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Self-Diffusion in Molten Salts. A Comparison Between Diffusion Theories and Experimental Data

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A comparison between the available self-diffusion data on pure molten salts and the predictions by different liquid diffusion theories is made. It is found that the Arrhenius equation $D=D_0 \exp(-Q/R\,T)$ describes the experimental data equally well (or better) than any of the other theoretically predicted equations. The hole model prediction ($Q=3.74\,R\,T_{\mathrm{m}}$) is found to be inaccurate. The free volume model and the local density fluctuation models describe the data less well than the other models considered. The cubic cell model leads to a correct correlation between self-diffusion and kinematic viscosity for several salts (but not all).

Several different models of liquids have been proposed, each leading to different equations regarding the transport properties. The complexity of the problems involved in theoretical descriptions of melts have led to the introduction of simplifying assumptions which in turn restrict the applicability of the theories (and the derived equations). The only possible way to ascertain the usefulness of a theory is to compare its predictions to experimentally obtained results. Every theoretical model gives a more or less detailed description of how to calculate the constants in the equations. In view of the approximate nature of the derivations it is however necessary first to investigate in a general way if the predicted temperature dependence (or any other readily controlled prediction) is supported or disproved by the experimental data. If an acceptable agreement is obtained the next step will be more detailed calculations of the constants (in the theoretical equations) whose values can be derived from independently measured quantities. The present paper covers only the first step above due to reasons to be discussed below.

The "proper" choice of the experimental data to be used as reference material is very difficult. A couple of different investigations of self-diffusion (and for that matter electrical conductivity and viscosity) have been carried out on several salts (in some cases even by the same worker). The difference between the observed values is sometimes considerable and although in most cases reasons are given why a certain investigation should be preferred to another, it is quite possible that a certain choice of data might affect the judgment of a certain theory in one way or the other. In order to avoid this risk all available self-diffusion data (which are not obviously in error) are used despite the fact that in some cases older data have been "superseded" by more recent material. It will be found that this procedure in no case affects the general conclusions drawn. In a recent paper[1] on self-diffusion in molten group II chlorides experimental data for only two salts out of eight are given while for the remaining salts only constants calculated according to the Arrhenius equation are tabulated:

$$D=D_0 \exp(-Q/R\,T). \tag{1}$$

D_0 is a constant, R is the gas constant, T is the temperature in degrees Kelvin, and Q is the "activation energy". Such a presentation is very unfortunate since the reader is limited to whatever use that can be made of these constants when quite possibly another interpretation might support (or disprove) some other model[2]. (It is true, however, that the Arrhenius equation describes most self-diffusion data equally well as or better than any other equation with the same number of adjustable constants.)

It has been general practice to describe the temperature dependence of the self-diffusion coefficient

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[1] J. O'M. Bockris, S. R. Richards, and L. Nanis, J. Phys. Chem. **69**, 1627 [1965].

[2] A carefully drawn plot of $\log(D)$ vs. T^{-1} is usually adequate in view of the obtained experimental accuracies.

(D) with the Arrhenius equation mentioned above, Eq. (1). It can be derived from the approach by EYRING et al.[3], who consider a mechanism where holes of ionic size in the liquid make jumps of the order of the interionic distance. The Arrhenius equation will be used in this paper as a standard to judge degree of success of a particular theoretical equation in describing the experimental data. (The discussion will be limited to self-diffusion in pure molten salts.)

The Hole Model

The hole model was originally developed by FÜRTH[4]. He regarded transport in molten salts as governed by jumps of cations and anions into vacancies large enough for a whole ion. This approach has been adopted by BOCKRIS and coworkers[1, 5–10]. Since the viewpoint of the original rate-theory[3] is in principle retained the theory leads to an equation of the Arrhenius type

$$D = D_0 \exp\left(-\frac{Q_h + Q_j}{R\,T}\right). \tag{2}$$

The activation energy is thus divided into two terms, Q_h corresponding to the work needed to create a "hole" large enough to accommodate the ion and Q_j corresponding to the energy needed by the ion to jump into this hole. It is also predicted that Q_j is small[5] and thus that Q_h predominates. Q_h and Q_j can be determined by self-diffusion experiments at elevated pressures. Such measurements have been performed by BOCKRIS et al.[7, 10] and the (still scarce) results are in general agreement with the prediction. The obtained precision is rather low, however, due to considerable experimental difficulties. Moreover, it is well known that the solubility of the pressure-transferring medium (an inert gas) increases with pressure. The contamination of the melt is difficult to estimate due to the lack of independent high-pressure data. Thus the apparent support to the hole model by the constant-volume results is very uncertain at present.

