

Fig. 3—Effect of ammonia concentration on copper recovery at different time intervals with mechanical agitation (Mech.) or ultrasound (c.w.—continuous wave or pulse).

To summarize, this laboratory-scale investigation has clearly established the positive influence of ultrasound on copper recovery from oxide ores in ammoniacal medium. A maximum recovery of copper of about 70 pct was obtained with the following leaching conditions: temperature, 298 K; particle size, $-300 + 150 \mu\text{m}$; ammonia concentration, 2.0 mol/L; and solids concentration, 10 g/L of slurry without sonication. The recovery increased up to 90 pct by the application of ultrasound. It was shown that the use of ultrasound decreased the leaching time by a factor of nearly 6 times and also decreased the reagent consumption compared to that during leaching using mechanical agitation. For the same particle size, ultrasound not only enhanced the extraction rate but also improved the yield. Other conditions remaining the same, intermittent use of ultrasound (pulsed ultrasound) had a better effect over the continuous use of ultrasound.

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Discussion of "Use of Solid Electrolyte Galvanic Cells to Determine the Activity of CaO in the CaO-ZrO₂ System and Standard Gibbs Free Energies of Formation of CaZrO₃ from CaO and ZrO₂"

K.T. JACOB

In a recent article, Tanabe and Nagata^[1] have used Ca₄P₂O₉ (4CaO·P₂O₅) as a solid electrolyte in a cell designed to measure the activity of CaO in the system CaO-ZrO₂ between 1572 and 1877 K. The article is interesting, not only because of new data obtained on an important system, but also because the authors have tried to extend the current experimental capabilities for measuring the activity of CaO to higher temperatures than is possible with the well-established CaF₂ solid electrolyte.^[2,3,4] At temperatures above 1300 K, CaF₂ begins to soften and it is difficult to use the material in solid-state cells. The only other solid electrolyte suitable for measuring the activity of CaO at higher temperatures is Ca β"-alumina. The β"-alumina phase is metastable in the CaO-Al₂O₃ system. It is stabilized by the addition of MgO, with the MgO/CaO molar ratio varying from 0.7 to 0.8. However, calcium β"-alumina is not in equilibrium with CaO. Hence, pure CaO cannot be used as a reference electrode, despite claims to the contrary by Kumar and Kay^[5] and Rog and Kozłowska-Rog.^[6] Several intermediate aluminates form at the interface between the electrolyte and the CaO reference electrode.^[7] Thus, the development of new solid electrolytes for measuring the activity of CaO at $T > 1300 \text{ K}$ is important for the development of the theoretical basis of extractive metallurgy and high-temperature ceramic processing. Earlier work by Tanabe *et al.*^[8] had established that Ca₄P₂O₉ is an ionic conductor with transference number of Ca²⁺ ion close to unity in the temperature range 1373 to 1873 K and oxygen partial pressure range from 10⁵ to 10⁻⁵ Pa.

It is revealing to compare the results obtained by Tanabe and Nagata^[1] for the system CaO-ZrO₂ with other measurements reported in the literature. Using measured values for the activity of CaO, Tanabe and Nagata^[1] derived values

J. TANABE and K. NAGATA: *Metall. Mater. Trans. B*, 1996, vol. 27B, pp. 658-62.

K.T. JACOB, Chairman and Professor, Materials Research Centre, and KSIIDC Chair, Department of Metallurgy, is with the Indian Institute of Science, Bangalore 560 012, India.

