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THE SURFACE TENSION OF MOLTEN SALTS

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I. INTRODUCTION

Molten salts and their mixtures in recent years have been finding ever-increasing application in industry as high-temperature liquids, lubricants, heat-carriers, fluxes, etc. The importance which is being attached to the study of both the bulk and the surface properties of molten salts is thus obvious. Moreover, the study of the physicochemical characteristics of salt melts is a necessary prerequisite for the investigation of the nature of the liquid state and the development of a general theory of liquids.

In view of the vast amount of accumulated information on the physicochemical properties of molten salts in recently published monographs and reviews[1-4] it was impossible to give sufficient attention to each property, including the surface tension of the salts. The increasing interest in experimental data on the surface tension of salts and the non-existence of sufficiently detailed reviews in this field suggest that a review of this type will be opportune and useful.

Before discussing published data on the surface tension of melts, we would point out that we have tried to cover, as completely as possible, papers describing the experimental study of the surface tension of salts and their mixtures; as far as the surface tension of oxide systems is concerned, we have restricted ourselves in the present review to a few papers containing data on the surface tension of the simplest compounds formed in these systems.

II. REVIEW OF EXPERIMENTAL WORK ON THE SURFACE TENSION OF MOLTEN SALTS AND THEIR MIXTURES

The surface tension (σ) of molten salts appears to have been measured for the first time in 1869 by Quinke[5], who used the stationary-drop and drop-weight methods[6-8] to find the capillary constants of melts formed by a number of salts of the alkali and alkaline earth metals. Experimentally, these measurements were unreliable. For example, the temperature of the melts was indefinite, a considerable temperature gradient was unavoidable, and during the measurements there was a danger of decomposition of the melts and contamination from the flame of the heater.

These unsatisfactory features of the determination of σ are also characteristic of the work of Traube[9] and Motylewski[10], who used the drop-weight method find the capillary constants of a large number of inorganic salts.

Bottomley[11] determined σ for $NaNO_3$ and KNO_3 melts using the capillary-ascent method, for which there is much greater theoretical justification[7].

Lorenz and coworkers[12-14] measured σ for $NaNO_3$, KNO_3, $PbCl_2$, $CdCl_2$, KCl, AgCl, and various KCl + $PbCl_2$ and $CdCl_2$ + $PbCl_2$ mixtures by the capillary-ascent method. Unsatisfactory methodological features of the studies are the possibility of contamination of the melt by corrosion products from the walls of the capillaries and the temperature gradient along the capillary.

Of considerable interest in the study of σ for fused salts is the work of Jaeger[15], which has now become classical. Jaeger was the first to measure σ for salts using the maximum gas-bubble pressure method[7,8,16-18], which is apparently the most reliable and convenient and which has subsequently been widely used. Jaeger developed thoroughly a method for measuring σ by this method in the temperature range from -80° to +1650°, and in the high-temperature range he introduced a number of improvements in technique aimed at preventing contamination of the salts, maintaining constant temperature, increasing the accuracy of the measurement of the temperature and pressure, etc. An unsatisfactory feature of his procedure is that the moment when the end of the capillary comes in contact with the surface of the melt is recorded visually, and this is extremely difficult at high temperatures. Jaeger determined the values of σ for almost 200 organic and 50 inorganic liquids. The latter included the alkali metal halides (with the exception of lithium bromide and iodide), nitrates, and sulphates; sodium and potassium metaborates, metaphosphates, molybdates, and tungstates; lithium metasilicate; potassium dichromate; thallium nitrate; sulphur monochloride; the trichlorides of phorphorus, arsenic, antimony, and bismuth; tribromides of phosphorus, arsenic, and bismuth; and phosphorus triiodide. All the substances studied have negative temperature coefficients $d\sigma/dt$. In some instances the value of $d\sigma/dt$ changes with temperature and the σ polytherms are slightly convex away from the temperature axis.

In a study of the properties of salt melts used as electrolytes in magnesium baths, Zhivov[19,20] used the maximum gas-bubble pressure method to measure σ for pure NaCl, KCl, and $MgCl_2$, the binary NaCl–KCl, NaCl–$MgCl_2$, and KCl–$MgCl_2$ systems, and sections of the ternary NaCl–KCl–$MgCl_2$ system at molar ratios KCl : NaCl = = 1 : 1 and 1 : 3. The 700° isotherms for the binary systems containing $MgCl_2$ showed points of inflection corresponding to equimolar mixtures of the components, and the 800° isotherm for the NaCl–$MgCl_2$ system also showed a maximum corresponding to 86 mole % $MgCl_2$. Zhivov (see Mashovets[21]) also measured σ for molten NaF + AlF_3 mixtures at AlF_3 concentrations up to 50 mole %, and molten NaF + AlF_3 (15 mole % and 33.4% AlF_3) + Al_2O_3 (up to 10 wt. %) and Na_3AlF_6 + Al_2O_3 (up to 17.5 wt. % Al_2O_3) mixtures. Within limits of accuracy of the measurements, the addition of Al_2O_3 does not influence the value of σ for the mixtures.

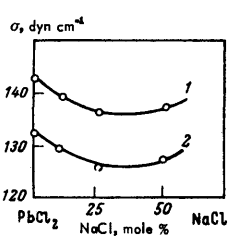


Fig. 1. Surface tension isotherms for the $PbCl_2$–NaCl system[25]: 1) 500°; 2) 600°.

Elchardus[22] used the maximum bubble-pressure method to measure σ for pure Na_3AlF_6 and its mixtures with NaF and AlF_3 (up to 20 wt. % additive). The temperature dependence of σ for Na_3AlF_6 is non-linear, and this is taken as an indication that cryolite dissociates in the molten state.

Jarrat and Prideaux[23] measured σ for melts using Sugden's version[7,24] of the maximum gas-bubble pressure method, using two capillaries; an advantage of this method is that it eliminates the measurement of the depth to which the end of the capillary is immersed in the melt. This method was used to find σ for molten $HgCl_2$ and $HgBr_2$ close to the melting points.

Barzakovskii[25,26] measured σ for the binary NaCl–KCl, $CaCl_2$–NaCl, and NaCl–$BaCl_2$ salt systems throughout the entire concentration range and for the NaCl–$PbCl_2$ system in the range 0–50 mole % NaCl. The isotherms for these systems are linear or slightly convex towards the composition axis; only the 500° and 600° isotherms for the NaCl–$PbCl_2$ system show minima corresponding to 30 mole % NaCl (Fig. 1).