Another check of the theory can be obtained by the relation

$$Q \approx Q_h = 3.74\,R\,T_m \tag{3}$$

where T_m is the melting temperature in degrees Kelvin. According to NANIS and BOCKRIS[6] "the numerical constant is bonded from theoretical considerations[11] by the limits 3.5 to 3.8". They have graphically performed a comparison[6] between the observed Q-values for self-diffusion and the melting points of some molten salts and also some noble gases and liquid metals. They find a general trend by which high-melting substances tend to have comparatively high activation energies. The agreement with Eq. (3) is, however, not very good (particularly bad for the molten salts). Thus it was felt necessary to investigate this matter in a more quantitative way[12] (see Table 1). If the "associated" salts (the zinc halides) are excluded it is still found that only 8 out of 53 values are close to (or inside) the predicted limits. The arithmetic mean of $Q/R\,T_m$ is, however, 4.0 ± 0.8[13] but the data in Table 1 indicate that the quantitative predictions by the hole model [in particular Eq. (3)] are inaccurate for almost any given salt.

The Free Volume Model

The free volume model was introduced by COHEN and TURNBULL[14] and has been discussed particularly by ANGELL[15–22]. The model liquid is composed of

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[3] S. GLASSTONE, K. J. LAIDLER, and H. EYRING, The Theory of Rate Processes, McGraw-Hill, New York 1941, p. 477.

[4] R. FÜRTH, Proc. Cambridge Phil. Soc. **37**, 281 [1941].

[5] J. O'M. BOCKRIS and G. W. HOOPER, Disc. Faraday Soc. **32**, 218 [1962].

[6] L. NANIS and J. O'M. BOCKRIS, J. Phys. Chem. **67**, 2865 [1963].

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[8] S. B. TRICKLEBANK, L. NANIS, and J. O'M. BOCKRIS, J. Phys. Chem. **68**, 58 [1964].

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[10] M. K. NAGARAJAN and J. O'M. BOCKRIS, J. Phys. Chem. **70**, 1854 [1966].

[11] F. H. STILLINGER, in "Selected Topics in Molten Salt Chemistry", ed. M. BLANDER, Interscience Publishers, Inc., New York 1963.

[12] A similar (but less comprehensive) comparison has been made by A. LUNDÉN, Trans. Chalmers Univ. of Technol. **241**, 6 [1961].

[13] All stated errors in this paper are standard deviations.

[14] M. H. COHEN and D. TURNBULL, J. Chem. Phys. **31**, 1164 [1959].

[15] C. A. ANGELL, J. Phys. Chem. **68**, 218 [1964].

[16] C. A. ANGELL, J. Phys. Chem. **68**, 1917 [1964].

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[22] C. A. ANGELL, E. J. SARE, and R. D. BRESSEL, J. Phys. Chem. **71**, 2759 [1967].

