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Activities of $MnCO_3$ in Disordered Solid-Solutions of the System $CaCO_3-MnCO_3$¹)

Aktivitäten von $MnCO_3$ in fehlgeordneten festen Lösungen des Systems $CaCO_3-MnCO_3$

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With Figures

Abstract

Phase equilibria work by Goldsmith and Graf (1957) and Capobianco and Navrotsky (1987) provides evidences that the mixing behaviour in the system $CaCO_3-MnCO_3$ can be approximated by an asymmetric mixing energy model for the disordered solid solutions outside the range of long-range and short-range order.

The activity coefficients of the component $MnCO_3$ as function of temperature and composition is given by the following equation:

$$\log \gamma^{1,T}_{MnCO_3} = X^2_{CaCO_3}\left[\left(\frac{955.15}{T} - 0.3939\right) - \left(\frac{2172.2}{T} - 2.256\right)(1 - X_{CaCO_3})\right](T \text{ in } {}^\circ K)$$

Decreasing excess energies with increase in temperature are indicated and positive excess entropies at least in the range of 570 to 860 °C. This fact may point to absence of short-range order in those solid solutions. Binodal and spinodal exsolution relations, metastable with respect to short-range order and to phase relations with ordered phases of kutnahorite composition, have been calculated by extrapolation to lower temperatures. The position of this solvus is compatible with relations shown by de Capitani and Peters (1981).

Zusammenfassung

Die Untersuchungen des Phasengleichgewichtes durch Goldsmith und Graf (1957) und Capobianco und Navrotsky (1987) zeigten, daß das Mischungsverhalten im System $CaCO_3-MnCO_3$ durch ein asymmetrisches Mischungsenergiemodell für fehlgeordnete feste Lösungen außerhalb der kurz- und weitreichenden Ordnung beschrieben werden kann.

Die Aktivitätskoeffizienten der $MnCO_3$-Komponente werden als Funktion der Temperatur und der Zusammensetzung durch folgende Gleichung gegeben:

$$\log \gamma^{1,T}_{MnCO_3} = X^2_{CaCO_3}\left[\left(\frac{955.15}{T} - 0.3939\right) - \left(\frac{2172.2}{T} - 2.256\right)(1 - X_{CaCO_3})\right](T \text{ in } {}^\circ K)$$

Eine Erniedrigung der Excessenergie bei Temperaturerhöhung wird beobachtet sowie eine positive Excessentropie zumindest in dem Bereich zwischen 570 °C und 860 °C. Dies spricht für das Fehlen einer Kurzbereich-Ordnung in diesen festen Lösungen. Die bimodalen und spinodalen Entmischungsverhältnisse, die im Hinblick auf die Kurzbereich-Ordnung und die Phasenbeziehungen zu den geordneten Phasen mit Kutnahoritzusammensetzung metastabil sind, werden durch Extrapolation zu niederen Temperaturen berechnet. Der Verlauf dieser Solvuskurve ist vergleichbar mit Ergebnissen, die von CAPITANI und PETERS (1981) angegeben werden. Im Gegensatz zu Interpretationen von CAPOBIANCO und NAVROTSKY (1987) muß angenommen werden, daß die Excessenergien bei höheren Temperaturen kleiner werden und die Aktivitäten der Komponenten sich den Konzentrationen annähern, d. h. $\gamma \rightarrow 1.0$.

Introduction

The join $CaCO_3-MnCO_3$ is of considerable importance and a key to study the mixing behaviour, and to deduce mixing relations in similar rhombohedral carbonate systems. The occurrence of the ordered phase kutnahorite in this system is restricted to quite low temperatures (GOLDSMITH 1983) and this fact permits an investigation of the mixing behaviour without interference of longrange order and its influence on the energetic properties of the solid solutions. New experimental work by CAPOBIANCO and NAVROTSKY (1987) stimulated this communication and it will be shown belaow that the phase equilibria studies of GOLDSMITH and GRAF (1957) and the model of mixing energy by SCHULTZ-GÜTTLER (1986) lead to results partly compatible and partly different from conclusions of the new experimental work.

