         | $14\,000 \pm 5700$ <sup>c</sup> |                          |                          |
|      | 1129    | $2.2 \pm 0.1$                                | $6.2 \pm 0.1$                         |                                 |                          |                          |
| RbCl | 1009    | $4.1 \pm 0.4$                                | $8.0 \pm 0.5$                         | 15 680 <sup>b</sup>             | 8020                     | 0.51                     |
|      | 1045    | $4.3 \pm 0.3$                                |                                       | $16\,400 \pm 1900$ <sup>c</sup> |                          |                          |
|      | 1070    | $4.0 \pm 0.5$                                |                                       |                                 |                          |                          |
|      | 1114    | $4.1 \pm 1.5$                                |                                       |                                 |                          |                          |
| CsCl | 944     | $6.1 \pm 0.3$                                | $9.3 \pm 0.3$                         | 16 740 <sup>b</sup>             | 8490                     | 0.51                     |
|      | 983     | $5.8 \pm 0.3$                                | $9.4 \pm 0.3$                         | $15\,800 \pm 1500$ <sup>c</sup> |                          |                          |
|      | 1034    | $4.5 \pm 1.0$                                | $8.6 \pm 1.0$                         |                                 |                          |                          |
|      | 1074    | $4.5 \pm 0.3$                                | $9.1 \pm 0.3$                         |                                 |                          |                          |
|      | 1129    | $4.4 \pm 0.6$                                | $9.7 \pm 0.6$                         |                                 |                          |                          |
| AgCl | 745     | $1.1 \pm 0.1$                                | $1.7 \pm 0.1$                         | 5130 <sup>d</sup>               | 2780                     | 0.54                     |
|      | 755     | $0.9 \pm 0.1$                                | $1.5 \pm 0.1$                         | $4\,700 \pm 540$ <sup>c</sup>   |                          |                          |
|      | 774     | $0.9 \pm 0.2$                                | $1.5 \pm 0.2$                         |                                 |                          |                          |

<sup>a</sup> ref. (12); <sup>b</sup> ref. (13), (14); <sup>c</sup> this work; <sup>d</sup> ref. (15).

Values of  $\Delta V_K$  are listed in tables 1-3. The uncertainties quoted correspond to 95 % confidence limits. The "activation volume"  $\Delta V_A$ , defined by eqn (1), was calculated from  $\Delta V_K$  using eqn (6),

