# ELECTROMOTIVE FORCE MEASUREMENTS IN THE SYSTEM AgNO<sub>3</sub> AND NaCl IN EQUIMOLAR NaNO<sub>3</sub>-KNO<sub>3</sub> MIXTURES AND THEIR COMPARISON WITH THE QUASI-LATTICE THEORY

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Electromotive force measurements in dilute solutions of Ag  $^+$  and Cl $^-$  ions in molten equimolar mixtures of NaNO<sub>3</sub> and KNO<sub>3</sub> demonstrate over the range of temperatures of 233–528° that the temperature coefficient of the association constant for the formation of the ion pair Ag  $^+$ -Cl $^-$  is, within the estimated experimental error, correctly given by the expression  $Z(\exp(-\Delta E/RT)-1)$  which has been derived from the quasi lattice model, where Z is the coördination number and  $\Delta E$  is the energy of ion pair formation and is a constant.  $K_1$  varies from 1050 (moles/mole solvent) $^{-1}$  at 233° to 133 (moles/mole solvent) $^{-1}$  at 528°. For possible values of Z=4, 5 and 6 average values of  $-\Delta E$  of 5.64, 5.36 and 5.12 kcal./mole, respectively, were calculated.

#### Introduction

In this paper are described measurements of the activity coefficients of  $AgNO_3$  in dilute solutions of  $Ag^+$  and  $Cl^-$  ions in molten equimolar mixtures of  $NaNO_3$  and  $KNO_3$  at five temperatures ranging from 233 to 528°. In previous papers, similar measurements in pure  $KNO_3^{3,4}$  and in pure  $Na-NO_3^{5,6}$  have been made and compared to the results based on the quasi-lattice model.<sup>6,7</sup> The comparison demonstrated that the temperature coefficient of the association constant  $K_1$ , for the formation of the ion pair  $Ag^+-Cl^-$  is correctly predicted by the expression derived from the theoretical calculations

$$K_1 = Z(\exp(-\Delta E/RT) - 1) = Z(\beta - 1)$$
 (1)

where Z is a coördination number,  $\beta = \exp(-\Delta E/RT)$ , and  $\Delta E$  is the energy of ion pair formation and is a constant.  $K_1$  was larger and  $\Delta E$  was more negative by about 1 kcal. in the solvent KNO<sub>3</sub> than in NaNO<sub>3</sub>. The purpose of this paper is to demonstrate the validity of equation 1 and the constancy of  $\Delta E$  over a larger range of temperatures than previously and to obtain information on the solvent effect in a mixed solvent.

### Experimental

The apparatus, materials and procedure were the same as have been described previously. In some batches of molten reagent grade alkali nitrates a precipitate was observed upon addition of  $\Lambda gNO_3$ . For the experiments particular batches from the manufacturers in which this precipitate was not observed were used. At 233 and 279° it was difficult to fabricate a reference electrode with a high enough conductance which did not leak. Consequently the galvanometer was somewhat sluggish and there was some scatter in the data at these temperatures. At 528° the reproducibility of the measurements was poorer than at the lower temperatures and was about  $\pm 1$  millivolt.

#### Results

As described previously,<sup>3,4</sup> electromotive force measurements were made in the concentration cell

$$Ag \begin{vmatrix} AgNO_3 \\ (Na-K)NO_3 \end{vmatrix} \begin{vmatrix} AgNO_3 \\ NaCl \\ (Na-K)NO_3 \end{vmatrix} Ag$$

for low concentrations of Ag<sup>+</sup> and Cl<sup>-</sup> ions. The addition of increments of NaCl to the right hand half cell at fixed concentrations of AgNO<sub>3</sub> in both half cells led to a change of e.m.f. from which the activity coefficient of AgNO<sub>3</sub> could be calculated

$$\Delta e.m.f. \cong \frac{2.303RT}{F} \log \gamma_{AgNO};$$
 (2)

where  $a_{AgNO_i} = N_{Ag}N_{NO_i}\gamma_{AgNO_i} \cong R_{AgNO_i}y_{AgNO_i}$  where the N are ion fractions and  $R_i$  is the mole ratio of the component i and