The phase equilibria study of GOLDSMITH and GRAF (1957) investigated reversibly the compositional changes of the three phase assemblage (Ca, Mn) CO_3, MnO and CO_2 over a large temperature interval (570–860 °C) with CO_2 pressures from 80 to 2000 bars. The large body of P–T and X (0.02 to 0.73 molefraction) is sufficient to draw conclusions about the mixing relations and to calculate the activities of $MnCO_3$ in solid solutions of (Ca, Mn) CO_3. On the other hand, the large range of temperatures, pressures and compositions employed in the experimental work will level out discrepancies in the determined activities due to errors in readings of temperature, pressure, composition, and due to kinetic factors and influences of crystal defects on the energies of the particular solid solution (SALJE 1986).

Thermodynamic Relations

The activities of $MnCO_3$ in the solid solutions may be derived from the experimental data of the three phase assemblages by a comparison of the fugacity of CO_2 under the particular run conditions with the fugacity of CO_2 for the pure phase equilibria $MnCO_3 \leftrightarrow MnO + CO_2$ at the same condition of temperature referenced to a standard state of total pressure.

All data points as given by GOLDSMITH and GRAF (1957) have been therefore recalculated to the standard state of 1 bar pressure and T for the solids by the following equation:

$$(1) \quad \log f_{CO_2}^{1\,\mathrm{bar},\,T} = \log f_{CO_2}^{P,T} + \Delta V_{\mathrm{solid}} (P - 1)/2.302\ RT$$

Equation (1) is derived from the general equation (2)

$$(2) \quad RT \ln f_{CO_2}^{P,T} = \Delta S^0_{\mathrm{reaction}} - \Delta H^0_{\mathrm{reaction}} - \Delta V_{\mathrm{solids}} (P - 1)$$

assuming enthalpy, entropy and volume change of the solids to be independent of T and P and that the excess volume of mixing is negligible. The reference fugacities of CO_2 for the endmember reaction $MnCO_3 = MnO + CO_2$ as function of temperature have been calculated from bracketing run and volume data given by Goldsmith and Graf (1957) and Huebner (1969) with fugacity coefficients for CO_2 tabulated by Perchuk (1977):

(3) $\log f_{CO_2}^{1\,\text{bar},\,T} = 8.88833 - 5759.927/T$ (T in °K)

The correlation coefficient of equation (3) is better than 0.9998, and the use of Perchuks fugacity coefficients for CO_2 indicates constancy of enthalpy and entropy of reaction over the whole P–T range.

The experimental activities are evaluated in this paper by calculating the fugacity of CO_2 under the particular P, T, X_{MnCO_3}– conditions (Goldsmith and Graf 1957), reduced to the standard state, and by subtracting the value of equation (3) for the given temperature. This is represented by equation

(4) $\log a_{MnCO_3}^{1\,\text{bar},\,T}$ (ss) $= (\log P\,\gamma_{CO_2}^{P,T} - 0.0944\,(P - 1)/T) - (8.88833 - 5759.927/T)$
(P bars, T °K)

Equation (4) uses only the particular values of pressure and temperature of the run data for the solid solutions and the fugacity coefficients of CO_2.

Therefore, errors in activities arise mainly due to inaccuracies in temperature, pressure, fugacity coefficients of CO_2 as well as calculated f_{CO_2} for pure $MnCO_3$ decomposition at the temperature of the activity measurements.

If precise thermodynamic data for all phases over the whole temperature range would be available, the reference fugacities at 1 bar and T could be calculated. The use of entropy data for $MnCO_3$, measured on natural material by Robie et al. (1984), to recalculate the decomposition curve of $MnCO_3$, synthetic material as used by Goldsmith and Graf (1957), showed discrepancies with bracketed runs. Errors up to 7% in recalculated fugacities and consequently pressures have been found.

For this reason, the least squares regression given by equation (3) will be used as reference fugacity.

