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The Influence of the Cation Composition on Anion-Equilibria in Molten Salt Mixtures

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In previous investigations [1] it has been shown that in reactions of molten salts the cation present can influence, to a remarkable degree, the equilibria in which formally only anions take part.

This effect is especially important in acid-base reactions of high polymeric acids.

In the following, a thermodynamic equation is derived for the equilibrium constant of an anion reaction in a melt with mixed cations, as a function of the equilibrium constants of the melts with single cations and the cation ratio. (This equation may, of course, be modified for equilibria between cations in melts with mixed anions.)

Let the anion equilibrium be of the type:

$$\mathrm{X}^{(-)} \rightleftharpoons \mathrm{Y}^{(-)}$$

(Examples: Anion equilibria:

$$S_2O_7^{2-}{}_{(melt)} \rightleftharpoons SO_4^{2-}{}_{(melt)} + SO_{3(gas)}$$
$$CO_3^{2-}{}_{(melt)} \rightleftharpoons O^{2-}{}_{(melt)} + CO_{2(gas)}$$
$$2Cl^-{}_{(melt)} + Br_{2(gas)} \rightleftharpoons 2Br^-{}_{(melt)} + Cl_{2(gas)}$$

Cation equilibria:

$$M_1{}^+{}_{(melt)} + M_{2(metal)} \rightleftharpoons M_2{}^+{}_{(melt)} + M_{1(metal)})$$

The equilibrium is established in a salt melt containing a mixture of the cations A and B (A, B), with mole fractions N_1 and N_2, together with the mixture of the anions X and Y (X, Y). — The ratio A : B = $N_1 : N_2$ is an independent variable. The ratio X : Y, however, always has to correspond to the value given by the equilibrium (I).

In accordance with usual convention, we define the activity a and the activity coefficient γ by means of the chemical potential:

$$\begin{aligned}\mu &= \mu^0 + RT \ln a \\ &= \mu^0 + RT \ln N + RT \ln \gamma\end{aligned}$$

where μ_0 is the chemical potential of the pure component, and μ that of the component with mole fraction N in a mixture.

In the following we have to consider 5 binary mixtures. The symbols used for these, and the corresponding subscripts used for N, a, and γ of the components are shown in Table 1.

Table 1.

Components	System	Subscripts
1 AX + AY	A(X,Y)	X(A), Y(A)
2 BX + BY	B(X,Y)	X(B), Y(B)
3 AX + BX	(A,B)X	A(X), B(X)
4 AY + BY	(A,B)Y	A(Y), B(Y)
5 (A,B)X + (A,B)Y	(A,B)(X,Y)	X(AB), Y(AB)

Hence the equilibrium constant of the mixed system (A, B) (X, Y):

$$K = \frac{a_{Y(AB)}}{a_{X(AB)}} = \frac{N_{Y(AB)}}{N_{X(AB)}} \cdot \frac{\gamma_{Y(AB)}}{\gamma_{X(AB)}} = K' \cdot \frac{\gamma_{Y(AB)}}{\gamma_{X(AB}}$$

has to be expressed as a function of the equilibrium constants of the two simple systems A(X,Y):

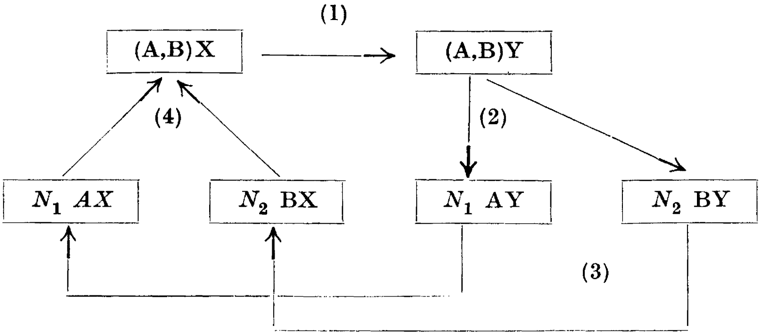
$$K_1 = \frac{a_{Y(A)}}{a_{X(A)}} = \frac{N_{Y(A)} \cdot \gamma_{Y(A)}}{N_{X(A)} \cdot \gamma_{X(A}} = K'_1 \cdot \frac{\gamma_{Y(A}}{\gamma_{X(A}}$$

and B(X,Y):

$$K_2 = \frac{a_{Y(B)}}{a_{X(B}} = \frac{N_{Y(B)} \cdot \gamma_{Y(B)}}{N_{X(B\ )} \cdot \gamma_{X(B)}} = K'_2 \cdot \frac{\gamma_{Y(B)}}{\gamma_{X(B}}$$

together with the ratio of A : B = $N_1 : N_2$ in the mixture.

