$$\Delta\phi_L = \phi_L(m_f) - \phi_L(m_i) \qquad (5)$$

The value for $\phi_L(m_f)$ was obtained from Parker's low-concentration data (*5*).

RESULTS AND DISCUSSION

Table I shows the heat of dilution of CsCl at 25° C. The last column in this table shows the values of ϕ_L calculated from the data of Stakhanova *et al.* (*8*), together with Parker's (*5*) value at 1*m*. The present results are 5 to 12 cal. per mole more positive. This could be due to an error of this magnitude in Parker's value at 1*m*.

Wood (*9*) showed that the partial molal entropies of normal strong electrolytes followed a single family of curves and could be correlated by a single parameter for each ion. The low-concentration data then available indicated that CsCl did not follow this correlation and was an "abnormal" electrolyte. The present results confirm this conclusion. The values of $T\overline{S}^E$ were obtained from the equation (*9*)

$$T\overline{S}^E = \overline{L}_2 - \overline{G}^E = \phi_L + m\,(d\phi_L/dm) - \nu RT \ln \gamma^{\pm} \qquad (6)$$

using the values of $\gamma^{\pm}$ from Robinson and Stokes (*6*) together with the ϕ_L from these measurements. The values of $d\phi_L/dm$ are from the slope of a large-scale graph of ϕ_L *vs.* *m*, using the present results and those of Parker.

The experimental values for $T\overline{S}^E$ are −385, −431, and −659 cal. per mole for $m = 1.5$, 2.0, and 3.0, respectively, as compared to the values predicted for a normal electrolyte (*9*) of 190, 45, and −179 cal. per mole for $m = 1.5$, 2.0, and 3.0, respectively. The most likely reason for abnormal behavior is ion-pairing, and there is other evidence to support the hypothesis that CsCl is ion-paired (*1, 2, 3*).

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Heats of Mixing of Some Aqueous Alkali Metal Chloride Solutions

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The heats of mixing CsCl with LiCl, CsCl with KCl, and KCl with LiCl were determined at various ionic strengths. The heat of mixing CsCl with KCl was very small and the coefficient RTh_0 changed rapidly with concentration, indicating that the like-charged pair interactions are smaller in this mixing and about as important as triplet interactions. For the CsCl with LiCl and KCl with LiCl mixings, the coefficient RTh_0 changed fairly slowly with concentration, indicating that like-charged pair interactions contribute more to RTh_0 than triplet interactions.

IN CONNECTION with a study of the heat of mixing alkaline earth chlorides with alkali metal chlorides, the heats of mixing CsCl with LiCl, CsCl with KCl, and KCl with LiCl were needed at ionic strengths of 1, 2, and 3. Wu *et al.* reported results at unit ionic strength (*10*). Stakhanova *et al.* (*3*) measured the heats of mixing LiCl with KCl and LiCl with CsCl, but their results were not accurate enough for our purposes.

EXPERIMENTAL

The lithium chloride and potassium chloride stock solutions were prepared from reagent grade salts. All impurities reported for these salts were less than 0.01%. The stock solutions were analyzed for chloride in a gravimetric silver chloride precipitation. The pH of both solutions was between 5 and 6.5.

Table I. Results of the Heat of Mixing Experiments at 25° C.

Mixture	I	N^a	$RTh_0{}^b$	$RTh_1{}^b$
CsCl-LiCl	0.5	6	−172 ± 11	−13 ± 11
	1	4	−192 ± 6	−7 ± 11
	2	5	−215 ± 4	−17 ± 7
	3	6	−229 ± 3	−22 ± 5
CsCl-KCl	1	7	8.0 ± 0.9	0.0 ± 1
	2	6	2.8 ± 0.2	−0.3 ± 0.4
	3	6	−1.7 ± 0.4	−0.7 ± 0.7
LiCl-KCl	2	8	−80.4 ± 0.5	−3.8 ± 0.7
	3	15	−93 ± 1	−5 ± 2

[a] *N* is the number of experiments.
[b] Units are cal. per kg. of solvent per ional² (Equation 1).