Semenchenko and Shikhobalova[27-30] used the maximum gas-bubble pressure method to study σ for a number of salt melts up to 1100°. As an improvement in technique they introduced a convenient method in which the moment when the end of the capillary came in contact with the melt was recorded by direct electrical contact. The values of σ were measured for Li_2SO_4, LiCl, $NaNO_3$, Na_2SO_4, NaCl, K_2SO_4, KCl, KBr, KI, RbCl, CsCl, $BaCl_2$ and the organic salts CH_3CO_2K and $C_2H_5CO_2K$, and also for mixtures of the binary systems $NaNO_3$–(NaF, NaCl, NaBr, NaI, CH_3CO_2K, and $C_2H_5CO_2K$), Na_2SO_4–(NaCl, NaI, KCl, KBr, and KI), and K_2SO_4–KCl at concentrations of the second component not exceeding 50 mole %, and for mixtures of the systems Li_2SO_4–(NaCl, KCl, RbCl, CsCl, and $BaCl_2$), LiCl–RbCl, and $NaNO_3$–(CH_3CO_2K and $C_2H_5CO_2K$) in the concentration range from 0 to 100%. The isotherms for all the systems are convex towards the composition axis. The isotherms for the Li_2SO_4–$BaCl_2$ system show a deep minimum which was attributed to the formation of the sparingly dissociated barium sulphate (Fig. 2). On the isotherms for the Li_2SO_4–(NaCl, KCl, RbCl, and CsCl) systems, small (1–2 mole %) horizontal sections were distinguished at low concentrations of the second component. The scatter in the experimental points in these ranges is scarcely greater than the error in the determination of σ (1.5–2% according to the authors), so that these isotherms can be regarded as smooth curves. On the basis of the data obtained, it was concluded that small quantities of the additives influence the value of σ and the crystallisation of the salt mixtures. The changes in σ and the limiting surface activity when various salts were added were compared with the values of the generalised moments of the ions according to the theory of Semenchenko[8,31]:

$$\mu = z/r, \qquad (1)$$

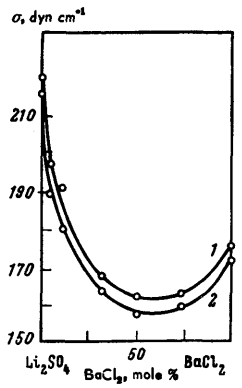


Fig. 2. Surface tension isotherms for the Li_2SO_4–$BaCl_2$ system[29,30]: 1) 1000°; 2) 1050°.

where z is the charge and r the radius of the ion. The adsorption of the surface-active components was calculated for a number of dilute mixtures.

King[32] measured σ for silicate systems up to 1600° using the hollow-cylinder detachment method which is a modification of the ring detachment method[7]. The values of σ were measured for 26 melts from the $CaO–SiO_2$, $MgO–SiO_2$, $MnO–SiO_2$, and $FeO–SiO_2$ systems, including some metasilicate compositions. Positive temperature coefficients of σ were observed for $CaSiO_3$, $MnSiO_3$, and a number of mixtures of the systems studied. This phenomenon was explained on the basis of theories regarding the breakdown of the structure of the melt. With increase in temperature the process of structure breakdown is displaced in such a way that the proportion of surface-active ions (SiO_3^{2-}) in the melt decreases; the resulting increase in σ is greater than the decrease in σ due to the decrease in the strength of the interaction between the particles with increase in temperature.

Mention may be made to the work of Shartsis and coworkers, who used the hollow-cylinder detachment method to measure σ for $MO–SiO_2$ (M = Li, Na, K, and Pb)[33,34] and $MO–B_2O_3$ (M = Li, Na, K, Ca, Sr, Ba, Zn, and Pb)[35–38] systems. The compositions of a number of systems were not brought to the metasilicate and metaborate compositions because of the limited miscibility of the components in the liquid phase.

Vajna[39] used the ring detachment method to measure σ for melts of pure cryolite and cryolite containing NaF, AlF_3, Al_2O_3, and CaF_2 additions (up to 15 wt.%).

Gromakov[40], who measured σ using Jaeger's method[15], proposed that the maximal pressures in the gas bubble be determined at two different depths of immersion of the end of the capillary in the melt, in order to eliminate the value of the density of the melt from the formula used in the calculation; this makes sense when the densities are unknown, although the error in the estimation of the density by this method is extremely large. Gromakov[41] also proposed a method for measuring the σ of small quantities of liquid by means of a capillary with thickened walls in the lower section; it was estimated that the error in the determination of σ is 10%. This method was used by Gromakov and Kostromin[42] to measure σ for a number of compositions of the $NaNO_3$–KNO_3–$RbNO_3$ ternary system.

The surface tension of systems formed by molten nitrates was also studied by Bokhovkin[43] ($AgNO_3$–KNO_3) and Manakin[44] ($NaNO_3$–KNO_3, $LiNO_3$–$NaNO_3$, and $LiNO_3$–KNO_3) by the maximum gas-bubble pressure method. In all the σ isotherms for the nitrate systems are either linear or only slightly convex towards the composition axis.

Peake and Bothwell[45] used the maximum gas-bubble pressure method to measure σ for the $BaCl_2$–KCl system, for which the 800° isotherm has a point of inflection corresponding to 35 mole % $BaCl_2$ (Fig. 3).

Peake and Neithamer[46] determined σ for the KCl–K_2SO_4 system; the isotherm is convex towards the composition axis.

Desyatnikov[47] used the maximum pressure and ring detachment methods to measure σ for NaCl, KCl, and $MgCl_2$ melts; the NaCl–KCl, NaCl–$MgCl_2$ and KCl–$MgCl_2$ binary systems; and sections of the NaCl–KCl–$MgCl_2$ ternary system at molar ratios NaCl : KCl = 1 : 3, 1 : 1, and 3 : 1. The σ isotherms for the NaCl–$MgCl_2$ and KCl–$MgCl_2$ systems show breaks (Fig. 4). The values of σ obtained for $MgCl_2$ are more reliable than those given by Zhivov[19].

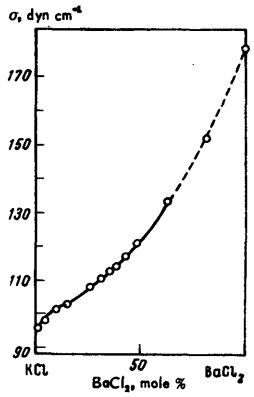


Fig. 3. 800° surface tension isotherm for the KCl–$BaCl_2$ system[45].

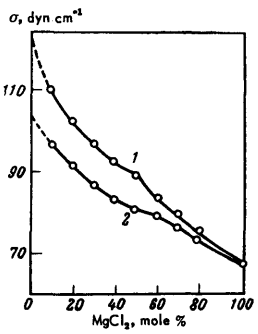


Fig. 4. 700° surface tension isotherm for the NaCl–$MgCl_2$ (1) and KCl–$MgCl_2$ (2) systems[47].

