

Thermodynamic Optimization of the Binary YbCl_3 - AECl_2 ($\text{AE} = \text{Mg, Ca, Sr, Ba}$) Systems

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By using the CALPHAD technique, an optimization of the binary YbCl_3 - AECl_2 ($\text{AE} = \text{Mg, Ca, Sr, Ba}$) systems was carried out. From measured phase equilibrium data and experimental integral properties, the YbCl_3 - AECl_2 phase diagrams were optimized and calculated. A set of thermodynamic functions was optimized based on an interactive computer-assisted analysis. The calculated phase diagrams and thermodynamic data are self-consistent.

1. Introduction

Molten salts are used as the solvent media in high-temperature chemical reprocessing of spent nuclear fuel of fast reactors. The phase diagrams of rare-earth metal halides in combination with alkali metal halide systems are of prime importance when considering those salt systems for possible use in this reprocessing application; specifically, the temperature and liquid composition at the eutectic reaction need to be known.

The phase diagrams of the YbCl_3 - AECl_2 ($\text{AE} = \text{Mg, Ca, Sr, Ba}$) systems have been measured by different research groups. One set of measurements was made by Blachnik et al.^[1,2] Their measurements included differential thermal analysis (DTA), x-ray diffraction (XRD), and, in the case of the YbCl_3 - MgCl_2 (CaCl_2) system, calorimetry of liquid formation at 1180 K. Their DTA apparatus was constructed in their laboratory and data were taken from heating curves with heating rates of $10^\circ \text{ min}^{-1}$ while using silicon as a nontransforming reference material. The earlier Blachnik paper on the YbCl_3 - MgCl_2 and YbCl_3 - CaCl_2 systems found them to be simple eutectic systems with no intermediate phases.^[1] Later Zheng et al. again with DTA and XRD examined these two systems and confirmed that both systems were simple eutectic systems.^[3] However, Zheng et al. reported peculiar and unexplained thermal arrests at ~ 939 K in the $\text{L}+\text{YbCl}_2$ two-phase region for the YbCl_3 - MgCl_2 system. YbCl_3 is not known to have any phase transformation in the solid form, and there is no intermediate phase to participate in a peritectic reaction, so the thermal effects are anomalous and not understood. The Zheng results are the basis for Fig. 1 and 2.

In the second Blachnik paper, the YbCl_3 - SrCl_2 and YbCl_3 - BaCl_2 systems were examined and both were found

to have well-developed eutectics.^[2] However, both systems were found to have intermediate phases with stoichiometries at AE_2YbCl_7 ($\text{YbCl}_3 \cdot 2\text{AECl}_2$) and AE_3YbCl_9 ($\text{YbCl}_3 \cdot 3\text{AECl}_2$). In the YbCl_3 - SrCl_2 system, both compounds form by peritectoidal reaction with $\text{YbCl}_3 + 2\text{SrCl}_2 \leftrightarrow \text{AE}_2\text{YbCl}_7$ at ~ 623 K and with AE_2YbCl_7 and AE_3YbCl_9 at ~ 473 K. These two peritectoid temperatures are much below the eutectic reaction and do not appear in Fig. 3 because the lowest temperature shown in the figure is 700 K. In the YbCl_3 - BaCl_2 system both compounds form peritectically with $\text{BaCl}_2 + \text{L}$ (42 mol % YbCl_3) $\leftrightarrow \text{YbAE}_3\text{Cl}_9$ at ~ 885 K and $\text{BaCl}_2 + \text{L}$ (44 mol.% YbCl_3) $\leftrightarrow \text{YbAE}_2\text{Cl}_7$ at ~ 873 K. Both SrCl_2 and BaCl_2 undergo crystallographic transformations at temperatures of ~ 1003 K for SrCl_2 and ~ 1195 for BaCl_2 . Some terminal solubility of YbCl_3 exists in the SrCl_2 system with an upper limit of ~ 5 mol%. This terminal solubility drops the polymorphic transformation in SrCl_2 precipitously from ~ 1103 to ~ 885 K. This drop in Fig. 3 is shown by a steep dashed line with no attempt to show the two-phase separation of the upper and lower polymorphs. No terminal solubilities have been reported for the other three systems, so in the YbCl_3 - BaCl_2 system of Fig. 4, the crystallographic transformation in BaCl_2 is shown as a horizontal dashed line. All experimental data for the invariant reaction in the four systems are summarized in Table 1.