Salt		Ref.	$D_0 \times 10^3$ (cm^2 s^{-1})	Q (cal mole^{-1})	T_m (°K)	$Q/R\,T_m$
$LiNO_3$	D^+	34	2.47	5490	537	5.15
	D^-		1.95	6340		5.94
$NaNO_3$	D^+	34	1.29	4970	580	4.32
	D^-		0.90	5080		4.41
$NaNO_3$	D^+	35	—	5000	580	4.34
$NaNO_3$	D^+	10	0.55	4300	580	3.73
$NaNO_3$	D^+	35a	2.0[a]	5340[a]	580	4.63
KNO_3	D^+	34	1.32	5530	607	4.59
	D^-		1.42	5760		4.78
KNO_3	D^+	35	—	5600	607	4.64
$CsNO_3$	D^+	34	1.13	5610	687	4.12
	D^-		1.78	6280		4.61
$CsNO_3$	D^+	10	1.79	6470	687	4.74
$AgNO_3$	D^+	34	0.49	3730	485	3.87
	D^-		0.31	3480		3.99
$AgNO_3$	D^+	36	0.32	3400	485	3.53
$TlNO_3$	D^+	35a	0.64[a]	4290[a]	479	4.51
NaCl	D^+	5	3.36	7860	1074	3.69
	D^-		3.02	8390		3.93
NaCl	D^+	1	2.1	7140	1074	3.35
	D^-		1.9	7430		3.49
NaCl	D^+	9	1.49	6800	1074	3.18
KCl	D^+	1	1.8	6880	1049	3.31
	D^-		1.8	7130		3.43
RbCl	D^+	5	2.51	8010	988	4.08
	D^-		1.67	7420		3.78
CsCl	D^+	5	1.73	7320	919	4.02
	D^-		2.46	7820		4.28
TlCl	D^+	37	0.76	4600	703	3.29
TlCl	D^+	38	0.73	4540	703	3.25
	D^-		0.79	4560		3.27
NaI	D^+	5	0.63	4030	924	2.20
	D^-		0.43	4420		2.41
NaI	D^+	8	1.09	5020	924	2.74
	D^-		1.88	7210		3.94
$CaCl_2$	D^+	1	0.38	6130	1045	2.95
	D^-		1.9	8860		4.27
$CaCl_2$	D^+	39	0.99	9910	1045	4.78
$ZnCl_2$	D^+	1	—	12200[a]	556	11.1
	D^-		—	11000[a]		9.8
$ZnCl_2$	D^+	40	58.5	15500	556	14.0
	D^-		137	16300		14.8
$SrCl_2$	D^+	1	0.21	5380	1146	2.37
	D^-		0.77	6880		3.02
$CdCl_2$	D^+	1	1.1	6840	841	4.09
	D^-		1.1	6800		4.07
$BaCl_2$	D^+	1	0.64	8960	1236	3.66
	D^-		2.0	9480		3.87
$PbCl_2$	D^+	41	0.773	6777	774	4.40
	D^-		0.895	6099		3.96
$PbCl_2$	D^+	38	1.47	7760	774	5.05
	D^-		2.55	7740		5.03
$ZnBr_2$	D^+	42	79	16060	667	12.1
$ZnBr_2$	D^+	43	405	19000	667	14.4
$ZnBr_2$	D^+	44	80	16900	667	12.8
	D^-	45	114	17050		12.9
$PbBr_2$	D^+	46	0.74	6500	646	5.06
	D^-		0.83	6100		4.75
Li_2CO_3	D^-	46a	0.014	9740	996	4.92
Na_2CO_3	D^+	47	10.0	12170	1124	5.45
	D^-		2.86	10620		4.76
			Mean value (Zn halides excluded)			4.04 ± 0.83

Tab. 1. Constants in the "ordinary" Arrhenius equation (1) as given by each worker ([a] = not given, calculated from given data). The agreement between the prediction by the hole model ($Q/R\,T_m = 3.5$ to 3.8) and the calculated values in the last column is seen to be poor. The stated error is a standard deviation.

simple spherical molecules and the diffusion process is assumed to occur by jumps (of molecular dimensions) made possible by momentary increases in the "cage" of neighbours due to redistribution of "free volume". In the latest version the approach according to Ref. [14] is replaced by a recent theory by Adam and Gibbs [23]. They assume that the translational motion of a given molecule occurs by rearrangement of a group of molecules. Postulating that these groups operate independently they could express the minimum size of such a group in terms of the (macroscopic) configurational entropy. Both these theories lead to essentially the same equations [24] for the temperature dependence of self-diffusion, equivalent conductivity (Λ), and viscosity (η)

$$D = D_0' \exp\left(-\frac{k}{T-T_0}\right) \tag{4}$$

(and corresponding equations for ΛT and $\eta^{-1} T$) where D_0' and k are constants and T_0 is the glass transition temperature (C-T approach) or the temperature at which the configurational entropy is zero (A-G approach). In both theories the attention is focussed on the behaviour of the liquid in the "low temperature region" (generally the supercooled liquid state).

