A new method for determining excess Gibbs energies in binary metal-carbonate solid solutions

W.H. Casey

P.A. Rock
M.M. McBeath
E.M. Walling
J. Chung

Department of Land, Air and Water Resources and the Department of Geology
Department of Chemistry
Department of Land, Air and Water Resources
Department of Chemistry
Department of Land, Air and Water Resources
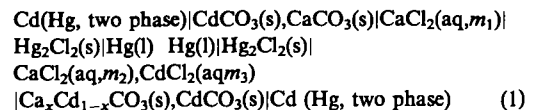*University of California, Davis, CA 95616, USA.*

The thermodynamic properties of carbonate solid-solution minerals can be determined more accurately using a new electrochemical cell than by conventional approaches. Our electrode involves a metal (e.g., Cd°) in contact with a slightly soluble salt of the metal (e.g., $CdCO_3$) and provides a measure of the activity of a dissolved salt with a common anion and a cation that is not directly electroactive (e.g., $CaCO_3(s)$). In some cases, two complete, interconnected, series-opposed, electrochemical cells are employed. These cells are a significant advance over conventional solubility measurements because: (i) reversibility can be determined quickly and unambiguously, (ii) they have higher sensitivity and precision than solubility experiments; and (iii) the cell measurements can be interpreted without appeal to complicated models of the solute speciation. The cells have been used to determine Gibbs energies of $Ca_xCd_{1-x}CO_3(s)$, $Ca_xSr_{1-x}CO_3(s)$, and $Ca_xMn_{1-x}CO_3(s)$ solids and work is underway on minerals in the $Ca_xMg_{1-x}CO_3(s)$ system.
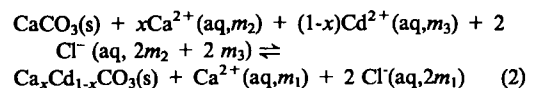
Introduction

The thermodynamic properties of carbonate solid-solutions, are difficult to study because secondary phases precipitate during a typical solubility experiment. Solubilities have been estimated by extrapolating transient concentration data (e.g., Plummer and Mackenzie, 1974) or by conducting the experiments in the presence of solutes that retard rates of precipitation (e.g., Busenberg and Plummer, 1989). Both methods have been criticized as inaccurate (see discussion in Mucci and Morse, 1990) but are widely used for lack of superior alternatives. Only in a few cases have these problems been approached electrochemically (e.g., Königsberger and Gamsjäger, 1990).

Experimental methods

We designed metal-carbonate electrodes of the third kind that avoid some of these difficulties. Our electrode involves a metal (e.g., Cd°) in contact with a slightly soluble salt of the metal (e.g., $CdCO_3(s)$) and provides a measure of the activity of a dissolved salt with a common anion and a cation that is not directly electroactive (e.g., $CaCO_3(s)$). The apparatus is referred to as a double cell when two complete, interconnected, electrochemical cells are employed in series opposition. A potential is generated in one cell by equilibrium with pure $CaCO_3(s)$ while the other contains a solid solution (e.g., $Ca_xCd_{1-x}CO_3(s)$). For example, a cell suitable for studying the $Ca_xCd_{1-x}CO_3(s)$ system is:

Cd(Hg, two phase)|CdCO₃(s),CaCO₃(s)|CaCl₂(aq,m_1)|
Hg₂Cl₂(s)|Hg(l) Hg(l)|Hg₂Cl₂(s)|
CaCl₂(aq,m_2),CdCl₂(aqm_3)
|Ca$_x$Cd$_{1-x}$CO₃(s),CdCO₃(s)|Cd (Hg, two phase)   (1)

The sum of the electrode reactions yields the equation for the net cell reaction:

$CaCO_3(s) + xCa^{2+}(aq,m_2) + (1-x)Cd^{2+}(aq,m_3) + 2$
$\quad Cl^-$ (aq, $2m_2 + 2m_3$) $\rightleftharpoons$
$Ca_xCd_{1-x}CO_3(s) + Ca^{2+}(aq,m_1) + 2$ Cl⁻(aq,$2m_1$)   (2)

Introduction of the Nernst equation and mean ionic activity coefficients yields:

$$E = E^0(x) - \frac{RT}{2F}\ln\left[\frac{4m_1^3\gamma_{\pm(CaCl_2,m_1)}^3}{m_2^x m_3^{1-x}(2m_2 + 2m_3)^2 \gamma_{\pm(CaCl_2,m_2)}^{3x}\gamma_{\pm(CdCl_2,m_3)}^{3(1-x)}}\right]$$