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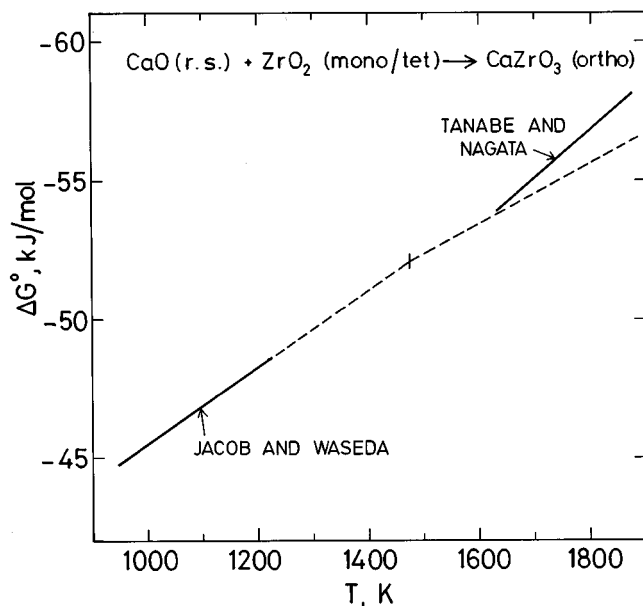


Fig. 1—Comparison of data for the standard Gibbs energy of formation of CaZrO_3 obtained by Tanabe and Nagata^[1] with that reported by Jacob and Waseda.^[4]

for activity of ZrO_2 using the Gibbs–Duhem relation. In Figure 5 of their article, the activity of CaO in the tetragonal solid solution is shown to obey Henry's law. When Henry's law is followed by a solute, the solvent must obey Raoult's law. It is therefore surprising that small negative deviations from Raoult's law are indicated for ZrO_2 in Figure 6 of Tanabe and Nagata.

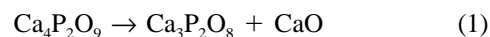
The standard free energy of formation of orthorhombic CaZrO_3 was calculated from activities of CaO and ZrO_2 in the two-phase region consisting of cubic zirconia solid solution and CaZrO_3 .^[1] The "second-law" enthalpy of formation of CaZrO_3 from tetragonal ZrO_2 and CaO obtained from the measurements of Tanabe and Nagata^[1] is $-25.2(\pm 4)$ kJ/mol at a mean temperature of 1725 K. The error limit given by Tanabe and Nagata (± 0.15 kJ/mol) is incorrectly assessed. The corresponding second-law enthalpy of formation from monoclinic ZrO_2 and CaO at 298.15 K is $-18.3(\pm 4)$ kJ/mol, using thermal functions for CaZrO_3 evaluated by Jacob and Waseda^[4] and those for ZrO_2 and CaO from Pankratz.^[9] The "third-law" enthalpy of formation of CaZrO_3 from monoclinic ZrO_2 and CaO at 298.15 K deduced from the results of Tanabe and Nagata^[1] shows a systematic draft of ~ 2 kJ/mol with the temperature of free energy measurement. The mean value is $-31.5(\pm 3)$ kJ/mol. The standard entropy of CaZrO_3 , calculated from the low temperature heat capacity measurements of King and Weller^[10] is used in the third-law evaluation. The large difference (13.4 kJ/mol) between the second-law and third-law values points to small but significant temperature-dependent systematic errors in the measurements of Tanabe and Nagata.^[1]

Jacob and Waseda^[4] have recently measured the standard Gibbs energy of formation of CaZrO_3 from monoclinic ZrO_2 and CaO with rock salt structure using a solid-state cell based on single-crystal CaF_2 as the electrolyte in the temperature range 950 to 1225 K. The second-law and third-law enthalpies of formation deduced from these meas-

urements are $-32.6(\pm 4)$ and $-30.4(\pm 3)$ kJ/mol, respectively, at 298.15 K. The two values agree within their error limits. The values also compare favorably with calorimetric data; $-30.5(\pm 4)$ kJ/mol of L'vova and Fedosev,^[11] $-31.4(\pm 4)$ kJ/mol of Korneev *et al.*,^[12] and $-34.2(\pm 4)$ kJ/mol of Muromachi and Navrotsky.^[13] The calorimetric value of $-40.8(\pm 1)$ suggested by Brown and Bennington^[14] is ~ 8 kJ/mol more negative than the average value of three other calorimetric determinations.^[11,12,13] The recent work of Jacob and Waseda was not cited in the article of Tanabe and Nagata.^[1]