Table II. Data for Heat of Mixing Experiments at 25° C. for 60-Ml. Dewar Calorimeter

CsCl–LiCl

CsCl Soln. in Vessel, Grams	LiCl Soln. in Vessel, Grams	CsCl Soln. in Pipette, Grams	LiCl Soln. in Pipette, Grams	$-q$ Exptl., Cal.	$-q$ Calcd.,[a] Cal.
$I = 0.5$					
0.00	48.46	8.83	0.00	−0.326	−0.315
7.50	41.14	9.21	0.00	−0.219	−0.228
14.34	35.30	9.04	0.00	−0.168	−0.156
51.67	0.00	0.00	8.69	−0.296	−0.294
43.82	7.37	0.00	8.73	−0.218	−0.222
37.23	13.60	0.00	8.76	−0.148	−0.166
$I = 1.0$					
0.00	47.54	9.20	0.00	−1.31	−1.32
9.12	47.09	9.46	0.00	−1.00	−0.98
53.40	0.00	0.00	8.41	−1.27	−1.28
45.15	7.11	0.00	8.56	−0.97	−0.96
$I = 2.0$					
0.00	49.85	10.32	0.00	−5.99	−6.00
59.14	0.00	0.00	8.76	−5.50	−5.55
49.34	8.61	0.00	8.57	−4.00	−3.90
0.00	49.76	10.38	0.00	−5.98	−6.02
8.71	41.76	10.43	0.00	−4.27	−4.24
$I = 3.0$					
0.00	39.66	5.67	0.00	−7.58	−7.56
5.10	35.70	5.67	0.00	−6.00	−5.97
9.76	32.34	5.85	0.00	−4.85	−4.85
50.36	0.00	0.00	4.33	−6.63	−6.56
45.10	3.88	0.00	4.54	−5.64	−5.73
40.76	7.61	0.00	4.44	−4.58	−4.64

CsCl–KCl

CsCl Soln. in Vessel, Grams	KCl Soln. in Vessel, Grams	CsCl Soln. in Pipette, Grams	KCl Soln. in Pipette, Grams	$-q$ Exptl., Cal.	$-q$ Calcd.,[a] Cal.
$I = 1$					
54.19	0.00	0.00	8.27	0.046	0.053
53.27	0.00	0.00	8.39	0.056	0.053
44.87	7.07	0.00	8.47	0.048	0.039
37.92	13.13	0.00	8.39	0.025	0.028
0.00	49.98	8.97	0.00	0.053	0.053
7.60	42.34	9.16	0.00	0.040	0.040
0.00	49.81	8.97	0.00	0.051	0.053
$I = 2$					
59.21	0.00	0.00	8.67	0.081	0.078
50.53	7.40	0.00	8.64	0.051	0.054
43.66	13.86	0.00	8.78	0.034	0.038
0.00	52.06	10.07	0.00	0.068	0.066
8.56	44.25	10.04	0.00	0.055	0.052
15.63	37.19	10.64	0.00	0.038	0.042
$I = 3$					
64.45	0.00	0.00	9.06	−0.082	−0.068
55.07	7.74	0.00	9.41	−0.056	−0.068
46.99	14.63	0.00	9.17	−0.054	−0.058
0.00	52.20	11.09	0.00	−0.140	−0.125
9.43	44.43	11.48	0.00	−0.057	−0.077
17.66	37.51	11.00	0.00	−0.036	−0.043

[a] Calculated from Equation 1 and the coefficients in Table I.

Technical grade cesium chloride (obtained from Penn Rare Metals Division of Kawecki Chemical Co., New York) was purified by precipitating the 1.2% sulfate impurity with a 0.005% excess of barium chloride. The other reported impurities in this salt were negligible, except for 0.1% rubidium. The stock solution was analyzed by a tetraphenylborate precipitation of the cesium ion. Duplicate determinations agreed to within 0.1%.

The calorimeter and the experimental procedure used for the CsCl with LiCl and the CsCl with KCl mixings have been described in detail elsewhere (*2*, *8*). Briefly, the calorimeter is a 60-ml. Dewar flask stirred by a magnetic stirrer. The temperature is sensed by a thermistor and electrical calibration is used. Tests (*2*, *8*) show that for high heats the calorimeter is accurate to about ±1%, and for low heats the accuracy is about ±0.01 cal. The initial temperature was adjusted to

