THERMODYNAMICS AND STRUCTURES OF MOLTEN SALTS

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INTRODUCTION

Thermodynamics is the science of the transformation of energies. The experimental methods which are utilized to determine thermodynamic data can be summarized as follows:

(i) determination of latent energies $\Delta H$ (by calorimetry);
(ii) determination of free energies $\Delta G$ (equilibria and e.m.f. measurements);
(iii) determination of $p\cdot v\cdot T$ relations (compressibility, density, etc.).

The bridge between thermodynamics and structure is the entropy $S$.

The word “structure” in relation to liquids ordinarily implies distances and short range order–disorder [including deviations from random distribution of the structural units (ions), the occurrence of particular configurations (ionic pairs, groupings, complexes)] and, finally, also the type of the bonding forces (that means the electronic distribution).

Any statistical description can give a more-or-less crude picture of the “true” structure only. Our main interest, therefore, is to derive the simplest possible model which is able to explain (with satisfying accuracy) the physical-chemical properties of molten salts. Consequently, the value of a model will depend to a certain degree on its practical applicability. This means that a certain model is not necessarily the best suited description for both thermodynamical processes like chemical equilibria and irreversible processes like conductivity and viscosity. But certainly the different models should not conflict in their consequences.

Thermodynamic experimental data can tell in principle only if a suggested structural model is possible or not, but they will frequently be unable to decide which one of several structures is correct or if a particular structure is the only one possible.

It is also important to keep Hildebrand’s warning in mind that, in principle, an insufficient model may still fit the activity ($\Delta G$) data well, but that when applied to $\Delta S$ and $\Delta H$ data much more serious disagreement will be evident.

$\Delta S$ determined by thermodynamical methods can be considered as the sum of two main contributions, the first expressing the capacity for thermal movements of the structural units (ions)—vibrational (rotational, translational, etc.) entropy, the second associated with the structural configurations in mixtures of different units (entropy of mixing).

In the following review, the thermodynamic contributions to the knowledge of the structure of molten salts and, perhaps still more important, the
corollary, namely the applicability of structural models in thermodynamic calculations will be discussed.

The review is divided into three parts, the first dealing with one component salt melts, with entropy effects of the vibrational type.

In the second part, mixtures of salts with a common ion, and the third, mixtures of different types of cations and anions (both dealing with entropies of mixing) are discussed.

ONE COMPONENT SALT MELTS

Two main thermodynamic quantities, the entropy of fusion $\Delta S_f$ and the change of volume by the melting process $\Delta V_f$ should relate the liquid structure to the structure of the solid substance.

The equation of Clausius-Clapeyron can be written

$$\Delta V_f = \frac{dT}{d\rho} \Delta S_f$$

where $T_f$ is the melting point and $\rho$ is the pressure. $dT/d\rho$ will depend on the difference in compressibility of the liquid and the solid phase.

Unfortunately, many of the older data of $\Delta S_f$ and $\Delta V_f$ quoted in the literature must be used critically. This is evident from the recent investigations of $\Delta S_f$ (Dworkin and Bredig\(^1\)) and $\Delta V_f$ (Schinke and Sauerwald\(^2\)) of the alkali halides which have simplified the empirical picture compared with the older data.

![Diagram](image)

*Figure 1. Entropy of fusion v. relative volume expansion at the melting point of the alkali halides*

If $\Delta S_f$ is plotted against $\Delta V_f$ the diagram is rather confusing, if, however, $\Delta S_f$ is plotted against $\Delta V_f/\nu_{liq}$ or $\Delta V_f/\nu_s$ respectively, all the data except for the lithium halides, seem to fall on one curve (*Figure 1*), indicating a general correlation between $\Delta S_f$ and the relative volume expansion in the
melting process (as suggested by Eucken).

\[ \Delta V_f^\text{liq}/V_{\text{liq}} \] should be related to the change in co-ordination number by the fusion process. According to Levy, Agron, Bredig and Danford\textsuperscript{3}, X-ray data indicate a higher co-ordination number of lithium (and caesium) compounds in the molten state compared with sodium iodide and potassium chloride. The lower values of \( \Delta S_f = S_{\text{liq}} - S_f \) of the lithium compounds could then be explained by an exceptionally low \( S_{\text{liq}} \) for the liquid halides. It is difficult, however, to correlate this conclusion regarding the lithium halides with the exceptionally high \( \Delta V_f^\text{liq}/V_f \) observed for these compounds. An alternative explanation (in line with Pauling's discussion of the effect of the relative ionic sizes on the properties of the halides) would be that the anion-anion "contact" in the solids gives rise to an abnormally high entropy of the solid state as the cations have a higher degree of vibrational freedom. The reason for the relatively small energies of fusion is also understandable from this point of view.