Despite of Zheng's report of thermal anomalies in the YbCl_3 - MgCl_2 system at ~ 939 K, Table 1 shows data from Zheng and from Blachnik to be in close compositional accord, though somewhat deviant in temperature. On this basis, the thermal anomalies were considered as spurious, and the Zheng data for the YbCl_3 - MgCl_2 and YbCl_3 - CaCl_2 systems were chosen as input for the optimization. This choice is justified because the Zheng melting points for the pure components were much closer to currently accepted melting points, which are in our local database labeled USERBASE, the Zheng experimental precisions of temperature measurement at ± 3 K were much better than the Blachnik uncertainties, and the Zheng values were confirmed by both heating and cooling data. The Blachnik data were the sole data for the other two systems and accordingly were used as input values with the following simplifications for the YbCl_3 - SrCl_2 system; terminal solubility of YbCl_3 in SrCl_2

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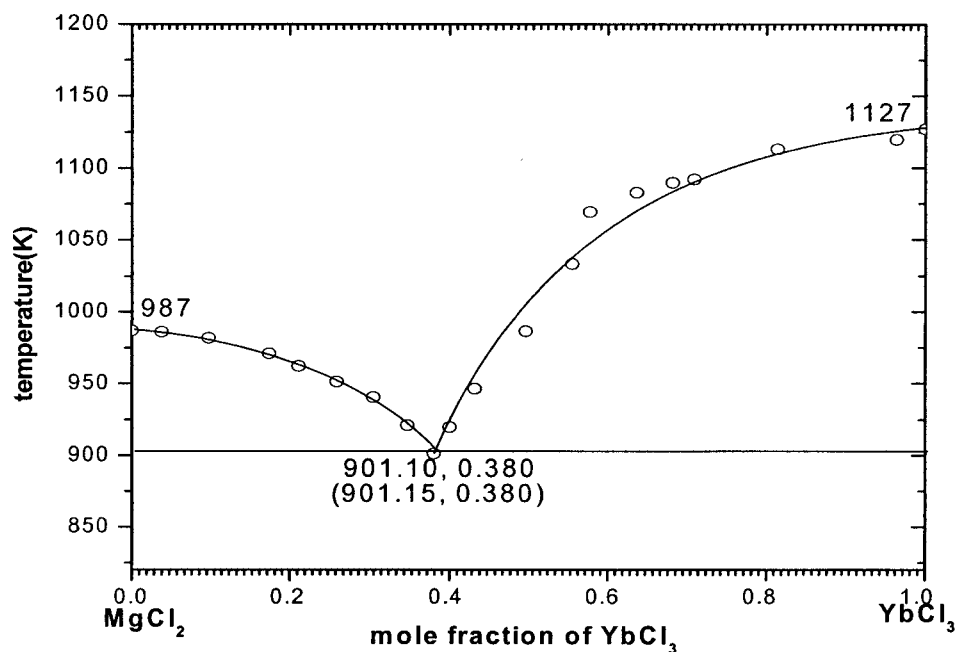


Fig. 1 Phase diagram of YbCl₃-MgCl₂. Solid lines – calculated; o – experimental points. Points along the 939K dashed line are considered spurious.

