Volumetric Properties of the Molten System (Li,K)-(Cl,NO_3)

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THE VOLUMES of many binary molten-salt mixtures, especially alkali salt mixtures, are closely approximated by the sum of the volumes of the pure components. In such instances, this property of volumetric additivity provides a very useful basis for estimating the molar volumes of mixtures from limited density data. For binary mixtures which deviate significantly from volumetric additivity, the concept of an ideal mixture which is exactly additive serves as a useful norm against which to reference real-liquid behavior.

The concept of additive volumes may be extended to ternary mixtures with a common ion such as LiCl-NaCl-KCl in a straightforward way. However, for ternary mixtures of reciprocal salt systems as (Li,K)-(Cl,NO_3) there is an ambiguity in the choice of components that leads to special difficulties when one attempts a straightforward extension of the additive-volume principle. This problem is considered here and a modified concept of volumetric additivity is proposed which does not involve logical difficulties and which is found to approximate closely real-solution behavior for two alkali metal reciprocal salt systems. These systems are (Li,K)-(Cl,NO_3) and (Na,K)-Cl,I).

Van Artsdalen and Yaffe (*8*) have reported density equations for the LiCl-KCl limiting binary of the (Li,K)-(Cl,NO_3) system. From the data in Table II of this article, the value of a in the density equation for 80.04 mole % KCl is computed by us to be 1.9597 rather than 1.9892 as reported in Table III of the same article. Density equations for the rest of the (Li,K)-(Cl,NO_3) system are presented here.

Bloom, Knaggs, Molloy, and Welch (*1*) have determined density equations along the pseudobinaries of the (Na,K)-(Cl,I) system—that is, for compositions which can be expressed as x NaCl + y KI or as x NaI + y KCl. In their article, the central maximum on the liquidus of the KCl-NaI pseudobinary cannot be a compound, as suggested by the authors, since the KI-NaCl liquidus shows only a simple eutectic. This maximum is most likely to be a two-phase region consisting of melt plus NaCl(c) or melt plus NaCl terminal solid solution. Thus, one would say that KI and NaCl constitute the "stable salt pair" of the (Na,K)-(Cl,I) system. However, this interpretation does not invalidate the intuitive structural ideas advanced by the authors.

APPARATUS AND PROCEDURE

The component nitrates were recrystallized from reagent grade materials, partially dried in an air oven, and then more completely dried by slowly heating through the melting point under a vacuum of about 10 microns. The alkali chlorides were purified by the method described by Boston and Smith for the LiCl-KCl eutectic (*2*), except that the apparatus was constructed of fused silica instead of borosilicate glass because of the high melting points of the pure chlorides. The preparation of mixtures and other handling of the purified compounds were carried out in an atmosphere box filled with high-purity nitrogen.

Density was measured by determining the buoyancy of a platinum bicone immersed in the fused salt and suspended by means of a platinum wire from one arm of an analytical balance. The bicone had a mass of 10 grams and a greatest diameter of 8 mm.; the suspension wire was 0.13 mm. in diameter; the depth of immersion was 4 to 5 cm., known to within ±0.5 mm.; and the balance had a sensitivity of 0.04 mg. under the conditions of measurement. The balance was supported by a massive mechanism which permitted screw-driven, vibration-free motion in the vertical and two horizontal directions. This arrangement was necessary in order to fix precisely the depth of immersion and to center the suspension wire in the small hole through which it entered the chamber which contained the molten salt. Computation of the volume of Pt submerged in the melt included the correction for thermal expansion of Pt.

Molten salts were contained in a fused-silica tube which was attached to a rigidly held metal cap by means of a tapered ground joint. The metal cap was fitted with a tube for evacuation and admission of nitrogen, with O-ring seals which served as vacuum-tight slip joints through which a stirrer and the thermocouple protection sheath entered, and with a special gland through which the platinum suspension wire entered. This gland could be closed around the platinum wire to give a vacuum-tight seal without kinking the wire and could be opened to permit free motion of the wire.

During the measurement, high purity nitrogen flowed out through the space around the suspension wire at a metered rate which was determined to be rapid enough to prevent backflow of air, but slow enough not to affect the measurements.