The X-ray data reveals no differences between the molten caesium chloride and caesium iodide structures. The difference in \( \Delta S_f \) between caesium chloride and caesium bromide or caesium iodide, therefore, should also be caused by differences in the solid lattices, the latter having a lower \( S_f \) because of the better packing in the 8-co-ordinated caesium iodide structure\textsuperscript{4}.

These data, therefore, appear to support the impression that the larger variations in \( \Delta S_f \) may be related mainly to the solid phase, which again indicates that the entropy of the liquid state at the melting point may reflect a corresponding state.

The results of investigations on the thermal expansion of alkali halides (Fischmeister\textsuperscript{5}) is another important consideration. He showed that fusion occurs at a "corresponding temperature" where the thermal lattice expansion of the solid halide relative to the 0\textdegree K distance is the same for all the alkali halides, in agreement with the classical theory of fusion of Lindemann.

Hence, it seems possible to relate the temperature of fusion of the alkali halides to properties of the solid halide only. As, however, the temperature of fusion corresponds to an equilibrium between solid and liquid, this statement should also imply that \( T_f \) represents a corresponding temperature for the liquid alkali halides. However, a simple structural interpretation of the small, but general variation of \( \Delta S_f \) in the sequence sodium, potassium, rubidium, has still not been given as far as the author is aware, nor has one for the important sequence in \( \Delta V_f \) fluorine > chlorine > bromine > iodine.

Some correlations are also apparent, when considering the more incomplete data on compounds of the type MX\textsubscript{2} (Table 1). In general, the values of \( \Delta S_f \) per atom in fluorite crystallizing compounds are lower than for the MX compounds, presumably because of the looser packing of the solid lattice.

The layer lattice of magnesium and ferrous chloride have a remarkable higher \( \Delta S_f \), which again is in agreement with the dense packing of these solid lattices.

In one case, however, \( \Delta S_f \) reveals a fundamental difference in the liquid structures. The lattice of beryllium fluoride is closely related to cristobalite, but the \( \Delta S_f \) values are more than 10 times larger. The reason obviously is the type of bonding in the liquid lattices. The Si—O—Si—O chain has a
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definitely higher degree of covalent bonding energy and tends to exist unbroken in the liquid state.

Table 1. The ionic radius ratio, m.p., heat of fusion and entropy of fusion of some MX₄ compounds

<table>
<thead>
<tr>
<th></th>
<th>r₋/r₊</th>
<th>T_f</th>
<th>ΔH_f</th>
<th>ΔS_f</th>
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<tbody>
<tr>
<td>CaF₂</td>
<td>1.25</td>
<td>(~1650)</td>
<td>7100</td>
<td>(~5)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.71</td>
<td>1055</td>
<td>6780</td>
<td>6.4</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>1.75</td>
<td>842-1</td>
<td>7220</td>
<td>8.6</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>1.99</td>
<td>923</td>
<td>9000</td>
<td>9.75</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>2.32</td>
<td>987</td>
<td>10300</td>
<td>10.5</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>2.18</td>
<td>950</td>
<td>10280</td>
<td>10.8</td>
</tr>
<tr>
<td>CdBr₂</td>
<td>1.90</td>
<td>841.2</td>
<td>7970</td>
<td>9.5</td>
</tr>
<tr>
<td>CdI₂</td>
<td>2.14</td>
<td>661.2</td>
<td>4950</td>
<td>7.5</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>552.7</td>
<td></td>
<td>4640</td>
<td>8.4</td>
</tr>
<tr>
<td>BeF₂</td>
<td>4.30</td>
<td>1070</td>
<td>(13000)</td>
<td>(12)</td>
</tr>
<tr>
<td>[SiO₄]₂</td>
<td></td>
<td></td>
<td>(1500)</td>
<td>(6.9)</td>
</tr>
</tbody>
</table>

Time does not allow a discussion of rotational contributions to the entropy of fused salts, as exemplified, for instance, by sulphates or nitrates.

The more refined structural models of the liquid state suggested, for instance by the "cell", the "hole" or the ionic pair models, have not progressed to the state where thermodynamic data can offer any decisive test.

