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Thermochimica Acta 470 (2008) 105–107
thermochimica acta
www.elsevier.com/locate/tca

Short communication

CaO solubility and activity coefficient in molten salts $CaCl_2$–x ($x = 0$, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl)

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Received 9 November 2007; received in revised form 1 February 2008; accepted 7 February 2008
Available online 15 February 2008

Abstract

CaO solubility in equimolar molten salts $CaCl_2$–x ($x = 0$, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl) was determined at 873–1223 K and activity coefficient calculated. CaO solubility in the binary salts is less than in $CaCl_2$, and the activity coefficient is greater than one. With increasing temperature CaO solubility increases and the activity coefficient decreases. The dependency of CaO activity coefficient on temperature in equimolar molten salts $CaCl_2$–x is

$CaCl_2$	$RT\ln\gamma_{CaO} = 6961 + 5.06\,T$ (K)	1123–1223 K
$CaCl_2$–NaCl	$RT\ln\gamma_{CaO} = 3985 + 17.67\,T$ (K)	923–1123 K
$CaCl_2$–KCl	$RT\ln\gamma_{CaO} = 2384 + 22.72\,T$ (K)	1073–1223 K
$CaCl_2$–$SrCl_2$	$RT\ln\gamma_{CaO} = 27245–1.13\,T$ (K)	1073–1223 K
$CaCl_2$–$BaCl_2$	$RT\ln\gamma_{CaO} = 17068 + 10.19\,T$ (K)	1223–1273 K
$CaCl_2$–LiCl	$RT\ln\gamma_{CaO} = 14724 + 0.72\,T$ (K)	923–1073 K

Keywords: CaO; Solubility; Activity coefficient; $CaCl_2$; Molten salt

1. Introduction

Because of low toxicity and high CaO solubility, $CaCl_2$ [1–3] and its mixtures $CaCl_2$–NaCl [4,5] and $CaCl_2$–KCl [6] have been widely used in research on metal electrorefining and electrowinning. CaO solubility in $CaCl_2$ was given by Neumann et al. [7] and Wenz et al. [8] over a wide temperature range. Perry and Macdonald [9] also reported the phase diagram of $CaCl_2$–CaO binary system. Freidina and Fray [10] determined melting points of $CaCl_2$–NaCl–CaO by DTA and gave the liquidus of $CaCl_2$ rich corner in the system. The liquidus line of CaO in $CaCl_2$–CaF_2 system was also reported in Perry's work [9], but CaO solubility in other $CaCl_2$ based salts is not found in literature. In present work, CaO saturated equimolar molten salts $CaCl_2$–x ($x = 0$, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl) were prepared and analyzed to determine CaO solubility and activity coefficient.

2. Experimental

CaO was calcined at 1200 °C for 4 h. $CaCl_2$, NaCl, KCl, $SrCl_2{\cdot}6H_2O$ and $BaCl_2{\cdot}H_2O$ were dried at 473 K (LiCl at 373 K) for 60 h. $CaCl_2$ was mixed with extra CaO (about 25 wt%, put in a nickel crucible (outer diameter 50 mm, height 50 mm) and was then heated in a sealed furnace under Ar. After the salt was kept at 1123 K for different times, the crucible was lifted out of the furnace and upper liquid (about 2 g) was scooped out quickly with a stainless spoon for the analysis of CaO concentration.

Sodium hydroxide solution was titrated by dibutyl orthophthalates solution of known concentration to determine the concentration of the sodium hydroxide solution. Hydrochloric acid solution was then titrated by the sodium hydroxide solution to determine the concentration of the hydrochloric acid solution.

The salts were crushed quickly in an agate mortar and titrated by the hydrochloric acid solution and CaO solubility in the salts was calculated as:

$$\text{Mass\%} = \frac{V \times c \times M}{2000m}100\% \qquad (1)$$

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0040-6031/$ – see front matter
doi:10.1016/j.tca.2008.02.007

Here, V (mL) and c (mol L^{-1}) present the volume and the concentration of the hydrochloric acid solution used in the titration process, M (g mol^{-1}) and m (g) present the molar weight of CaO and the weight of the salts and mass% is CaO solubility.

