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THERMODYNAMICS OF THE $AgCl–Ag_2SO_4$ SYSTEM

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ABSTRACT

The phase diagram of the $AgCl–Ag_2SO_4$ system was determined. It is of the simple eutectic type with a eutectic temperature of 304°C at 31.5 mole % Ag_2SO_4. Deviations from Raoult's law are slightly negative. Solutions of AgCl in Ag_2SO_4 follow the Temkin model; solutions of Ag_2SO_4 in AgCl exhibit some SO_4^{2-}-vacancy dimers.

INTRODUCTION

Mixtures of 1–1 with 1–2 salts provide an interesting test for theories of liquid structure. The entropy of mixing depends on whether the anions are randomly distributed in spite of their different charges, or whether the introduction of a divalent ion will produce vacancies in the liquid. Thermodynamic studies of such salt solutions are most easily carried out using galvanic formation cells, but this method could not be used for the system reported here (data for which were required for another study[1]) because an electrode reversible to the sulfate ion in this melt does not exist and because it was found in preliminary experiments that Cl_2 reacts with Ag_2SO_4 to produce SO_3 and/or SO_2.

The necessary thermodynamic data can also be determined from concentration cells with liquid junction, Ag|AgCl; AgCl, Ag_2SO_4|Ag in the present instance, but there is some disagreement about the interpretation of such cells. Thus, Bell and Flengas[2] regard the liquid junction as negligible, whereas Stern[3] interprets the entire cell EMF as a junction potential. The most sophisticated use of concentration cells for the determination of phase diagrams was worked out by Øye[4] who determined the phase diagram of the $Li_2SO_4–Ag_2SO_4$ system and obtained good agreement with the diagram established previously from cooling curves. The method appears to be precise but requires somewhat elaborate instrumentation. For this reason the more conventional methods of cooling curves and differential thermal analysis (DTA) were used in the present work. The only previous study of this system appears to be that of Sokolov[5] who used a "visual polythermal method" to determine the liquidus and a few points below the eutectic.

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EXPERIMENTAL

Cooling curves

Mixtures of AgCl and Ag_2SO_4 (Fisher, certified reagent grade) were weighed into fused silica tubes 8 inch long and 8 mm in diameter. The tube containing a particular mixture was placed into the central hole of a 2 inch diameter copper cylinder set in a vertical tube furnace preheated to above the melting point of the mixture. The hot junction of a Platinel II thermocouple (Engelhard Industries), calibrated against a National Bureau of Standards reference Pt–Pt–13% Rh thermocouple, was placed into the melt. After the melt had been well stirred and the temperature stabilized the furnace was turned off. The output of the thermocouple was measured by a Leeds and Northrup Model 8690 potentiometer and a Photovolt varicord recorder in parallel. This arrangement permitted frequent calibration of the recorder. Halts and changes of slope of the cooling curves were determined on the recorder. Each composition was run at least twice and only points agreeing within ±2° were retained for the phase diagram. The thermocouple was frequently calibrated against the melting point of AgCl.

DTA

The DTA apparatus utilized in this investigation was a DuPont Model 900 differential thermal analyzer. The DTA samples of AgCl–$AgSO_4$ mixtures (50–100 mg) were placed in a 4-mm quartz glass sample holder. A chromel–alumel thermocouple was inserted into the center of the sample material. A thermally inert reference sample, Al_2O_3, was placed into two adjacent quartz holders. Thermocouples were placed into each of these holders. The third thermocouple measures the temperature of the heating block while the other two thermocouples give the temperature difference (ΔT) between the sample and reference. The heating block assembly was then covered with a thermal shield and then the entire sample cell assembly was enclosed within a bell jar The heating block was programmed to give a linear temperature rise of 20°C/min. The samples were heated in stationary air to a few degrees above their melting point and held at this temperature for several minutes. The heater was then turned off and the sample allowed to cool. DTA curves were obtained while the sample was cooling. Upon reaching room temperature the sample was heated again to its melting point and cooled a second time. This was done to assure good mixing of the samples and reproducible results. Upon the start of a run on a new sample mixture a new sample thermocouple was used to avoid any contamimation by previous sample mixtures.

