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THERMODYNAMIC CALCULATIONS ON PHASE EQUILIBRIA INVOLVING FUSED SALTS. PART II. SOLID SOLUTIONS AND APPLICATION TO THE OLIVINES

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ABSTRACT. A theory is developed for ideal solutions of ionic salts giving Roozeboom Type I phase diagrams, based on the assumption that the mole fraction of an ion in a phase is equal to the number of specified ions present divided by the total number of ions of all species in the phase. When applied to solid solutions of fayalite and forsterite the theory predicts for the components heats of fusion, 25,200 and 29,300 cal mole^{-1} respectively, which differ considerably from the value, 14,000 cal mole^{-1} for each component, calculated by Bowen and Schairer (1935), who assumed ideal behavior for the undissociated molecules. Orr (1953) found a calorimetric heat of fusion of 22,000 cal mole^{-1} for fayalite. When applied to solid solutions of Mg_2SiO_4 and Mg_2GeO_4, where there is a common cation, the theory predicts that ideal solution theory for undissociated molecules may be used. The data of Ringwood (1956) for this system show, however, practically no separation between liquidus and solidus, and do not admit of the calculation of heats of fusion. The behavior of the system Mg_2GeO_4 + Fe_2SiO_4 with no common ion is predicted. Mg_2SiO_4 and Mn_2SiO_4, with a common anion, behave like forsterite and fayalite.

INTRODUCTION

In Part I a theory was developed for the crystallization of ionic salts and was applied to ideal systems giving eutectics without solid solution. In this paper the theory is extended to apply to the Roozeboom Type I phase diagram for a continuous range of solid ideal solution between two compounds.

The classical theory of such ideal solid solutions for nonelectrolytes gives

$$R \ln(x_{1l}/x_{1s}) = \Delta H_1(1/T_1-1/T) + \Delta C_{p1}\ln T/T_1 - T_1\Delta C_{p1}\,(1/T_1-1/T) \quad \ldots\ldots(1),$$

$$R \ln[(1-x_{1l})/(1-x_{1s})] = \Delta H_2(1/T_2-1/T) + \Delta C_{pa}\ln T/T_2 - T_2\Delta C_{p2}(1/T_2-1/T) \quad \ldots\ldots(2),$$

where x_{1l} and x_{1s} are the mole fractions of substance (1) in liquid and solid solution, ΔH_1 and ΔH_2 are the molar heats of fusion of substances (1) and (2) at the respective melting points T_1 and T_2 °K, and ΔC_{p1} and ΔC_{p2} are the increases in specific heat at constant pressure per mole on melting substances 1 and 2.

Bowen and Schairer (1935) in a classical paper, applied equations (1) and (2) with $\Delta C_{p1} = \Delta C_{p2} = 0$, to solid solutions of Fe_2SiO_4 (fayalite) and Mg_2SiO_4 (forsterite) and showed that good agreement with experimental data could be obtained with $\Delta H_1 = \Delta H_2 = 14{,}000$ cal mole^{-1}.

At first sight this agreement appears convincing. It seems, however, that fayalite and forsterite would be unlikely to have the same molar heats of fusion in view of their very different melting points (1205°C for fayalite and 1890°C for forsterite); it would be expected that the entropies of melting would be more clearly equal than found by Bowen and Schairer. Moreover Orr (1935) has determined the heat of fusion of fayalite with a value, 22.000 cal mole^{-1}, considerably greater than that obtained by Bowen and Schairer.

It so happens because of their valence type that fayalite and forsterite give a different type of formula for melting behaviour when treated ionically

and molecularly. It will be shown below that the ionic treatment gives results more consistent with Orr's value than the classical molecular treatment.

GENERAL THEORY

For equilibrium between solid and liquid solution we have for a salt which ionizes

$$a\mu_{+s} + b\mu_{-s} = a\mu_{+1} + b\mu_{-1} \quad \text{.....(3),}$$

where the μ's are chemical potentials and the suffices apply to solid (s) and liquid (l): one molecule of the salt gives a positive and b negative ions, and if the system is ideal, we have, as in Part I,

$$\left(x_{+1}^{a}\, x_{-1}^{b}\right) \Big/ \left(x_{+s}^{a}\, x_{-s}^{b}\right) = K_T = Q_l/Q_s \quad \text{.....(4).}$$

K_T depends only on temperature and pressure and x_+ and x_- are the mole fractions of ions treated individually. Q is defined in Part I. If x_1 and x_2 are the mole fractions of substances (1) and (2), it follows that, if there is no common ion.

$$R \ln[(x_{1l}a_1)^{a_1}(x_{1l}b_1)^{b_1}] - R \ln[(x_{1s}a_1)^{a_1}(x_{1s}b_1^{b_1}] = \Delta H_1(1/T_1 - 1/T) + \Delta C_{p1} \ln T/T_1 - T_1\Delta C_{p1}(1/T_1 - 1/T) \quad \text{.....(5).}$$

$$R \ln\{[(1-x_{1l})a_2]^{a_2}[(1-x_{1l})b_2]^{b_2}\} - R \ln\{[(1-x_{1s})a_2]^{a_2}[(1-x_{1s})b_2]^{b_2}\} = \Delta H_2(1/T_2 - 1/T) + \Delta C_{p2} \ln T/T_2 - T_2\Delta C_{p2}(1/T_2 - 1/T) \quad \text{.....(6).}$$

