[AMERICAN JOURNAL OF SCIENCE, VOL. 262, APRIL 1964, P. 541-544]

THERMODYNAMIC CALCULATIONS ON PHASE EQUILIBRIA INVOLVING FUSED SALTS. PART III. APPLICATION TO POLYMERIC ANIONS

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ABSTRACT. Polymeric anions do not contribute appreciably to the depression of the freezing point in fused salt systems. $\alpha CaSiO_3$ and diopside form nearly perfect solutions containing polymeric anions, with respective heats of fusion of approximately 14,000 and 22,000 cals $mole^{-1}$. $\alpha CaSiO_3$ forms imperfect solutions with CaF_2, for which mean ionic activity coefficients have been calculated.

INTRODUCTION

In Parts I and II (Bradley, 1962) phase equilibria involving fused salts were treated in terms of an ionic product. Since there is general agreement that considerable ionic dissociation occurs in most fused salt systems, it would appear imperative to use an ionic product in the discussion of both chemical and physical equilibria, but the precise nature of the product is open to question. The writer used ionic mole fractions given by the number of ions of a particular species divided by the total number of ions present, whereas Temkin (1945) defined the ionic mole fraction as the ratio of the number of ions of one species to the total number of ions of the same sign. Since writing Parts I and II the author has had his attention drawn to a paper by Herasymenko and Speight (1950), who adopted the same convention as the writer in discussing redox equilibria in melts. These authors point out that Temkin's formulation gives an artificial result in the system 1 mole of Na_2CO_3 + 0.1 mole of $BaCl_2$, for which the sum of the cations is 2.1 moles and of the anions 1.2 moles, giving, according to Temkin ionic fractions, $[Na^+] = 2/2.1 = 0.953$; $[Ba^{++}] = 0.1/2.1 = 0.047$; $[CO_3^{--}] = 1/1.2 = 0.834$; $[Cl^-] = 0.2/1.2 = 0.166$. Hence, according to Temkin, the effective concentration of the chloride ion is 3.5 times that of the barium ion, whereas as regards the effect of $BaCl_2$ on the lowering of the freezing point of Na_2CO_3 the ions Ba^{++} and Cl^- should, for ideal solutions, act equally, irrespective of sign.

When departures from ideality occur owing to large differences in charge and sign between comparable ions of two salts, the lack of ideality can be expressed in a "hold-all" mean ionic activity coefficient $f_\pm$ given by

$$-R\ln f_\pm Q = \Delta H\,(1/T - 1/T_m) \qquad \text{..... 1,}$$

where Q is the ionic product, T_m the melting point in °K, and ΔH the heat of fusion of the salt which crystallizes; the effect of specific heat is neglected. Some examples of this coefficient are given below for melts containing polymeric anions. Departures of $f_\pm$ from unity arise from non-zero heats of mixing of the salts and from departures of the entropy of mixing from ideality.

IONIC PRODUCTS FOR SYSTEMS CONTAINING LARGE POLYMERIC ANIONS

It will be recalled that the ionic product is the product of the ionic mole fractions multiplied by a "normalizing" constant chosen to make the ionic product of the pure fused salt to be unity.

Consider for simplicity a salt AB which forms a polymeric anion of average degree of polymerization n, i.e. $AB \rightarrow A + 1/n\ B_n$ (for simplicity ionic charges have been omitted). Then for one mole of AB the ionic mole fractions are $1/(1 + 1/n)$ for A and $(1/n)/(1 + 1/n)$ for B, giving an ionic product proportional to $(1/n)^{1/n}/(1 + 1/n)^{(1+1/n)}$. Now if n is sufficiently large $(1/n)^{1/n}$ approximates very closely to unity: this can be seen from the fact that $\mathrm{Lim}_{n \rightarrow \infty} \log (1/n)^{1/n} = \mathrm{Lim}_{n \rightarrow \infty} -(1/n) \log n = 0$. The ionic product is then unity for the pure salt. If we have p moles of AB and 100-p moles of CD and if both B and D form large polymers, the ionic product of AB will be p/100 and of CD(100-p)/100.

It follows that polymeric ions, as would be expected, do not function in depressing the freezing point. Similar considerations apply if we have p moles of A_2B to 100-p moles of CD, B, and D forming polymers. Since the total number of ions is then $100 - p + 2p = 100 + p$, the ionic mole fractions are $2p/(100 + p)$ for A and $(100 - p)/(100 + p)$ for C, and the ionic products are $4p^2/(100 + p)^2$ for A_2B and $(100 - p)/(100 + p)$ for CD. Both of these become unity for the pure salts.

These remarks will be illustrated by two systems involving $\alpha CaSiO_3$.