SALT MIXTURES WITH ONE COMMON ION

These systems are particularly suitable for the study of the entropy of mixing of ionic species in relation to their size and shape, charge and structure of the outer electronic shell.

Starting with heat effects, most of the systems investigated are known to have a negative heat of mixing. This already indicates an important difference between solid and liquid ionic solutions, ΔH_mix of the former being, almost without exception, positive. The endothermic formation of solid solutions of ions of different size is qualitatively explained by a loss in the lattice energy caused by the change of the nearest neighbour distance in the ionic lattice (as for instance expressed by Vegard’s law).

The negative ΔH_mix values on the other hand are in agreement with the picture of a second nearest neighbour interaction⁶.

Assuming constant cation–anion distances in the liquid mixture of the two components M₁X and M₂X, the sum of the (positive) potential energies M₁...M₁... + M₂...M₂...M₂ is always larger than 2(M₁...M₂), if the radii of M₁ and M₂ are different.

Considering this effect only

\[ ΔH_{\text{mix}} \approx KU N_{M_1} (1 - N_{M_1}) (d_1 - d_2/d_1 + d_2)^2 \]

where \( K \) is a constant, \( N \) the ionic fraction, \( U \) the lattice energy and \( d_1 \) and \( d_2 \) are the interionic distances characteristic for the two pure components.

In some recent, very accurate calorimetric determinations of the heat of mixing of alkali nitrates, Kleppa⁷ has shown that this formula is in excellent agreement with the experimental results.
agreement with the experiments as far as the variation of $\Delta H_{\text{mix}}$ with the interionic distance is concerned. The absolute values of $\Delta H_{\text{mix}}$, however, seem to be smaller than expected from the second nearest neighbour interactions only.

Negative deviations from ideality, of the same order of magnitude, are also present in mixtures of potassium and lithium fluoride, chloride and bromide, and they decrease with increasing size of the larger common ion.

In Table 2 is collected a number of data for binary salt mixtures with a common ion. Except for the calorimetric figures of Kleppa and co-workers, $\Delta H$ is calculated from activity data, assuming ideal entropy of mixing.

<table>
<thead>
<tr>
<th>System</th>
<th>$T$ (°C)</th>
<th>$\Delta H/\mathcal{N}(1-\mathcal{N})$ (kcal)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Li–Rb) NO$_3$</td>
<td>345</td>
<td>-2.47</td>
<td>Kleppa and Hersh$^a$</td>
</tr>
<tr>
<td>(Li–K) NO$_3$</td>
<td>345</td>
<td>-1.76</td>
<td></td>
</tr>
<tr>
<td>(Li–Na) NO$_3$</td>
<td>345</td>
<td>-0.46</td>
<td></td>
</tr>
<tr>
<td>(Li–K) F</td>
<td>775</td>
<td>-1.2</td>
<td>Aukrust, Bjorge,</td>
</tr>
<tr>
<td>(Li–K) Cl</td>
<td>775</td>
<td>(0.9–1.0)</td>
<td>Flood and Förland$^b$</td>
</tr>
<tr>
<td>(Li–K) Br</td>
<td>775</td>
<td>-0.8</td>
<td></td>
</tr>
<tr>
<td>K (Br–Cl)</td>
<td>800</td>
<td>+0.53</td>
<td>Toguri, Flood and</td>
</tr>
<tr>
<td>Na (Br–Cl)</td>
<td>800</td>
<td>+0.35</td>
<td>Förland$^b$</td>
</tr>
<tr>
<td>Li (Br–Cl)</td>
<td>800</td>
<td>+0.15</td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{2}$Mg (Br–Cl)</td>
<td>800</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>K (CrO$_4$–Cr$_2$O$_7$)</td>
<td>650</td>
<td>+0.5</td>
<td>Flood and Muan$^a$</td>
</tr>
<tr>
<td>Na (CrO$_4$–Cr$_2$O$_7$)</td>
<td>405</td>
<td>+0.3</td>
<td></td>
</tr>
<tr>
<td>(Ag–Rb) Br</td>
<td>600</td>
<td>-2.58</td>
<td>Hildebrand and</td>
</tr>
<tr>
<td>(Ag–K) Br</td>
<td>600</td>
<td>-1.48</td>
<td>Salstrom$^c$</td>
</tr>
<tr>
<td>(Ag–Na) Br</td>
<td>600</td>
<td>+1.05</td>
<td></td>
</tr>
<tr>
<td>(Ag–Li) Br</td>
<td>600</td>
<td>+1.88</td>
<td></td>
</tr>
<tr>
<td>(Ag–Rb) NO$_3$</td>
<td>350</td>
<td>-1.19</td>
<td>Kleppa, Clarke and Hersh$^d$</td>
</tr>
<tr>
<td>(Ag–K) NO$_3$</td>
<td>350</td>
<td>-0.45</td>
<td></td>
</tr>
<tr>
<td>(Ag–Na) NO$_3$</td>
<td>350</td>
<td>+0.59</td>
<td></td>
</tr>
<tr>
<td>(Ag–Li) NO$_3$</td>
<td>350</td>
<td>+0.65</td>
<td></td>
</tr>
</tbody>
</table>

