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# The binary diagram water + barium chloride

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## Abstract

As part of a larger work on the production of solid metal by FFC electro-deoxidation in liquid salts, some candidate raw materials (i.e. hydrated salts) were studied with respect to thermal equilibria, in particular de-hydration. This paper presents the first complete review and critical assessment of the thermal equilibria of the hydrates of  $\text{BaCl}_2$ . A consistent set of optimised equations is presented for the water pressure within the bi-phase regions of the binary system  $\text{H}_2\text{O}-\text{BaCl}_2$ , along with a complete update of the corresponding  $T-X$  phase diagram. Finally, it is suggested that the hemi-hydrate ( $\text{BaCl}_2 \cdot 1/2 \text{H}_2\text{O}$ ) is only barely stable, and that the formation of hemi-hydrate (from  $\text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{BaCl}_2$ ) is driven by entropy only. An important correction to Holmes (J. Chem. Thermodynamics 28 (1996) 1325; J. Chem. Thermodynamics 29 (1997) 1363) is pointed out. **To cite this article: J. Fenstad, D.J. Fray, C. R. Chimie 9 (2006).**

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## 1. Introduction

As part of a larger work on producing solid metal by salt electro-deoxidation [1,2], a study was undertaken to map the properties of candidate raw materials, both for the main constituent of the salt electrolyte [3] and for salt additives. One potential additive is  $\text{BaCl}_2$ , an end member of the binary system reported here. This additive is commercially available as the hydrated chloride, and needs to be de-hydrated prior to use in the high temperature electrolytic process. The end member  $\text{BaCl}_2$  stands out (amongst the alkali earth chlorides) due to its relatively low molar solubility in water. In this respect it is more similar to  $\text{NaF}$  than to either  $\text{CaCl}_2$  or  $\text{SrCl}_2$ . The low solubility is readily linked to the relative ease with which  $\text{BaCl}_2$  loses its crystal water, i.e. the

barium chloride hydrates are relatively unstable [4–7] at atmospheric pressure (and below). However, when pressurised, the hemi-hydrate is reported to persist as high as 270 °C [8,9], thus ordinary  $T-X$  diagrams do not reveal the hemi-hydrate's instability at normal pressures. The most complete and recent  $T-X$  diagram for this system is from Kessis and Pascal [9], who combined the liquidus from Benrath and Lechner [8] with their own data for decomposition temperatures of the hydrates. Many key papers for this system are of early date, but they are quite consistent with recent papers, suggesting that the experimental methods were fairly 'mature' already in 1940. Some disagreements can be attributed to the particulars of each method, while others are attributable to differing levels of salt purity. This paper aims to present the first complete review and critical assessment of the stable phase equilibria of the  $\text{H}_2\text{O}-\text{BaCl}_2$  binary, and to provide vapour isobars and phase boundaries in a compact graphical form, and as a consistent set of optimised and versatile equations.

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## 2. Peritectic decomposition temperatures

Benrath and Lechner [8] and Eddy and Menzies [10] are the two most extensive and accurate investigations of the H<sub>2</sub>O-rich liquidus. Since these two are indistinguishable below 120 °C, we accept their temperature for BaCl<sub>2</sub>·2 H<sub>2</sub>O decomposition (102 °C) over the recommendations from Kessis and Pascal [9] and Tenu and Counioux [11], which are 3 K higher and coincides closely with another thermal arrest (water boiling). Kessis and Pascal [9] also reported BaCl<sub>2</sub>·1/2 H<sub>2</sub>O decomposition at a temperature of 2 K higher than Benrath and Lechner's [8], with an error of ± 3 K. Arbitrarily, 2 K was subtracted from the reported temperature [9] for decomposition of the monohydrate, to harmonise with the other investigations. Thus, 207 and 270 °C were selected for the decomposition temperature of mono- and hemi-hydrate, respectively.

## 3. Liquidi

The extensive liquidus data of Benrath and Lechner [8] and Eddy and Menzies [10], and from several other sources was summarised by Tenu and Counioux [11, 12], who modelled these liquidi (up to 200 °C). Tenu's fairly original mathematical approach provided a consistent set of equations, which main weakness is they cannot be re-arranged to an explicit form, i.e. neither  $T(X)$  nor  $X(T)$ . Thus, numeric approximation is needed to utilise Tenu's optimisation.

### 3.1. Liquidus equations

All liquidi of this system up to 270 °C could be reproduced accurately by second order polynomials with respect to composition, i.e. explicit  $T(X^2)$  functions.

### 3.2. Optimised liquidi

Up to 102 °C, the original sources for experimental  $T-X$  pairs are abundant, thus explicit  $T(X)$  functions were generated directly from these, yielding the following liquidus:

$$T/^\circ\text{C} = -166.9 + 7500 X_{\text{BaCl}_2} - 41\,500 X_{\text{BaCl}_2}^2$$

For the range 102–207 °C (monohydrate saturation), less experimental solubility data are available. Thus, the present optimisation was based on smoothing functions from Tenu and Counioux [11] and Monnin [13] that were thermodynamically consistent. Unfortunately, the solubility product ( $K_{\text{sp}}$ ) from Monnin [13] was not

based on solubility data alone, but was defined (and optimised) in terms of a particular model for the dilute liquid. Thus, this  $K_{\text{sp}}$  was made redundant by Holmes and Mesmer [14] who provided new data (and a different model) for the dilute liquid. Equations from Tenu and Counioux [11] related to solubilities only, and numeric  $T-X$  data could be extracted, to optimise an explicit  $T(X)$  function:

$$T/^\circ\text{C} = -610 + 19\,670 X_{\text{BaCl}_2} - 106\,050 X_{\text{BaCl}_2}^2$$

which may be combined with vapour pressure data [15] to confirm (independently) the liquid phase model of Holmes and Mesmer [14]. One solubility datum from Holmes and Mesmer [14] allowed a tentative liquidus function between 207 and 270 °C:

$$T/^\circ\text{C} = -868 + 26\,100 X_{\text{BaCl}_2} - 143\,000 X_{\text{BaCl}_2}^2$$

Beyond 270 °C, reasonable estimates could not be made for the liquidus compositions (Fig. 1).

## 4. Equilibrium vapour pressures

### 4.1. Vapour-pressure equations

With respect to vaporisation equilibria for H<sub>2</sub>O + BaCl<sub>2</sub>, there has been a steady trickle of relevant papers over the last 100 years. Holmes and Mesmer [19] provided smoothed (refined) data for the osmotic coefficients for aqueous salts over a wide temperature range. Osmotic data may be used with present  $T(X)$  functions for the liquidi, to generate explicit equations for the vapour pressure over the liquid solutions in equilibrium with solid hydrates. No attempts were made to estimate the equilibria involving liquid + anhydrous BaCl<sub>2</sub>, because of the lack of experimental data. Even if relevant data were available, such a vapour equation would be valid only in a limited temperature range, since these high temperatures causes the simple binary H<sub>2</sub>O–BaCl<sub>2</sub> to gradually degenerate into a complex reciprocal system [16] involving molecules and ions formed by combination of H<sub>2</sub>O, HCl, BaCl<sub>2</sub> and BaO. We noted, however, that extrapolation of vapour pressure data for dilute solutions (Azizov and Akhundov [17] and Matuzenko et al. [18]) indicate that Holmes' model predict ~ 10% too high vapour pressures (near the liquidus) at 350 °C, i.e. the extrapolative ability [14] may possibly drop off rapidly above 270 °C.

Moreover, this liquid model [14,19] is strikingly complex. This allows small typing errors to remain un-

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