

## PHASE RULE INVESTIGATIONS OF SALT SYSTEMS \*

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### ABSTRACT

General information is given on the topology of salt systems. The thermal methods most commonly employed in phase rule investigations of these systems are briefly overviewed and some examples of their application are reported.

### INTRODUCTION

The interest devoted to salt systems during the last few decades has been both theoretical (study of interaction in the molten state, characterization of ionic glasses and mesomorphic phases, etc.) and practical (use of salt systems as reaction media, as components of solid electrolyte cells, as non-aqueous ionic solvents, as circulating media in homogeneous reactors, as material useful for energy storage, etc.).

Accurate phase rule studies are of fundamental importance, because reliable information concerning phase relations is an essential prerequisite for all theoretical and/or practical developments in the field.

### SOME DEFINITIONS

#### *A heterogeneous system*

This is any system formed of two or more homogeneous physically distinct portions, each of which may or may not be a continuum and may or may not belong to the same state of aggregation.

#### *A phase*

This is any homogeneous portion of a heterogeneous system [e.g., at given  $T$ ,  $p$  values, a crystalline polymorph and its melt represent two phases of a

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\* Presented at the International Summer School of Calorimetry and Thermal Analysis, 1–5 October 1984, Belgirate, Italy.

one-component system (not necessarily a system containing only one chemical species); two molten mixtures of different composition represent two phases of a two-component system (not necessarily a system containing only two chemical species) exhibiting liquid layering; etc.]. In salt systems, solid crystalline, plastic crystalline, liquid crystalline, isotropic liquid, glassy, and vapor phases can be found. In the  $T, p, x$  space, each phase has its own stability range although, not infrequently, a phase may be capable of existing beyond this range in a metastable state.

### *A phase transition*

This is a transformation from a phase initially present in the system (phase I) into a different one (phase II) occurring (in the absence of metastability phenomena) when a variable on which the system depends varies sufficiently to move the point representative of the system across the boundary of the stability field of phase I into that of phase II.

In the phase rule investigations discussed here the vapor phase, although unavoidably present, is ignored. Consequently, only condensed  $T$  vs.  $x$  isobaric phase diagrams (usually taken at atmospheric pressure) are considered, and the number of degrees of freedom (variance,  $v$ ) to be taken into account is

$$v = n_i - \phi + 1 \quad (1)$$

where  $n_i$  = number of independent components, and  $\phi$  = number of condensed phases. Invariant, univariant, bivariant, etc., equilibria correspond to  $\phi = n_i + 1$ ,  $n_i$ ,  $n_i - 1$ , etc., respectively.

### PHASE TRANSITION ORDER

For the sake of simplicity, only one-component systems are considered in this section.

A transition, trs, from a phase II stable at  $T < T_{\text{trs}}$  to a phase I stable at  $T > T_{\text{trs}}$  is classified "first order" when, at the transition point

$$\left( \frac{\partial \mu^{\text{II}}}{\partial p} \right)_T \neq \left( \frac{\partial \mu^{\text{I}}}{\partial p} \right)_T \quad (2)$$

and

$$\left( \frac{\partial \mu^{\text{II}}}{\partial T} \right)_p \neq \left( \frac{\partial \mu^{\text{I}}}{\partial T} \right)_p \quad (3)$$

From conditions (2) and (3) it follows that

$$\left( \frac{\partial \Delta \mu}{\partial p} \right)_T = \left( \frac{\partial \mu^{\text{I}}}{\partial p} \right)_T - \left( \frac{\partial \mu^{\text{II}}}{\partial p} \right)_T = \Delta_{\text{trs}} V_m \neq 0 \quad (4)$$

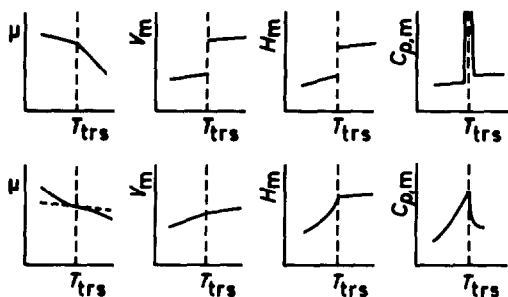


Fig. 1. Changes in some thermodynamic quantities for first-order (top) and second-order (bottom) phase transitions.