Equimolar molten salts $CaCl_2$–x (x = NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl) were mixed separately with CaO (25 wt%), placed in the nickel crucible separately, and heated to high temperatures. The melting points of the mixed salts $CaCl_2$–x (x = NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl) are lower than that of $CaCl_2$, equilibrium time for CaO dissolution in the salts should be longer than that of CaO dissolution in molten $CaCl_2$. Therefore, the first sample was taken after 4 h holding at the high temperatures and the time interval was kept for 4 h in the subsequent sampling process. All chemicals are of analytical grade.

3. Results and discussions

Variation of CaO concentration in molten $CaCl_2$ with time is presented in Fig. 1. After 3 h dissolution in molten $CaCl_2$ at 1123 K CaO reached saturation and its concentration was constant.

CaO solubility in molten $CaCl_2$ reported by Neumann et al. [7], Wenz et al. [8] and Perry and Macdonald [9] is plotted in Fig. 2 together with CaO solubility obtained in present work. Our data are somewhat greater than that reported in the references.

Fig. 3 shows CaO solubility at different temperatures in equimolar $CaCl_2$–x (x = 0, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl). At 1123–1273 K, CaO solubility in $CaCl_2$ is 14.9–16.0 wt% and is higher than in the binary salts. Molten $CaCl_2$–KCl has the smallest CaO solubility (4.0–4.2 wt% at 1023–1223 K), and the greatest solubility is in $CaCl_2$–LiCl, 6.87 wt% at 873 K. CaO solubility in all salts increases with increasing temperature but with different temperature gradients. The temperature gradient in $CaCl_2$–LiCl and $CaCl_2$–$SrCl_2$ is greater than in $CaCl_2$–x (x = 0, NaCl, KCl and $BaCl_2$).

There is a two-phase equilibrium between solid CaO and CaO dissolved in the molten salts. The chemical potentials of CaO in both phases are equal:

$$\mu^{\mathrm{s}} = \mu^{\mathrm{l}} \qquad (2)$$

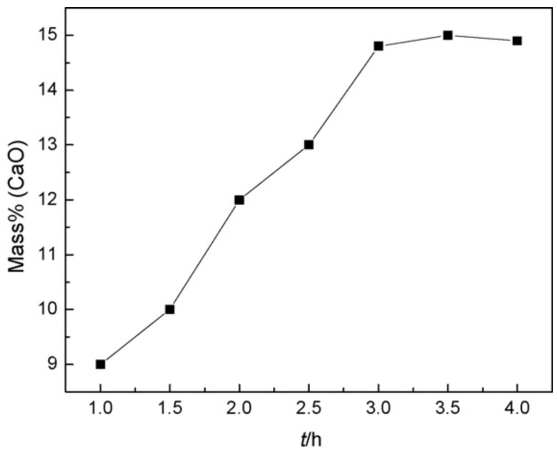

Fig. 1. Variation of CaO concentration in molten $CaCl_2$ with time at 1123 K.

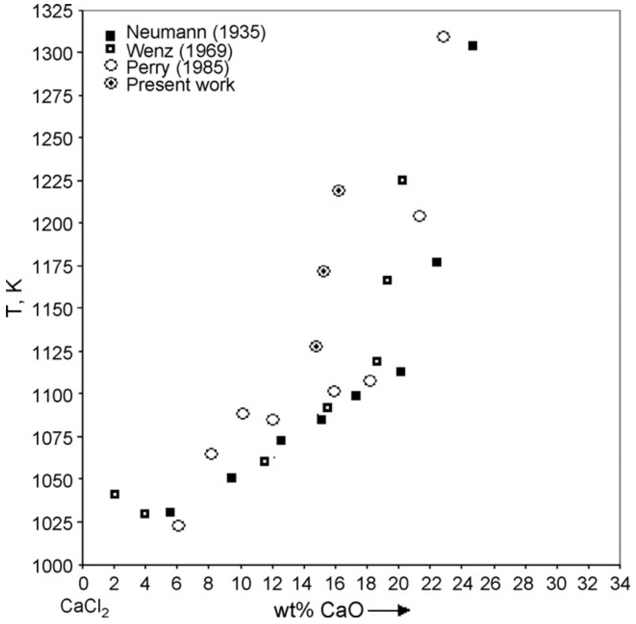

Fig. 2. Liquidus line of $CaCl_2$–CaO binary system.