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[23] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 [1965].

[24] In the original equation by Cohen and Turnbull a factor $T^{1/2}$ is included in the pre-exponential term. This factor does not arise in the Adam-Gibbs approach. It has been disregarded in the later papers [19–22] (its effect on the predicted temperature dependence is very weak).

ANGELL[15, 16, 19] has been able to show that the equivalent conductivity of supercooling salt mixtures indeed follows Eq. (4) and that k has about the same value for all systems (with univalent anions) studied. T_0 can be correlated with the mean cationic strength (a table of T_0-values obtained in this way is given in Ref. [17]). Finally, the glass transition temperature has been measured directly in some systems[22].

It has been argued[16] that the precision of the experimental self-diffusion data is too low to detect the influence of the constant T_0 in Eq. (4). Nevertheless the real test of the theory must be a direct comparison between the predicted equation and the observed data. Such a comparison is difficult since the temperature T_0 of most pure salts is well below the melting temperature T_{m}. It has already been found[16] that the agreement between predicted and observed equivalent conductivity values is less good when T is greater than about $1.7\,T_0$. (The "constant" k is slightly temperature dependent in this range.) Thus the prospects for a sucessful description of the available self-diffusion data (which in most cases are obtained at temperatures well above T_0) are somewhat dim. A meaningful comparison between the observed self-diffusion data and the theoretical Eq. (4) must include the use of the predicted T_0-value (since otherwise the equation reduces to a variant of the Arrhenius equation with another adjustable constant added). Thus Eq. (4) with the predicted T_0 inserted was least squares fitted[25] to the experimental data ($T_0 \pm 15\,°\mathrm{K}$ was also tried[26] in order to ascertain if the predicted T_0 indeed gives the best fit). D_0' and

Salt		Ref.	$D_0' \times 10^5$ (cm^2 s^{-1})	k (°K)	T_0 (°K)	Temp. range expressed in T_0	$T_{D=0}$ (°K)
$LiNO_3$	D^+	34	8.3	269	385	1.4−1.6	450
	D^-		4.1	312			
$NaNO_3$	D^+	34	19.7	721	285	2.1−2.3	460
	D^-		13.5	747			
$NaNO_3$	D^+	35	19.9	741	285	2.1−2.3	460
$NaNO_3$	D^+	10	16.3	688	285	2.2−2.4	440
$NaNO_3$	D^+	35a	26.3	772	285	2.1−2.2	460
KNO_3	D^+	34	26.6	1100	237	2.6−2.8	490
	D^-		27.1	1160			
KNO_3	D^+	35	29.7	1090	237	2.5−2.8	480
$CsNO_3$	D^+	34	34.8	1930	210	3.2−3.6	520
	D^-		50.3	1570			
TlCl	D^+	37	30.3	1100	240	3.2−3.5	470
TlCl	D^+	38	27.9	1020	240	3.0−3.4	460
	D^-		25.5	1070			
NaI	D^+	5	33.2	995	285	3.3−3.8	520[a]
	D^-		23.0	1150			
NaI	D^+	8	53.3	1300	285	3.4−3.8	610
	D^-		64.8	1820			
$CaCl_2$	D^+	39	24.2	2250	380[b]	2.9−3.2	870
$ZnCl_2$	D^+	1	3.10	746	450[b]	1.3−2.0	610[c]
	D^-		1.62	663			
$ZnCl_2$	D^+	40	3.6	874	450[b]	1.3−1.8	620[c]
	D^-		4.8	906			
$BaCl_2$	D^+	1	97.4	2840	330[b]	3.8−4.5	920
	D^-		26.6	2540			
$CsNO_3$	D^+	10	54.8	1711	210	3.4−3.8	570
$AgNO_3$	D^+	34	9.9	592	225	2.2−2.5	380
	D^-		8.1	695			
$AgNO_3$	D^+	36	8.0	588	225	2.2−2.7	370
$TlNO_3$	D^+	35a	10.6	652	240[b]	2.0−2.5	390
NaCl	D^+	5	161	2320	290	3.8−4.3	790
	D^-		137	2480			
NaCl	D^+	9	145	1789	290	3.8−4.3	650
RbCl	D^+	5	112	2450	240	4.2−4.8	740
	D^-		67	2130			
CsCl	D^+	5	75	2210	220	4.3−4.9	710
	D^-		103	2380			
$PbCl_2$	D^+	41	10.2	930	385	2.0−2.2	590
	D^-		14.6	837			
$PbCl_2$	D^+	38	16.6	1120	385	2.0−2.2	630
	D^-		24.2	1040			
$ZnBr_2$	D^+	42	16.2	1340	450	1.5−2.0	690[c]
$ZnBr_2$	D^+	43	16.1	1450	450	1.5−1.9	690[c]
$ZnBr_2$	D^+	44	13.3	1480	450	1.5−1.8	690[c]
	D^-	45	11.1	1340			
$PbBr_2$	D^+	46	6.5	690	385[b]	1.7−2.1	560
	D^-		8.6	663			
Na_2CO_3	D^+	47	203	2770	410[b]	2.2−2.6	930
	D^-		71	2410			