$$\left(\frac{\partial \Delta \mu}{\partial T}\right)_p = \left(\frac{\partial \mu^I}{\partial T}\right)_p - \left(\frac{\partial \mu^{II}}{\partial T}\right)_p = -\Delta_{\text{trs}} S_m \neq 0 \quad (5)$$

$$T_{\text{trs}} \Delta_{\text{trs}} S_m = \Delta_{\text{trs}} H_m \neq 0 \quad (6)$$

i.e., discontinuities (see Fig. 1) are expected to occur at  $T_{\text{trs}}$  in molar volume,  $V_m$ , and molar entropy,  $S_m$ , and the amount of energy required,  $\Delta_{\text{trs}} H_m$ , is to be supplied isothermally at  $T_{\text{trs}}$ . Accordingly, the molar heat capacity,  $C_{p,m}$ , of the system must be infinite at  $T_{\text{trs}}$ \*

A phase transition is classified "second order" when, at the transition point

$$\left(\frac{\partial \mu^{II}}{\partial p}\right)_T = \left(\frac{\partial \mu^I}{\partial p}\right)_T \quad (7)$$

and

$$\left(\frac{\partial \mu^{II}}{\partial T}\right)_p = \left(\frac{\partial \mu^I}{\partial T}\right)_p \quad (8)$$

Discontinuities are expected to occur in such thermodynamic quantities as compressibility,  $\beta = -(1/V_m)(\partial V_m/\partial p)_T$ , thermal expansivity,  $\alpha = (1/V_m)(\partial V_m/\partial T)_p$ , and heat capacity,  $C_{p,m}/T = (\partial S_m/\partial T)_p$ . The amount of energy required,  $\Delta_{\text{trs}} H_m$ , is supplied non-isothermally, which causes the

\* Experimentally, any transition—even when high-purity materials are employed—occurs across a non-infinitesimal temperature interval so that finite (although apparent)  $C_{p,m}$  values can be measured (see Fig. 2).

It is, moreover, to be stressed that many transitions classified as first order (e.g., on the basis of X-ray diffractometric evidence) often occur more or less gradually (i.e., across a larger or smaller temperature interval), due to some associated order-disorder process.

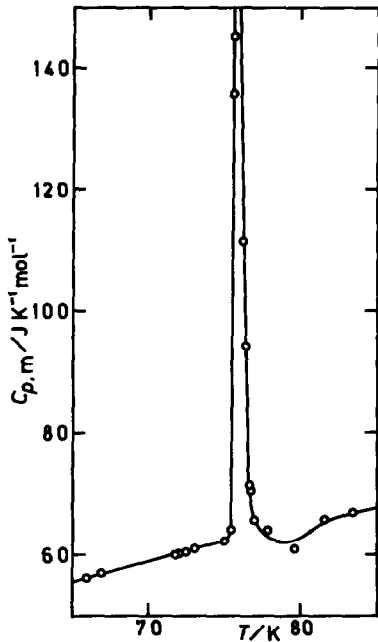


Fig. 2. First-order intercrystalline phase transition, detected in tetramethylammonium chloride with adiabatic equilibrium calorimetry by Chang and Westrum [1].

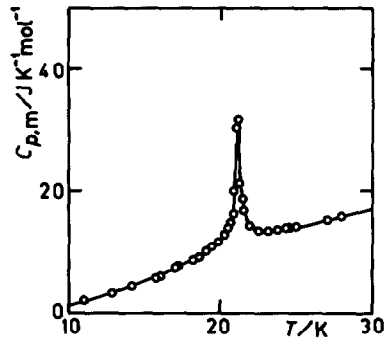


Fig. 3. Second-order "lambda" shaped phase transition, detected in sodium ethanoate with adiabatic equilibrium calorimetry by Franzosini et al. [2].

curve  $C_{p,m}$  vs.  $T$  to assume a characteristic "lambda" shape in the transition region, with a maximum at  $T_{\text{trs}}$  (see Fig. 3) \*\*.