Other effects, however, must also be taken into account when considering mixtures where the common ion is the smaller one, as demonstrated in unpublished data of Toguri et al.$^a$ from exchange equilibria between hydrogen chloride–hydrogen bromide gas mixtures and mixed bromide–chloride salt melts.

Again assuming ideal entropy of mixing, $\Delta H_{\text{mix}}$ in these systems is endothermic and decreases in the sequence potassium–sodium–lithium.

Positive deviations from ideality are also evident in mixtures of CrO$_4^{2−}$–Cr$_2$O$_7^{2−}$, and here again it is larger in the potassium than in the sodium system$^b$.

Hence, in mixtures where the larger "lattice forming" ions differ, heat
effects similar to those of the formation of solid solutions seem to be dominating. Probably, therefore, packing effects in the mixtures contribute to the heat of mixing.

The mixing of molecules of unequal size is known to give a volume expansion. The pure components represent a better packing than the mixed state, the packing effect, therefore, generally will be expected to be endothermic.

It does not seem unreasonable to assume that similar packing effects may also be predominating in ionic mixtures where the larger ions are of unequal size. The solubility gap in the acid range of the SiO₂–MO systems may also be considered from this point of view.

A quantitative approach to the calculation of this effect is still missing.

One should also keep in mind the possibility of unsymmetrical deviations from ideality of the two components, an ion fitting better in a lattice of larger than of smaller ions. Effects of this kind are evident in some of Kleppa’s systems, but are possibly of greater importance in the chloride–bromide mixtures.

In mixtures of silver and alkali salts still other effects may have to be considered. The formation of bromide (Hildebrand and Salstrom⁶) as well as nitrate mixtures (Kleppa) of the silver–lithium and silver–sodium salts is endothermic, whereas the formation of the silver–potassium and silver–rubidium mixtures is exothermic. Thurmond¹¹ has suggested as an explanation for this that the contribution of covalent character of the silver–bromine bond is changed when silver is replaced by alkali ions, and this theory according to Kleppa is suggested by the data on the nitrate mixtures*.

Finally, it should be mentioned that very few data are available on the deviation from ideality in mixtures of the type

\[(M₁ - M₁₁)X₂ \text{ or } M(X₁ - X₁₁)₂\]

The former may be even more ideal than the corresponding \((M₁ - M₁₁)X\) mixtures (compare CaCl₂–FeCl₂)³⁰.

Therefore, although we still seem to be far from even a qualitative description of the deviations from ideality in binary salt mixtures with one common ion, it is a reasonable assumption that if \(\Delta H_{\text{mix}} < zRT\) \((2z = \text{coordination number of the second nearest neighbour})\), the ionic mixture is random and what we might call a regular mixture. When, however, \(\Delta H_{\text{mix}} \rightarrow zRT\) deviations from a random distribution should be expected;

* In a recent paper of Lumsden⁹ a radically new theory is given of the heat of mixing of molten salts with a common ion. The coulombic interactions between the ions are neglected. The heat of mixing is explained as a result of two opposite effects: an exothermic nearest neighbour effect attributed to the polarizability of the ions (resulting in a term similar to the coulombic second nearestighbour interaction term), and an endothermic second nearest neighbour effect, attributed to non-polar London interactions. The theory was applied with success to the calculation of some binary phase diagrams of alkali halides but, unfortunately, this is due to an error in calculation.

According to Blander¹4, however, the calorimetric \(\Delta H\) values in the alkali–silver as well as the alkali–thallium salt systems are in good agreement with the calculated values, when coulombic exothermic interactions are combined with endothermic London interactions.
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a preferential occurrence of $M_1 \ldots M_1$ and $M_{II} \ldots M_{II}$ second nearest
neighbours if $\Delta H_{mix}$ is positive, and of $M_1 \ldots M_{II}$ neighbours if $\Delta H_{mix}$ is nega-
tive. Deviation from random distribution is clearly indicated in Kleppa’s
lithium–caesium and lithium–rubidium nitrate mixtures.