Table III. Data for Heat of Mixing Experiments at 25° C. for Twin Calorimeter

LiCl-KCl

$-q$ (Exptl.), Cal.	$-q$ (Calcd.), Cal.	X_i[a]	X_f[b]	Wt.$_i$[b], Grams	Wt.$_f$[b], Grams
		$I = 2$			
−12.92	−12.92	0.0000	0.0589	654.5	695.5
−11.30	−11.36	0.0589	0.1113	695.5	736.5
−10.11	−10.02	0.1113	0.1645	645.6	686.7
− 8.85	− 8.83	0.1645	0.2118	686.7	727.9
−12.08	−12.05	1.0000	0.9405	657.0	698.6
−10.87	−10.85	0.9405	0.8875	698.6	740.3
− 9.71	− 9.79	0.8875	0.8342	656.8	698.8
− 8.68	− 8.73	0.8342	0.7871	698.8	740.6
		$I = 3$			
−16.36	−16.73	0.0000	0.0290	656.3	675.9
−15.74	−15.95	0.0290	0.0568	675.9	695.9
−15.29	−14.74	0.0568	0.0827	695.9	715.5
−13.65	−13.91	0.0827	0.1072	715.5	735.1
−13.39	−13.10	0.1072	0.1336	646.1	665.8
−12.79	−12.41	0.1336	0.1588	665.8	685.8
−11.78	−11.65	0.1588	0.1826	685.8	705.7
−11.93[c]	−10.87	0.1826	0.2049	705.7	725.5
−15.74	−15.80	1.0000	0.9679	621.1	641.7
−15.04	−14.89	0.9679	0.9379	641.7	662.2
−13.73	−13.59	0.9379	0.9107	662.2	682.0
−13.54	−13.44	0.9107	0.8839	682.0	702.7
−12.47	−12.77	0.8839	0.8554	622.7	643.5
−11.77	−11.96	0.8554	0.8289	643.5	664.1
−11.09	−11.25	0.8289	0.8040	664.1	684.5
−10.57	−10.72	0.8040	0.7805	684.5	705.2

[a] X_i is the initial mole fraction of KCl in the vessel and X_f is the final mole fraction after the pipette is opened.

[b] Wt.$_i$ is the initial weight of solvent in the vessel and Wt.$_f$ is the final weight of solvent in the vessel after the pipette is opened. The mole fraction in the pipette is either one or zero.

[c] This data point was not included in the final fit.

25.00 ± 0.02° C., and the pipette was opened. Electrical calibration followed completion of the measurement of the heat of mixing. In addition to the 8-ml. pipettes used by Rooney, a set of 4-ml. pipettes was constructed; these were used for the CsCl–LiCl measurements at $I = 3$. The procedure for opening the pipettes was also changed. Instead of pulling up on the center piece of the pipette, the outer piece was pulled up. This gave faster mixing of the solutions and reduced the volume of solution needed in the calorimeter vessel to 37 ml. for the 4-ml. pipettes and 47.5 ml. for the 8-ml. pipettes. The heat of opening of the pipettes was −0.007 ± 0.005 cal. for the large (8-ml.) pipettes and −0.010 ± 0.005 cal. for the small (4-ml.) pipettes. The vessel solution resulting from the first pipette opening was used as the vessel solution for the next run. Similarly, the resulting solution was used for the third experiment. This procedure was repeated, with the other component used as a vessel solution. In this way, the mole fraction range 0 to 0.4 and 1.0 to 0.6 was covered. The amount of solution in the vessel and in the pipette was determined by weight to an accuracy of 0.2% for vessel solution and 0.1% for the pipette solution.

The procedure and the calorimeter employed in the KCl–LiCl mixings have been described in detail previously (*9*). Briefly, the calorimeter consists of two 750-ml. vessels surrounded by air in a constant-temperature bath. The temperature difference is measured by an 80-junction thermopile connected between the two vessels. There are four 25-ml. pipettes in each vessel and electrical calibration is used. The tests (*9*) show that the calorimeter is accurate to about ±0.5% for high heats and ±0.005 cal. for low heats.

The experimental data were fit to the equation (*9*)

$$\Delta H_m \text{ (cal. per kg. of solvent)} = y(1-y)I^2[\mathrm{RTh}_0 + \mathrm{RTh}_1(1-2y)] \quad (1)$$

using the method of least squares. ΔH_m is the heat of mixing, y is the mole fraction of the salt of larger formula weight, I is the ionic strength, RTh_0 is a measure of the magnitude of the interaction, and RTh_1 is a measure of asymmetry. The uncertainty of the constants in Equation 1 was calculated at the 95% confidence level.

RESULTS AND DISCUSSION

The results of the measurements are given in Table I. The data for the CsCl with LiCl and CsCl with KCl mixing experiments are given in Table II. The data for the LiCl with KCl mixings are given in Table III. As a check on the operation of the 60-ml. Dewar calorimeter, Wu *et al.*'s measurements of LiCl with CsCl and KCl with CsCl at $I = 1$ were repeated. The result for LiCl with CsCl, $\mathrm{RTh}_0 = -192 \pm 6$ and $\mathrm{RTh}_1 = -7 \pm 11$, agrees well with Wu *et al.*'s result, $\mathrm{RTh}_0 = -194.6$ and $\mathrm{RTh}_1 = -8.9$. The result for LiCl with KCl, $\mathrm{RTh}_0 = -8.0 \pm 0.9$ and $\mathrm{RTh}_1 = 0 \pm 1$, is also in reasonable agreement with Wu *et al.*'s result, $\mathrm{RTh}_0 = -6.4$ and $\mathrm{RTh}_1 = -0.1$. Comparison of the present results with those of Stakhanova *et al.* shows differences in RTh_0

ranging from 4 to 24 (*3*). On the basis of the inherent sensitivity of the two calorimeters used and the good agreement with Wu *et al.*, the present results are believed more accurate.