$\alpha CaSiO_3$ (PSEUDO-WOLLASTONITE) AND DIOPSIDE

An example in which both species probably form chain-like anions in the melt is provided by $\alpha CaSiO_3$, pseudo-wollastonite, and diopside, studied by Bowen and Schairer (1942). The structure of $\beta CaSiO_3$ was thought to be based on rings of $Si_3O_9^{---}$ (Barnick, 1936). The work of Dornberger-Schiff, Libeau, and Thilo (1955) shows that $\beta CaSiO_3$ also contains anionic chains. It is probable that the chain structure is present in $\alpha CaSiO_3$ formed from the β polymorph at about 1150°C, and also in the melt, although it is likely that there will be some degree of coiling of the chains in the melt.

$\alpha CaSiO_3$ and diopside appear to form ideal solid solutions, as would be expected if they have similar structures. We assume $CaSiO_3 \rightleftarrows Ca^{++} + \frac{1}{n}(SiO_3)_n^{2n-}$; $CaMg(Si_2O_6) \rightleftarrows Ca^{++} + Mg^{++} + \frac{1}{m}(Si_2O_6)_m^{4m-}$ where n and m are large. If we take p moles of $CaMgSi_2O_6$ and 100 – p moles of $\alpha CaSiO_3$ the total number of g-ions is $2p + 100 - p = 100 + p$ and the number of g-ions of calcium is $100 - p + p = 100$; the number of g-ions of magnesium is p. As before we have neglected the presence of the polymeric anions. The ionic products are $400p/(100 + p)^2$ for diopside and $100/(100 + p)$ for $\alpha CaSiO_3$, both of which become unity for the pure species. The data in table 1 may be calculated from the results of Bowen and Schairer (1942). ΔH has been calculated from equation 1 with $f_{\pm} = 1$. It may be noted that the same results for the calculations are obtained if n varies somewhat with temperature.

The heat of fusion of $\alpha CaSiO_3$ is thus about 14,000 cals mole $^{-1}$ and of diopside 21,900 cals mole^{-1}. The latter value agrees with that given by White (1909, p. 486), who made a direct determination, namely 22,900 ± 3,240 cals mole^{-1}.

TABLE 1

Mole % diopside (p)	T, °K	ΔH, cals
0	1813	—
10.5	1768	14,100
20.9	1723	13,080
35.8	1673	13,180
47.6 (eutectic)	1631	15,800
100	1664	21,940

The treatment above differs radically from that of Bååk and Ölander (1955) for the same system. These authors plotted log (mole fraction $Ca_3Si_3O_9$) against 1/T, i.e. they did not use ionic products. and they assumed on the basis of the erroneous structure of Barnick (1936) that $\alpha CaSiO_3$ forms rings of $Si_3O_9^{---}$ in the melt. Their heat of fusion per molecule of $CaSiO_3$. 13,600 cals $mole^{-1}$ comes out at about the same value as that found in this paper.

$\alpha CaSiO_3$ AND CaF_2

It is not surprising that this system is far from ideal. It was studied experimentally by Bååk and Ölander (1955) and was treated theoretically on the assumption of a ring structure for $CaSiO_3$ and without using ionic products. Taking p moles of CaF_2 and 100 – p moles of $\alpha CaSiO_3$ the respective ionic products are $2700p^2/(100 + 2p)^3$ and $100/(100 + 2p)$. Values of the mean ionic activity coefficient have been calculated in table 2, based on heats of fusion of 7100 and 14,000 cals $mole^{-1}$ for CaF_2 and $\alpha CaSiO_3$ respectively. The values of $f_\pm$ in brackets are those given by Bååk and Ölander.

TABLE 2

T, °K	p (mole % CaF_2)	$f_\pm$ CaF_2	$f_\pm$ $\alpha CaSiO_3$
1691	100	1	
1663	90.9	0.968(0.998)	
1530	71.9	0.831(0.887)	
1474	64.0	0.788(0.843)	
1400 (eutectic)	59.0	0.711(0.749)	0.725(1.003)
1423	57.9		0.744(1.087)
1466	55.0		0.837(1.209)
1513	50.0		0.922(1.304)
1633	33.1		1.083(1.333)
1813	0		1 (1)

CONCLUSION

These results illustrate the use of ionic fractions with polymeric anions. They also reveal the different results sometimes obtained when calculations are made in terms of ionic products rather than mole fractions and illustrate the fact that large structural differences between salts tend to give rise to imperfect

solutions. It should be emphasized that departures from ideality may arise (a) from association of ions, (b) from a non-zero heat of mixing, (c) from a non-ideal entropy of mixing, or (d) from all these factors simultaneously. The freezing point method is not very diagnostic as to the nature of ionic species in ionic melts. The point of view of this paper is that $\alpha CaSiO_3$ and diopside when fused probably resemble the crystals in structure, that the ideal solutions formed on mixing can best be interpreted in this way, and that ionic products in melts containing large polymeric ions can be treated in a simple manner. The non-ideality of the solutions of $\alpha CaSiO_3$ and CaF_2 indicate that further factors must be introduced, such as the heat of mixing.

ACKNOWLEDGMENT

My thanks are due to Professor P. Gray for useful discussions on fused salts.

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