$$\frac{R_{\rm AgNO_3}}{N_{\rm Ag}} = 1 + R_{\rm NaC1} + R_{\rm AgNO_3}$$

which is close to unity in dilute solutions so that within the experimental precision,  $y_{AgNO_3} = \gamma_{AgNO_3}$ . The concentrations of ions for which data are reported are well below concentrations at which a ported are well below concentrations at which a precipitate was observed visually. Values of  $-\log \gamma_{\rm AgNO_3}$  are given in Table I for different values of  $R_{\rm AgNO_3}$  and  $R_{\rm NaCl}$  at 233, 278, 385, 479 and 528°. The experimental results at 385° are plotted in Fig. 1 for  $R_{\rm AgNO_3} = 0.2 \times 10^{-3}$  and 2.2  $\times$  10<sup>-3</sup>. The comparison in Fig. 1 of the concentration dependence of the experimental results with calculations based on the symmetric and the asymmetric approximations based on the quasilattice model indicates that the concentration dependence of the asymmetric approximation is closer to the experimental results. In Fig. 2 are plotted values of  $-\log \gamma_{\rm AgNO_3}$  versus  $R_{\rm Cl}$  at  $R_{\rm AgNO_3}$   $\cong 0.2 \times 10^{-3}$  at five temperatures ranging from 233 to 528°. The points at 233 and 278° represent points from four separate sets of measurements, at 385 and 479 from one and at 528 from three. One low set of measurements at 528° which was not plotted was rejected.

#### Discussion

The solid lines of Fig. 2 represent values of  $-\log \gamma$  from the calculations based on the asymmetric approximation<sup>4,5</sup> for the values of Z and  $\Delta E$  listed in Table II where the range of values of 4 to 6 probably covers all reasonable values of Z. Within the estimated error of the measurements the values of  $\Delta E$  for any given value of Z are constant at all temperatures at which measurements were made. This demonstrates that over  $\alpha$ 

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<sup>(4)</sup> J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960).

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<sup>(6)</sup> M. Biander and J. Braunstein, Ann. N. Y. Acad. Sci., 79, 838 (1960).

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#### TABLE I

ACTIVITY COEFFICIENTS CALCULATED FROM E.M.F. CHANGE OF HALF CELLS CONTAINING SOLUTIONS OF AgNO<sub>3</sub> IN EQUIMOLAR MIXTURES OF NaNO<sub>3</sub> AND KNO<sub>3</sub> UPON ADDITION OF CHLORIDE