The extreme case, $\Delta H > zRT$, will result in either a demixing (positive
$\Delta H_{mix}$) or in the formation of an ordered $M_1 \ldots M_{II} \ldots M_I$ structure,
corresponding formally to the formation of a complex compound $M_I[M_{II}X_2]$.
In both cases, the system $M_I X – M_{II} X$ might behave as two more-or-less ideal
binaries, in the latter case of the components

$$M_I X – M_I [M_{II} X_2]$$
and  $$M_I [M_{II} X_2] – M_{II} X$$

Examples of this kind are found in the systems potassium chloride–magnesium chloride and potassium chloride–ferrous chloride, where a
compound $K_2[MgCl_4]$ or $K_2[FeCl_4]$ seems to explain the phase diagram liquidus
lines fairly well\(^4\),\(^5\). Similarly, the formation of complexes like $AlF_6^{3–}$ and
$AlF_4$ explains the phase diagram sodium fluoride–aluminium fluoride\(^6\).

Extensive cryoscopic measurements in dilute solutions of low melting salt
solvents have indicated the formation of real complexes (see, for instance,
papers by Kordes, van Artsdalen, Rolin and others). The use of the term
“complex” in molten salt system has caused some controversy, but it is
outside the framework of this review to deal with questions of terminology.

Another principal question, however, is connected with the entropy
of mixing of ions with different volume or charge. In the “complex” treatment
outlined above the underlying concept was that one might assume the validity
of the ideal equation of the entropy of mixing

$$\Delta S = - R(N_1 \ln N_1 + N_2 \ln N_2)$$

where

$$N_1 = n_{M_I}/n_{M_{II}} + n_{M_{II}}$$

$n$ is the number of ions in the mixture (Temkin mixture).

How far this equation can be trusted when $M_I$ and $M_{II}$ differ in volume,
shape or charge cannot be answered yet, as independently determined
$\Delta S$ and $\Delta H$ values are not available at present for simple ionic mixtures of
noble gas ions.

It is known from molecular mixtures that mixing of molecules of different
volume is normally associated with an expansion accompanied by an
additional entropy increase. The entropy of mixing is larger than that
corresponding to ideal solutions (compare also the athermal solutions).

As the ionic compounds in the solid, and still more in the liquid, state
ordinarily have more open structures, compared with molecular or metallic
systems, one would expect the volume effect to be of less importance in
the entropy of the ionic systems. This, however, must be proved experiment-
ally and it may turn out to be difficult since a large difference in ionic
volume would normally also mean a large $\Delta H_{mix}$ and, hence, deviations from
random distribution.

The simplest possible systems of this kind are probably mixtures of pyro-
and ortho-ions, such as $CrO_4^{2–}$–$Cr_2O_7^{2–}$, where some data are available
from the careful investigations of the potassium and sodium systems by
Muan, in connection with the redox equilibrium with $\text{O}_2(g)$ and $\text{Cr}_2\text{O}_3(s)$.

As mentioned, these data indicate small but positive deviations from
ideality, hence it is strictly opposite to what would have been expected
for athermal monomer–dimer mixtures. The volume effect, therefore, seems
to be dominated by the $\Delta H$ term. This is also suggested by the strong
demixing tendency in the acid range of the silicate and borate systems.

From this it seems likely that the size and even the shape of the ions
appear not to affect seriously the applicability of Temkin’s activity formula.
This also is in line with the observation that the liquidus lines in calcium
borosilicate phase diagrams (where heats of fusion are known from calorimetric
investigations) can be calculated from a very simple mixture model
of ortho-, pyro- and meta-ions (like $(\text{BO}_3)_3^3$–, $(\text{SiO}_3)_3^4$–, and where also the
formation of mixed borosilicate ions like $[\text{BSiO}_6]^5$– and $[(\text{B, Si})\text{O}_{2-3}]_3^2$ seems
clearly proved17. (Compare also mixtures of sulphate and sodium meta-
silicate18.)

The entropy effects arising from a difference in charge between the mixed
ions is another important, but still not definitely answered, question. Calcium
chloride can be dissolved in the solid sodium chloride lattice by replacing
two Na$^+$ with one Ca$^{2+}$ leaving a neighbouring cationic site empty. This
means that the solid Na$^+$–Ca$^{2+}$ solutions should be comparable with mono-
er–dimer mixtures, as treated by Flory and several others.