In general terms, the order of a transition should be that of the derivative of  $\mu$  which exhibits a discontinuity at  $T_{\text{trs}}$  [3].

#### CLASSIFICATION AND GRAPHICAL REPRESENTATION OF SALT SYSTEMS

For the sake of simplicity, only uni-univalent salts are considered in this section and ionic charge signs are omitted. Thus, cations and anions are represented as A, B, C, and X, Y, Z, respectively. Moreover, it is assumed that only crystalline solids and isotropic melts are present.

\*\* For the sake of completeness, it must be added that some authors feel that a distinction should be made between true second-order transitions (examples of which, however, are virtually unknown), and "lambda" transitions (frequently met). A discussion of the rationale of this distinction is unnecessary here.

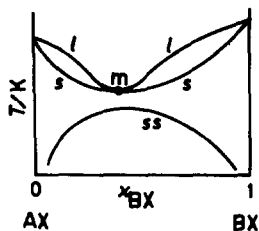


Fig. 4. Phase diagram of a binary with common anion exhibiting a continuous series of solid solutions (with a minimum,  $m$ ); further cooling causes demixing in the solid state:  $l$ , liquidus;  $s$ , solidus;  $ss$ , subsolidus.

### *A binary*

This is a system of three ionic species, such as A, B, X (binary with common anion), or A, X, Y (binary with common cation), and (at constant  $p$ ) its phase diagram can be represented in a  $T$  vs.  $x$  plane (see Fig. 4).

### *A ternary*

This is a system of four ionic species, such as A, B, C, X (ternary with common anion), or A, X, Y, Z (ternary with common cation), and its phase diagram can be represented by a prism, the base of which is the so-called composition triangle (see Fig. 5).

### *A reciprocal ternary*

This is a system of four ionic species, such as A, B, X, Y (i.e., two cations and two anions) and its phase diagram can be represented by a prism, the base of which is the so-called composition square (see Fig. 6).

More complex systems are not considered here.

In any system, the set of characteristic points (such as eutectics, peritectics, dystectics, monotectics, etc.), and curves and/or surfaces which form

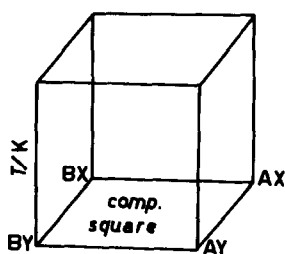
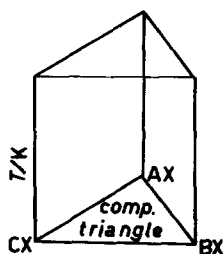


Fig. 5. Three-dimensional representation of a ternary with common anion.

Fig. 6. Three-dimensional representation of a reciprocal ternary.

the lower boundary of the isotropic liquid region is called the “liquidus” (see, e.g., Fig. 4). That which forms the upper boundary of the crystalline region is called the “solidus”. Finally, that relevant to transformations at  $T < T_{\text{solidus}}$  is called the “subsolidus”.

## PHASE RULE INVESTIGATIONS

### *Preliminary remarks*

In principle, the thorough phase rule investigation of a system requires:

(i) accurate definition of the liquidus, solidus and subsolidus boundaries; and, moreover,

(ii) complete information on the thermophysics of the component salts (and the intermediate compounds, if any), i.e., on the temperatures,  $T_{\text{trs}}$ , and enthalpy changes,  $\Delta_{\text{trs}}H_m$ , of the phase transitions, and on the molar heat capacities,  $C_{p,m}$ , of the different phases ( $\Delta_{\text{trs}}H_m$  and  $C_{p,m}$  values being needed to develop a variety of thermodynamic considerations on the system).