	A	DDITION OF			
Temperature 233°		Temperat	ure 385°	Temperature 528°	
$R_{\text{AgNO8}} = 0.198 \times 10^{-8}$		$R_{\text{AgNO3}} = 0.2017 \times 10^{-3}$		$R_{\text{AgNO3}} = 0.2016 \times 10^{-3}$	
$Rcl \times 10^3$	—log γΑεΝΟ3	$R_{\rm Cl} \times 10^3$	−log γAgNO₃	$R_{\rm Cl} \times 10^2$	-log γagNOs
0.082	0.029	0.207	0.022	0.333	0.021
0.082	0.065	.640	.077	.756	.045
		.918	.109	1.168	.069
$R_{ t AgNO} = 0.200  imes 100$	10 -3		. 138	1.614	.093
$R_{\rm Cl} \times 10^3$	-log	1.174	. 194	1.014	.106
	γAgNO3	1.683			.125
0.035	0.011	2.370	. 264	2.350	.123
.080	.023	2.946	. 320	2.809	
.170	.063	$R_{ m AgNO}$	08 = ( 10 -3	$R_{AeNO} = 0.2015$	3 = 4 10 -3
.200	.087		log	$R_{\rm Cl}  imes 10^{3}$	log
$R_{ ext{AgNO}}$	10-3	$R_{\rm Cl} \times 10^3$	YAENO3		γΑ <sub>2</sub> ΝΟ3
	-log	0.435	0.038	0.448	$0.023^a$
$R_{\rm Cl} \times 10^{8}$	γAgNO3	. 664	.058	. 0936ª	. 0524
0.059	0.025	.995	.087	1.314	.0624
R <sub>AgNO</sub> 0.2014 >	10-3	1.303	. 115	1.918	.0894
	-log	1.654	. 149	$2.278^a$	$.108^{a}$
$R_{ m Cl}  imes 10^{ m s}$	YAgNO3	1.997	. 185	$R_{ m AgNO}$	03 = 0 10 -3
0.050	0.017	RARNO	08 =		$-\log$
. 087	. 029	2.200 >	-log	$R_{\rm Cl}  imes 10^{\rm s}$	YAgNO8
. 141	. 058	$R_{\mathrm{Cl}}  imes 10^{3}$	$\gamma_{\rm AgNO3}$	0.528	0.031
. 193	.078	0.270	0.0252	1.24	.070
Temperatu	ıre 278°	. 460	. 0443	1.95	. 108
$R_{AgNO} \ 0.2013 >$	3 == C 10 = 3	. 725	.0664	2.75	. 149
	-log	1.01	. 0909	3.79	. 200
$R_{\rm Cl}  imes 10^{3}$	γAgNO3	1.32	.112	4.68	. 242
0.157	0.039	1 00	147	-	
	100	1.68	. 141	KARNO	98 —
.407	. 103			$R_{AgNO}$ $0.203$	< 10 −8
. 407 . 541	.140	Temperat	ure 479°	$0.203 \Rightarrow$ $R_{\rm Cl} \times 10^3$	7 10 -8 - log γλ <sub>8</sub> ΝΟ3
. 407 . 541 . 805	. 140 . 201	Temperat Ragno 0.2018	ure 479°  10 =  × 10 -3  — log	0.203 >	< 10 <sup>-8</sup> −log
.407 .541 .805 .943	.140 .201 .231	Temperat $R_{\rm AgNC}$ 0.2018 : $R_{\rm Cl}  imes 10^3$	ture 479°  0s =  × 10-s  —log  γAgNO	$0.203 \Rightarrow$ $R_{\rm Cl} \times 10^3$	-log γλαΝΟ3
. 407 . 541 . 805	. 140 . 201	Temperat $R_{\rm AgNC}$ $0.2018$ $R_{\rm Cl} \times 10^8$ $0.153$	oure 479°  > 10 -8  -log  > Agno  0.011	$0.203 > R_{Cl} \times 10^{3}$ $0.203$	10-8 -log γλ <sub>g</sub> NO3 0.0069
.407 .541 .805 .943 1.154 RAENO	.140 .201 .231 .288	Temperat $R_{AgN} = 0.2018$ $R_{Cl} \times 10^{8}$ $0.153$ $0.275$	oure 479° 08 =  × 10~8	$0.203 \Rightarrow$ $R_{\text{Cl}} \times 10^3$ $0.203$ $.437$	10-8 -log γλ <sub>8</sub> Nos 0.0069 .0195
.407 .541 .805 .943 1.154 RAENO 0.2003 >	.140 .201 .231 .288	Temperat $R_{\rm AgN}$ 0.2018 $0.2018$ $0.153$ $0.153$ $0.724$	ture 479°  03 =  × 10 -3  —log γAgNO  0.011  .019 .054	$0.203 \Rightarrow$ $R_{\text{Cl}} \times 10^3$ $0.203$ $.437$ $.677$	10 <sup>-8</sup> -log γλ <sub>8</sub> N03 0.0069 .0195
$.407$ $.541$ $.805$ $.943$ $1.154$ $R_{AKNO}$ $0.2003 > R_{Cl} \times 10^{3}$	.140 .201 .231 .288 2 = -log yAgNO3	Temperat $R_{AgN} = 0.2018$ $R_{Cl} \times 10^{8}$ $0.153$ $0.275$	oure 479°  > 10 - 8  × 10 - 8  — log γAgNO  0.011  .019 .054 .070	$0.203 \Rightarrow$ $R_{Cl} \times 10^{3}$ $0.203$ $.437$ $.677$ $1.03$	10 <sup>-8</sup> -log γλ <sub>8</sub> Nο3 0.0069 .0195 .0327 .0529
$.407$ $.541$ $.805$ $.943$ $1.154$ $0.2003 >$ $R_{\rm Cl} \times 10^3$ $0.083$	.140 .201 .231 .288	Temperat $R_{\rm AgN}$ 0.2018 $0.2018$ $0.153$ $0.153$ $0.724$	ture 479°  03 =  × 10 -3  —log γAgNO  0.011  .019 .054	$\begin{array}{c} 0.203 \\ R_{\text{Cl}} \times 10^{3} \\ 0.203 \\ .437 \\ .677 \\ 1.03 \\ 1.22 \\ 1.58 \end{array}$	10 <sup>-8</sup> -log γλ <sub>6</sub> No <sub>3</sub> 0.0069 .0195 .0327 .0529 .0641 .0818