In this way, the calculated CO_2 pressures are compatible with the equilibrium pressures of the endmember reaction for $MnCO_3$ and also with the pressure data for the three phase assemblages used to calculate activities since furthermore the same synthetic starting material has been used by Goldsmith and Graf (1957). The entropy measurements of Robie et al. (1984) have been made with natural material and there may be some slight difference in the physical properties of this material compared with the synthetic reagent grade rhodochrosite used by Goldsmith and Graf (1957). Furthermore, all entropy values above 550 °K are extrapolated. The systematic decrease of ΔH_{298} with increase in temperature (1 kJ from 830 to 1050 °K) may be related to this extrapolation.

The problem of fugacity coefficients of CO_2 has been dealt with by Kerrick and Jacobs (1981) and Bottinga and Richet (1981), and the results of the different adaptions of the P–V–T data to various equations of state give differences up to 10% absolute. A comparison of data given by Bottinga and Richet (1981), Shmonov and Shmulovich (1975), Kerrick and Jacobs (1981), Kramer (1963), Perchuk (1977) and Majudar and Roy (1956) shows the highest fugacity coefficients of CO_2 under given P–T conditions for the letter three investigations. The smallest values are given by Bottinga and Richet (1981). Since most adaptions are based on measurements by Kennedy (1954), and the P–V–T data for CO_2 of Greenwood (1969) reproduce these quite well over a similar temperature, but more restricted pressure range, it is felt, that the fugacity coefficients of PERCHUK (1977), MAJUDAR and ROY (1956) and KRAMER (1963) may be quite reasonable to use in the lower pressure range where experimental data overlap with data from KENNEDY (1954) for CO_2.

Activity calculations for solid solutions of carbonates may be influenced by the precision of the variation of the activity coefficient of CO_2 with temperature and pressure of the various adaptions cited above, and this will introduce an additional source of error by comparing results of different authors.

It is estimated that the calculated activities of carbonates may be accurate to about 10% relative, considering the sources of errors.

Since the data for the three phase assemblages of GOLDSMITH and GRAF (1957) are not isothermal, but isobaric measurements, the calculation of the interaction parameter for any mixing model is not as straightforward as shown, for instance, by CAPOBIANCO and NAVROTSKY (1987).

A selection of reversed compositional data have been plotted, therefore, a function of temperature at constant pressures of 82.8, 200.1 and 1028.1 bars, and the equilibrium temperatures at mole fractions of 0.05, 0.1, 0.15, 0.2, 0.3, 0.4 and 0.5 of $MnCO_3$ have been interpolated. This compositional interval is quite well covered with data, and interpolations are precise. With this set of P–T data at constant compositions a series of equations of $\log f_{CO_2}$ as a function of the inverse of temperature could be calculated in the same way as done for the reaction $MnCO_3 = MnO + CO_2$ (equation 3).

Since all data thus calculated refer to a standard state of 1 bar, the differences in slope of the curves at constant composition from the slope of the endmember reaction gives directly the excess partial enthalpy of $MnCO_3$ in the solid solutions.

The differences concerning the intercept are likewise related to the partial entropies and partial excess entropies of $MnCO_3$ in the solid solutions.

The activities of $MnCO_3$ are given by the difference of the values at specific temperatures and compositions, and the activity coefficients are derived by division by composition. A least squares fit of the activity coefficients of $MnCO_3$ to the asymmetric mixing model of THOMPSON (1967) over the compositional range from 0 to 50 mole% $MnCO_3$ showed high correlation coefficients (>0.97) and makes it very likely that the remaining compositional interval of high $MnCO_3$ contents, plagued by backward reactions as stated by GOLDSMITH and GRAF (1957), can be described as well by this model.