In the molten sodium chloride–calcium chloride mixtures, however, the
electroneutrality might be satisfied in a less drastic way by a somewhat
looser cationic packing surrounding a Ca$^{2+}$ ion, and this arrangement may
be better described by an entropy equation like Temkin’s (corrected for
deviations from random distribution). The difference, however, between
Temkin’s equation and the monomer–dimer–entropy equation of Flory
is rather small compared with the limits of error in the experimental
data.

In the system silver bromide–lead bromide (according to calculations
by Førland), the Temkin entropy equation seems to fit the experimental
data of Salstrom better than the equation of Flory.

The same may also be true for the Na–Ca–CO$_3$ mixtures. When, however,
less than 7 mole per cent CaO is added to calcium fluoride, according to
Bååk, the density definitely indicates that a liquid structure with anionic
vacancies is formed (and this is in agreement with the variation in conduct-
itivity with composition). In these liquid mixtures positive deviations from
ideality definitely seem to be present (immiscibility gap). (In the calcium
oxide–calcium chloride mixtures, however, negative deviations are present.)

Systems could also be mentioned where models with “defects” (vacancies
or ions in interstitial positions) might be favourable.

Equilibria in the system (FeO–Fe$_2$O$_3$)$_{\text{liquid}}$–O$_2(g)$ can be described more
simply by defect-models, similar to those applied to spinel solid solutions,
than by the conventional Temkin models. It is possible spinel or spinel-like
structural models, with anion or cation vacancies, might also represent an
improvement even for salt melts of the simple 1:1 type compared with the
conventional Temkin model; compare the system magnesium oxide–
aluminium oxide.

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Concerning the acid silicates and borates, which include the large field of the technical glasses, only a single thermodynamic contribution will be mentioned. The characteristic of the models of these systems is that it might be convenient to operate with two kinds of cation positions, the lattice forming (Si, Al, etc.) and the lattice modifying (K, Na, Ca, etc.).

A comparison of binary phase diagrams of silica shows that addition of caesium or rubidium oxide have the same cryoscopic effect as potassium and sodium aluminate. Förlanď³³ explains this by a simple structural model.

The acid silicates are considered as a mixture of oxygen ions in unbroken Si—O—Si and broken Si—O—M⁺—O—Si bridges. Then, in accordance with the Temkin model

\[ a_{SiO₄} = N_{Si} N_{O^{-}} \]

where \( N_{Si} \) is the fraction of Si atoms in the “network forming” positions, and \( N_{O^{-}} \) is the fraction of oxygen ions in the unbroken bridges.

It seems reasonable from an electrostatic point of view to assume that the two oxygen ions in a broken bridge are tied together with a pair of Cs⁺ ions, as indicated above. Then

\[ N_{O^{-}} = \frac{2n_{SiO₄}}{2n_{SiO₄} + n_{CsO₃}} \]

and \( N_{Si} = 1 \).

On addition of potassium aluminate, aluminium occupies a network-forming position, whereas the K⁺ ions serve to conserve the electroneutrality

\[ Si—O—Al—O—Si— \quad K⁺ \]

hence

\[ N_{O^{-}} = 1 \text{ and } N_{Si} = \frac{n_{SiO₄}}{n_{SiO₄} + n_{KAlO₃}} \]

which in the dilute range gives values of \( a_{SiO₄} \) which are nearly identical with those calculated for the case of the caesium oxide addition.

A more differentiated model can be based on SiO₄—tetrahedral groups having 0, 1, 2, 3 or 4 corners common with other groups—expressed by the symbols SiO₄, SiO₃₂, SiO₃, etc. In the dilute acid range this model gives results identical with those of the model of broken and unbroken oxygen bridges (assuming the SiO₂₃ groups in pairs). Acid–base reactions and other chemical properties might be satisfactorily treated with these models³⁷.

SALT MIXTURES WITHOUT A COMMON ION

As a definition of the ideal entropy of mixing, we will accept the Temkin equation

\[ \Delta S = \Delta S_+ + \Delta S_- = -R(\Sigma N_+ \ln N_+ + \Sigma N_- \ln N_-) \]

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which implies that the cations are distributed at random among cation positions, the anions among the anion positions, without preference for any particular ionic pairs such as $M_i X_i$.