$.407$ $.541$ $.805$ $.943$ $1.154$ $R_{AKNO}$ $0.2003 > R_{Cl} \times 10^{3}$	.140 .201 .231 .288 \$\frac{10^{-3}}{-\log \gamma_{ANO3}}\$ 0.016 .072	Temperat $R_{\rm AgN}$ 0.2018 $0.2018$ $0.2018$ $0.153$ $0.153$ $0.275$ $0.724$ $0.08$	ure 479° 10-8 × 10-8 -log γA <sub>6</sub> NO 0.011 .019 .054 .070 .099 .134	$\begin{array}{c} 0.203 \times \\ R_{\rm Cl} \times 10^{3} \\ 0.203 \\ .437 \\ .677 \\ 1.03 \\ 1.22 \\ 1.58 \\ 2.15 \end{array}$	10 <sup>-8</sup> —log γλ <sub>8</sub> No <sub>3</sub> 0.0069 .0195 .0327 .0529 .0641
$.407$ $.541$ $.805$ $.943$ $1.154$ $0.2003 >$ $R_{\rm Cl} \times 10^3$ $0.083$	.140 .201 .231 .288 2 = 10 <sup>-3</sup> -log yAgNO3 0.016	$R_{AgNO} = 0.2018$ $R_{Cl} \times 10^{s}$ $0.153$ $0.275$ $0.724$ $0.08$ $0.402$	ure 479°  = × 10 <sup>-3</sup>	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50	C 10-8 -log 74kr03 0.0069 .0195 .0327 .0529 .0641 .0818 .1104
.407 .541 .805 .943 1.154 RANNO 0.2003 > RC1 × 103 0.083 .313 .614	.140 .201 .231 .288 2 = (10 <sup>-3</sup> -log yaknos 0.016 .072 .142	Temperat RANNO 0.2018 1 RCI × 10 <sup>8</sup> 0.153 .275 .724 1.008 1.402 1.911	ure 479° 10-8 × 10-8 -log γA <sub>6</sub> NO 0.011 .019 .054 .070 .099 .134	0.203 > Rct × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19	<ul> <li>10<sup>-8</sup>         —log         γλενοз         0.0069         .0195         .0327         .0529         .0641         .0818         .1104         .1290         .1618</li> </ul>
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 103 0.083 .313 .614 RAINO 0.199 ×	.140 .201 .231 .288 = 10-3 -log yAsNos 0.016 .072 .142	Temperat RANNO 0.2018 1 RCI × 10 <sup>8</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227	ure 479° 10-8 × 10-8 -log γA <sub>6</sub> NO 0.011 .019 .054 .070 .099 .134 .155	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50	<ul> <li>10<sup>-8</sup>         —log         γλεΝοз         0.0069         .0195         .0327         .0529         .0641         .0818         .1104         .1290         .1618</li> </ul>
.407 .541 .805 .943 1.154 RANNO 0.2003 > RC1 × 103 0.083 .313 .614	.140 .201 .231 .288 2 = (10 <sup>-3</sup> -log yaknos 0.016 .072 .142	Temperat RASNO 0.2018 10.103 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944	ure 479°  = × 10-8	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  RAING 2.19 ×	C 10-3
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 103 0.083 .313 .614 RAINO 0.199 × RCI × 103 0.049	.140 .201 .231 .288 .288 .2 = -log .288 .2 = -log .248 .248 .248 .248 .248 .248 .248 .248	Temperat RANNO 0.2018 1 RC1 × 10* 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944	Control of the contro	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  RAINIC ROLL × 103 RCi × 103	C 10 <sup>-8</sup> -log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλεΝος
.407 .541 .805 .943 1.154 RARNO 0.2003 > RCI × 103 0.083 .313 .614 RARNO 0.199 × RCI × 103	.140 .201 .231 .288 = (10-3 -log yarnos 0.016 .072 .142 s = (10-8 -log yarnos	Temperat RASNO 0.2018 10.103 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944	ure 479°  = × 10-8	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rain × 103 0.254	<ul> <li>10<sup>-8</sup>         —log         γλεΝος</li> <li>0.0069         .0195         .0327         .0529         .0641         .0818         .1104         .1618</li> <li>25<sup>-8</sup>         —log         γλεΝος         0.0107</li> </ul>