The salts were heated by an electric tube furnace which was raised and lowered by a rack-and-pinion drive that permitted moving and then repositioning the furnace in a precise way. The furnace winding was provided with shunts so that different power inputs could be applied to each 5-cm. length of furnace core in order to minimize thermal gradients. The temperature level was controlled by means of a Chromel-Alumel thermocouple which actuated a Leeds and Northrup Model G Speedomax coupled with a Leeds and Northrup DAT controller. The temperature of the fused salt was measured with a calibrated platinum-to-platinum-rhodium thermocouple sheathed in a thin-walled, fused-silica tube and read with a Leeds and Northrup Model K-3 Universal Potentiometer. The thermocouple in its sheath was immersed in the salt melt and moved up and down (through the O-ring seal) to test for the absence of temperature gradients. During a measurement, the thermocouple element was placed opposite the platinum bicone.

The fused salt was stirred previous to density determinations by means of a suitably shaped fused-silica rod which was moved up and down through an O-ring seal. In the preliminary phases of the research, melts were not stirred and a surprising degree of difficulty was encountered from density gradients due to insufficient mixing even after several hours at a given temperature, although the powdered components had been blended previously. Such gradients were most readily detected by a consequent stabilization of the position of the platinum bicone which, in turn, reduced the apparent sensitivity of the balance.

Density measurements were made only after thermal equilibration for about 30 minutes at each temperature. The temperature was raised stepwise with a density measurement at each step and then lowered stepwise with a density measurement at each step. The absence of hysteresis to within the experimental precision for such sets of data was considered a least measure of internal consistency.

Consideration was given to the thermal decomposition of the nitrate ion to form the nitrite ion and oxygen at elevated temperatures. Although the melts were not analyzed for nitrite, the investigation reported here was paralleled by an extensive study of the ultraviolet absorption spectra of melts covering the same concentration ranges. The nitrite ion when present in fairly low concentrations was readily detected by an optical absorption at about 360 mμ due to the band of its lowest-energy electronic transition. From these spectrophotometric studies plus density measurements on nitrate-nitrite mixtures, it was concluded that such small nitrate decomposition as may have occurred was not a significant source of error in the density equations which are reported.

Some previous workers have claimed that the sinker method of density measurement generally gives values which are too low because of condensation of salt vapors on the suspension wire. The salt mixtures described here have a low volatility over the temperature ranges studied. Nevertheless, various experimental checks were made to determine the weight of salt condensate on the wire and the error which this introduced. It was concluded for the data reported here that errors due to salt condensate were very much smaller than the precision of the measurements.

No corrections were made for the surface tension force which is exerted by the melt on the suspension wire. From surface tension values for pure alkali nitrates it is estimated that this correction is of the order of +0.3 to 0.5% of the density values computed from the equations reported here. Values for mixed nitrates are unavailable. However, 0.3 to 0.5% is the order of precision for density equations of mixtures, so that the application of an estimated correction is of doubtful value.

EXPERIMENTAL RESULTS

In this work, the temperature dependence of the density ρ at a fixed composition is expressed by the customary linear relation $\rho = \alpha - \beta t$, where α and β are functions of composition, but not temperature and t is the temperature in ° C. This empirical relation is regarded as a power-series expansion in t with truncation after the first power. The data are fitted to the linear relation by the method of least squares.

Concentrations are expressed in terms of mole fractions of component salts or in terms of cation and anion fractions of component ions. The cation fraction of potassium N_K in a mixture of potassium and lithium salts is defined as $N_K = n_K/(n_K + n_{Li})$, where n_K and n_{Li} are the gram-atoms of K and Li, respectively. Likewise, the anion fraction of chloride N_{Cl} in a mixture of chloride and iodide salts is defined as $N_{Cl} = n_{Cl}/(n_{Cl} + n_I)$, where n_{Cl} and n_I are the gram-atoms of Cl and I, respectively. The molar volume, V^0, of a mixture is computed from the relation $V^0 = \sum W_i N_i/\rho$, where N_i is the ionic fraction of ions of species i, W_i is the gram-formula weight of ions of species i, ρ is the density in grams per cubic centimeter, and the summation is over all species of ions.