RESULTS

The phase diagram is shown in Fig. 1. Agreement between the cooling curves and DTA is quite good. The melting point of AgCl was found to be 455°C, in agreement with the commonly accepted value[6], and that of Ag_2SO_4 was 658±1°C,

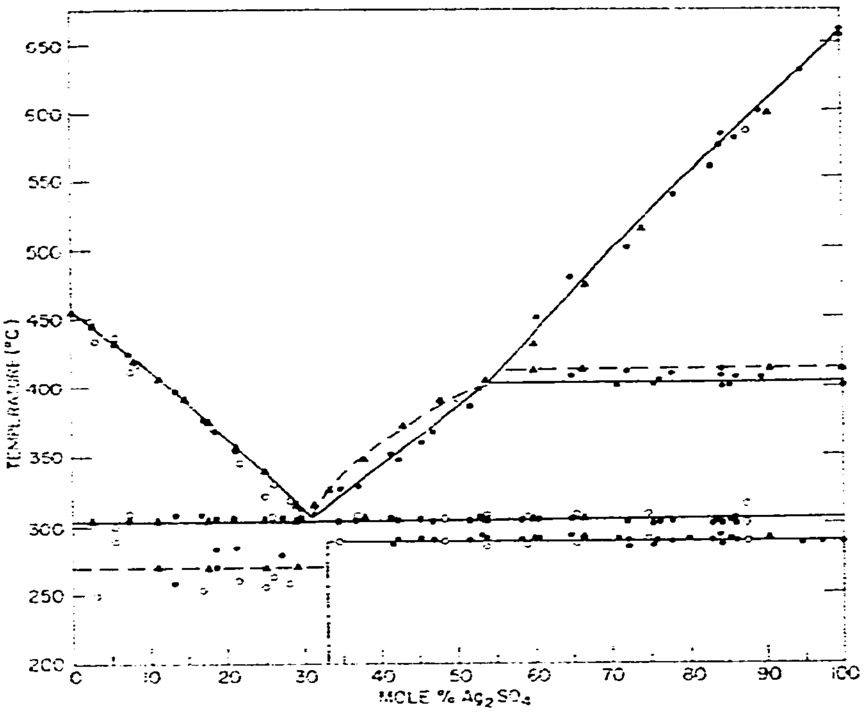

Fig. 1. Phase diagram of the $AgCl–Ag_2SO_4$ system; ●, cooling curves; ○, DTA; ▲, Ref. 5.

compared to the literature value of 660 °C (Ref. 6). The slight decomposition of this salt occurring just above the melting point may account for the slightly lower value. The liquidus lines on both sides of the eutectic agree quite well with the data of Sokolov[5] except for the β-Ag_2SO_4-liquid line which runs slightly lower on our diagram. Our value of the α–β transition is about 7° lower than the generally accepted value of 412 °C, but the high-temperature form of α-Ag_2SO_4 appears to supercool easily. In fact, Hedvall, Lindner and Hartler[7] have claimed that the true transition lies at 430 °C. Our value of the eutectic temperature, 304 °C, and eutectic composition, 31 mole % Ag_2SO_4, agree with Sokolov's values.

The state of the diagram below the eutectic is not so clear. Sokolov had reported a few points near 270 °C between 70 and 90 mole % AgCl and at 291 °C between 54 and 100 mole % Ag_2SO_4 without discussing them. We found a transition at 289 ± 2 °C from 35 mole % to pure Ag_2SO_4, *i.e.* there appears to exist a previously unreported Ag_2SO_4-transition at this temperature. We also find a transition in the AgCl-rich melts near 270 °C, but it is apparently very sluggish since both DTA and cooling curves give scattered results between 240 and 280 °C. The transition was observed in melts up to 97 mole % AgCl, but not in pure AgCl itself. Since the phase diagram in this region is suggestive of the existence of a compound of composition $2AgCl \cdot Ag_2SO_4$ which decomposes in the solid state below the eutectic, an attempt was made to prepare such a compound. Various procedures, such as melting the appropriate $AgCl–Ag_2SO_4$ composition and equilibrating it for more than a week at

250 °C, were unsuccessful. X-ray diffraction patterns showed only lines characteristic of AgCl and Ag_2SO_4 mixtures. Attempts to prepare the compound from aqueous solution were foiled by the low solubility of AgCl. The lower left portion of the phase diagram is thus still uncertain.