Strelets, with Desyatnikov[48,49] and Bondarenko[50,51] measured σ for the salt mixtures used in the electrolytic production of magnesium. The values of σ were measured from melts of an isoconcentrate section (10 wt.% $MgCl_2$) of the $MgCl_2$–$CaCl_2$–KCl–NaCl system at NaCl : KCl ratios of 1 : 6, 1 : 3, 1 : 1, and 6 : 1, and of isoconcentrate sections (10 wt.% and 20 wt.% $MgCl_2$) of the $MgCl_2$–$BaCl_2$–KCl–NaCl system at NaCl : KCl ratios of 2 : 1, 1 : 1, and 1 : 2, and also of the $BaCl_2$–$MgCl_2$, $BaCl_2$–NaCl, and $MgCl_2$–$BaCl_2$–NaCl (8 sections at 10 wt.% $BaCl_2$ intervals) systems. The isotherm for the $BaCl_2$–$MgCl_2$ system shows an inflection at 10–15 mole % $BaCl_2$ (Fig. 5); this is attributed to compound formation.

Bordman and coworkers[52] used the maximum gas-bubble pressure method in a glass apparatus to measure σ for 13 binary systems formed by salts with common cations or anions: AgCl–AgBr, AgBr–AgI, NaBr–KBr, KCl–KBr, $NaNO_3$–KNO_3, $CdCl_2$–$CdBr_2$, $PbCl_2$–NaCl, $PbCl_2$–$CdCl_2$, $CdCl_2$–KCl, $PbCl_2$–KCl, $PbCl_2$–AgCl, AgCl–KCl, and AgBr–KBr. The isotherms for most of the systems are linear or slightly convex towards the composition axis. The 600° isotherm for the $PbCl_2$–KCl system has a minimum at 40 mole % $PbCl_2$; this minimum is now shown by the 500° isotherm (Fig. 6). The 700° isotherm for the $CdCl_2$–KCl system passes through a maximum at 80 mole % $CdCl_2$ and through a point of inflection at the equimolar component ratio (Fig. 7). These points on the σ isotherms were attributed to the presence of ionic complexes of the type MCl_3^- in the melts. As a criterion for ideal behaviour in the binary system the authors used Zhukhovitskii's equation[53], rewritten by Guggenheim[54] for an equimolar mixture in the form

$$\sigma = {}^1/_2(\sigma_1 + \sigma_2) - (\sigma_2 - \sigma_1)^2 a/8kT, \qquad (2)$$

where σ, σ_1, and σ_2 are the surface tensions of the mixture and the pure components, k is the Boltzmann constant, and a the mean area occupied by a molecule in the surface layer, assumed to be equal to the sum

$$a = {}^1/_2\left(\frac{M_1}{d_1 N}\right)^{2/3} + {}^1/_2\left(\frac{M_2}{d_2 N}\right)^{2/3}, \qquad (3)$$

where M_1, M_2, d_1, and d_2 are the molecular weights and densities of the components, and N is Avogardro's number. For all the systems studied, with the exception of the $PbCl_2$–$CdCl_2$ system, the experimental value of σ shows a negative (up to 4%) deviation from the value calculated from Eqn. (2)†.

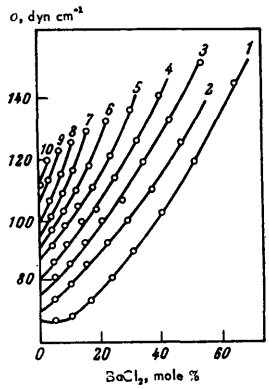


Fig. 5. 750° surface tension isotherms for $MgCl_2$–NaCl–$BaCl_2$ systems[50,51]. NaCl concentration (wt.%): 1) 0; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50; 7) 60; 8) 70; 9) 80; 10) 90.

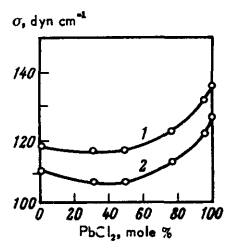


Fig. 6. Surface tension isotherms for the KCl–$PbCl_2$ system[52]: 1) 500°; 2) 600°.

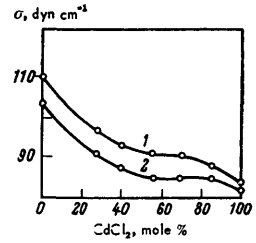


Fig. 7. Surface tension isotherms for the KCl–$CdCl_2$ system[52]: 1) 600°; 2) 700°.

Callis and coworkers[55] used the ring detachment method to determine σ up to 1000° for sodium phosphate melts at Na_2O/P_2O_5 oxide ratios from 1 to 2.2, that is, including sodium meta- and pyro-phosphates. The values of σ and $d\sigma/dt$ differ considerably from those given by Jaeger[15]. It was found that the value of σ is higher, the higher the concentration of basic oxide in the melt. The value obtained for σ and the densities of the melts were used to estimate the apparent molecular weights of the phosphates in the melt.

Dahl and Duke[56] used the maximum gas-bubble pressure method to determine σ for melts formed by $AgNO_3$–$NaNO_3$, $AgNO_3$–KNO_3, and $PbCl_2$–(LiCl, NaCl, KCl, RbCl, and CsCl) mixtures. In the $PbCl_2$–MCl systems the nature of the σ isotherms at 575° changes with increase in the dimensions of the alkali metal ion. Thus in the $PbCl_2$–LiCl system the isotherm is linear and in the $PbCl_2$–NaCl system the isotherm is convex towards the composition axis and does not show the minimum reported by Barzakovskii[25]; the σ isotherms for the $PbCl_2$–(KCl, RbCl, and CsCl) systems have minima which become deeper on going from potassium to caesium (Fig. 8). The values of σ for silver nitrate are anomalously high. The

† Conclusions regarding the extent of the deviation from ideal behaviour shown by a system on the basis of calculations from Eqn. (2) for the equimolar composition alone can of course be only approximate.

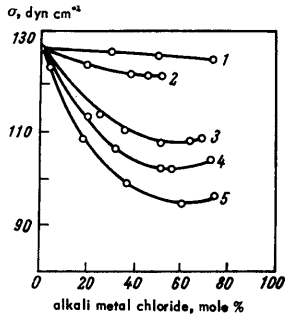


Fig. 8. 575° surface tension isotherms for the $PbCl_2$–(LiCl, NaCl, KCl, RbCl, and CsCl) systems[56]:
1) LiCl; 2) NaCl; 3) KCl; 4) RbCl; 5) CsCl.

