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Transport parameters for the molar electrical conductivities of molten alkali nitrates at high pressures

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Abstract. The temperature and pressure dependence of the electrical conductivities of the molten alkali nitrates are expressed in terms of molar and constant volume quantities. Values of activation energy and volume of activation are obtained, and the results are discussed in terms of liquid transport theories.

Glossary of symbols

A, B	empirical or theoretical parameters in transport property equations
C	potential energy term in Adam-Gibbs theory [Equation (13)]
ΔC_p	change in constant pressure specific heat at T_0
D	diffusion coefficient
D_i	diffusion coefficient of ion i
E_p	isobaric Arrhenius activation energy [Equation (3)]
E_V	isochoric Arrhenius activation energy [Equation (4)]
F	Faraday constant
$\Delta G_0^\ddagger$	standard partial molar free energy of activation
$(\Delta H_\mathrm{h})_p, (\Delta H_\mathrm{h})_V$	molar enthalpy of hole formation at constant pressure or constant volume
ΔH_j	molar enthalpy of activation for a jump process
$\Delta H_0^\ddagger$	standard partial molar enthalpy of activation
K	pre-exponential constant in Cohen and Turnbull relation
M	molecular weight
R	gas constant
S_c	molar configurational entropy [Equation (14)]
S_c^*	configurational entropy of cooperative region
ΔS_fus	molar entropy change on fusion
$\Delta S_0^\ddagger$	standard partial molar energy of activation
T	temperature
T_0	lower temperature limit of mobility
T_fus	melting point
U	molar internal energy
$(\Delta U_\mathrm{h})_p, (\Delta U_\mathrm{h})_V$	molar internal energy of hole formation at constant pressure or constant volume
$\Delta U_0^\ddagger$	standard partial molar internal energy of activation
$\Delta U_\mathrm{j}^\ddagger$	molar internal energy of activation for a jump process
V	molar volume
V_f	molar free volume, $V - V_0$
V_0	limiting molar volume; molar volume at T_0
V_s	molar volume of solid
$\bar{V}$	molar volume intermediate between V and $V^\ddagger$
$V^\ddagger$	molar volume of system in activated state
ΔV	activation volume [Equation (5)]
ΔV_fus	molar volume change on fusion
ΔV_j	volume change associated with an ionic jump process
$\Delta V_0^\ddagger$	standard partial molar volume of activation
k	term in Adam-Gibbs theory [Equation (16)]

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p	pressure
r_{+-}, r_{++}, r_{--}	friction coefficients
v_f	molecular free volume in Cohen and Turnbull theory
v^*	critical volume permitting diffusive displacement in Cohen and Turnbull theory
$\bar{v}_m$	mean molecular volume
$w(T)$	cooperative rearrangement probability
z_i	valence of ion i
z_+, z_-	valence of positive, negative ions
Λ	equivalent or molar electrical conductivity
$\bar{\alpha}$	mean expansion coefficient in the range T to T_0
β	thermal pressure coefficient $(\partial p/\partial T)_V$
γ	constant in Cohen and Turnbull theory
η	viscosity
κ	isothermal compressibility, $-(1/V)(\partial V/\partial p)_T$
$\Delta\mu$	potential energy hindering cooperative rearrangement
π	internal pressure, $(\partial U/\partial V)_T$ [Equation (6)]
$\pi^{\ddagger}$	internal pressure in activated state
ρ	density
σ	specific conductivity

1 Introduction

Recent studies in this laboratory have been concerned with the temperature and pressure coefficients of the electrical conductivity of molten salts. Results of the measurement of specific conductivities of the alkali metal nitrates have been described by Barton *et al.* (1968). The externally-heated pressure assembly used in that work was later used for the determination of the densities of the nitrate melts to pressures of 2 kbar and temperatures from the melting point to 500°C (Barton *et al.*, 1970; Bannard *et al.*, to be published).

The availability of these liquid $p-V-T$ data over the same range of temperature and pressure enables a more complete analysis of the transport properties to be made in terms of the constant volume principle (Barton, 1971a). The isobaric temperature dependence E_p, which is customarily obtained from Arrhenius plots, relates to a system in which a change in density accompanies the temperature change, and the importance of isochoric or constant volume parameters in normalising the system to one with a constant density of conducting species cannot be over-emphasized.

Relations suitable for describing the experimental results may be derived as follows (Barton, 1971a)[similar expressions have been previously used for fluidity and diffusion (Collins, 1957; Nagarajan and Bockris, 1966) as well as electrical conductivity (Brummer and Hills, 1961; Barton *et al.*, 1968)]:

$$\ln\Lambda = f_1(p, V, T)\,,$$

and from the equation of state $f_2(p, V, T) = 0$,

$$\ln\Lambda = f_3(p, T)$$

$$d\ln\Lambda = \left(\frac{\partial\ln\Lambda}{\partial T}\right)_p dT + \left(\frac{\partial\ln\Lambda}{\partial p}\right)_T dp\,. \tag{1}$$

Differentiating with respect to $(1/T)$ at constant volume yields

$$\left[\frac{\partial\ln\Lambda}{\partial(1/T)}\right]_V = \left[\frac{\partial\ln\Lambda}{\partial(1/T)}\right]_p - T^2\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial\ln\Lambda}{\partial p}\right)_T\,. \tag{2}$$

The *isobaric* energy of activation is familiar,

$$E_p = RT^2\left(\frac{\partial\ln\Lambda}{\partial T}\right)_p = -R\left[\frac{\partial\ln\Lambda}{\partial(1/T)}\right]_p\,. \tag{3}$$