DISCUSSION

Information on the nature of the solutions can be obtained from the two ends of the liquidus since most theoretical treatments are based on dilute solution theory, *i.e.*, they are limiting laws. If the temperature dependence of the heat of fusion is taken into account[8], then

$$\Delta H_f = \Delta H_f^0 - \int_T^{T_0} \Delta C_p \qquad (1)$$

where ΔH_f and ΔH_f^0 are the enthalpies of fusion at temperature T and the melting point T_0, and $\Delta C_p = C_p(\text{liq}) - C_p(\text{solid})$. For the salts of this study ΔC_p is small and its temperature dependence is unknown. Hence $\Delta C_p = \Delta a$. The usual equation for the activity of the solvent

$$\frac{\mathrm{d}\ln a_1}{\mathrm{d}\left(\frac{1}{T}\right)} = \frac{-\Delta H_f}{R} \qquad (2)$$

can then be written as

$$\ln a_1 = \frac{-\Delta H_f^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \Delta a\left(\frac{T_0}{T} - 1 - \ln\frac{T_0}{T}\right) \qquad (3)$$

Some information on the number of new particles introduced by the solute can be obtained from the Van't Hoff relation

$$T_0 - T \simeq \frac{RT_0^2}{\Delta H_f}\,\nu N_2 \qquad (4)$$

where N_2 is the mole fraction of solute and ν is the number of independent particles different from those of the solvent introduced by the dissolution of one solute molecule.

In applying the above equation to the present system the following data were used[6]:

	AgCl	*Ag_2SO_4*
T_0(°K)	728	930
ΔH^0(kcal/mol)	3.08	4.06
Δa(cal·deg^{-1}·mol^{-1})	1	0

Applying Eqn. (4) to the dilute solution ends of the liquidus gives $\nu = 1$ for Ag_2SO_4 in AgCl and $\nu = 1.2$ for AgCl in Ag_2SO_4 compared to the value of unity expected from the stoichiometry of the compounds and the fact that Ag^+ is common to solute and solvent.

In considering the distribution of ions in a molten salt solution two models have generally been considered. In the Temkin model the salts are considered to be completely ionized and the solution consists of interpenetrating anion and cation quasi-lattices, the mixing on each lattice being completely random. For two salts with a common cation only the anions would mix randomly. If such a solution is ideal in the Temkin sense the activity of each component is equal to its mole fraction, even if the charges of the ions are not the same. In the present case this would mean that Cl^- and SO_4^{2-} are randomly distributed on the anion lattice. For ions with unequal charges there exists, however, another possibility. Thus, if Ag_2SO_4 dissolves in AgCl it may create a vacant site associated with the SO_4^{2-} ion, *i.e.* the anion lattice behaves as a mixture of monomers and dimers. The assumption made is that SO_4^{2-} and its associated vacancy are twice as large as Cl^- and the entropy of mixing of the anions is that of the dimer (SO_4^{2-}-vacancy) with the monomer Cl^-.

The above two models predict different entropies of mixing. In terms of Eqn. (3) they predict different activities. For the Temkin model the activity of each component is equal to its mole fraction in the melt. For the vacancy model the activity of each component is defined as equal to its equivalent ionic fraction so that

$$a_{AgCl} = \frac{n_{AgCl}}{n_{AgCl}+2n_{Ag_2SO_4}}, \qquad a_{Ag_2SO_4} = \frac{2n_{Ag_2SO_4}}{n_{AgCl}+2n_{Ag_2SO_4}} \tag{5}$$

where the n's are mole numbers.

Using the activities as defined by the two models in Eqn. (3) the liquidus temperature T can be calculated for the two ends of the phase diagram. The comparison is shown graphically in Fig. 2. For dilute solutions of Ag_2SO_4 in AgCl the