Figure 1 compares the extrapolated results of Jacob and Waseda^[4] for the standard Gibbs energy of formation of CaZrO_3 with values reported by Tanabe and Nagata.^[1] The change in slope at 1478 K corresponds to phase transition from monoclinic to tetragonal ZrO_2 . The enthalpy of transition is 8.075 kJ/mol.^[9] Below the transition temperature standard state for ZrO_2 is the monoclinic form, and above 1478 K standard state is the tetragonal form. There is good agreement between the two sets of data^[1,4] at 1572 K, but the results diverge with increasing temperature. Since the cell designs in the two studies are almost identical, based on the model design of Allibert *et al.*,^[2] the source of this discrepancy probably arises from different chemistry at the electrolyte/electrode interfaces. Nevertheless, the maximum difference at the highest temperature of measurement is only ~ 2 kJ/mol. The overall agreement between the two studies is reasonable.

Reasonable values for the free energy of formation of CaZrO_3 obtained by Tanabe and Nagata^[1] may be construed as evidence for the correct functioning of the solid-state cell based on $\text{Ca}_4\text{P}_2\text{O}_9$ as the electrolyte. A scrutiny of the phase diagram for the system $\text{CaO-P}_2\text{O}_5$ ^[15] indicates that $\text{Ca}_4\text{P}_2\text{O}_9$ is stable in contact with pure CaO used as a reference electrode. However, if the activity of CaO falls below a critical value, $\text{Ca}_4\text{P}_2\text{O}_9$ will decompose to $\text{Ca}_3\text{P}_2\text{O}_8$ ($3\text{CaO}\cdot\text{P}_2\text{O}_5$). The value of the critical activity can be calculated from the standard free energies of formation of the two phosphates. The standard free energy change for the reaction



obtained from three sources^[16-19] is plotted as a function of temperature in Figure 2. The results are reasonably concordant. At a temperature of 1700 K, $\text{Ca}_4\text{P}_2\text{O}_9$ becomes unstable when the activity of CaO is less than 0.53 (± 0.06). The activities of CaO measured by Tanabe and Nagata^[1] fall below this value. A thin layer of $\text{Ca}_3\text{P}_2\text{O}_8$ is therefore expected to have formed at the interface between $\text{Ca}_4\text{P}_2\text{O}_9$ and the working electrodes during the high-temperature exposure. The large time lapse recorded by Tanabe and Nagata^[1] before obtaining the first stable electromotive force is indicative of the formation of $\text{Ca}_3\text{P}_2\text{O}_8$ during the incubation period. It is often difficult to identify thin layers of product phases by conventional X-ray diffraction analysis of electrode pellets. More sophisticated techniques such as cross-sectional transmission electron microscopy and microprobe analysis are required for identifying thin layers at the interface.

Despite the formation of a new phase, the cells employed by Tanabe and Nagata^[1] can measure the correct activity of CaO if $\text{Ca}_3\text{P}_2\text{O}_8$ is also an ionic conductor with transference number of Ca^{2+} ion close to unity. The reasonable value for