The equation for the activity coefficients of $MnCO_3$ as function of composition and temperature thus derived is given by equation

$$(5)\quad \log \gamma^{1\,\mathrm{bar},T}_{MnCO_3} = X^2_{CaCO_3}\left[\left(\frac{955.15}{T} - 0.3939\right) - \left(\frac{2172.2}{T} - 2.256\right)(1 - X_{CaCO_3})\right]$$

and the activities may be calculated by equation.

$$(6)\quad \log a^{1\,\mathrm{bar},T}_{MnCO_3} = \log \gamma^{1\,\mathrm{bar},T}_{MnCO_3} + \log X_{MnCO_3}$$

The use of the GIBBS-DUHEM relation and equation (6) permits the evaluation of the interaction parameters as a function of temperature. The excess mixing energy of the system $CaCO_3-MnCO_3$ is given by equation

$$(7)\quad \Delta G^{exc.} = X_{CaCO_3}X_{MnCO_3} - [(4370.4 - 1.807\ T)\ X_{CaCO_3} + (9339.8 - 6.965\ T)\ X_{MnCO_3}]\ (\mathrm{cal.,\ {}^\circ K,\ mole})$$

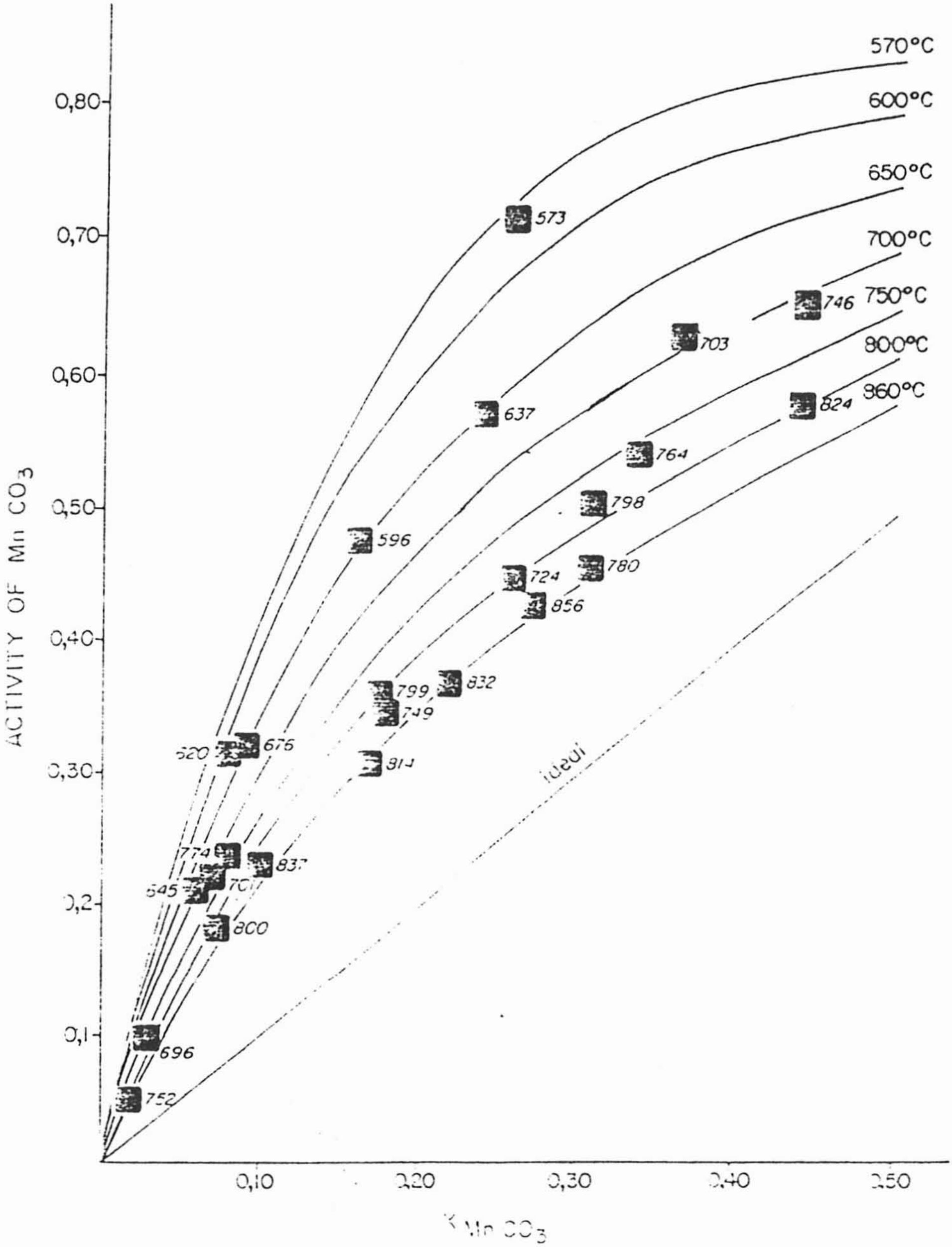

Fig. 1. Activities of $MnCO_3$ in solid solutions of (Ca, Mn) CO_3 as calculated from phase-equilibria data by GOLDSMITH and GRAF (1957). Size of symbols indicates ± 1 mole% and ± 0.01 absolute in activity.

Note decreasing activities with increase in temperature.

The excess mixing energy decreases with increasing temperature, and the values of the interaction parameter are comparable with data given by de Capitani and Peters (1981). These autors used a physical interpretation of the interaction parameter and calculated about 1.4 kcal/mole and 1.1 cal/mole K as excess enthalpy and excess entropy for the equimolar composition of the disordered solid solution. The corresponding values from equation (7) are 1.7 kcal/mole and 1.1 cal/mole K.

Figure (1) shows the experimental activities (equation 4) from all data points given by Goldsmith and Graf (1957), including the ones not used for fitting (14 points). Solid lines are calculated by equations (5) and (6) for temperatures from 570 to 860 °C. One notes in this figure that at constant composition activities are decreasing with increase in temperature over the compositional range.