Unfortunately, the literature offers few examples of such investigations. It is found that:

(i) information on solidus and subsolidus is available rather frequently for binaries in the superambient region, but very infrequently for binaries in the subambient region, or for ternaries in general \*; and

(ii) adequate thermophysical information is available for only a limited number of salts.

A wide variety of experimental techniques (whose application, of course, is not confined to salt mixtures) has been employed in salt system investigations: an incomplete list is given below.

### *The visual polythermal method*

This method—popular with Russian authors, who have employed it to study countless systems—is efficient (though its application is restricted to liquidus) and basically very simple. It consists of direct visual recording of either the temperature of initial crystallization when a melt is cooled, or that at which the last crystal disappears when a solid is heated. Details of the procedure can be found, e.g., in ref. 4.

More sophisticated devices allowing the use of an inert atmosphere, observation of the melt through crossed polaroids, quick remelting of

\* This is why the most common graphical representation of a ternary merely consists of the projection on the composition triangle (or square) of the intersection curves of the liquidus with a set of selected isothermal planes.

partially frozen samples, etc., have been developed in recent years (see, e.g., ref. 5).

### *Thermoanalytical techniques*

ICTA [6] defines as thermoanalytical “a group of techniques in which a physical property of the substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program” \*\*. Those most commonly used for phase rule investigations of salt systems will now be briefly described.

#### *Classical thermal analysis*

Temperature is measured at given time intervals. The breaks recorded in the heating or cooling curves indicate at which temperatures phase changes of any kind occur (provided the amounts of energy involved are sufficient to cause noticeable breaks).

#### *Differential thermal analysis (DTA)*

In  $\Delta T = (T_{\text{sample}} - T_{\text{reference material}}) = f(T)$  traces, a “peak” is recorded when a temperature difference arises between the sample and the inert reference material due to the occurrence of a phase transition in the sample. DTA devices can also be used for obtaining semiquantitative information on  $\Delta_{\text{trs}}H_{\text{m}}$  values.

Very frequent examples of the application of this method can be found in the current literature.

#### *Differential scanning calorimetry (DSC)*

In  $\Delta P$  vs.  $t$  traces ( $\Delta P$ , differential power input between the sample and the inert reference material;  $t$ , time;  $T$ , dependent linearly on  $t$ ; sample and reference material maintained continuously at equal temperature), a “peak” is recorded when a differential energy supply is required by the sample, due to the occurrence of a phase transformation.

DSC allows one to obtain reliable  $T_{\text{trs}}$  and  $\Delta_{\text{trs}}H_{\text{m}}$  data, on the one hand, and semiquantitative  $C_{p,m}$  values, on the other hand, by applying the so-called ordinate displacement procedure. Frequent examples of the application of this method are to be found in the recent literature.

#### *Thermomicroscopy*

Light transmission of the system is studied as a function of  $T$ , usually using a hot-stage Kofler polarizing microscope. Baum et al. [8], for example, have successfully employed this technique in  $T_{\text{trs}}$  measurements for several metal alkanoates.

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\*\* The ICTA (International Confederation for Thermal Analysis) nomenclature is widely accepted, though some authors disagree with it to a certain extent (see, e.g., ref. 7).

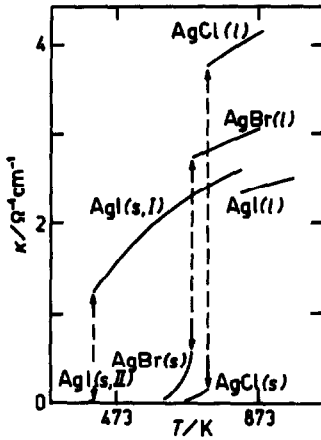


Fig. 7. Specific conductance of solid and liquid silver halides [9].

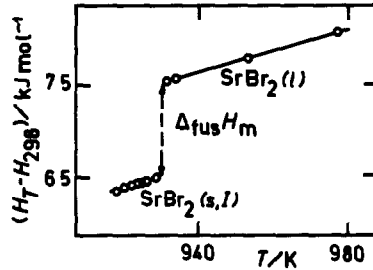


Fig. 8. Drop calorimetric data on liquid (*l*) and solid-alpha (*s, I*) strontium bromide [15].