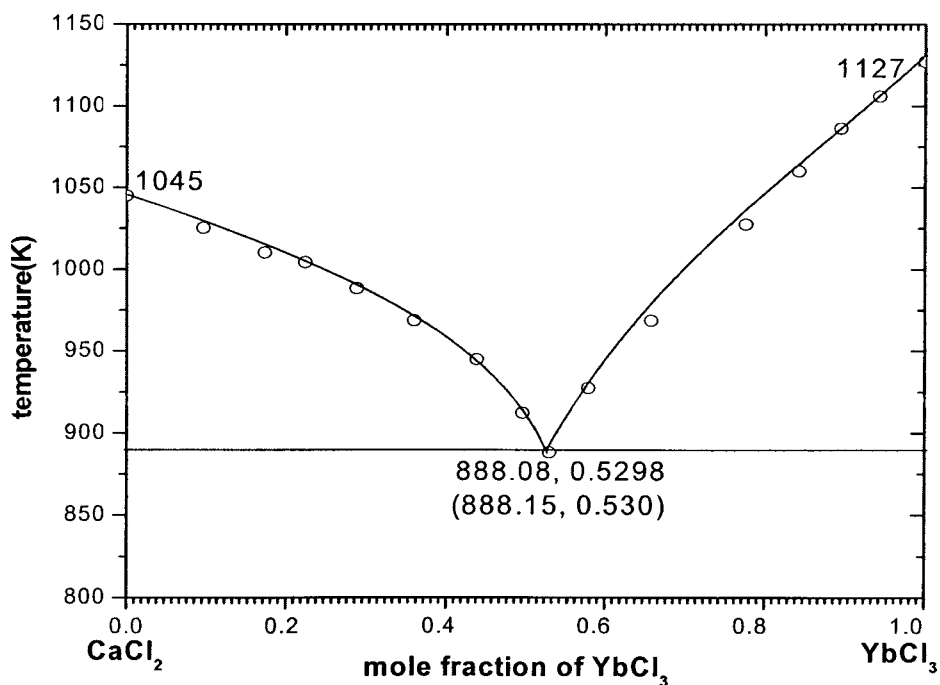


Fig. 2 Phase diagram of YbCl₃-CaCl₂. Solid lines – calculated; o – experimental points. Points along the 939K dashed line are considered spurious.

was not considered, and the peritectoidally formed compounds were neglected because their formation was well below the temperature range of interest.

To continue our previous work,^[4-6] the thermodynamic optimizations of YbCl₃-AECl₂ (AE = Mg, Ca, Sr, Ba) systems have been performed for this paper. The thermo-

dynamic properties for mixing of the liquid phases were described with a modified quasi-chemical model in the pair-approximation for short-range ordering model.^[7] Using the optimized thermodynamic parameters to construct phase diagrams, good agreement between the calculated and the experimental phase diagrams were observed.