The activities calculated from data given by Capobianco and Navrotsky (1987) compare reasonable well with the data shown in Fig. (1), but it may be mentioned that their values at intermediate compositions (X_{MnCO_3} between 0.4 and 0.7) are generally higher by about 5 to 8 %, relative. This may be the result of using a different set of activity coefficients for CO_2 than used in this work, or it may be related to some differences in the physical state of the samples used. In the compositional range cited, the solubilities of $MnCO_3$ are generally about 5 to 7 mole% lower than determined by Goldsmith and Graf (1957). The correspondance at $X_{MnCO_3} = 0.851$ is better than 2% relative.

Discussion

If the heat treated material of Capobianco and Navrotsky (1987) corresponds more to perfect physical state of the carbonate, equation (5) will give minimum values.

One can conclude, therefore, that the asymmetric mixing model approximates quite well the experimental data. Deviations of about 5 to 10% relative may be easily explained by sources of errors already discussed. At low X_{MnCO_3} in the range 0.01 to 0.1, slight changes in composition of almost not more then 0.3 to 0.9 mole% in $MnCO_3$ of the solid solutions reduces the error to zero. This is the case for the compositions of 2 mole% (Goldsmith and Graf 1957) with an error of over 45% relative. Using a composition of 1.7 mole% gives perfect agreement with the base line. Using a composition of 0.03 instead of 0.035 (Capobianco and Navrotsky 1987) reduces the error of −10% to zero. Since accuracies of better than 1 mole% can seldom be obtained by X-ray diffraction methods used in the works of both authors, errors in this compositional interval are to be considered as not significant.

Deviations at higher mole fractions may be explained by incomplete reactions as evidenced by some very short runs, cited by Goldsmith and Graf (1957).

The fact of decreasing activities with increase in temperature indicates decreasing excess energies with temperature, at least in the range 570 to 860 °C. At constant excess enthalpy in the system this means positive excess entropy due to mixing, as also given by equation (7). The system $CaCO_3-MnCO_3$ behaves apparently normal with respect to a disordered solid solution at temperatures above the influence of long range order. Furthermore, it appears that no short range order exists in these solid solutions, already a few tens degree above the miscibility gap (Goldsmith and Graf 1957).