The experimental results are summarized in Tables I and II. Table I lists the compositions of binary salt mixtures in terms of the mole fraction of a specified component, the constants α and β in the density equations, the standard deviation for the least squares fit, and the experimental temperature range.

Table II summarizes data for ternary mixtures. The first two columns specify the composition in terms of N_K and N_{NO_3}. For one composition ($N_K = 0.750$, $N_{NO_3} = 0.750$) the density was determined at only two temperatures. These density values are separately reported in Table II, in the column of α values and the temperatures at which they were measured are reported in the column of temperature ranges.

Table I. Density Equations for Binary Mixtures

Compn., Mole Fraction	$\rho = \alpha - \beta t$		Std. Dev.	
	α, g./cc.	$\beta \times 10^4$, g./cc./° C.	$\times 10^3$, G./Cc.	Exptl. Temp. Range, ° C.
$LiNO_3$		$LiNO_3$-KNO_3 System		
0	2.110	7.33	0.8	346-505
0.107	2.102	7.35	0.3	318-452
0.245	2.083	7.29	0.6	294-425
0.375	2.055	6.96	0.4	306-454
0.500	2.033	6.83	0.7	275-473
0.625	2.010	6.57	0.6	328-476
0.680	1.997	6.38	0.9	219-445
0.801	1.974	6.23	0.2	264-350
0.876	1.954	5.99	0.4	257-403
1.000	1.922	5.56	0.5	276-420
$LiNO_3$		$LiNO_3$-LiCl System		
0.900	1.911	5.37	0.7	278-446
0.799	1.903	5.38	1.0	340-497
0.700	1.889	5.24	0.4	378-497
KNO_3		KNO_3-KCl System		
0.913	2.101	7.28	0.9	349-540
0.795	2.090	7.12	1.3	429-580
0.702	2.069	6.80	1.5	485-633

Table II. Density Equations for Ternary Mixtures of (Li,K)-(Cl,NO_3)

Compn.		$\rho = \alpha - \beta t$		Std. Dev.	Exptl.
Cation fraction, K^+	Anion fraction, NO_3^-	α, g./cc.	$\beta \times 10^4$, g./cc./° C.	$\times 10^3$, G./Cc.	Temp. Range, ° C.
0.250	0.500	1.919	5.57	0.4	350-398
0.250	0.750	1.965	6.18	0.7	296-376
0.410	0.250	1.911	5.51	3.2	302-473
0.410	0.500	1.951	5.77	1.0	253-450
0.410	0.750	1.999	6.50	0.7	300-449
0.750	0.750	1.799	...	...	366.9
0.750	0.750	1.781	...	...	395.8

There are four previous determinations of the density function for molten KNO_3, all of which are in fair agreement (*1, 4, 5, 6*). The equation reported here for KNO_3 agrees particularly well with the most recent of these determinations (*1*). The results reported here for molten $LiNO_3$ are intermediate to two previous determinations (*4, 5*).

DISCUSSION

Additive volume considerations will first be applied to the limiting binaries of the (Li,K)-(Cl,NO_3) system. Then, the formalism of volumetric additivity will be extended to ternary mixtures of a reciprocal salt system and the consequences of this extension will be illustrated for the (Li,K)-(Cl,NO_3) and (Na,K)-(Cl,I) reciprocal systems.

For a binary mixture of molten salts the additive molar volume, V^A, may be defined by a relation such as $V^A = V_2^0 + N_1(V_1^0 - V_2^0)$ where V_1^0 and V_2^0 are the molar volumes of the pure constituents and N_1 is the mole fraction of constituent number 1. The conventional deviation from volumetric additivity for a mixture then becomes $\delta = V^0 - V^A$, where V^0 is the real molar volume of the mixture For liquid mixtures at temperatures below the melting point of a pure constituent, the molar volume of the pure salt as a hypothetical netastable liquid will be defined and computed by extrapolating the linear density *vs.* temperature equation into the supercooled liquid region.