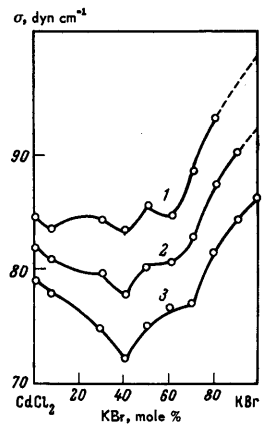


Fig. 9. Surface tension isotherms for the KBr–$CdCl_2$ system[59]:
1) 600°; 2) 700°; 3) 800°.

values of σ for $ZnCl_2$ melts are lower than those for melts formed by LiCl, NaCl, KCl, $PbCl_2$, $NaNO_3$, KNO_3, and $AgNO_3$[57].

Ellis et al.[58] measured σ for the alkaline earth metal halides $BaBr_2$, $SrCl_2$, $SrBr_2$, $CaBr_2$, and CaI_2. For these salts, σ increases with increase in the dimensions of the cation. Ellis and coworkers[59] also studied σ for a diagonal section of the $CdCl_2$–KBr ternary reciprocal system. The σ isotherms showed a minimum at 40 mole % KBr and a point of inflection at 60 mole % KBr (Fig. 9), indicating, in the opinion of the authors, the existence of ionic complexes $CdCl_4^{2-}$ and $CdBr_4^{2-}$ in the melts; this was confirmed by the Raman spectra. The increase in the depth of the minimum on the isotherms with increase in temperature is related to the increase in the disorder and variety of the species in the melt.

Greenwood and Wade[60] determined σ for $GaCl_3$ melts and Greenwood and Worrall[61] determined σ for $GaBr_3$ and Ga_2Cl_4 melts.

Bradbury and coworkers[62,63] used the hollow-cylinder detachment method to measure σ for melts of the Na_2O–P_2O_5, K_2O–P_2O_5, and CaO–P_2O_5 binary systems from the metaphosphate composition to the pyrophosphate composition (with the exception of the CaO–P_2O_5 system) and also for $NaPO_3$ + NaF mixtures (up to 15 mole % NaF). The surface tension of the melts in all the systems increases with increase in the concentration of basic oxide or NaF in the mixture; by analogy with the silicates[32], this was attributed to breakdown of the structure of the melt‡.

Frame and coworkers[68] give values of σ for the low-melting salts KCNS, $NaNO_2$, $K_2Cr_2O_7$, and $KClO_3$, obtained by Sugden's version of the maximum gas-bubble pressure method[24]. For these salts (with the exception of $NaNO_2$) σ and σ/dt are not constant and depend on the temperature and the time for which the salt is kept above its melting point. This is related to possible decomposition of the salt or to bond redistribution. Comparison of the values of σ for alkali metal halides and nitrates shows that the influence of the dimensions of the cation is greater, the smaller the anion.

Bloom and coworkers[69] used the maximum gas-bubble pressure method to measure the surface tension of melts formed by NaCl, NaBr, NaI, KCl, KBr, KI, $NaNO_3$, $NaNO_2$, KNO_3, $AgNO_3$, $PbCl_2$, the binary $NaNO_3$–$NaNO_2$, KNO_3–KNO_2, $NaNO_3$–$AgNO_3$, KNO_3–$AgNO_3$, and $PbCl_2$–NaCl systems, and a diagonal section of the ternary reciprocal KCl–NaI system. It was suggested that the deviation of the values of σ for the salt mixtures from the values corresponding to ideal solutions be explained on the basis of theories of the surface enthalpy of mixing H^S:

$$H^s/a = \sigma - Td\sigma/dT, \qquad (4)$$

where a is the surface area and $d\sigma/cT = -\Delta S^S/a$. The formation of an ionic complex in the melt leads to a decrease in enthalpy in the bulk phase and also to a decrease in the surface enthalpy of mixing:

$$\Delta\sigma = \Delta H^s/a - T\Delta S^s/a, \qquad (5)$$

that is, when an ionic complex is formed $\Delta\sigma < 0$, if $\Delta H^S/a < 0$ and $\Delta S^S/a > 0$. For the $NaNO_3$–$AgNO_3$ and $PbCl_2$–NaCl systems, small negative deviations from the values for ideal mixtures (~ 7%) were observed. For the KCl–NaI, $PbCl_2$–RbCl[56], and $CdCl_2$–KCl[52] systems, the curves obtained by plotting $\Delta H^S/a$ against the mole fraction of the second component show maxima corresponding to 50 mole % NaI and RbCl and 75 mole % KCl. Generally speaking, the method for estimating $\Delta H^S/a$ assumed that $d\sigma/dT$ is constant over a wide temperature range, and the use of the values of $d\sigma/dT$ to calculate $\Delta H^S/a$ requires that σ be measured with a fairly high accuracy, and this is not always true.

Popel' and Esin[70] measured σ for the CaO–SiO_2–Al_2O_3 and CaO–SiO_2–MgO ternary oxide systems by stationary-drop and maximum gas-bubble pressure methods; values of σ were obtained for calcium metasilicate in the range 1460–1520°. The same methods were used by Manakov and coworkers[71] to determine σ for potassium metaniobate at 1400°.

Lantratov[72] used the gas-bubble pressure method to measure σ for melts formed by the salt systems used as electrolytes in the preparation of metallic sodium. The

‡ In systems of the type MPO_3–MX (where X = halide, SO_4^{2-}, etc.), chemical reaction takes place, accompanied by the separation of reaction products[64-67]. Bradbury and coworkers[62,63] apparently made no allowance for this feature and measured σ for non-equilibrium mixtures of indefinite composition.

$CaCl_2$–NaCl binary system and sections of the $BaCl_2$–$CaCl_2$–NaCl ternary system at $CaCl_2$: $BaCl_2$ ratios of 3 : 1 and 3 : 2 were studied. NaF and CaF_2 additives (up to 10 wt. %) were found to be surface-inactive with respect to these systems.

Janz and Lorenz[73,74] measured σ for aggressive carbonate melts up to 1000° in an atmosphere of CO_2 by the solid detachment method[7]. The solid detached from the surface consisted of the elongated tip of a gold–palladium sphere, which was also used to determine the density. Values of σ were obtained for melts formed by Li_2CO_3, Na_2CO_3, K_2CO_3, and the Na_2CO_3–K_2CO_3 binary system.

Addison and Coldrey[75] used the gas-bubble pressure method to measure σ for molten $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$, $TlNO_3$, NH_4NO_3, $AgNO_3$, $NaNO_2$, and KNO_3. The values of σ found for $TlNO_3$ were 25% lower than those given by Jaeger[15]. The values of σ for the molten nitrates and chlorides of the alkali and alkaline earth metals and magnesium close to the melting points were compared with the radii of the cations: the values of σ for the alkali metal salts decrease from Li to Cs; the values of σ for the alkaline earth metal salts increase from Mg to Ba (Fig. 10). This nature of the change in σ was attributed to the increase in the covalent forces in the subgroup formed by the alkaline earth metals and magnesium.