These equations simplify (no common ion) to

$$R(a_1 + b_1)\ln(x_{1l}/x_{1s}) = (\Delta H_1 - T_1\Delta C_{p1})(1/T_1 - 1/T) + \Delta C_{p1} \ln T/T_1 \quad \text{.....(7),}$$

$$R(a_2 + b_2)\ln[(1-x_{1l})/(1-x_{1s})] = (\Delta H_2 - T_2\Delta C_{p2})(1/T_2 - 1/T) + \Delta C_{p2} \ln T/T_2 \quad \text{.....(8).}$$

For all applications of interest the two salts are of the same type, i.e., $a_1 = a_2$, $b_1 = b_2$. Moreover, there is usually a common ion, the mole fraction of which is independent of the proportions of the two components, as explained in Part I, and the mole fraction of which is the same in liquid and solid solution.

THE SYSTEM Mg_2SiO_4–Fe_2SiO_4

If we apply equations (5) and (6) to olivine $a_1 = a_2 = 2$, and x_- is constant.

Hence:

$$2R \ln(x_{1l}/x_{1s}) = (\Delta H_1 - T_1\Delta C_{p1})(1/T_1 - 1/T) + \Delta C_{p1} \ln T/T. \quad \text{.....(9),}$$

$$2R \ln[(1-x_{1l})/(1-x_{1s})] = (\Delta H_2 - T_2\Delta C_{p2})(1/T_2 - 1/T) + \Delta C_{p2} \ln T/T_2 \quad \text{.....(10).}$$

Equations (9) and (10) differ from those employed by Bowen and Schairer in so far as the logarithms on the left are multiplied by the factor 2. It follows that if we neglect the specific heat terms the values of ΔH_1 and ΔH_2 are twice those found by Bowen and Schairer.

From the equations of Orr (1953) the value of ΔCp for fayalite at the melting point is found to be 7.5 cal mole^{-1}. It will be assumed that ΔCp for

forsterite is the same. The smoothed experimental data of Bowen and Schairer were used to plot

$$2\log_{10}(x_{1l}/x_{1s}) - \frac{\Delta Cp_1}{R}\log_{10} T/T_1 \text{ and } 2\log_{10}[(1-x_{1l})/(1-x_{1s})] - \frac{\Delta Cp_2}{R}\log_{10} T/T_2$$

versus 1/T. From the slopes of the straight lines obtained the values of $(\Delta H_1 - \Delta C_{p1}T_1)$ and $(\Delta H_2 - \Delta C_{p2}T_2)$ were found, and hence ΔH_1 and ΔH_2 could be calculated. For fayalite $\Delta H = 25{,}200$ cal mole^{-1} and for forsterite $\Delta H = 29{,}300$ cal mole^{-1}.

The "theoretical" curves are:

$$\log_{10}(x_l/x_s) = 1550\ (1/1478 - 1/T) + 1.887\log_{10}(T/1478)$$

$$\log_{10}[(1-x_l)/(1-x_s)] = 1420\ (1/2163 - 1/T) + 1.887\log_{10}(T/2163)$$

where x refers to fayalite.

In order to calculate x_l and x_s from these equations we write

$$(1-x_l)/(1-x_s) = \lambda_1\ ,\ (\lambda_1<1)$$

$$x_l/x_s = \lambda_2\ ,\ (\lambda_2>1) \qquad \text{.....(11),}$$

giving

$$x_l = \lambda_2(1-\lambda_1)/(\lambda_2-\lambda_1) \qquad \text{.....(12),}$$

$$x_s = (1-\lambda_1)/(\lambda_2-\lambda_1) \qquad \text{.....(13).}$$

The smooth curve in figure 1 is plotted from these values. The circles are taken from Bowen and Schairer's experimental smoothed curves. It will be seen that the agreement is good.

It follows that, as Bowen and Schairer concluded, fayalite and forsterite form ideal solid solutions. The heats of fusion found by these authors, however, require revision. It is worth noticing that the inclusion of a specific heat term may give an appreciable effect on the calculated heats. Without this term the phenomena may have a pseudo ideality. It should be noticed also that if

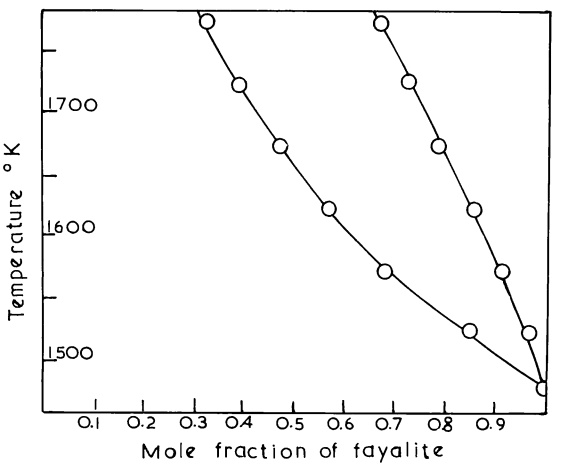

Fig. 1.

the mean activity coefficient of the ions is the same in each phase then a pseudo ideality will be observed.