where μ^{s} and μ^{l} represent the chemical potentials of solid CaO and CaO in the molten salts, respectively. Chemical potential can be expressed as the function of activity:

$$\mu^{\mathrm{s}} = \mu^{\mathrm{o}}(T, p) + RT\ \ln a^{\mathrm{s}}_{\mathrm{CaO}} \qquad (3)$$

$$\mu^{\mathrm{l}} = \mu^{\mathrm{o}}(T, p) + RT\ \ln a^{\mathrm{l}}_{\mathrm{CaO}} \qquad (4)$$

$a^{\mathrm{s}}_{\mathrm{CaO}}$ and $a^{\mathrm{l}}_{\mathrm{CaO}}$ express the activity of pure solid CaO and CaO in the salts. The chemical potentials in Eq. (3) and (4) are equal, and therefore, $a^{\mathrm{s}}_{\mathrm{CaO}} = a^{\mathrm{l}}_{\mathrm{CaO}} = 1$, and

$$\gamma^{\mathrm{l}}_{\mathrm{CaO}} = x^{-1}_{\mathrm{CaO}} \qquad (5)$$

$\gamma^{\mathrm{l}}_{\mathrm{CaO}}$ and $x^{\mathrm{l}}_{\mathrm{CaO}}$ in Eq. (5) present the activity coefficient of dissolved CaO and its solubility in mole fraction in the salts, respectively.

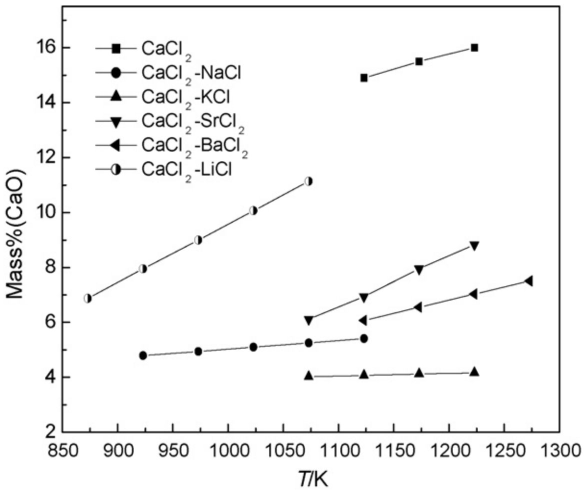

Fig. 3. CaO solubility in equimolar molten salts $CaCl_2$–x (x = 0, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl).

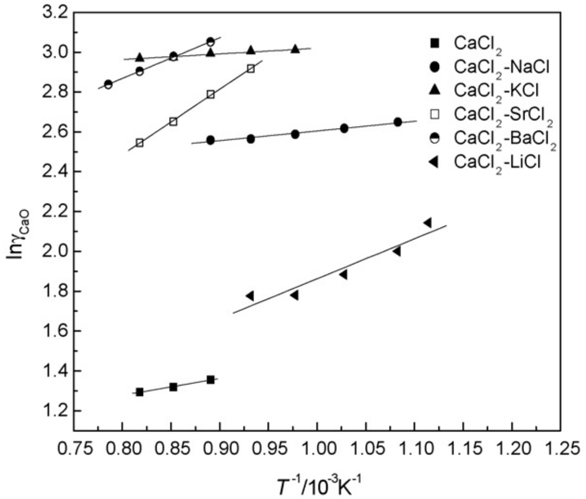

Fig. 4. Dependency of CaO activity coefficient on temperature in equimolar molten salts $CaCl_2$–x ($x = 0$, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl).