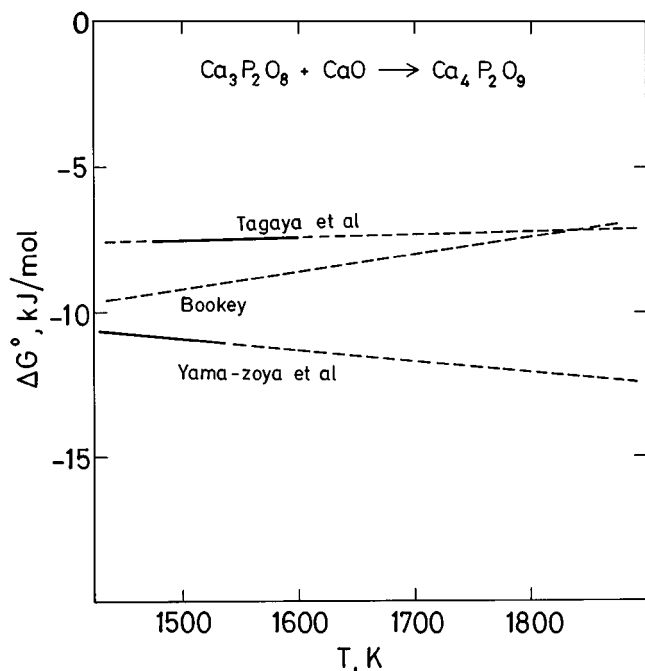


Fig. 2—Variation of the standard free energy of formation of tetracalcium phosphate from tricalcium phosphate and calcium oxide with temperature—comparison of data from three laboratories.^[16–19]

free energy of formation of CaZrO_3 obtained by Tanabe and Nagata suggests that this is indeed the case. However, the transport properties of $\text{Ca}_3\text{P}_2\text{O}_8$ need to be established by independent measurements before cells based on the $\text{Ca}_4\text{P}_2\text{O}_9/\text{Ca}_3\text{P}_2\text{O}_8$ couple can be validated for the measurement of the activity of CaO over a wide range.

As the activity of CaO is lowered further at the measuring electrode, $\text{Ca}_3\text{P}_2\text{O}_8$ will in turn decompose to other phosphates ($\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}_7\text{P}_{10}\text{O}_{32}$, CaP_2O_6 , $\text{Ca}_2\text{P}_6\text{O}_{17}$, and $\text{CaP}_4\text{O}_{11}$).^[15] The critical activity of CaO for the decomposition of $\text{Ca}_3\text{P}_2\text{O}_8$ to $\text{Ca}_2\text{P}_2\text{O}_7$ at 1700 K evaluated from the thermodynamic data^[20] is 9.6×10^{-5} . Unfortunately, accurate values for the free energies of formation of the other phosphates are not available for estimating their thermodynamic stability ranges. Even when these calcium-deficient phosphates form, correct results for activity of CaO can be obtained if the phosphates are ionic conductors. As discussed by Jacob *et al.*,^[21] thermodynamic stability and transport properties of phases in the microsystem near the electrolyte/electrode interface can impose constraints on the design of galvanic cells. The melting points of the phosphates also decrease with depletion of CaO .

In summary, further research is needed on transport properties of other calcium phosphates, especially $\text{Ca}_3\text{P}_2\text{O}_8$, in order to specify the range of activity of CaO that be measured using $\text{Ca}_4\text{P}_2\text{O}_9/\text{Ca}_3\text{P}_2\text{O}_8$ bielectrolyte combination. The behavior of the cell based on $\text{Ca}_4\text{P}_2\text{O}_9$ is more complex than that outlined by Tanabe and Nagata.^[1]

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Prediction on Thermodynamic Properties of Ternary Molten Salts from Wilson Equation

DONG-PING TAO and XIAN-WAN YANG

To make up for a shortcoming of classical thermodynamics, many empirical or semiempirical models based on the theory of regular solutions have been developed for predicting the thermodynamic properties of ternary and even multicomponent systems. A common characteristic among them is to be much more empirical, namely, if only binary data are used to predict the thermodynamic properties of a ternary system, the deviations of predicted values will be larger; and if it is desirable for the values to match the required accuracy, a portion of experimental data of a ternary system has to be employed in the fitting computation.

DONG-PING TAO, Associate Professor and Director of Metallurgical Principles Laboratory, and XIAN-WAN YANG, Professor, Chairman of the Academic Committee and Former President of the University are with the Department of Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, People's Republic of China.
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