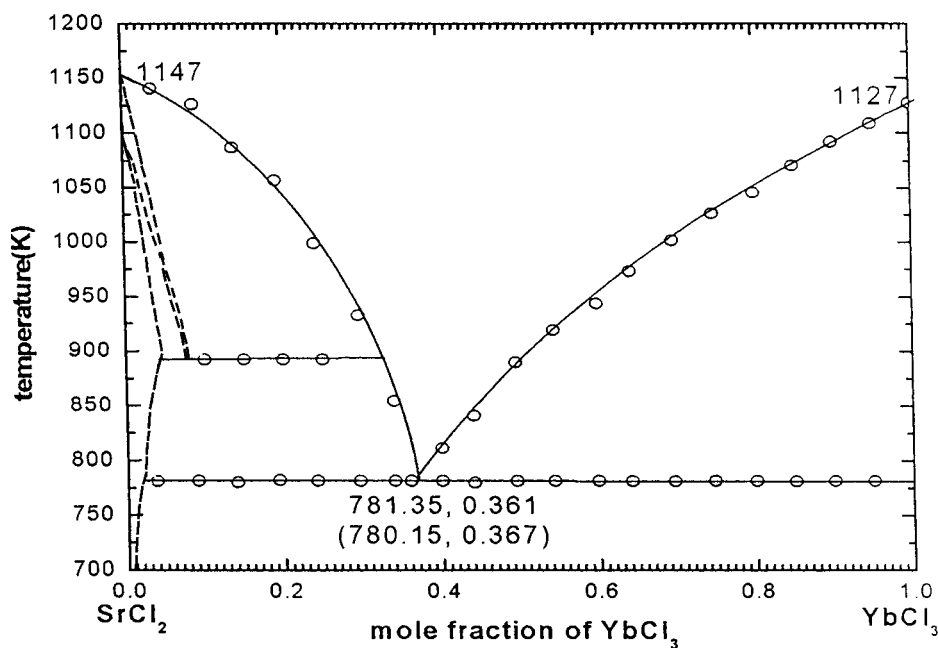


Fig. 3 Phase diagram of $\text{YbCl}_3\text{-CaCl}_2$. Solid lines – calculated; o – experimental points; dashed lines – speculative.

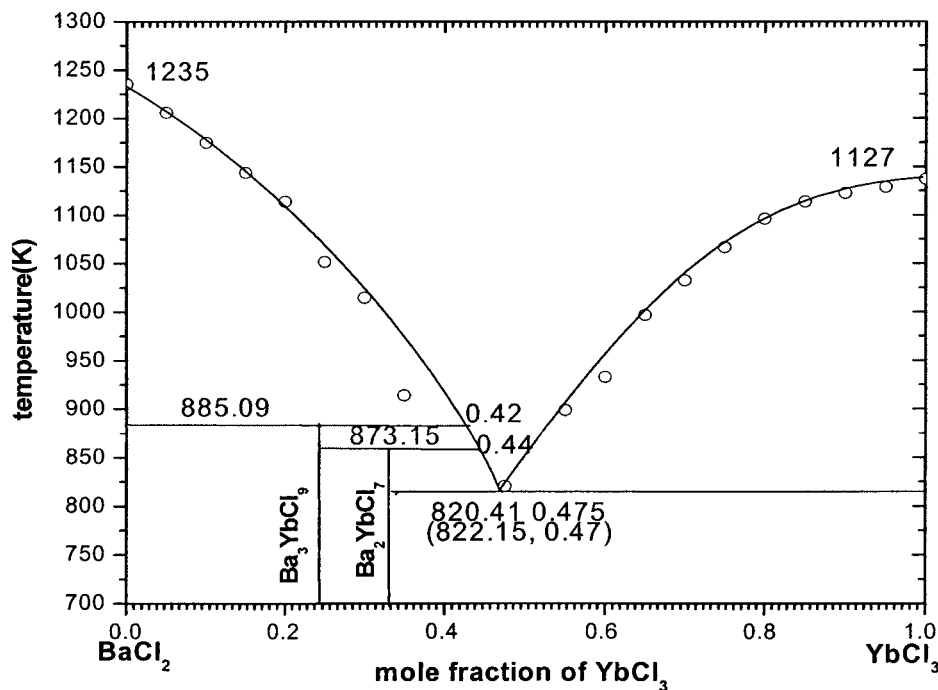


Fig. 4 Phase diagram of $\text{YbCl}_3\text{-BaCl}_2$. Solid lines – calculated; o – experimental points

2. Model

In the 1990s, a modification of the quasichemical theory of Guggenheim^[8,9] was made by Pelton and Blander^[10-12] to optimize phase diagrams with short-range ordering such as some molten salt systems. If A and B are the real components in an A-B solution system, three pseudo-

components AA, BB, and AB are considered in the new approach:

$$(\text{A-A})_{\text{pair}} + (\text{B-B})_{\text{pair}} = 2(\text{A-B})_{\text{pair}} \quad (\text{Eq 1})$$

If the first-nearest-neighbor pairs are used in a one-lattice pair model, the Gibbs energy of “reaction” 1, Δg , is the

Table 1 Experimental data of the YbCl₃-AECI₂ phase diagrams

System	Melting point, AECI ₂ , K	Type of phase diagram	Composition, mol% YbCl ₃	Temperature(a), K	Ref
MgCl ₂ -YbCl ₃	980	Eutectic	37.4	928 (E)	1
	997	Eutectic	38.0	901 (E)	3
CaCl ₂ -YbCl ₃	1044	Eutectic	40.0	868 (E)	1
	1045	Eutectic	53.0	888 (E)	3
SrCl ₂ -YbCl ₃	1143	Eutectic	36.7	708 (E)	2
	47.0	822 (E)	...
BaCl ₂ -YbCl ₃	1236	Peritectic	44.0	872 (P)	2
	42.0	885 (P)	...