Morris and coworkers[76] used an assembly similar to that described by Janz and Lorenz[73] to measure σ for the $PbMoO_4$–$Bi_2(MoO_4)_3$ system. The temperature coefficients $d\sigma/dt$ for all compositions change with change in temperature.

Lehman[77] measured σ for melts of the KCl–$CaCl_2$ and CsCl–$CaCl_2$ systems§.

Sokolova and Voskresenskaya[78–80] used the maximum gas-bubble pressure method to study σ for the NaCl–$BaCl_2$ system and for the NaBr–K_2SO_4 diagonal section of the Na, K ‖ Br, SO_4 ternary reciprocal system. Reshetnikov's equation[81] in the form

$$\sigma = \sigma_1 + \frac{(\sigma_2 - \sigma_1)x}{x + k(1-x)}, \qquad (6)$$

where σ, σ_1, and σ_2 are the surface tensions of the mixture and the pure components, x the mole fraction of the second component, and k a constant, is applicable to the isotherms.

Sokolova and coworkers obtained values of σ for the metaphosphates of lithium, sodium, potassium, caesium, calcium, strontium, and barium[82] and the $LiPO_3$–$NaPO_3$, $NaPO_3$–$Ca(PO_3)_2$, and KPO_3–$Ba(PO_3)_2$ binary systems[83]. These and published data were used to construct curves giving the dependence of σ on the generalised moments μ – see Eqn. (1) – of the cations and anions forming the salt[82,84] (Figs. 11 and 12). The nature of the change in the dependence of σ on μ for the cation of the alkaline earth metal salts was compared[82] with the possible difference in the degree of dissociation of these salts[85] and the existence of MX^- ions in the melts. The values for some radium salts were estimated by interpolation from the plots of σ against μ. On the basis of the experimental facts it was suggested[84] that the values of σ for the alkali metal metaphosphates are independent of the length of the $(PO_3^-)_n$ polyanion chain and that a decisive part is played by the terminal PO_4^{2-} groups. Values of σ were determined for zinc metaphosphate and the binary $NaPO_3$–$Zn(PO_3)_2$ and KPO_3–$Zn(PO_3)_2$ systems (Figs. 13 and 14), for which the equilibrium diagrams were also studied[86]. The same authors[87] also studied σ for a number of nitrate and nitrite–nitrate salt mixtures.

Wu and coworkers[88] used the maximum gas-bubble pressure method to study σ for the FeO–Fe_2O_3–P_2O_5 system (up to 20 mole % P_2O_5), a number of (FeO–Fe_2O_3)–CaO–P_2O_5 mixtures, and the CaO–P_2O_5 system up to the metaphosphate composition.

Yakobashvili and Frumin[89,90] used the drop-weight method to obtain the values of σ for pure CaF_2 and for CaF_2 containing added CaO, MgO, SiO_2, ZrO_2, TiO_2, and Al_2O_3.

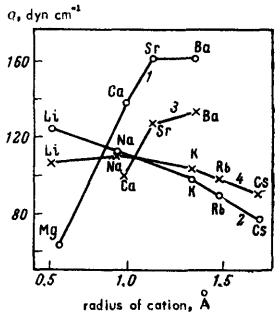


Fig. 10. Dependence of the surface tension of the chlorides and nitrates of the alkali and alkaline earth metals and magnesium on the radius of the cation[75]:
1) Group II chlorides at 1000°; 2) Group I chlorides at 800°; 3) Group II nitrates close to the melting point; 4) Group I nitrates at 425°.

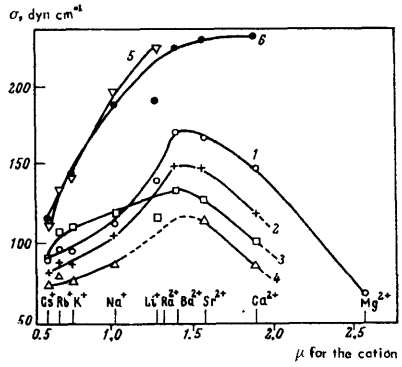


Fig. 11. Dependence of the surface tension of salts of the alkali and alkaline earth metals and magnesium at the melting points on the generalised moments of the cations[82]:
1) chlorides; 2) bromides; 3) iodides; 4) nitrates; 5) sulphates; 6) metaphosphates.

§ We have no information on the method of measurement or the shape of the σ isotherms, since only an abstract was available.

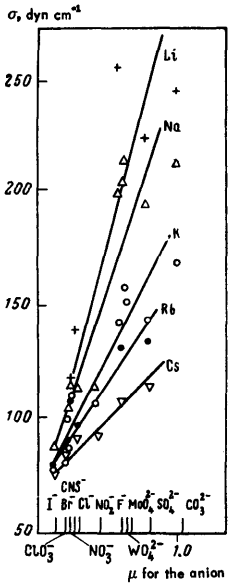


Fig. 12. Dependence of the surface tension of alkali metal salts at the melting point on the generalised moments of the anions [84].

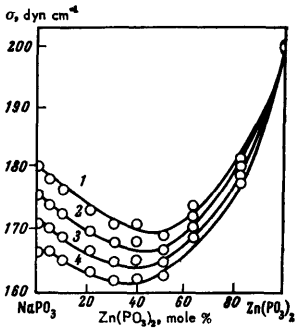


Fig. 13. Surface tension isotherms for the $NaPO_3$–$Zn(PO_3)_2$ system [86]:
1) 800°; 2) 900°; 3) 1000°: 4) 1100°.

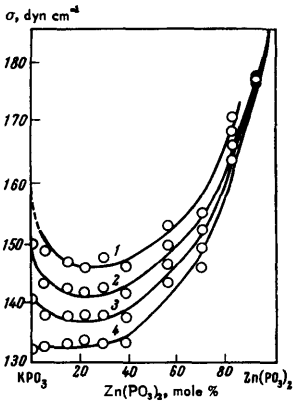


Fig. 14. Surface tension isotherms for the KPO_3–$Zn(PO_3)_2$ system [86]:
1) 800°; 2) 900°; 3) 1000°; 4) 1100°.

Nikitin and coworkers [91] used the stationary-drop method to determine the values of σ for pure CaF_2 and for CaF_2 containing added CaO, SiO_2, Al_2O_3, and MgO in the range 1470–1550°.

Moiseev and Stepanov [92] used the maximum gas-bubble pressure method in an atmosphere of CO_2 to measure σ for melts formed by Li_2CO_3, Na_2CO_3, K_2CO_3, and the binary systems and the ternary system based on these carbonates.