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 103 0.083 .313 .614 RAINO 0.199 × RCI × 103 0.049	.140 .201 .231 .288 .288 .2 =	Temperat  RANNO 0.2018  ROI × 103  0.153 .275 .724  1.008  1.402  1.911 2.227 2.613 2.944  RANNO 2.200	ure 479°  10-8  10-8  -log γA <sub>6</sub> Nο  0.011  .019  .054  .070  .099  .134  .155  .181  .201	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rain × 103 0.254 .569	C 10 <sup>-8</sup> -log γλ <sub>4</sub> Nos 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλ <sub>4</sub> Nos 0.0107 .0264
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 10 <sup>3</sup> 0.083 .313 .614 RAINO 0.199 × RCI × 10 <sup>3</sup> 0.049 .188	.140 .201 .231 .288 .288 .2 =	Temperat  RANNO 0.2018  RCI × 103  0.153 .275 .724  1.008  1.402 1.911 2.227 2.613 2.944  RANNO RCI × 103	ure 479°  10-8  10-8  -log γΑεΝο  0.011  .019  .054  .070  .099  .134  .155  .181  .201  Σε = -log γΛεΝο  γΛεΝο  10-3  -log γΛεΝο  10-3  -log γΛεΝο  γΛεΝο  10-8	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rain × 103 0.254 .569 .774	C 10 <sup>-8</sup> -log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλεΝος 0.0107 .0264 .0358
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 10 <sup>3</sup> 0.083 .313 .614 RAINO 0.199 × RCI × 10 <sup>3</sup> 0.049 .188 .438	.140 .201 .231 .288 .288 .2 =	Temperat  RANN 0.2018  RCI × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RANN 2.200  RCI × 10 <sup>3</sup> 0.188	Unre 479°  10-8  10-8  -log  7AgNO  0.011  .019  .054  .070  .099  .134  .155  .181  .201  .201  .201  .201  .201  .202  .203  .203  .204  .201  .204  .201  .204  .204	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rci × 103 0.254 .569 .774 1.160	C 10 <sup>-8</sup> -log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλεΝος 0.0107 .0264 .0358 .0546
.407 .541 .805 .943 1.154  RAKNO 0.2003 >  ROI × 103 0.083 .313 .614  RAKNO 0.199 ×  ROI × 103 0.049 .188 .438 .687 1.068	.140 .201 .231 .288 	Temperat  RANNO 0.2018  RCI × 103 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RANNO RCI × 103 0.188 .478	ure 479°  10-8  10-8  -log γΑεΝο  0.011  .019  .054  .070  .099  .134  .155  .181  .201  Σε = -log γΛεΝο  0.0134  .0302	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rci × 103 0.254 .569 .774 1.160 1.39	C 10 <sup>-8</sup> —log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> —log γλεΝος 0.0107 .0264 .0358 .0546 .0636
.407 .541 .805 .943 1.154 RAINO 0.2003 > RCI × 10 <sup>3</sup> 0.083 .313 .614 RAINO 0.199 × RCI × 10 <sup>3</sup> 0.049 .188 .438 .687	.140 .201 .231 .288 .288 .200 .200 .200 .200 .200 .200	Temperat  RAENO 0.2018  Roi × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RAENO 2.200  Roi × 10 <sup>3</sup> 0.188 .478 .722	Control of the contro	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19 Rci × 103 0.254 .569 .774 1.160 1.39 1.70	C 10 <sup>-8</sup> —log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> —log γλεΝος 0.0107 .0264 .0358 .0546 .0636 .0767
.407 .541 .805 .943 1.154  RAKNO 0.2003 >  ROI × 103 0.083 .313 .614  RAKNO 0.199 ×  ROI × 103 0.049 .188 .438 .687 1.068	.140 .201 .231 .288 	Temperat RASNO 0.2018 $^{\circ}$ 0.2018 $^{\circ}$ 0.103 $^{\circ}$ 0.153 $^{\circ}$ 275 $^{\circ}$ .724 $^{\circ}$ 1.008 $^{\circ}$ 1.402 $^{\circ}$ 1.911 $^{\circ}$ 2.227 $^{\circ}$ 2.613 $^{\circ}$ 2.944 $^{\circ}$ RASNO $^{\circ}$ RCI $^{\circ}$ 1.018 $^{\circ}$ 4.78 $^{\circ}$ .722 $^{\circ}$ 1.023	Control of the contro	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Rci × 103 0.254 .569 .774 1.160 1.39 1.70 1.97	C 10 <sup>-3</sup> —log γλεΝος 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-3</sup> —log γλεΝος 0.0107 .0264 .0358 .0546 .0636 .0767 .0906