Ringwood (1958), in calculations on solutions of Mg_2SiO_4 in the spinel Ni_2GeO_4, has also used an ionic product for forsterite of the form $[Mg^{2+}]\,2\,[SiO_4^{-4}]$, based on the work of Temkin (1945). It should be noted, however, that Ringwood defines $[Mg^{2+}]$ as the ratio of the number of specified ions to the total number of lattice sites available to them, i.e. $[Mg^{2+}] = n_{Mg2+}/(n_{Mg2+} + n_{Ni2+})$.

THE SYSTEM Mg_2SiO_4–Mg_2GeO_4

It is of interest that Ringwood (1956) found that Mg_2SiO_4 and Mg_2GeO_4 form solid solutions with no difference in composition between solid and liquid. For this mixture with a common cation the mole fraction of Mg^{2+} is constant and the molecular mole fractions may be used direct. Equations (9) and (10) give, putting x_1 = the mole fraction of Mg_2SiO_4,

$$R \ln (x_{1l}/x_{1s}) = (\Delta H_1 - T_1\Delta C_{p1})(1/T_1 - 1/T) + \Delta C_{p1} \ln T/T_1 = 0 \quad \text{.....(14)},$$

$$R \ln [(1 - x_{1l})/(1 - x_{1s})] = (\Delta H_2 - T_2\Delta C_{p2})(1/T_2 - 1/T) + \Delta C_{p2} \ln T/T_2 = 0 \quad \text{.....(15)},$$

which can hold for all values of T only if $T = T_1 = T_2$ (Prigogine and Defay, 1954, p. 369). The phase diagram is then a horizontal line between T_1 and T_2. In fact there is a drop in melting point from Mg_2SiO_4 (1890°C) to Mg_2GeO_4 (1855°C), so that presumably there is a slight separation between liquidus and solidus. It is clear, however, that the data of Ringwood do not allow the heats of fusion to be calculated.

THE SYSTEM Mg_2GeO_4–Fe_2SiO_4

Presumably Mg_2GeO_4 and Fe_2SiO_4 will form solid solutions with a much wider gap between liquidus and solidus. Such solutions, if formed, would not

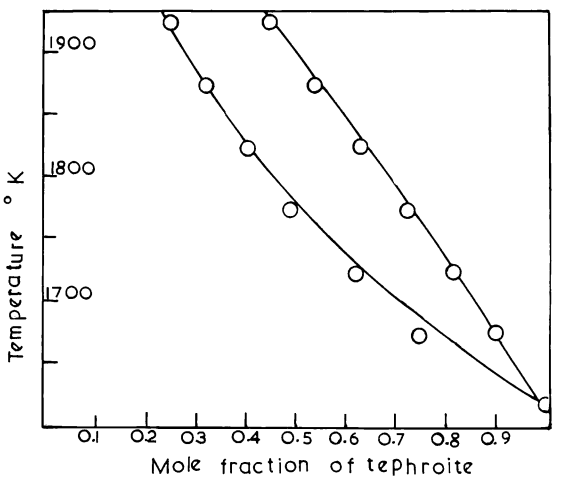

Fig. 2.

be expected to obey equations (9) and (10), since there is no common ion; equations (7) and (8) would apply, with $(a_1 + b_1) = 3 = (a_2 + b_2)$.

THE SYSTEM Mg_2SiO_4–Mn_2SiO_4

Glasser and Osborn (1960) have studied the solid solutions between Mn_2SiO_4 (tephroite) and Mg_2SiO_4. Their curves may be analyzed as above, taking ΔCp to be the same as before. This gives

$$\log_{10} x_l/x_s = 1550(1/1618 - 1/T) + 1.887 \log_{10} T/1618 \quad \text{.....(16),}$$

$$\log_{10} [(1 - x_l)/(1 - x_s)] = 1100(1/2163 - 1/T) + 1.887 \log_{10} T/2163 \quad \text{.....(17),}$$

where x is the mole fraction of tephroite. These curves are plotted in figure 2, where the circles are taken from Glasser and Osborn's smoothed curve. The agreement is within a few percent. The heats of fusion calculated from equations (16) and (17) are 26,150 cal $mole^{-1}$ for tephroite and 26,240 cal $mole^{-1}$ for forsterite. The value for forsterite is probably a little low, but in this analysis one has not the advantage of knowing ΔCp for one at least of the components.

It is hoped to extend this work to other silicate systems, including imperfect solutions.

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