Tab. 2. Constants in the ADAM-GIBBS equation (4) calculated by least squares fitting. The constant k differs widely for different salts. A table of the "reference temperature" $T_{D=0}$ suggested in the discussion of the LDF-models is also included. The given value is a mean obtained from A_0 and A_2 of D^+ and D^-. [a] = Only A_0 used in this calculation since $A_2 \approx 0$. [b] = Calculated according to Ref. [16]. [c] = Higher than the melting point.

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[25] A. HALD, Statistical Theory with Engineering Applications, John Wiley & Sons, New York 1952, p. 522.

[26] According to Ref. [17] the accuracy of the predicted T_0-values is ± 10 °K or better.

k for all studied salts are given in Table 2 since Eq. (4) constitutes a novel approach and thus these values cannot be found elsewhere.

The linear regression analysis[25] shows, that

a) In no case are the data best fitted using the predicted value of T_0.

b) For only 3 salts are the data better fitted by Eq. (4) using the predicted T_0 while for 9 salts the ordinary Arrhenius equation (1) gives better fit (the remaining 6 salts are equally well fitted by both equations).

c) The obtained k-values are within experimental error equal for D^+ and D^- of the same salt (and the results by different workers are also in satisfactory agreement with each other).

d) The obtained k-values differ considerably for different salts.

The results calculated from data obtained at temperatures close to T_0 where Eq. (4) is expected to be strictly valid ($LiNO_3$, $ZnCl_2$, $ZnBr_2$, and perhaps $PbBr_2$) agree with the general conclusions above. Thus it is improbable that the discrepancies between the predictions and the observations are due to the (comparatively) high experimental temperatures only, and it can be concluded that the theory by Cohen and Turnbull (and by Adam and Gibbs) describes (the available) self-diffusion data less well than the ordinary Arrhenius equation. The success of Eq. (4) in reproducing (conductivity) data of glass-forming liquids close to their T_0 is, however, a good reason to continue the study of the free-volume theory in that connection.

The Local Density Fluctuation (LDF) Model

According to this model by Swalin[27] diffusion in liquids (molten metals) results from local density fluctuations causing the molecules to move small (and variable) distances. In contrast to the free volume model the LDF model does not stipulate a critical (minimum) void size before diffusion will occur. Using the transition state theory Swalin obtained an equation for the self-diffusion coefficient (D)

$$D = A\,T^2 \tag{5}$$

where A is a constant depending on the particular liquid in question. Eq. (5) has been criticized by Reynik[28] who has pointed out that in the derivation of the equation from the transition state theory a factor T^{-1} has been omitted. The correct form of the equation should be

$$D = A\,T\,. \tag{6}$$

A crude calculation by Nachtrieb[29] gives an equation similar to Eq. (6) which is claimed to give good agreement with experimental self-diffusion data of liquid In, Sn, Cu, Na, Ga, K, Hg, and Ag[28]. In order to investigate if Eqs. (5) and (6) are able to describe molten salt diffusion as well the equations

$$D = A_0 + A_1\,T\,, \tag{7}$$

$$D = A_2 + A_3\,T^2\,, \tag{8}$$

were least squares fitted to the data[25]. According to the predicted Eqs. (5) and (6) the constants A_0 and A_2 should then come out equal to zero.