.407 .541 .805 .943 1.154  .2003 >  .2003 >  .2003 >  .313 .614  .313 .614  .314  .318 .438 .438 .438 .687 1.068  .348 .348	.140 .201 .231 .288 .288 .2 = -log .288 .2 = -log .248 .0016 .072 .142 .10-s .142 .10-s .006 .036 .097 .153 .237	Temperat  RASNO 0.2018  Roi × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RASNO Roi × 10 <sup>3</sup> 0.188 .478 .722 1.023 1.248	Control of the contro	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Ratnot × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61	C 10 <sup>-8</sup> -log γλεΝο3 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλεΝο3 0.0107 .0264 .0358 .0546 .0636 .0767 .0906 .1182
.407 .541 .805 .943 1.154  RAINO 0.2003 >  RCI × 103 0.083 .313 .614  RAINO 0.199 ×  RCI × 103 0.049 .188 .438 .687 1.068  RAINO 0.199 ×  RCI × 103	.140 .201 .231 .288 	Temperat RASNO 0.2018 $^\circ$ 0.2018 $^\circ$ 0.153 $^\circ$ 275 $^\circ$ .724 $^\circ$ 1.008 $^\circ$ 1.402 $^\circ$ 1.911 $^\circ$ 2.227 $^\circ$ 2.613 $^\circ$ 2.944 $^\circ$ RASNO $^\circ$ RCI $^\circ$ 101 0.188 $^\circ$ 478 $^\circ$ .722 $^\circ$ 1.023 $^\circ$ 1.248 $^\circ$ 1.507	Control of the contro	0.203 > Rc1 × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19 Rappin × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61 3.11	Continue   Continue
.407 .541 .805 .943 1.154  .2003 >  .20	.140 .201 .231 .288 	Temperat RASN'S 0.2018 $^{\circ}$ 0.2018 $^{\circ}$ 0.103 $^{\circ}$ 0.153 $^{\circ}$ 275 $^{\circ}$ .724 $^{\circ}$ 1.008 $^{\circ}$ 1.402 $^{\circ}$ 1.911 $^{\circ}$ 2.227 $^{\circ}$ 2.613 $^{\circ}$ 2.944 $^{\circ}$ RASN'S $^{\circ}$ 7.22 $^{\circ}$ 1.102 $^{\circ}$ 0.188 $^{\circ}$ 478 $^{\circ}$ 7.722 $^{\circ}$ 1.248 $^{\circ}$ 1.507 $^{\circ}$ 1.857	Control of the contro	0.203 > Rci × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19  Ratnot × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61	C 10 <sup>-8</sup> -log γλεΝο3 0.0069 .0195 .0327 .0529 .0641 .0818 .1104 .1290 .1618 C 10 <sup>-8</sup> -log γλεΝο3 0.0107 .0264 .0358 .0546 .0636 .0767 .0906 .1182
.407 .541 .805 .943 1.154  .2003 >  .20	.140 .201 .231 .288 	Temperat  RANN 0.2018  Roi × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RANN 2.200  Roi × 10 <sup>3</sup> 0.188 .478 .722 1.023 1.248 1.507 1.857 2.404	Control of the contro	0.203 > Rc1 × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19 Rappin × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61 3.11	Continue   Continue
.407 .541 .805 .943 1.154  .2003 >  .2003 >  .2003 >  .2003 >  .313 .614  .313 .614  .3199 ×  .318 .438 .687 1.068  .3199 ×  .318 .438 .687 1.068  .3199 ×  .318 .438 .687 1.068  .3199 ×  .318 .438 .687 1.068	. 140 .201 .231 .288 	Temperat  RANN 0.2018  Roi × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RANN 2.200  Roi × 10 <sup>3</sup> 0.188 .478 .722 1.023 1.248 1.507 1.857 2.404	Control of the contro	0.203 > Rc1 × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19 Rappin × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61 3.11	Continue   Continue
.407 .541 .805 .943 1.154  .2003 >  .2003 >  .2003 >  .2003 >  .313 .614  .313 .614  .3199 ×  .318 .438 .687 1.068  .3199 ×  .318 .438 .687 1.068  .3199 ×  .318 .413 .769 .933	.140 .201 .231 .288 	Temperat  RANN 0.2018  Roi × 10 <sup>3</sup> 0.153 .275 .724 1.008 1.402 1.911 2.227 2.613 2.944  RANN 2.200  Roi × 10 <sup>3</sup> 0.188 .478 .722 1.023 1.248 1.507 1.857 2.404	Control of the contro	0.203 > Rc1 × 103 0.203 .437 .677 1.03 1.22 1.58 2.15 2.50 3.19 Rappin × 103 0.254 .569 .774 1.160 1.39 1.70 1.97 2.61 3.11	Continue   Continue