(a) E, eutectic point; P, peritectic point

nonconfigurational Gibbs energy change for the formation of 2 mol (A-B) pairs, and it is composition and temperature dependent. Then the Gibbs energy of A-B system is represented by Eq 2:

$$G = (n_A g_A^0 + n_B g_B^0) + RT(n_A \ln X_A + n_B \ln X_B) + RT \left(n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right) + \frac{n_{AB}}{2} \Delta g_{AB} \quad (\text{Eq 2})$$

where n_i is the number of moles of i , n_{ij} is the number of moles of the i - j pair; X_i is the mole fraction of i , X_{ij} is mole fraction of the i - j pair, and Y_i is the equivalent fraction of i .

In Eq 2, X_{ij} and Y_i are defined as follows:

$$X_{ij} = n_{ij} / (n_{AA} + n_{BB} + n_{AB}) \quad (\text{Eq 3})$$

$$Y_A = Z_A n_A / (Z_A X_A + Z_B n_B) = Z_A X_A / (Z_A X_A + Z_B X_B) = 1 - Y_B \quad (\text{Eq 4})$$

According to the mass conservation law, one can get the following equation in the A-B binary system:

$$Z_A n_A = 2n_{AA} + n_{AB} \quad (\text{Eq 5})$$

$$Z_B n_B = 2n_{BB} + n_{AB} \quad (\text{Eq 6})$$

or:

$$2X_A = 2X_{AA} + X_{AB} \quad (\text{Eq 7})$$

$$2X_B = 2X_{BB} + X_{AB} \quad (\text{Eq 8})$$

The mole pair Gibbs energies of A-B pairs, i.e., g_{AA}^0 , g_{BB}^0 , and g_{AB}^0 are defined according to the following expression:

$$g_{AA}^0 = \frac{2g_A^0}{Z_{AA}}, g_{BB}^0 = \frac{2g_B^0}{Z_{BB}} \quad (\text{Eq 9})$$

$$g_{AB}^0 = \Delta g_{AB}^0 + g_{AA}^0 \frac{Z_{AA}}{Z_{AB}} + g_{BB}^0 \frac{Z_{BB}}{Z_{BA}} = \Delta g_{AB}^0 + \left(\frac{2g_A^0}{Z_{AB}} + \frac{2g_B^0}{Z_{BA}} \right) \quad (\text{Eq 10})$$

where g_i^0 is molar Gibbs energy of pure i , and Z_{ij} is the coordination number of the i - j pair. Z_{ij} and Z_i , the coordination number of i , which can be different and a function of pair composition.

$$\frac{1}{Z_A} = \frac{1}{2n_{AA} + n_{AB}} \left(\frac{2n_{AA}}{Z_{AA}^A} + \frac{n_{AB}}{Z_{AB}^A} \right) \quad (\text{Eq 11})$$

$$\frac{1}{Z_B} = \frac{1}{2n_{BB} + n_{AB}} \left(\frac{2n_{BB}}{Z_{BB}^B} + \frac{n_{AB}}{Z_{AB}^B} \right) \quad (\text{Eq 12})$$

The molar energy of A-B pairs Δg_{AB} is a function of mole fractions of i - j pairs and can be expressed as follows:

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum_{i \geq 1} g_{AB}^i X_{AA}^i + \sum_{j \geq 1} g_{AB}^j X_{BB}^j \quad (\text{Eq 13})$$

or

$$\Delta g_{AB} = \Delta g_{AB}^0 + \sum g_{AB}^{ij} X_{AA}^i X_{BB}^j \quad (i + j \geq 1) \quad (\text{Eq 14})$$

For both Eq 13 and 14, in practice one will always have either $i = 0$ or $j = 0$.