The density data for the $LiNO_3$-KNO_3 binary are extensive and precise. At 400° and 500° C., the pure components and all of their mixtures are real liquids. Deviations from additivity are positive and attain a maximum at 500° C. of 0.30 cc. or 0.6%. At 300° C., all of the mixtures studied are real liquids, but pure KNO_3 is not. The deviations (all positive but one) attain a maximum of 0.12 cc. or 0.3%. At 200° C., only three of the eight mixtures studied are real liquids and both of the pure nitrates are below their melting points. Nevertheless, the molar volumes of these three real-liquid mixtures at 200° C. are represented to within less than 0.1% by the extrapolated additive molar volumes.

Data for the $LiCl$-$LiNO_3$ and KCl-KNO_3 binaries were obtained only at the nitrate-rich end because the melting points of these systems rise rapidly with increasing chloride content and soon exceed the temperature range within which the nitrate ion is usefully stable. Additive molar volumes for these systems were computed at 400° C. by extrapolating the density equations of Van Artsdalen and Yaffe for the pure chlorides. At 400° C., LiCl is more than 200° C. below its melting point and KCl is nearly 400° C. below. The $LiCl$-$LiNO_3$ binary (up to $N_{Cl} = 0.3$) showed a maximum deviation of about 0.4%, and the KCl-KNO_3 binary (up to $N_{Cl} = 0.3$) showed a maximum deviation of about 0.1%.

Van Artsdalen and Yaffe (*8*) reported that the LiCl-KCl binary at 800° C. was additive to within 0.1%. One of the mixtures which they studied, 58.8 mole % LiCl, is liquid at 400° C. If the density equations for the pure chlorides are extrapolated to 400° C., one finds that the 58.8 mole % LiCl mixture is still additive to within 0.1%.

For all four of the limiting binary systems ($LiCl$-KCl, KCl-KNO_3, KNO_3-$LiNO_3$, $LiNO_3$-$LiCl$) the deviations from additivity which are quoted above are estimated to be less than the probable error, except for the $LiNO_3$-KNO_3 binary at 400° and 500° C. for which a deviation of $+ (0.5 \pm 0.3)\%$ with a maximum near the equimolar composition is estimated.

Additivity for Reciprocal Systems. Volumetric additivity implies that the volume of a mixture equals the sum of the volumes of the pure components of which the mixture is comprised. The three components of a reciprocal salt system may be chosen equally well in four ways from among four thermodynamically equivalent constituent salts. A specified mixture may thus be prepared in four ways. For each of these four ways, the amount of each of the three components is uniquely defined, but for each way a different value of the sum of the volumes of the pure components will generally be obtained.

These considerations will be developed and applied in a quantitative way in the following paragraphs. It is useful to formulate statements in terms of a specific system. For this purpose (Li,K)-(Cl,NO_3) is chosen. It is also useful to employ the molar volume which, being an intensive quantity, reduces the independent composition variables to two for which the ionic fractions N_K and N_{Cl} are chosen.

The volumetric-additivity concept may be described by four equations, two of which may be written as

$$V_1^A = V^0_{LiNO_3} + N_{Cl}(V^0_{KCl} - V^0_{KNO_3}) + N_K(V^0_{KNO_3} - V^0_{LiNO_3}) \qquad (1)$$

$$V_2^A = V^0_{LiCl} + (1 - N_{Cl})(V^0_{LiNO_3} - V^0_{LiCl}) + N_K(V^0_{KNO_3} - V^0_{LiNO_3}) \qquad (2)$$

These four relations will be referred to as Equations 1, 2, etc. They define the additive molar volumes, $V_1^A, \ldots, V_4^A$, from which the conventional deviations from additivity δ^A are obtained by the four relations, $\delta_i^A = V^0 - V_i^A$ ($i = 1, \ldots, 4$), where V^0 is the real molar volume of the mixture.

For each ternary composition of a given system there are, in general, four distinct values of the deviation from additivity. One can imagine that there may be systems for which all four values of α_i^A are equal for every composition (the equality of any two for every composition implies the equality of all four) and we shall refer to this case as strict ternary additivity.