$$\Delta V_A = \Delta V_K + \beta RT. \quad (6)$$

TABLE 2.—ACTIVATION VOLUMES AND ENERGIES FOR FUSED BROMIDES

| salt | temp./K | $\Delta V_K/(\text{cm}^3/\text{mol})$ | $\Delta V_A/(\text{cm}^3/\text{mol})$ | $(E_A)_P/(\text{J/mol})$        | $(E_A)_V/(\text{J/mol})$ | $(E_A)_V/(\text{J/mol})$ |
|------|---------|---------------------------------------|---------------------------------------|---------------------------------|--------------------------|--------------------------|
| LiBr | 869     | $-1.9 \pm 0.7$                        | $-0.3 \pm 0.7$                        | 8 860 <sup>a</sup>              | 9060                     | 1.02                     |
|      | 870     | $-1.4 \pm 0.4$                        | $0.2 \pm 0.4$                         | 9 850 $\pm$ 800 <sup>c</sup>    |                          |                          |
|      | 914     | $-2.3 \pm 0.8$                        | $-0.5 \pm 0.8$                        |                                 |                          |                          |
|      | 922     | $-1.9 \pm 0.4$                        | $-0.1 \pm 0.4$                        |                                 |                          |                          |
| NaBr | 1047    | $0.3 \pm 0.3$                         | $3.1 \pm 0.3$                         | 9 920 <sup>b</sup>              | 6410                     | 0.65                     |
|      | 1062    | $0.3 \pm 0.1$                         | $3.2 \pm 0.1$                         | 9 800 $\pm$ 700 <sup>c</sup>    |                          |                          |
|      | 1094    | $0.0 \pm 0.1$                         | $3.1 \pm 0.1$                         |                                 |                          |                          |
|      | 1119    | $-0.3 \pm 0.3$                        | $3.0 \pm 0.3$                         |                                 |                          |                          |
|      | 1131    | $-0.2 \pm 0.2$                        | $3.2 \pm 0.2$                         |                                 |                          |                          |
|      | 1145    | $-0.3 \pm 0.3$                        | $3.2 \pm 0.3$                         |                                 |                          |                          |
| KBr  | 1015    | $3.9 \pm 0.5$                         | $7.2 \pm 0.5$                         | 15 580 <sup>b</sup>             | 8350                     | 0.54                     |
|      | 1050    | $3.7 \pm 0.3$                         | $7.4 \pm 0.3$                         | 15 100 $\pm$ 4 800 <sup>c</sup> |                          |                          |
|      | 1105    | $3.2 \pm 0.3$                         | $7.5 \pm 0.3$                         |                                 |                          |                          |
| RbBr | 988     | $5.5 \pm 0.5$                         |                                       | 15 500 <sup>b</sup>             | 7930                     | 0.51                     |
|      | 999     | $5.2 \pm 0.5$                         |                                       | 13 300 $\pm$ 2 700 <sup>c</sup> |                          |                          |
|      | 1008    | $5.0 \pm 0.5$                         |                                       |                                 |                          |                          |
|      | 1075    | $4.3 \pm 0.5$                         | $9.1 \pm 0.5$                         |                                 |                          |                          |
|      | 1122    | $3.8 \pm 0.4$                         |                                       |                                 |                          |                          |
| CsBr | 956     | $6.3 \pm 0.4$                         | $10.6 \pm 0.4$                        | 16 410 <sup>b</sup>             | 8880                     | 0.54                     |
|      | 1002    | $5.7 \pm 0.1$                         | $10.6 \pm 0.1$                        | 15 500 $\pm$ 700 <sup>c</sup>   |                          |                          |
|      | 1069    | $5.5 \pm 0.3$                         | $11.5 \pm 0.3$                        |                                 |                          |                          |
|      | 1098    | $5.2 \pm 0.1$                         | $11.6 \pm 0.1$                        |                                 |                          |                          |
|      | 1128    | $5.1 \pm 0.6$                         | $12.1 \pm 0.6$                        |                                 |                          |                          |
| AgBr | 727     | $0.7 \pm 0.2$                         | $1.3 \pm 0.2$                         | 4 620 <sup>d</sup>              | 2840                     | 0.61                     |
|      | 753     | $0.6 \pm 0.2$                         | $1.2 \pm 0.2$                         | 4 680 $\pm$ 200 <sup>c</sup>    |                          |                          |
|      | 791     | $0.5 \pm 0.5$                         | $1.2 \pm 0.5$                         |                                 |                          |                          |
|      | 813     | $0.4 \pm 0.2$                         | $1.2 \pm 0.2$                         |                                 |                          |                          |
|      | 850     | $0.6 \pm 0.5$                         | $1.5 \pm 0.5$                         |                                 |                          |                          |

<sup>a</sup> ref. (12); <sup>b</sup> ref. (13), (14); <sup>c</sup> this work; <sup>d</sup> ref. (16).

$\Delta V_A$  is independent of temperature within experimental error. We define "activation energies" corresponding to constant pressure and constant volume conditions by eqn (7),

$$\begin{aligned} (E_A)_P &= -R[\partial \ln \Lambda / \partial (1/T)]_P; \\ (E_A)_V &= -R[\partial \ln \Lambda / \partial (1/T)]_V. \end{aligned} \quad (7)$$

Using eqn (2), these energies are related by

$$(E_A)_V = (E_A)_P - T(\partial P / \partial T)_V \Delta V_A \quad (8)$$

$(E_A)_V$  was calculated for each salt. For the alkali halides other than CsCl and CsI,  $(\partial P / \partial T)_V$  was calculated using eqn (3) and literature values of expansivity<sup>9</sup> and compressibility.<sup>10, 11</sup> The  $(E_A)_P$  values used in eqn (8) were also taken from the literature. Values of  $\Delta V_K$ ,  $\Delta V_A$ ,  $(E_A)_P$ ,  $(E_A)_V$  and  $(E_A)_V/(E_A)_P$  are listed in tables 1-3.