3. Optimization

All thermodynamic data of pure components come from the FACTBASE^[13] and USERBASE, and the latest published thermodynamic data are stored in the USERBASE.

The Gibbs energies of fusion are given by:

$$\Delta G_{\text{fus}}^0 = A + BT + CT^2 + DT \ln T + E/T \quad \text{J mol}^{-1} \quad (\text{Eq 15})$$

Section I: Basic and Applied Research

Table 2 Thermodynamic properties of pure compounds

Compounds	T_{fus}, K	Phase	$A \times 10^{-3}$	B	$C \times 10^3$	D	$E \times 10^{-5}$
MgCl ₂	987	S	-676.337	242.257	-10.711	-54.584	5.561
	...	L	-634.331	499.203	0.000	-92.048	0.000
CaCl ₂	1045	S	-361.373	-3567.260	-54.628	338.822	-39.802
	...	L	-815.002	585.175	0.000	-102.533	0.000
SrCl ₂	1147	S ₁	-734.624	3645.780	190.713	-476.337	-19.594
	...	S ₂	-847.874	749.736	0.000	-123.010	0.000
	...	L	-847.537	587.487	0.000	-104.600	0.000
BaCl ₂	1235	S ₁	-881.525	371.704	-633.799	-73.257	0.839
	...	S ₂	-914.091	749.701	0.000	-123.846	0.000
	...	L	-879.498	614.467	0.000	-108.784	0.000
YbCl ₃	1127	S	-959.810	242.379	-46.650	-94.684	0.000
	...	L	-941.499	271.711	0.000	-121.336	0.000

Table 3 Calculated coefficients for the U₂Cl₃-AEC₂ systems

System	$C_1, j = 0$	$C_1, j = 1$		$C_1, j = 2$		$C_1, j = 4$
		X_{AA}	X_{BB}	X_{AA}	X_{BB}	
MgCl ₂	1557.72	-1024.00	-7285.63	10,826.72	0.0000	0.0000
CaCl ₂	1985.50	-1487.52	-4650.64	0.0000	0.0000	0.0000
SrCl ₂	-4423.22	3392.29	1199.10	0.0000	0.0000	0.0000
BaCl ₂	-5830.50	5114.45	4400.40	-3,411.76	-11,226.52	8622.40

Table 2 shows coefficients for the free energies of pure compounds for the liquid and solid state of the various components from which the coefficients in Eq 15 can be derived.

All collected data including phase diagram data and the descriptions of pure components that are already available are used together to optimize the thermodynamic properties and phase diagrams by using a simple computer program.

For calculation of the phase diagrams, an initial determination of the Z_{ij} is needed. On the basis of past experience with mixed salt systems, values for the coordination numbers were set at $Z_{YbYb} = Z_{AA} = 6$, where the selection was based on experimental input.^[14] In the authors studies of rare-earth (Re) chloride-metal chloride systems of the type $\text{ReCl}_3\text{-MCl}_n$ ($n = 1$ or 2) system, a tendency to form an intermediate phase of the type $\text{ReCl}_3 \cdot 3\text{MCl}_n$, $[\text{ReM}_3\text{Cl}_3(1 + n)]$ has been found. Such phases occur in the $\text{YbCl}_3\text{-SrCl}_2$ and $\text{YbCl}_3\text{-BaCl}_2$ systems; however, YbSr_3Cl_9 is not stable in our temperature range of interest, but YbBa_3Cl_9 is stable to 885 K.^[2] On the basis of this information with A-Yb pair ratio occurring at 3:1, the values of $Z_{YbYb} = Z_{AA} = 6$ and $Z_{AYb} = 2$, and $Z_{YbA} = 6$ were selected for all alkaline earth elements through the calculations.