It then follows, that in an ideal mixture

$$a_{M_i X_i} = N_{M_i} N_{X_i}$$

where $N_{M_i}$ and $N_{X_i}$ are the cationic and anionic fractions respectively. In a mixture of $M_i$, $M_{II}$ cations and with $X_i$, $X_{II}$ anions much more serious deviations from ideality are generally expected if $\Delta G \approx \Delta H \gg O$ for the double decomposition

$$M_i X_i + M_{II} X_{II} = M_{II} X_i + M_i X_{II}$$

because

$$\gamma_{M_i X_i} \gamma_{M_{II} X_{II}} \ll \gamma_{M_{II} X_i} \gamma_{M_i X_{II}}$$

($\gamma =$ activity coefficient).

Again an ideal entropy of mixing would be expected (regular mixtures) if

$$\Delta G \approx \Delta H \ll zRT$$

From a thermodynamic cyclic process based on ionic exchange equilibria, Flood, Førland and Grjothen\textsuperscript{24} derived the relationship

$$RT \ln \gamma_{M_i X_i} = N'_{M_{II}} N'_{X_{II}} \Delta G^o + \ln \gamma_{M_i \gamma_{X_i}}$$

(1)

where $N'$ is the fraction of equivalents (mole/charge), and the $\gamma_{M_i}$ and $\gamma_{X_i}$ terms are specially defined. They include contributions from binary and pseudobinary systems of the ions involved.

In the case of regular mixtures (ideal entropy of mixing = random distribution), considering the nearest neighbour interaction effects only, a very similar equation

$$RT \ln \gamma_{M_i X_i} = N'_{M_i} N'_{X_i} z\Delta E$$

(2)

can be derived from a lattice model, where $z$ is the co-ordination number and $\Delta E$ is the energy of the nearest neighbour bond reaction:

$$\Delta E = (\epsilon_{M_{II} - X_i} + \epsilon_{M_i - X_{II}}) - (\epsilon_{M_i - X_i} + \epsilon_{M_{II} - X_{II}})$$

(1) and (2) become identical when $\Delta G = \Delta H = z\Delta E$, that means if $\Delta S$ of the double decomposition reaction is equal to zero and if the approximation

$$\Delta H \approx z\Delta E$$

is valid, and if further the term $\ln \gamma_{M_i}, \gamma_{X_i}$ is neglected.

The equation (2) fits astonishingly well the FeO activity data in slags at 1600\textdegree C\textsuperscript{24}, but gives positive deviations from ideality which are far too high for sodium fluoride and potassium chloride mixtures\textsuperscript{35} indicating that the equation in general will be valid in the very dilute range only.
THERMODYNAMICS AND STRUCTURES OF MOLTEN SALTS

Recently Watt and Blander\textsuperscript{26} have published data on the activity coefficient of silver nitrate in mixtures of Ag\textsuperscript{+}, K\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−}, in a range diluted with respect to Ag\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2−}. A very accurate value of \(\Delta G\) for the double decomposition reaction

\[
\text{AgNO}_3\text{liq} + \frac{1}{2} \text{K}_2\text{SO}_4\text{liq} = \frac{1}{2} \text{Ag}_2\text{SO}_4\text{liq} + \text{KNO}_3\text{liq}
\]

can not be evaluated for lack of thermodynamic information on silver sulphate but according to the best available data

\[
\Delta G_{638^\circ K} \simeq -5.6 \pm ca. 0.3 \text{ kcal} \simeq zRT
\]

In a mixture where \(N_{SO_4^{2-}} = 10^{-2}\) and \(N_{Ag} \simeq 10^{-3}\), \(\gamma_{AgNO_3}\) is calculated in astonishing agreement with the experimental value as far as the sign of the deviation and the order of magnitude is concerned (\textit{Table 3}). The measurements, however, indicate increasing negative deviations from ideality with increasing temperature and this abnormal behaviour is not explained by the available data.

\begin{table}[h]
\centering
\begin{tabular}{l|c|c|c|c}
 & \(N_{Ag}^+\) & \(N_{SO_4^{2-}}\) & \(\gamma \text{ exp.}\) & \(\gamma \text{ calc.}\) \\
\hline
\textit{T}_{638} & 0.0059 & 0.0197 & 0.900 & 0.92 \\
\textit{T}_{732} & 0.0059 & 0.0193 & 0.885 & 0.93 \pm 0.02 \\
\end{tabular}
\caption{The activity coefficient of silver nitrate in mixtures of Ag\textsuperscript{+}, K\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−}.}
\end{table}

A thorough testing of the first approximation formula on systems with low \(\Delta G\) relative to \(zRT\), however, is still lacking.