range of temperatures of 295° and a range of values of  $K_1$  varying by a factor of about eight in this system equation 1 predicts the temperature coefficient of  $K_1$ .

The comparison of  $K_1$  and  $\Delta E$  in the three solvents NaNO<sub>3</sub>, NaNO<sub>3</sub>-KNO<sub>8</sub> (50-50 mole %), and

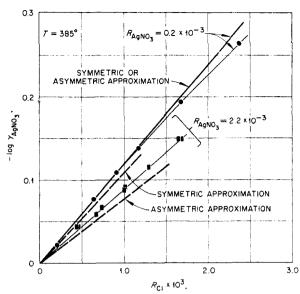


Fig. 1.— - log  $\gamma_{AgNO3}$  versus  $R_{Cl}$  at 385° compared with theoretical calculations.

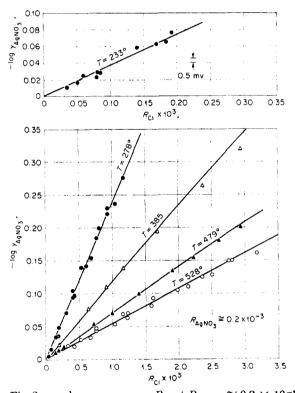


Fig. 2.—  $-\log \gamma_{\rm AgNO3}$  versus  $R_{\rm Cl}$  at  $R_{\rm AgNO3} \cong 0.2 \times 10^{-8}$  at five temperatures compared with calculations based on the asymmetric approximation.

Table II  ${\rm Values~of~} \Delta E {\rm ~and~} Z ({\rm exp}(-\Delta E/RT)-1) {\rm ~Obtained~} {\rm from~}$  the Comparison of the Data with the Theory

T(°K.)	$\widetilde{Z} = 4$	$-\Delta E \text{ (kcal. } Z = 5$	$Z = \hat{G}$	$K_{i} = E$ $Z(\beta - 1)$	Estimated error in $K_1$ (%)
506	5.6	5.4	5.2	1050	±10
551	5.57	5.33	5.13	644	$\pm 4$
658	5.67	5.38	5.15	302	$\pm 3$
752	5.72	5.40	5.13	180	$\pm 3$
801	$5.6_{2}$	$5.2_{8}$	$5.0_{0}$	133	±7

KNO<sub>3</sub> at 385° is made in Table III. The results at other temperatures are comparable. The value

#### TABLE III

Comparison of the Values of  $K_1$  and  $\Delta E$  in NaNO<sub>3</sub>, NaNO<sub>3</sub>-KNO<sub>5</sub> (50-50 Mole %), and KNO<sub>3</sub> at 385°

		NaNO <sub>3</sub>	(50-50 mole )	%) KNO.
$K_1$ (mole/mole KNO <sub>3</sub> ) <sup>-1</sup>		205	302	455
$-\Delta E$ (kcal./mole)	Z = 4	5.17	5.67	6.18
$-\Delta E$ (kcal,/mole)	Z = 5	4.88	5.38	5.89
,	Z = 6	4.65	5.15	5.68

of  $\Delta E$  in the mixture is the average of the values in the pure NaNO<sub>3</sub> and KNO<sub>3</sub> and it appears that for any one value of  $Z^8$ 

$$\Delta E_1(\text{NaNO}_3 - \text{KNO}_3) = N_{\text{Na}} \Delta E_1(\text{NaNO}_3) + N_{\text{K}} \Delta E_1(\text{KNO}_2) \quad (3)$$