Measurement of E at known molalities (m_1, m_2 and m_3), together with values of the mean ionic activity coefficients, gives $E^0(x)$ for the cell reaction:
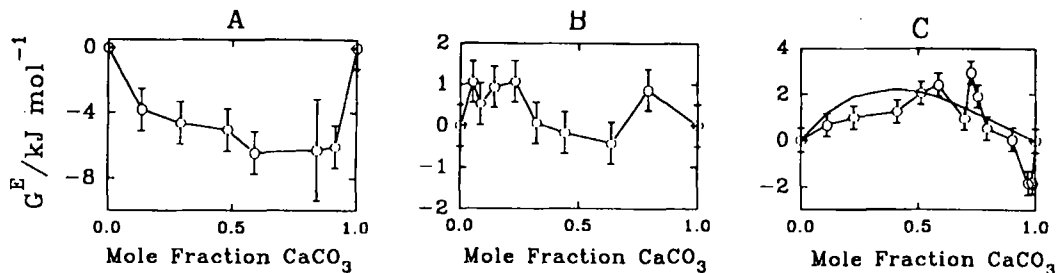
$CaCO_3(s) + (1-x) Cd^{2+}(aq) \rightleftharpoons$
$\quad Ca_xCd_{1-x}CO_3(s) + (1-x) Ca^{2+}(aq)$ (4)
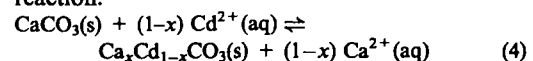
FIG 1: Measured G^E values with mineral composition for three solid solutions. A: $Ca_xCd_{1-x}CO_s$ (from Rock *et al.*, in press); B: $Ca_xMn_{1-x}CO_3$ (McBeath *et al.*, in prep.); and C: $Ca_xSr_{1-x}CO_3$ (Casey *et al.*, submitted). The line through C corresponds to the G^E values recommended Plummer and Busenberg (1987).

from which $\Delta G^0_f[Ca_xCd_{1-x}CO_3(s)]$ can be calculated. Similar cells can be constructed for studying other solid-solution minerals.

Results and discussion

Excess Gibbs energies for mixing (G^E) in three binary carbonate systems are shown in Fig. 1. In the $Ca_xCd_{1-x}CO_3(s)$ system, the G^E values are consistently less than zero for $0.0 < x < 1.0$, indicating that the solid solutions are stable relative to a mechanical mixture of the end-member components. Conversely, solids in the $Ca_xMn_{1-x}CO_3(s)$ system are stable only in the region $0.25 < x < 0.75$ (Fig. 1B). In the $Ca_xSr_{1-x}CO_3(s)$ system (Fig. 1C), G^E values are positive for the compositional range $0.0 < x < 0.85$, indicating that these solid solutions are unstable relative to a mechanical mixture of the end-member compositions. Although such compositions can be synthesized, they spontaneously unmix with time. Evidence that the cell reactions are reversible includes demonstration of Nernstian response to changes in electrolyte composition, and an absence of significant hysteresis in cell current-voltage and current-temperature (10–35°C) plots. These results are strong evidence that the cell method is achieving a metastable equilibrium state over the time course of the electrochemical measurements.

Summary

This electrochemical method provides a direct measure of the desired thermodynamic data, as opposed to techniques that obtain similar data from small differences between large numbers. The precision of the measured cell voltages for reversible double cells is in the range of ± 0.05 to 0.50 mV, which makes the method sufficiently sensitive to detect small changes in the Gibbs energies. In addition, calculation of the Gibbs energies does not require a model for speciation of solutes in complex mixtures, there is also no correction for a liquid-liquid junction potential, and the reversibility of the cell reaction can be established.

References

Casey, W. H., Rock, P. A., Chung, J-B, Walling E. M., and M. M. McBeath (submitted) *Geochim. Cosmochim. Acta.*

Königsberger, E. and Gamsjäger, H. (1990) *Mar. Chem.*, **30**, 317–27.

McBeath, M. M., Rock, P. A., Casey, W. H. (in prep.) *Geochim. Cosmochim. Acta.*

Mucci, A. and Morse, J. W. (1990) *Aquatic Sciences*, **3**, 217–54.

Plummer, L. N. and Mackenzie, F. T. (1974) *Amer. J. Sci.*, **274**, 61–83.

Plummer, L. N. and Busenberg, E. (1987) *Geochim. Cosmochim. Acta*, **51**, 1393–411.

Plummer, L. N. and Busenberg, E. (1989) *Geochim. Cosmochim. Acta*, **53**, 1189–208.

Rock, P. A., Casey, W. H., McBeath, M. M. and Walling, E. M. (1994) *Geochim. Cosmochim. Acta* (submitted).