If \(\Delta H > zRT\) deviations from random distribution are to be expected. Blander, Blankenship, and Newton\textsuperscript{27} have measured the silver nitrate activities in systems of Ag\textsuperscript{+}, K\textsuperscript{+} (or Na\textsuperscript{+}), Cl\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} at low Ag\textsuperscript{+} and Cl\textsuperscript{−} concentrations. In these systems, \(\Delta G\) for the double decomposition reactions

\[
\text{AgNO}_3 + \text{KCl (NaCl)} = \text{AgCl} + \text{KNO}_3 (NaNO_3)
\]

are \(\simeq 3 zRT\).

These deviations are accounted for in a theory which is in good agreement with the experimentally observed change of \(a_{AgNO_3}\) with the concentration of chloride ions in the melt.

The theory is based on a model of ions of equal size. The purely coulombic forces, therefore, would result in a mixture at random, but an additional non-coulombic interaction is assumed between the ions of a certain ionic pair (AgCl) in nearest neighbour positions. The interaction energy and the co-ordination number are both empirically determined parameters.

In accordance with the theory, the parameters are independent of temperature, the theory thus also leads to a correct prediction of the temperature coefficient of the activity function.

When applying the model to Ag\textsuperscript{+}, K\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}\textsuperscript{−} mixtures, however, the results are less encouraging as the empirical interaction energy (\(z\) assumed constant) in this system increases with increasing temperature.
H. FLOOD

The difference between the random and non-random distribution equations in dilute solutions of M₁ and X₁ in M₁X₁ can be expressed by the equations

Random
\[ \ln \gamma_{M_1X_1} = N'_{M_1} N'_{X_1} z \frac{\Delta E}{RT} \]  

(2)

Non-random
\[ \ln \gamma_{M_1X_1} = N'_{M_1} N'_{X_1} z \left[ \left( \frac{\Delta E}{RT} \right) + \frac{1}{2} \left( \frac{\Delta E}{RT} \right)^2 + \frac{1}{6} \left( \frac{\Delta E}{RT} \right)^3 + \ldots \right] \]  

(3)

The difference in \( \gamma \) calculated from the two equations is 0·5 per cent when \( \Delta E/RT = 0·1 \) and 2 per cent when \( \Delta E/RT = 0·2 \). Therefore, an influence of the deviation from random distribution would be expected when \( \Delta H \rightarrow (0·5 - 1)RT \) (compare Hill, Woolner and Alvares²⁸).

As both the development of the quasi-lattice theory and its experimental testing are apparently in rapid progress, any further comment on this stage may seem premature. Braunstein, Blander et al.²⁷, have recently developed an alternative, promising, approach to the calculation of activities in alkali-silver-nitrate-halide mixtures, similar to the treatment of the stepwise complex formation in water solutions.

In general, the present theories of the diluted salt solutions can not be expected to be applicable outside the very dilute range as interactions outside the nearest neighbour sphere then have to be taken into account. Very little work has yet been done on the important question of the calculation of activities in multi-component ionic systems outside the dilute range.

Recent investigations of Toguri, Flood and Førland⁸ on bromide-chloride exchange equilibria in molten halide mixtures have shown that it seems possible to estimate the additional terms in the equation of \( \ln \alpha_{M_1X_±} \) from the deviation from ideality in the binary mixtures involved.

One may, as a first approximation, consider the quaterionic system as two simultaneous pseudo-binaries,

(i) as a cation mixture of \( M_1(X_1X_1) \) and \( M_1(X_1X_2) \) where the deviation from ideality has a mean value of the values in the pure \( X_1 \) and \( X_1X_1 \) systems,

(ii) as an anion mixtures of \( (M_1M_1)_1X_1 \) and \( (M_1M_1)_1X_1 \) where the deviation from ideality has a mean value of the values in the pure \( M_1 \) and \( M_1M_1 \) systems.

The application of activity equations of the type
\[ \ln \gamma_{M_1X_1} = bN^2_{M_1X_1} \text{ etc.} \]
to the binary and pseudo binary systems results in an equation identical with one derived earlier by Førland⁸ from a structural model of randomly distributed cations and anions, taking into account interactions of the nearest and second nearest neighbours only.

The general applicability of this approach has to be tested in future work. Details will soon be published elsewhere.

References
THERMODYNAMICS AND STRUCTURES OF MOLTEN SALTS

27 H. Flood. Unpublished data.