Owens and Mayer [93] determined the values of σ for $NaPO_3$–Li_2SO_4, $NaPO_3$–Na_2SO_4, $NaPO_3$–Rb_2SO_4, and $NaPO_3$–UO_2SO_4 mixtures; as in the work of Bradbury and coworkers [62,63], no allowance was made for possible chemical interaction between the components [65], leading to the liberation of SO_3.

Campbell and Williams [94] used the maximum gas-bubble pressure method in the range 130–170° to determine σ for $LiClO_3$ and its mixtures with H_2O (up to a mole fraction of 0.236) and with $LiNO_3$ (up to a mole fraction of 0.213).

Bertozzi and Sternheim [95] used the solid detachment method [7] to determine σ for 13 binary systems formed by the nitrates of the alkali metals and silver.

Mellors and Senderoff [96] studied σ for melts formed by the NaF–LiF–ZrF_4 ternary system (from 2.9 mole % to 60 mole % ZrF_4 in mixtures with the eutectic NaF : LiF = = 2 : 3) in the range 750–850°. On the basis of a comparison of σ and the surface enthalpy H^S/a (4) with the logarithm of the ZrF_4 concentration, it was concluded that the melts contain the $[ZrF_7]^{3-}$ ion. The $[ZrF_6]^{2-}$ ion, which is stable in the solid state, was not detected in the melts.

III. SURFACE TENSION OF ONE-COMPONENT SALT SYSTEMS

1. Surface Tension of Molten Salts at the Melting Point

Examination of the literature on the surface tension of molten salts shows that up to the present, values of σ have been determined more or less reliably for almost a hundred individual salts.

In Table 1 we have collected the published values of σ for pure salts at the melting point or at temperatures close to the melting point. The melting points were taken from various sources [15,68,97] and the surface tension values are those of Jaeger [15] and later workers, since the reliability of the results of earlier studies [5,6,9–14] is doubtful. Some of the values of σ given in Table 1 were obtained by analytical or graphical extrapolation from published data. The values of σ given in Table 1 were obtained with different degrees of experimental accuracy, which in a number of specific instances could not be estimated. In most instances the error in the determination of σ apparently amounts to not less than ±1% of the measured quantity, particularly in the high-temperature range.

2. Temperature Dependence of the Surface Tension of Molten Salts

The investigation of the temperature dependence of the surface tension of molten salts is one of the important problems associated with the surface properties of melts.

TABLE 1. Surface tension of molten salts at the melting point.

Salt	M.p., °C	σ, dyn cm⁻¹	Refs.
Lithium salts			
LiF	840	255.2	15
LiCl	680	140.2	15
$LiNO_3$	254	118.4	15
		115.4	75
Li_2CO_3	726	244.1	74,92
Li_2SO_4	852	224.4	15
		226	29,30
$LiBO_2$	845	264.8	15
$LiSiO_3$	1201	381	15
	at 1200	~355	34
$LiPO_3$	675	191.1	82
$LiClO_3$	128	88.6	94
Sodium salts			
NaF	990	201.6	15
NaCl	801	114.1	15,19,26, 28,76
		116.4	69,2,3
NaBr	768	106.5	15
		98	69
	at 755	102.8	79
NaI	660	88.2	15,69
$NaNO_2$	281	124.5	68
		119.4	69
	277	121.2	75
$NaNO_3$	312	120.7	15
		119.0	27
		116.9	52
		116.6	75
		113	2,3 см.[42–44]
Na_2CO_3	858	211.7	74,92
Na_2SO_4	884	196.3	15
	at 900	192.6	29,30
Na_2MoO_4	687	215.1	15
Na_2WO_4	694	204.4	15
$NaPO_3$	620	209.5	15
		194	55
		192.5	62,63
	623,5	189.5	82
$Na_4P_2O_7$	994	248	55
		~243	63
$NaBO_2$	965	201.6	15
Na_2SiO_3	at 1570	307	32
	at 1100	300	34
Na_3AlF_6	1000	145.5	21
		148.3	39
Potassium salts			
KF	858	143.2	15
KCl	at 800	96.1	25
	780	97.4	15,19,29,45
		98.3	69
KBr	734	88 8	15,29
		90.6	59
		89.5	69
KI	681	78.3	15,29
		79.5	69
KNO_2	435	107.6	75
KNO_3	339	112.9	15
		109.3	69,2,3
		113.5	56
	334	110.8	75
$CaSiO_3$	at 1570 in the range 1460—1520	400 465	32 70
Strontium salts			
$SrCl_2$	873	169.0	58
$SrBr_2$	643	149.5	58
SrI_2	507	115.0	75
$Sr(NO_3)_2$	at 615	128.4	82
$Sr(PO_3)_2$	1010	228.3	
Barium salts			
$BaCl_2$	at 1000	171.0	25
	962	177	29
		165	45
	960	170	79
$BaBr_2$	847	153	58
$Ba(NO_3)_2$	595	134.8	75
$Ba(PO_3)_2$	868	224.5	82
Copper salts			
CuCl	at 450	95	99
Silver salts			
AgCl	455	179	52,3
AgBr	434	154	52,3
AgI	552	116	52
$AgNO_3$	212	170.2	15
		171	43
		150	56
		148	69
		152.1	75
Zinc salts			
$Zn(BO_2)_2$	at 900	130	36
$Zn(PO_3)_2$	862	199.2	86
Cadmium salts			
$CdCl_2$	568	90	52,3
K_2CO_3	899	168.2	см.[42–44]
K_2SO_4	1069	144.5	74,92
		144	15
		142.3	30
		137	46
K_2MoO_4	919	152.5	79
K_2WO_4	921	158.2	15
$K_2Cr_2O_7$	396	140	15
		129	68
$KClO_3$	368	84	15
		81	68
KCNS	173	101.5	68
KPO_3	820	161.2	15
	810	140.0	63
		148.2	82
$K_4P_2O_7$	1090	~185	63
KBO_2	946	136.6	15
$K_2Nb_2O_6$	1400	150	71
Rubidium salts			
RbF	765	132.0	15
RbCl	720	98.3	15,29
RbBr	685	90.7	15
RbI	642	80.3	15
$RbNO_3$	304	109	15,43,75
Rb_2SO_4	1055	135	15
Caesium salts			
CsF	692	107.1	15
CsCl	646	91.3	15
		93	29
CsBr	631	83.6	15
CsI	620	75.4	15
$CsNO_3$	414	92.0	15
		92.5	75
Cs_2SO_4	1015	113.1	15
$CsPO_3$	724	118.0	82
Ammonium salts			
NH_4NO_3	170	101.9	75
		99.7	98
Magnesium salts			
$MgCl_2$	at 733	135.8	19
	at 750	~68	47,48
$MgSiO_3$	at 1570	378	32
Calcium salts			
CaF_2	in the range 1470—1550	280	91
	at 1400	400	90
$CaCl_2$	772	148.6	25,26,48—51,72
$CaBr_2$	730	119.6	58
CaI_2	740	85.8	58
$Ca(NO_3)_2$	at 560	101.6	75
$Ca(PO_3)_2$	969	229.6	63
		230.2	82
	at 1025	~235	88
$CdBr_2$	567	~70	52
		86	58
Mercury salts			
$HgCl_2$	at 293	56.1	23
$HgBr_2$	at 241	64.5	23
Gallium salts			
$GaCl_3$	77.7	27.3	60
Ga_2Cl_4	172.4	56.2	61
$GaBr_3$	122.5	35.2	61
Thallium salts			
$TlNO_3$	206	117.5	15
		94.8	75
Tin salts			
$SnCl_2$	250	100	15
Lead salts			
$PbCl_2$	501	142.8	25
		136	52,56,3
		137	69
$PbMoO_4$	1090	166.0	76
$Pb(BO_2)_2$	at 900	100	36
$PbSiO_3$	at 1000	~240	33
Antimony salts			
$SbCl_3$	73.2	50	15
Bismuth salts			
$BiCl_3$	233	71.2	15
$Bi_2(MoO_4)_3$	630	165	76
Manganese salts			
$MnSiO_3$	at 1570	415	32
Iron salts			
$FeSiO_3$	at 1570	363	32