The values of RTh_0 for the CsCl with LiCl and the KCl with LiCl mixings are large, and change by 20 to 30% in the concentration range 1 to 3*m*. The concentration dependence could be due to either ion atmosphere effects on like-charged pairs, or triplet interactions (*1, 5, 9*). The 20 to 30% change in RTh_0 indicates that these effects are only 20 to 30% as large as the like-charged pair interactions. This behavior is similar to the behavior of most alkali chloride mixtures (*3, 4, 9*).

The results of the CsCl with KCl mixings are more unusual. The value of RTh_0 is comparatively small; this means that the heat of interaction of a Cs^+–K^+ pair is almost the average of the heat of interaction of a Cs^+–Cs^+ pair and a K^+–K^+ pair, since this is the change in pair interactions that takes place in the mixing process (*1*). The other interesting thing about the CsCl with KCl mixing is that RTh_0 changes sign as the concentration increases. This is the first example of this for a symmetrical mixture. Evidently, the like-charged pair interactions are small enough that, at high concentrations, triplet interactions are large enough to change the sign of RTh_0. Because of this change in sign, this mixture at $I = 3$ violates the sign-predicting rule of Young and coworkers (*6, 10, 11*). This is not too surprising, since the rule really predicts like-charged pair interactions (*7*), and it is the triplet interactions that produce a negative RTh_0 in this mixing at $I = 3$.

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Ternary Systems: Water–Alkali Metal Hexafluorosilicates

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The existence of $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSif_6$, and $CsLiSiF_6$ was discovered from solubility measurements on the systems M_2SiF_6–Li_2SiF_6–H_2O at 25° C. ($M = Na$, K, Rb, Cs). X-ray data indicate that these salts are orthorhombic, $a = 8.680$, $b = 6.500$, $c = 7.026$; orthorhombic, $a = 9.600$, $b = 9.143$, $c = 9.300$; orthorhombic, $a = 9.823$, $b = 5.805$, $c = 7.560$; orthorhombic, $a = 11.230$, $b = 9.693$, $c = 8.783$; and hexagonal, $a = 11.334$, $c = 9.271$ A., respectively. The space groups of $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ are *Pcam* or *Pca2₁*, *Pbcn*, and *P6₃22*, respectively. Solid solutions occur in the systems M_2SiF_6–Rb_2SiF_6–H_2O ($M = K$, Cs). The remaining systems are simple. The isothermally invariant saturated solutions in the systems M_2SiF_6–Na_2SiF_6–H_2O ($M = K$, Rb, Cs) are: K_2SiF_6, 0.096 ± 0.002, Na_2SiF_6, 0.759 ± 0.019; Rb_2SiF_6, 0.138 ± 0.001, Na_2SiF_6, 0.789 ± 0.014; Cs_2SiF_6, 0.83 ± 0.01, Na_2SiF_6, 0.793 ± 0.011%, respectively.

AQUEOUS TERNARY SYSTEMS of alkali metal hexafluorosilicates were investigated by solubility and x-ray methods in a search for double salts with no hydrogen bonding. The suggestion has been made that such double salts are actually complex salts, structures of two ions only (*2*). This idea is supported by the discovery of $Na_3Li(SiF_6)_2$, $NaLiSiF_6$, $KLiSiF_6$, $RbLiSiF_6$, and $CsLiSiF_6$ reported here, particularly in view of the known tendency of the lithium ion to form complexes and the absence of double salts in the alkali metal hexafluorosilicate systems where the ion was not present.

EXPERIMENTAL

Solubility. The hexafluorosilicate salts were prepared as described earlier (*2*). Analyzed lithium hexafluorosilicate solutions were used instead of the solid in the preparation of half of the mixtures in each of the systems M_2SiF_6—Li_2SiF_6—H_2O ($M = Na$, K, Rb, Cs). Mixtures of known composition were equilibrated at 25° C. for 30 to 60 days. The saturated solutions were analyzed finally either for total solids and one metal, except cesium, or directly for two metals.

In the first procedure, which was applied to the sys-