### Thermoelectrometry

An electrical property of the system is studied as a function of  $T$ . The sharp changes in specific conductance occurring when silver halides undergo phase transitions are shown in Fig. 7 [9].

It must be stressed, however, that every thermoanalytical technique suffers from the disadvantage of being a non-equilibrium procedure employed to attempt investigation of equilibria. "The samples are subjected to constant rates of cooling or heating. The length of a temperature halt in straight thermal analysis or the area under a peak in DTA has to be determined for a process, not as a measurement on a system at equilibrium" [10]. This disadvantage becomes particularly marked when subsolidus relations are concerned, due to the (usually) extremely slow equilibration rate. Thus, caution is always required when evaluating the results obtained.

Moreover, employment of most of the techniques mentioned above is usually restricted to the superambient region. Routine measurements below room temperature (down to about 100 K) can only be performed by DSC.

### Adiabatic equilibrium calorimetry

Adiabatic equilibrium calorimeters must undoubtedly be regarded as the most effective devices available for phase rule investigations. In improved versions, data acquisition is computerized: the drift readings of the calorimeter temperature before and after each energy input, and the current and potential readings during each input are usually recorded, as well as the initial, final, and mean temperatures, the resistance of the heater, etc. A distinction must be made between cryogenic and superambient devices; for a more extensive account, see Westrum et al. [11], and West and Westrum [12], respectively.



TABLE 1

Transition temperatures and enthalpy changes for sodium propanoate

Transition	$T_{\text{trs}}$ (K)		$\Delta_{\text{trs}}H_m$ (kJ mol <sup>-1</sup> )	
	ad. cal.	DSC	ad. cal.	DSC
<i>s</i> , III → <i>s</i> , II	467	470	3.21	7.4 <sup>a</sup>
<i>s</i> , II → <i>s</i> , I	491	494	4.36	
<i>s</i> , I → <i>l</i>	561.9	562.4	13.28	13.4

<sup>a</sup> DSC only allowed measurement of the cumulative enthalpy change, due to the closeness of the two transitions. This figure must therefore be compared with the sum  $3.21 + 4.36 = 7.57$ .

By way of illustration, the results obtained by Ferloni et al. [13] and Franzosini et al. [14] on sodium propanoate using DSC and adiabatic equilibrium calorimetry are compared in Table 1.

The systematic, though not large, differences between the  $T_{\text{trs}}$  values are probably due to the fact that DSC is a non-equilibrium technique. By contrast, substantial agreement exists between the enthalpy changes, though greater precision is obviously obtained with adiabatic calorimetry. Unfortunately, the latter technique—due to its complication—has not yet found extensive employment in phase rule investigations of salt systems.

### Drop calorimetry

Obtaining satisfactory adiabatic behavior is increasingly problematical as temperature increases. The application of adiabatic calorimetry becomes difficult when  $T > 900$  K. Drop calorimetry is, therefore, preferred for thermophysical investigations on high melting systems. Measurements are made of the overall enthalpy change, ( $H_{\text{final}} - H_{\text{initial}}$ ), occurring in a sample when dropped from an oven kept at  $T_{\text{initial}}$  (K) into a receiving calorimeter (often of the metal block type), where the temperature  $T_{\text{final}}$  (K) is finally reached. As an example, the results of Dworkin and Bredig [15] on the liquid (*l*) and solid-alpha (*s*, I) strontium bromide are plotted in Fig. 8; trustworthy information can be obtained on  $\Delta_{\text{fus}}H_m$ , as well as on the molar heat capacity,  $C_{p,m} = (\partial H_m / \partial T)_p$ , of both phases.

Further details of the experimental methods listed in this section, and information on other techniques less commonly employed in phase rule investigations on salt systems, can be found, inter alia, in ref. 16.

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