For strict ternary additivity to hold, the sums of the molar volumes of the reciprocal pairs must be equal—that is

$$V^0_{LiCl} + V^0_{KNO_3} = V^0_{LiNO_3} + V^0_{KCl} \qquad (3)$$

This relation implies that the molar volume of any one constitutent may be computed from a knowledge of the molar volumes of the other three. For the system (Li,K)-(Cl,NO_3), Equation 3 fails by 1.07 cc. at 396° C., when one uses the density equations reported here for the nitrates and extrapolates the equations of Van Artsdalen and Yaffe for the chlorides. This 1.07 cc. is 1.9% of the molar volume of KNO_3 and 4% of the extrapolated molar volume of LiCl. These deviations are substantially greater than those for the limiting binary systems discussed above. For the (Na,K)-(Cl,I) system at 700° C., it is computed from the data of Bloom, Knaggs, Molloy, and Welch (*1*) that Equation 3 fails by 1.78 cc. or 2.6% of the molar volume of KI and 4.9% of the molar volume of NaCl.

Additivity for Pseudobinaries. The pseudobinaries have been a source of some confusion in the literature. Along the KCl-$LiNO_3$ pseudobinary the relation

$$N_{Cl} - N_K = 0$$

holds, while along the KNO_3-$LiCl$ pseudobinary the relation

$$N_{Cl} + N_K = 1$$

holds. Each of these relations reduced each of the isotherms given by Equations 1, 2, etc., to an equation in one composition variable. Along the KCl-$LiNO_3$ pseudobinary V_1^A (Equation 1) reduces to a function with the mathematical form of a binary additivity relation. Furthermore, V_3^A or V_4^A must equal V_1^A (we choose $V_3^A = V_1^A$), whereas V_2^A and V_4^A are not equal and do not have the formal properties of binary additivity. Along the KNO_3-$LiCl$ pseudobinary, V_2^A and V_4^A have the mathematical form of binary additivity relations and are equal, while V_1^A and V_3^A are different.

Previous workers have chosen to define deviation from additivity for pseudobinaries as the deviations from those additivity expressions which have the mathematical form of binary additivity relations. According to this definition, the deviations from additivity for the KCl-$LiNO_3$ pseudobinary would be defined to be δ_1^A, while the deviation δ_2^A would be ignored, and the deviations from additivity for the KNO_3-$LiCl$ pseudobinary would be defined to be δ_2^A while δ_1^A would be ignored. It may easily be shown that if Equation 3 does not hold, then it is impossible for more than one pseudobinary molar-volume isotherm to be linear so that so-called deviations from additivity are an unavoidable artifact of this method of treating data.

From the data of Bloom, Knaggs, Molloy, and Welch (*1*) for the pseudobinaries of the (Na,K)-(Cl,I) system we compute that the 700° C. isotherm for the KI-NaCl pseudobinary is a linear function of composition to within an uncertainty of about 0.4%, whereas the isotherm for KCl-NaI shows substantial positive deviations from linearity. When the latter deviations are smoothed to fit the function $\delta^A = \delta^A_{max} \cos(\pi N_{Cl})$, δ^A_{max} is $(1.5 \pm 0.2)\%$. At the composition where all ionic fractions are equal, V_1^A and V_2^A differ by 1.7% at 700° C. so that a deviation from linearity of at least 0.85% for one pseudobinary isotherm is unavoidable.

Quasilinear Additivity. As an alternative to linear additivity the authors have chosen a function which, for mnemonic purposes, may be written as

$$V^Q = N_K N_{Cl} V^0_{KCl} + N_K N_{NO_3} V^0_{KNO_3} + N_{Li} N_{Cl} V^0_{LiCl} + N_{Li} N_{NO_3} V^0_{LiNO_3} \qquad (4)$$

but which readily reduces to an equation in two ionic fraction variables. This equation has the following useful properties, none of which is possessed by the criteria for strict ternary additivity. First, Equation 4 defines a single deviation parameter, $\delta^Q = V^0 - V^Q$. Second, for binary compositions, Equation 4 transforms into the equations for binary additivity and at the composition of each of the four pure salts it yields the empirical value for the molar volume.

(Thus, Equation 3 need no longer hold.) Third, Equation 4 reduces to a linear isotherm, when either the anionic fraction alone or the cationic fraction alone is held constant. Because of this property, V^Q is referred to here as the quasi-additive molar volume and δ^Q is referred to as the deviation from quasi-additivity.

In Equation 4, each molar volume of a pure susbstance is weighted by the product of the corresponding cationic and anionic fractions and this product equals the Temkin expression for the concentration of the pure substance in the mixture (*3*, *7*). Thus, $(N_K N_{Cl})$ equals the Temkin concentration for KCl in the melt.