The values of the temperature coefficients for molten salts are often not indicated at all, or are given with no estimate of the accuracy of the determination; this applies to an even greater extent to the temperature coefficients for salt mixtures. In the present review, therefore, we shall restrict ourselves to general points. The surface tension of most of the salts studied decreases with increase in temperature; the course of the σ polytherms is given by the equation $\sigma = a - bt$, where a and b are empirical constants. Almost invariably the absolute value of $b = -d\sigma/dt$ does not exceed 0.1 dyn cm^{-1} deg^{-1}. For some salts, however, the values of $d\sigma/dt$ are close to zero (for example, $MgCl_2$ [20,47] and metaphosphates [82]) or even positive (silicates [32]). This phenomenon is apparently due to a change in the structure of the melts with increase in temperature (decrease in the size of the particles, dissociation), leading to the accumulation of surface-inactive particles in the melt [32,82]. The values of $d\sigma/dt$ are generally constant within the temperature ranges studied, but in a number of instances it has been found that the values of $d\sigma/dt$ are not constant, for example, for certain fluorides, nitrates, sulphates [15], molybdates [73], the low-melting $KClO_3$, KCNS, and $K_2Cr_2O_7$ [68], and Na_3AlF_6 [22]. It is possible that in some instances this is due to decomposition of the salts, leading to a change in composition.

IV. SURFACE TENSION OF BINARY SALT SYSTEMS

In the study of the surface tension of binary system, the problems of the nature of the shapes of the σ isotherms and their classification, interpretation, and analytical expression are of greatest interest. Despite the general character of these problems for binary systems of different type (organic, metallic, oxide, salt, etc.), they cannot yet be regarded as completely solved. In particular, the extent to which the value of σ for binary systems is sensitive to change in the structure of the bulk phase and the correspondence between the shape of the σ isotherms and the interaction between the components of the melt, reflected by the equilibrium diagram, are not yet clear. It is not possible in the present paper to examine in detail the literature dealing with all these problems. Of the most interesting topics we may mention the studies of Trifonov [100] (the general classification of σ isotherms for binary organic systems) and Teitel'baum [101] (factors influencing the shape of σ isotherms), the Zhukhovitskii [53]–Guggenheim [54] equation mentioned above, and the work of Esin [102] (oxide systems) and Eremenko and coworkers [103] (metallic systems).

Since information on σ isotherms has been published for more than 50 binary salt systems, it was of interest to use this material to investigate the correspondence between the shape of the σ isotherms and the equilibrium diagrams. For this purpose we compared the σ isotherms and equilibrium diagrams for three groups of binary salt systems (Tables 2–4); the fusibility data were taken from a handbook [104] and the concentrations of the components are given in mole fractions or mole %.

1. Binary Salt Systems with the Formation of Solid Solutions or Eutectics

Of the 26 binary salt systems in the first group, 25 of the systems give isotherms which are linear or convex towards the composition axis (Table 2). In accordance

TABLE 2. Binary salt systems with formation of solid solutions or eutectics

System	Type of equilibrium diagram (Ref. 104)	Shape of σ isotherm	Refs.
LiCl—RbCl	eutectic	convex towards composition axis	30
LiCl—$PbCl_2$	»	linear	56
$LiNO_3$—$NaNO_3$	»	ditto	44
$LiNO_3$—KNO_3	solid solutions with minimum	convex towards composition axis	44,52
$LiPO_3$—$NaPO_3$*	?	ditto	83
NaCl—KCl	solid solutions	linear, convex towards the K composition axis	19,25,47
NaCl—$CaCl_2$	eutectic	convex towards composition axis	25,26,72
NaCl—$BaCl_2$	»	ditto	25,79
NaCl—$PbCl_2$	»	» with a minimum	25,26,56,69
NaBr—KBr	solid solutions with a minimum	convex towards composition axis	52
$NaNO_3$—$NaNO_2$	ditto	ditto	69
$NaNO_3$—KNO_3	»	linear	44,52
$NaNO_3$—$RbNO_3$	solid solutions	convex towards composition axis	42
$NaNO_3$—$AgNO_3$	solid solutions with a peritectic	ditto	56,69
Na_2CO_3—K_2CO_3	solid solutions with a minimum	»	74,92
KCl—KBr	ditto	»	52
KCl—AgCl	eutectic		52
KCl—K_2SO_4	solid solutions with a minimum	»	46
KBr—AgBr	ditto	»	52
KNO_3—KNO_2	»	»	69
KNO_3—$RbNO_3$	solid solutions with a minimum	convex towards composition axis	42
AgCl—AgBr	ditto	ditto	52
AgCl—$PbCl_2$	eutectic		52
AgBr—AgI	solid solutions with a minimum	convex towards composition axis	52
$CdCl_2$—$CdBr_2$	ditto	ditto	52
$CdCl_2$—$PbCl_2$	eutectic	»	52

* System assigned conditionally to Group I.

TABLE 3. Binary salt systems with compound formation.