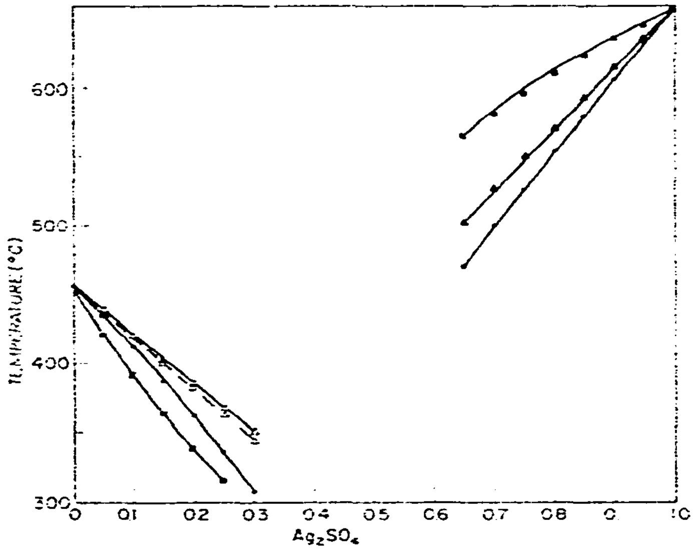

Fig. 2. Calculated and experimental liquidus; ●, experimental; △, ▲, Temkin model; --, with ΔC_p correction; ■, vacancy model.

experimental curve lies between the two models suggesting that the mixing on the anion lattice is not entirely random, but that some SO_4^{2-}-vacancy dimers exist. The effect of neglecting the Δa term is also shown and is evidently small. For dilute solutions of AgCl in Ag_2SO_4 the experimental liquidus lies very much closer to the Temkin model, as might be expected from the introduction of a monovalent ion. The discrepancy between the two curves may be due to an error in the enthalpy of fusion of Ag_2SO_4 which is not known precisely.

The only other binary silver salt system of the same valence type is the AgCl–Ag_2S system studied by Bell and Flengas[2]. In contrast to the present case they found that dilute solutions of Ag_2S in AgCl followed the Temkin model very closely but that deviations for solutions of AgCl in Ag_2S were accounted for by the selfassociation of Ag_2S. Such association is evidently absent in Ag_2SO_4.

Eqn. (3) can also be used to calculate the activities of each component. In Fig. 3 are shown the values of the more significant activity coefficient $\gamma_i = a_i/X_i$, where X_i is the mole fraction. Since Δa is very small, the second term of Eqn. (3) has been omitted from the calculation. As expected from the negative deviations of the experimental liquidus from the Temkin equation (Fig. 2) the deviations from "ideality" are slightly negative. As required by the Gibbs–Duhem equation the deviations for both components are in the same direction.

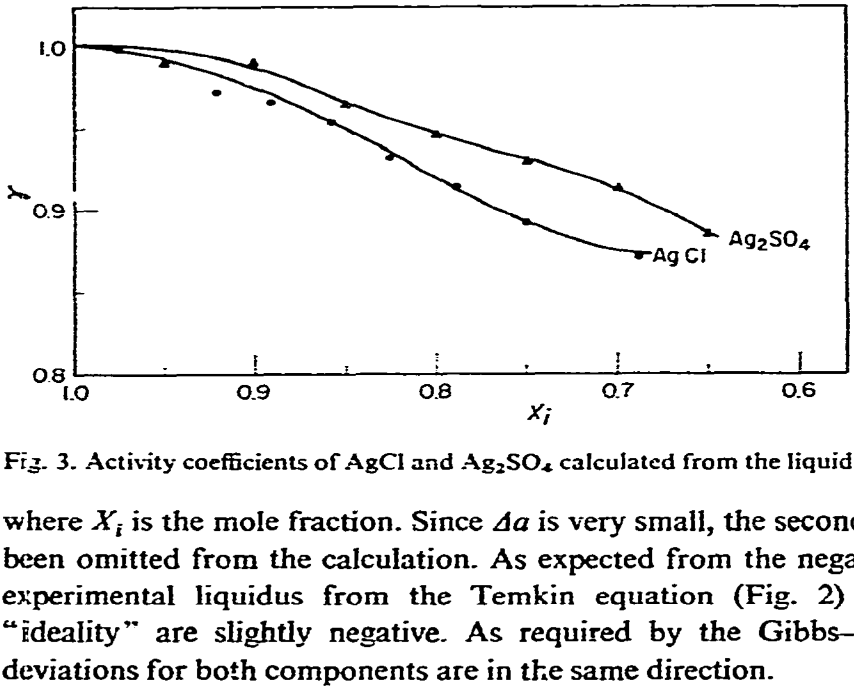

Fig. 3. Activity coefficients of AgCl and Ag_2SO_4 calculated from the liquidus.

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