In the new approach, the molar energy of A-B pairs, Δg_{AB} is a function of mole fractions of i - j pairs shown in Eq 13 and 14. However, different kinds of expressions can be selected. To suit the form of the FACTBASE, the Margules expression (Eq 16) is put to use in the present work:

$$\Delta g_{AB} = \sum X_{AB} X_n^j (C_1 + C_2 T) \quad (\text{Eq 16})$$

where n can be AA and BB, and C_1 and C_2 correspond to enthalpy of mixing and excess entropy, respectively. In this system, $j = 0, 1, 2, 4$. Table 3 shows all the coefficients for the $\text{YbCl}_3\text{-AEC}_2$ binary systems.

The expression for the Gibbs energy of formation of the intermediate compound C_1 and C_2 is as follows:

$$\Delta G_{f(A_m B_n)}^0 = a + bT, \quad \text{J mol}^{-1} \quad (\text{Eq 17})$$

The authors calculated the coefficients of two intermediate compounds Ba_3YbCl_9 and Ba_2YbCl_7 . The optimized coefficients for Ba_3YbCl_9 :

$$\Delta G_{f(\text{Ba}_3\text{YbCl}_9)}^0 = 22095.82 - 31.25T \quad \text{J mol}^{-1}$$

The optimized coefficients for Ba_2YbCl_7 :

$$\Delta G_{f(\text{Ba}_2\text{YbCl}_7)}^0 = -9920.29 + 5.876T \quad \text{J mol}^{-1}$$

4. Calculations and Discussion

According to the thermodynamic data optimized above, the $\text{YbCl}_3\text{-AEC}_2$ phase diagrams were calculated by using the THERMOCALC computer program. The assessed phase diagrams are shown in Fig. 1-4. The solid lines in the figures represent the calculated data, and the spots represent the experimental data. The numbers in the parentheses are the experimental critical points. It can be seen that the calculated phase boundaries and invariant points agree well with the experimental data.

For the $\text{YbCl}_3\text{-MgCl}_2$ system (Fig. 1), the calculated eutectic point is at 901.00 K with the composition of 38.00 mol% YbCl_3 . A peritectic-like line was reported by Zheng et al.^[3] at 939 K but was not found by Blachnik et al.,^[1] and there is no polymorphic transition in YbCl_3 ; without further corroboration, the experimental points must be considered spurious and are most likely due to an impurity effect. For the $\text{YbCl}_3\text{-CaCl}_2$ system (Fig. 2), the calculated eutectic temperature is 888.08 K with a liquidus composition of 52.98 mol% YbCl_3 . For the $\text{YbCl}_3\text{-SrCl}_2$ system (Fig. 3), the calculated eutectic temperature is 781.35 K with a liquidus composition of 36.15 mol% YbCl_3 . Solid SrCl_2 exists in two polymorphic forms with a crystallographic transformation in the pure material near 1103 K, but with a solubility of YbCl_3 in SrCl_2 of up to 5 mol% as reported by Blachnik et al.,^[2] the transition drops precipitously to ~885 K; the SrCl_2 -rich region in Fig. 3 is drawn to show that the phase rule requires a two-phase field between the high and low temperature forms of SrCl_2 at off-stoichiometric compositions, but the dashed lines are purely speculative with no experimental basis except there is some terminal solubility of YbCl_3 in SrCl_2 . Indeed, in the calculations the terminal solubility was ignored with the assumption that the terminal solubility was not likely to significantly affect either the temperature or liquid composition of the eutectic reaction.

As shown in Fig. 4, two incongruently melting compounds Ba_3YbCl_9 and Ba_2YbCl_7 are observed in the $\text{YbCl}_3\text{-BaCl}_2$ system. The peritectic temperatures of compounds Ba_3YbCl_9 and Ba_2YbCl_7 are 885.09 and 873.15 K, respectively. The eutectic in this system were calculated at 820.41 K with 47.50 mol% YbCl_3 . Also, there are two kinds of states in the solid BaCl_2 .

5. Conclusions

In general, the calculated phase boundaries agree well with the experimental data. However, for the $\text{YbCl}_3\text{-SrCl}_2$ system, the results are different to some extent. The thermodynamic properties of the intermediate compounds were estimated. The calculated phase diagrams and optimized thermodynamic parameters are thermodynamically self-consistent.

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