The thermodynamic relation between K', K'_1 and K'_2 can be derived from the following cyclic process:



1) 1 mole (A,B)X is transformed reversibly into (A,B)Y:

$$\begin{aligned} \Delta\mu_1 &= \mu_{(A,B)Y} - \mu_{(A,B)X} \\ &= -RT \ln K = -RT \ln K' - RT \ln \frac{\gamma_{Y(AB)}}{\gamma_{X(AB)}} \end{aligned}$$

2) 1 mole (A,B)Y is separated into N_1 mole AY and N_2 mole BY:

$$\begin{aligned} \Delta\mu_2 &= N_1\, \mu^0{}_{AY} + N_2\, \mu^0{}_{BY} - \mu_{(A,B)Y} \\ &= -RT\, (N_1 \ln a_{A(Y)} + N_2 \ln a_{B(Y)}) \\ &= -RT\, (N_1 \ln N_1 + N_2 \ln N_2) - RT\, (N_1 \ln \gamma_{A(Y)} + N_2 \ln \gamma_{B(Y)}) \end{aligned}$$

3) N_1 mole AY is transformed reversibly into AX, and N_2 mole BY into BX:

$$\begin{aligned} \Delta\mu_3 &= N_1\, (\mu^0{}_{AX} - \mu^0{}_{AY}) + N_2\, (\mu^0{}_{BX} - \mu^0{}_{BY}) \\ &= N_1 \cdot RT \ln K_1 + N_2 \cdot RT \ln K_2 \\ &= N_1 \cdot RT \ln K'_1 + N_2 \cdot RT \ln K'_2 \\ &\qquad + N_1 \cdot RT \ln \frac{\gamma_{Y(A)}}{\gamma_{X(A)}} + N_2 \cdot RT \ln \frac{\gamma_{Y(B)}}{\gamma_{X(B}} \end{aligned}$$

4) N_1 mole AX and N_2 mole BX are mixed to form 1 mole (A,B)X:

$$\Delta\mu_4 = \mu_{(A,B)X} - (N_1 \cdot \mu^0{}_{AX} + N_2 \cdot \mu^0{}_{BX}) =$$

$$= RT\ (N_1 \ln N_1 + N_2 \ln N_2) + RT\ (N_1 \ln \gamma_{A(X)} + N_2 \ln \gamma_{B(X)})$$

For the total cycle, the sum of the changes in chemical potential is zero, hence it follows that:

$$\log K' = N_1 \log K'_1 + N_2 \log K'_2 \tag{1}$$

$$+ \left(N_1 \log \frac{\gamma_{Y(A)}}{\gamma_{X(A)}} + N_2 \log \frac{\gamma_{Y(B)}}{\gamma_{X(B)}} - \log \frac{\gamma_{Y(AB)}}{\gamma_{X(AB)}}\right)$$

$$+ (N_1 \log \gamma_{A(X)} + N_2 \log \gamma_{B(X)})$$

$$- (N_1 \log \gamma_{A(Y)} + N_2 \log \gamma_{B(Y)})$$

From this equation it can be seen that if all of the 5 binary mixtures behaved ideally, then log K would be a linear function of the cation composition of the melt.

The expression: $\log K = N_1 \log K_1 + N_2 \log K_2$ will ordinarily be valid as a first approximation.

The additional terms in the expression for log K' contain activity coefficients corresponding to deviations from ideal solutions in the 5 binary mixtures. All these coefficients can, at least in principle, be determined independently (*e. g.* from the melting diagrams).

It is important, however, that the activity terms ordinarily tend to cancel each other.

This will be the case for the second term if the deviations from ideal mixtures in the three mixtures A(X,Y), B(X,Y), and (A,B) (X,Y) are of the same sign. The term is insignificant if the deviations of the (A,B) (X,Y) system are equal to the average of the deviations of the two systems A(X,Y) and B(X,Y).

In the same way, the third and fourth terms will affect log K' in opposite directions if the deviations from ideal solutions in the two systems (A,B)X and (A,B)Y are of the same sign. The linear relationship between log K' and N can therefore be expected to be approximately valid even in systems where the single binary mixtures show considerable deviations from ideality.

In a subsequent paper, formula (1) will be compared with experimental results on the thermic decomposition of dichromate into chromate, chromium trioxide, and oxygen in the presence of mixed cations.

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SUMMARY

A thermodynamic expression is derived for the equilibrium constant of an anion equilibrium in a melt with mixed cations. As a first approximation:

$$\log K = N_1 \log K_1 + N_2 \log K_2$$

where K_1 and K_2 are the equilibrium constants for the melts with single cations and N_1 and N_2 are the mole fractions of the cations in the mixture. — The exact formula includes terms containing a number of activity coefficients, which are related to 5 simple binary mixtures.

REFERENCE

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