Deviations from quasi-additivity, δ^Q, for the (Li,K)-(Cl,NO_3) system were computed and found to be less than 0.5% for all compositions, except one—namely, $N_K = 0.41$ and $N_{Cl} = 0.50$—for which δ^Q was about 0.9%. The uncertainty in the ternary density data was considered to be about 0.2% and the uncertainty in δ^Q to be 0.4 to 0.6%, depending on the chloride content. The 0.9% deviation was out of line with the deviations for neighboring compositions and did not seem to represent a trend.

By comparison, when these same data for the (Li,K)-(Cl,NO_3) system are tested for strict ternary additivity, it is found that to within the uncertainty of the deviations (0.4 to 0.6%) at least one V_i^A will represent the data for a given mixture about as well as V^Q, but at least one other V_i^A will give a decidedly poorer representation. Furthermore, different concentration ranges are best represented by different V_i^A.

The quasi-additivity isotherms of pseudobinaries are represented by parabolas, one of which is

$$V^Q = V^0_{LiNO_3} + N_{Cl}(V^0_{KNO_3} + V^0_{LiCl} - 2V^0_{LiNO_3}) + N^2_{Cl}(V^0_{KCl} + V^0_{LiNO_3} - V^0_{KNO_3} - V^0_{LiCl})$$

for $N_K - N_{Cl} = 0$ (the $LiNO_3 - KCl$ pseudobinary).

These parabolas, of course, intersect at the common composition ($N_{Cl} = \frac{1}{2}$) and, when Equation 3 holds, reduce to the formalism of binary additivity.

The molar-volume isotherms of the (Na,K)-(Cl,I) pseudobinaries were tested for quasi-additivity at 700° C. using the data of Bloom and coworkers. The molar volumes along the KCl-NaI pseudobinary may be represented fairly well by a parabolic function which differs from the quasi-additivity function by a maximum of +(0.6 ± 0.2)%. The molar volumes along the KI-NaCl pseudobinary show positive deviations from quasi-additivity which average 0.6%, but which do not follow any simple function of concentration.

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Thermodynamic Equilibrium in the Ethyl Alcohol–Ethyl Ether–Water System

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THE VAPOR PHASE DEHYDRATION of ethyl alcohol, catalyzed by Dowex 50 hydrogen as ion exchange resin to give ethyl ether and water, has been studied.

$$2C_2H_5OH = (C_2H_5)_2O + H_2O \qquad (1)$$

The work deals specifically with the equilibrium relationships in this system. The existence of the reaction, while not unknown, has often been ignored by past investigators whose primary concern was with some competing reaction of ethyl alcohol. In studying the vapor phase esterification of acetic acid with ethyl alcohol, Herrman (*6*) found that the equilibrium constant for this reaction appeared to vary with the total pressure. This suggests the presence of a side reaction, possibly ether formation. Klem (*9*), repeating Herrman's experiments, found the same effect. He prepared, by distillation, an acid-free sample of the reaction product for analysis by the authors. The analysis showed a considerable concentration of ether. In several studies of this esterification (*2*, *7*, *13*, *14*), the side reaction to ethyl ether was not considered. The authors, in a preliminary investigation of the reaction of isobutylene and ethyl alcohol to give *tert*-butyl ethyl ether, also found large amounts of diethyl ether in the product. Cope and Dodge (*5*) studied the hydration of ethylene with emphasis upon the formation of ethyl ether as well as ethyl alcohol. Their work specifically shows that one cannot neglect the possibility of ether formation. Hence, information on the dehydration of ethyl alcohol to ethyl ether would appear to be of value in a number of reactions involving ethyl alcohol.

Cope (*4*) has considered the thermal data necessary to predict the equilibrium constant for Reaction 1 as a function of temperature, and has made corrections to improve existing data where possible. He lists his best estimates (*5*), with an outline of the corrections made, the reliability, and the shortcomings. The temperature dependence of the equilibrium constant as calculated from these thermal data is shown as the broken line in Figure 1.

Cope and Dodge also critically discuss the experimentally determined values of the equilibrium constant, which are

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