The linear relation derived from equations 3 for values of  $\beta$  appreciably greater than unity

$$\ln K_1(\text{NaNO}_2-\text{KNO}_2) \cong N_{\text{Na}} \ln K_1(\text{NaNO}_2) + N_{\text{K}} \ln K_1(\text{KNO}_2)$$
 (4)

is suggested by the results. Equations 3 and 4 are

(8) Slightly different values of Z in these two pure molten nitrates should not make any effective difference.

of a type first suggested by Flood and co-workers.9

Differences between the solvents NaNO<sub>3</sub> and KNO<sub>3</sub> may be ascribed (a) to the differences in the "polarization" of electrons in Ag<sup>+</sup>-Cl<sup>-</sup> pair "bonds" by the solvent cation<sup>5</sup> or (b) to a coulombic effect, which in a mixture of two cations and two anions of different sizes, aside from contributions due to other types of interactions, will lead to a negative contribution to the energy of association of the small cation with the small anion (i.e., Ag<sup>+</sup> and Cl<sup>-</sup> in KNO<sub>3</sub>).<sup>10</sup> This negative contribution will be greater for a given small anion and small cation pair the greater the differences in the sizes of the two cations or of the two anions. As both these effects are in the same direction they cannot be separated easily.

Acknowledgment.—The authors would like to thank Professor J. Braunstein of the University of Maine and Dr. R. F. Newton for many valuable discussions.

(9) See for example H. Flood, T. Forland and K. Grjotheim, Z. anorg. u. allgem. Chem., 276, 289 (1954).

(10) If the interionic distance for  $Ag^+-Cl^-$  is  $d_1$ , for  $Ag^+-NO_2^ d_2$ ,  $M^+-Cl$   $d_3$ , and  $M^+-NO_3^ d_4$  it is easy to demonstrate the well known fact that if  $d_1>d_1$  and  $d_4>d_1$  then the coulombic term  $-e^2(1/d_1+1/d_4-1/d_2-1/d_3)$  is negative if the  $d_1$  are additive sums of ionic radii so that  $d_1+d_4=d_3+d_4$ .

## SPECTROPHOTOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANT OF SILVER CHLORIDE IN PYRIDINE<sup>1</sup>

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A new spectrophotometric method for the determination of the dissociation constants for equilibria of the type AB  $\rightleftharpoons$  A + B is described. The method yields  $K=8.4\times10^{-6}$  for the dissociation constant of silver chloride in anhydrous pyridine.

#### Introduction

Although the dissociation constants of approximately thirty compounds have been determined conductometrically<sup>3-5</sup> using pyridine as a solvent, the dissociation constant of silver chloride has not been reported.

A spectrophotometric method has been developed for the determination of the dissociation constant of silver chloride in pyridine and is of interest because of its possible applications to other non-aqueous solvents. Previously described aqueous spectrophotometric methods for the determination of equilibrium constants normally involve media buffered with respect to one of the species produced on dissociation. For example, to determine the dissociation constant of an acid, (1) the pH at which the acid is half neutralized is determined spectrophotometrically, (2) the acid is placed in a

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buffer of known pH and the ratio of the acid to its conjugate base determined from the known molar absorptivities, (3) the absorbance of the acid in three different buffers is measured and three simultaneous equations are solved to find K, (4) a variation of the Benesi-Hildebrand plot is employed or (5) in salt solutions of constant ionic strength, the Type II plot is used. (10)

Such methods cannot be used in low dielectric constant solvents because of the formation of ion triplets, quadrupoles, etc., and the inability to make suitable estimates of ionic activity coefficients in any but the most dilute of solutions. The method described below is applicable to solutions containing only the solute, AB, which dissociates according to the scheme  $AB \rightleftharpoons A + B$ , and requires the determination at a suitable wave length of the absorbance as a function of the analytical concentration of AB. The restrictions of the method require

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