The regression analysis[25] shows, however, that for only one salt (NaI according to Ref. [5]) is the constant A_2 within experimental error equal to zero and that the constant A_0 is never equal to zero. (An inspection of available self-diffusion data on molten metals[28, 29] shows that A_0 is different from zero in those cases also, a fact that obviously has been overlooked.) Thus it is found that while D might *vary* linearly with T, D is not directly proportional to T (or T^2) for molten salts (and not for molten metals either). Neither Eq. (5) nor Eq. (6) are in their present form able to correctly describe the observed data which means that the LDF models must be modified in order to take into account the need of a constant term in Eqs. (5) and (6). Such a term might be introduced by measuring the temperature relative to a reference temperature $T_{D=0}$ where D is supposed to become zero. [These temperatures $T_{D=0}$ can be calculated from A_0 in Eq. (7) or A_2 in Eq. (8). Approximatively the same value is obtained in both cases[30].] The meaning (if any) of these calculated "reference" temperatures is of course unclear. Most obtained values (see Table 2) fall 100 to 400 °K below the melting points of the salts. For two salts ($ZnCl_2$ and $ZnBr_2$) $T_{D=0}$ comes out higher than the melting points. This fact means merely that not even Eqs. (7) and (8) are able to describe those data satisfactorily. It is likely that similar discrepancies had been discovered for other salts too if their

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[27] R. A. Swalin, Acta Met. **7**, 736 [1959].

[28] R. J. Reynik, Appl. Phys. Letters **9**, 239 [1966].

[29] N. H. Nachtrieb, Adv. Phys. **16**, 309 [1967].

[30] Within 10%.

$D:s$ had been studied over a wide range (i. e. two orders of magnitude).

Neither of the local density fluctuation models is in its present form able to satisfactorily describe self-diffusion in molten salts (and obviously not self-diffusion in liquid metals either) [30a].

The Cubic Cell Model

Houghton [31] has developed a cubic cell model for viscous flow and self-diffusion in liquids based on the Navier-Stokes equation. He is able to relate the friction coefficient for a molecule interacting with its neighbours to the diffusivity, kinematic viscosity and cell dimensions. The model leads to an equation

$$D = C_1 \frac{T\varrho}{\eta} = C\,T \exp(-Q_\nu/R\,T) \qquad (9)$$

where C_1 and C are constants, ϱ is the density, η is the viscosity, and Q_ν is the activation energy of the kinematic viscosity $\nu = \eta/\varrho$. Thus Eq. (9) can be used to predict the self-diffusion coefficient of a liquid once the kinematic viscosity is known. (C_1 is equal to $R\,\lambda^2/24\,M$, where λ is the linear dimensions of the cubic cell and M is the molecular weight.)

A similar equation is arrived at by Walls and Upthegrove [32]. Einstein's relation between the diffusion coefficient (D) and the mobility (M' = velocity per unit force), $D = k\,T\,M'$ (where k in this case is the Boltzmann constant) is used as a starting point. A relation between mobility and kinematic viscosity is then obtained by geometrical reasoning, the final result being an equation almost identical to Eq. (9). The constant C_1 in this case contains the atomic radius and a geometrical parameter postulated to be the same for a given class of liquids. Walls and Upthegrove then modify their equation by introducing the expression for η derived by Eyring et al. [33].

Equation (9) shows that a plot of $^{e}\log(D/T)$ versus T^{-1} should have a slope equal to $-Q_\nu/R$. A comparison between experimentally observed values of Q_ν and the values calculated from self-diffusion data using Eq. (9) is made in Table 3. The agreement is satisfactory for all studied nitrates and also for RbCl, CsCl, $CaCl_2$, $PbCl_2$, and $PbBr_2$ while on the other hand NaCl, NaI, $ZnCl_2$, and $BaCl_2$ show considerable discrepancies.