Table 1
Liner regression of logarithm of CaO activity coefficient against temperature reciprocal in equimolar molten salts $CaCl_2$–x ($x = 0$, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl)

Molten salts	CaO activity coefficient	T (K)
$CaCl_2$	$\ln\gamma_{CaO} = 0.6064 + 840.0(T, K)^{-1}$	1123–1223
$CaCl_2$–NaCl	$\ln\gamma_{CaO} = 2.118 + 486.5(T, K)^{-1}$	923–1123
$CaCl_2$–KCl	$\ln\gamma_{CaO} = 2.736 + 284.1(T,K)^{-1}$	1023–1223
$CaCl_2$–$SrCl_2$	$\ln\gamma_{CaO} = -0.139 + 328.2(T,K)^{-1}$	1073–1223
$CaCl_2$–$BaCl_2$	$\ln\gamma_{CaO} = 1.238 + 203.7(T,K)^{-1}$	1123–1273
$CaCl_2$–LiCl	$\ln\gamma_{CaO} = 0.140 + 200.4(T,K)^{-1}$	873–1073

CaO activity coefficient in all the salts is >1, showing positive deviation from the ideal solution. CaO activity coefficient in equimolar $CaCl_2$–x (x = NaCl, KCl, $SrCl_2$ and $BaCl_2$) is large (about 14–22), indicating that CaO was repulsed strongly in these salts. CaO activity coefficient in $CaCl_2$ and $CaCl_2$–LiCl is small (about 3–9), suggesting CaO repulsion is weaker in these salts. The CaO activity coefficient in $CaCl_2$–x follows the following increasing order:

$$CaCl_2 \rightarrow LiCl \rightarrow NaCl \rightarrow SrCl_2 \rightarrow KCl \rightarrow BaCl_2$$

According to the regular solution model, CaO activity coefficient can be expressed as:

$$RT \ln \gamma_{CaO} = A + BT \tag{6}$$

Fig. 4 shows the relationship between the logarithm of CaO activity coefficient and temperature reciprocal in the salts. The activity coefficient decreases with increasing temperature and has less temperature gradient in $CaCl_2$–x ($x = 0$, $BaCl_2$ and LiCl) than in $CaCl_2$–x (x = NaCl, KCl, $SrCl_2$). From Eq. (5) CaO solubility at different temperatures can then be calculated. Table 1 lists the linear regression of the logarithm of CaO activity coefficient against temperature reciprocal.

Acknowledgements

The authors would like to express sincere appreciation to Prof. D.J. Fray in University of Cambridge for valuable advice. This work was supported financially by NSFC (Contract No. 50674027), for which the authors are grateful.

References

[1] T.H. Okabe, M. Nakamura, T. Oishi, K. Ono, Metall. Trans. B 24 (1993) 449–455.
[2] C.Z. Chen, D.J. Fray, T.W. Farthing, Nature 407 (2000) 361–364.
[3] K. Ono, R.O. Suzuki, JOM 54 (2002) 59–61.
[4] X.Y. Yan, D.J. Fray, Metall. Mater. Trans. B 33 (2000) 685–693.
[5] E. Gordo, G.Z. Chen, D.J. Fray, Electrochim. Acta 49 (2004) 2195–2208.
[6] V.L. Cherginets, T.P. Rebrova, Electrochem. Commun. 2 (2000) 97–99.
[7] B. Neumann, C. Kroger, H. Juttner, Zeitschrift feur Elektrochemie 41 (1935) 725–736.
[8] D.A. Wenz, I. Johnson, R.D. Wolson, J. Chem. Eng. Data 14 (1969) 250–252.
[9] G.S. Perry, L.G. Macdonald, J. Nucl. Mater. 130 (1985) 234–241.
[10] E.B. Freidina, D.J. Fray, Thermochim. Acta 356 (2000) 97–100.