System	Compound (Ref. 104)	Shape of σ isotherm	Refs.
Li_2CO_3—Na_2CO_3	$Li_2CO_3 \cdot Na_2CO_3$	convex towards composition axis	92
Li_2CO_3—K_2CO_3	$Li_2CO_3 \cdot K_2CO_3$	ditto	92
NaCl—$MgCl_2$	$NaCl \cdot MgCl_2$; $2NaCl \cdot MgCl_2$	inflection at 50 mole % $MgCl_2$, *maximum* at 86 mole % $MgCl_2$, inflection at 50 mole %	20,47
NaCl—$CdCl_2$	$2NaCl \cdot CdCl_2$	convex towards composition axis	52
$NaPO_3$—$Ca(PO_3)_2$	$4NaPO_3 \cdot Ca(PO_3)_2$	ditto	83
$NaPO_3$—$Zn(PO_3)_2$	$NaPO_3 \cdot Zn(PO_3)_2$	minimum at 50 mole %	86
KCl—$MgCl_2$	$KCl \cdot MgCl_2$; $2KCl \cdot MgCl_2$	inflection at 50 mole %	20,47
KCl—$CaCl_2$*	$KCl \cdot CaCl_2$	?	77
KCl—$BaCl_2$	$KCl \cdot BaCl_2$ or $2KCl \cdot BaCl_2$	inflection at 35 mole % $BaCl_2$	45
KCl—$CdCl_2$	$KCl \cdot CdCl_2$; $4KCl \cdot CdCl_2$	inflection at 50 mole % KCl, maximum at 20 mole % KCl	52
KCl—$PbCl_2$	$KCl \cdot PbCl_2$; $2KCl \cdot PbCl_2$	minimum at 55 mole % KCl	52,56
KNO_3—$AgNO_3$	$KNO_3 \cdot AgNO_3$	convex towards composition axis	43,56,69
KPO_3—$Ba(PO_3)_2$**	?	inflection at 70–80 mole % KPO_3	83
KPO_3—$Zn(PO_3)_2$	$KPO_3 \cdot Zn(PO_3)_2$	minimum at 70 mole % KPO_3	86
RbCl—$PbCl_2$	$RbCl \cdot 2PbCl_2$; $RbCl \cdot PbCl_2$; $2RbCl \cdot PbCl_2$	minimum at 55 mole % RbCl	56
CsCl—$CaCl_2$*	$CsCl \cdot CaCl_2$	?	77
CsCl—$PbCl_2$	$xCsCl \cdot yPbCl_2$; $CsCl \cdot PbCl_2$	minimum at 55 mole % CsCl	56
$MgCl_2$—$BaCl_2$	compound of unknown composition	inflection at 15 mole % $BaCl_2$	50,51

* Shape of σ-isotherm for the system not known to us (see footnote on p. 505).

** System assigned conditionally to Group II.

TABLE 4. Diagonal sections of ternary reciprocal systems.

System	Type of diagonal	Shape of σ isotherm	Refs.
Li_2SO_4—NaCl	stable diagonal	convex towards composition axis	29
Li_2SO_4—KCl	ditto	ditto	29
Li_2SO_4—RbCl	from ΔH – stable diagonal of singular system	»	29
Li_2SO_4—CsCl	reversibly-reciprocal system	»	29
Li_2SO_4—$BaCl_2$	from ΔH – stable diagonal	minimum at 30 mole % $BaCl_2$	29
		minimum at 15 mole % KCl	69
NaI—KCl	unstable diagonal		
NaBr—K_2SO_4	from ΔH – unstable diagonal	convex towards composition axis	79
KBr—$CdCl_2$	from ΔH – unstable diagonal	inflection at 60 mole % KBr, minimum at 40 mole % KBr	59

with conclusions from the Zhukhovitskii equation[53], linear isotherms are observed when the values of σ for the pure components are close to one another. In this group a minimum is observed only on the σ isotherms for the NaCl–$PbCl_2$ system. Electrical conductivity and e.m.f. data for this system[105] suggest that the melts contain unstable ionic complexes.

2. Binary Salt Systems with Compound Formation

The second group consists of binary systems for which the equilibrium diagrams indicate the formation of compounds (Table 3). This group also contains the KCl–$CaCl_2$ and CsCl–$CaCl_2$ systems, for which the nature of the isotherms is unknown[77]. This group also contains the KPO_3–$Ba(PO_3)_2$ system, for which the equilibrium diagram has not been studied but in which the possibility of compound formation is confirmed by the tendency of potassium salts to form ionic complexes with the salts of bivalent cations[2]. A characteristic feature is that the σ isotherms for 11 systems of this group show singular points (extremal points, points of inflection, and breaks), the isotherms being linear or convex towards the composition axis in only five instances. It is possible that in these last systems the compounds which crystallise from the liquid phase dissociate. The absence of interaction between the components in the liquid phases of the KNO_3–$AgNO_3$ and NaCl–$CdCl_2$ systems, whose isotherms show no singular points, is confirmed by data on a large number of their properties[2].

Thus the interaction between the components of binary salt systems, reflected by the equilibrium diagram, is in a number of instances also revealed on the σ isotherms; here the composition corresponding to a singular point on the σ isotherms does not always correspond to the composition of the compound crystallising, as is in general possible[3].

3. Diagonal Sections of Ternary Reciprocal Systems

The experimental material on σ for ternary reciprocal systems is insufficient to enable any conclusion to be reached regarding the relationships between the equilibrium diagrams and the shapes of the σ isotherms for the diagonal sections. In the third group, 8 such sections have been studied, and the diagrams are known for only 4 of these (Table 4). The classification of the remaining pairs of salts in a given system type and the form of the diagonals[106] was estimated approximately on the basis of Kablukov's rule[107] from the magnitude and sign of the heats of the exchange reactions ΔH_{298}, calculated from the heats of formation of the reacting compounds[108].

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Thus the surface tension isotherms for binary salt systems with solid solution or eutectic formation generally show no singular points; the surface tension isotherms for binary systems with interaction between the components usually show singular points — extrema, points of inflection or breaks. The surface tension of salt melts is a property which to a certain extent is sensitive to change in the structure of the melts.

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THE CYCLISATION OF ALKYNES AND THEIR DERIVATIVES

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I. INTRODUCTION

In recent years the polymerisation of alkynes has been attracting increasing attention with the discovery of new aspects of this diverse process. Up to recently, the polymerisation of acetylene yielded only oligomers of linear structure (vinylacetylene, divinylacetylene, etc.), or high-molecular products of the cuprene type. Instances of the cyclisation of acetylene with the formation of aromatic compounds, particularly benzene, were known, but the methods of synthesis were imperfect and the mechanism of synthesis was not clear. A review of the state of the problem may be found in the monograph of Newland and Vogt[1].

The cyclisation of acetylene and its derivatives was presented in a new light after Reppe's discovery of active catalysts that permit the selective preparation of the corresponding cyclic oligomers under mild conditions[2]. Later, numerous papers appeared in which catalysts suitable for the most diverse examples were recommended. Control of the course of the reactions and high yields made cyclisation a process of practical interest. It was