The cubic cell model and the model by Walls and Upthegrove are thus able to predict the temperature dependence of many salts without relying upon adjustable constants. Further systematic studies of self-diffusion and kinematic viscosity of molten salts are, however, needed before it is known if this fact can be used to provide further insight into the mechanism(s) of diffusion in (at least some classes of) molten salts.

No attempt has been made in this paper to calculate the constants in the theoretical equations from the descriptions in the original (theoretical) papers and make a comparison with the constants obtained in the least squares fittings since the discussions above have already shown that all the models considered have more or less serious shortcomings. The local density fluctuation models are in their present form unable to give a correct equation relating D and T (this is the case for molten metals as well). The free volume model is successful in describing equivalent conductivity close to and below the melting point but the use of the constant T_0 (which is central in this theory) leads to a description of D which is inferior to that of the ordinary Arrhenius equation. The hole model leads to a variant of the Arrhenius equation (and describes consequently the observed data at least as well as any other model) but the prediction of the magnitude of the activation energy is inaccurate. The cubic cell model is able to predict the temperature dependence of D for many molten salts without use of adjustable constants but there are also many exceptions. It can finally be mentioned that the "ordinary" Arrhenius equation is at least as good as any other equation as a convenient and accurate representation of experimental self-diffusion data.

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[30a] Note added in proof: S. A. Rice and N. H. Nachtrieb, Adv. Phys. **16**, 351 [1967], find that D at constant density should be proportional to $T^{3/2}$. As a support they cite constant pressure data for molten Hg and Na, finding a linear dependence of D upon $T^{3/2}$. The need of a constant term in the equation as in Eq. (7) and (8) is not taken care of in this case either which means that the equation by Rice and Nachtrieb has to be modified in the same way as the LDF equations in order to become able to describe the experimental data (for both metals and salts).

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Salt		Ref.	$C \times 10^7$ ($cm^2 s^{-1} T^{-1}$)	Q_v Calculated (cal mole^{-1})	Observed	Ref.
$LiNO_3$	D^+	34	16.4	4390	5290	48
	D^-		13.1	5260		
$NaNO_3$	D^+	34	7.7	3750	3470	48
	D^-		5.5	3870		
$NaNO_3$	D^+	35	8.0	3710	3470	48
$NaNO_3$	D^+	10	3.9	3000	3470	48
$NaNO_3$	D^+	35a	12.3	4150	3470	48
KNO_3	D^+	34	8.0	4320	3990	48
	D^-		8.1	4490		
KNO_3	D^+	35	8.1	4360	3990	48
$AgNO_3$	D^+	34	3.4	2680	3450	49
	D^-		3.2	3190		
$AgNO_3$	D^+	36	2.0	2330	3450	49
$TlNO_3$	D^+	35a	4.3	3210	2870	49
NaCl	D^+	5	12.2	5910	10400	48
	D^-		10.6	6320		
NaCl	D^+	9	4.9	3910	10400	48
RbCl	D^+	5	8.8	5920	5040	49
	D^-		4.4	4690		
CsCl	D^+	5	6.2	5260	6300	49
	D^-		9.3	5900		
NaI	D^+	5	2.1	1850	6460	48
	D^-		1.7	2560		
NaI	D^+	8	4.1	3090	6460	48
	D^-		6.2	4960		
$CaCl_2$	D^+	39	3.2	7670	9600	48
$ZnCl_2$	D^+	1	40	10800	23100	49
	D^-		11.0	9400		
$ZnCl_2$	D^+	40	310	14000	23100	49
	D^-		710	14900		
$BaCl_2$	D^+	1	6.4	7150	19300	49
	D^-		1.5	6030		
$PbCl_2$	D^+	41	3.4	5100	6270	48
	D^-		4.1	4480		
$PbCl_2$	D^+	38	7.0	6230	6270	48
	D^-		9.4	5780		
$PbBr_2$	D^+	46	3.8	5040	5400	48
	D^-		4.3	4700		

Tab. 3. Constants in the cubic cell model equation (9) obtained by least squares fitting. The agreement between the calculated and observed Q_v-values is satisfactory (in view of the obtained accuracies) except for NaCl, NaI, $ZnCl_2$, and $BaCl_2$.

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