These results are in contradiction to conclusions derived by Capobianco and Navrotsky (1987). They claim an increase of excess energy with temperature by

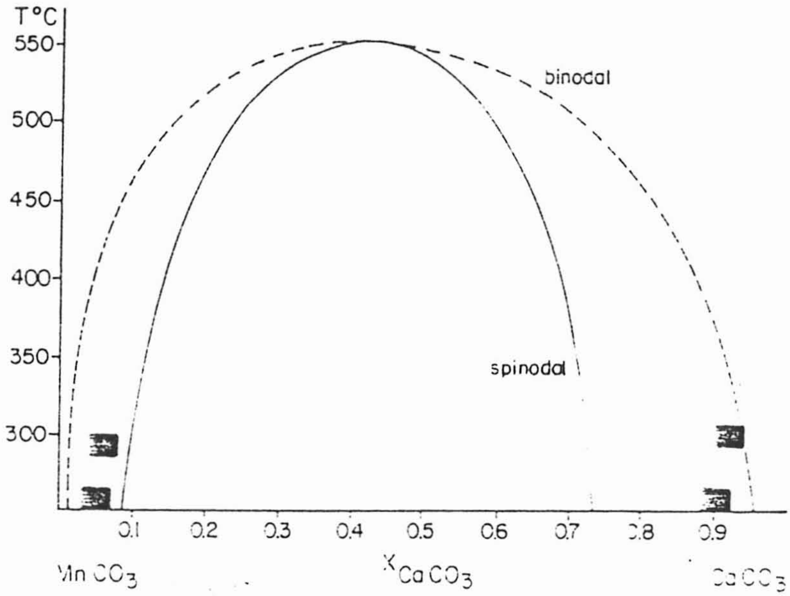

Fig. 2. Metastable binodal and spinodal relations in the system $CaCO_3-MnCO_3$ for disordered solid solutions (SCHULTZ-GÜTTLER 1986). Short- and long-range order will affect strongly the position of this metastable miscibility gap. Data from FRANKE and HOFER (1986) at 295 °C and 250 °C are shown. Very flat slopes in $\delta\Delta G^{Mix}/\delta x$ at the calcic part may explain metastable results (lack of driving force to exsolve).

combining their phase equilibria work at 700 °C with low temperature precipitation work by BOYNTON (1971). But, the formation of metastable solid solutions at low temperature in regions of miscibility gaps is well known in the system $CaCO_3-MgCO_3$ (SCHULTZ-GÜTTLER 1986, GOLDSMITH 1983, MACKENZIE et al. 1983) and $CaCO_3-MnCO_3$ (GOLDSMITH and GRAF 1957, FRANKE and HOFER 1986). Unfortunately, no cell constants are given by BOYNTON (1971) to estimate any possible short range order in those samples.

Short range order in samples used by CAPOBIANCO and NAVROTSKY (1987) for calorimetric work may be an explanation for the sigmoidal shape of the excess enthalpy of mixing as determined by them. The mixing model as given by equation (7) however indicates positive excess enthalpy and entropy over the whole composition range. These values will be reduced by short range order or long range order.

In the absence of those, it is possible to extrapolate the data to lower temperatures. In that case, the system shows a metastable (with respect to long- and short-range order) solvus as shown in Figure (2), and calculated by using equation (7). Some experimental data which may be of importance with respect to the solvus for the disordered case have been given by FRANKE and HOFER (1986). The compositions of the coexisting phases at 295 and 250 °C are plotted in Fig. (2). It is clear that much caution has to be taken, but the pairs of compositions agree satisfactorly with the calculated compositions.

To complete the binodal relations shown, the spinodal has been calculated and displayed. These binodal and spinodal relations are strongly affected by long and short range order as discussed for the similar system $CaCO_3-MgCO_3$ by SCHULTZ-GÜTTLER (1986).

It is interesting to note that the compositions of all published natural occurrences of coexisting pairs of Mn-calcites/kutnahorites and Ca-rich rhodochrosites/kutnahorites displayed by PEACOR et al. (1987) are enclosed by the calculated solvus for disordered solid solutions in the system $CaCO_3-MnCO_3$ shown in Fig. (2). The non-stoichiometric compositions of the kutnahorites may indicate a relativ low degree of long-range order in those phases, and the solubilities of Ca in rhodochrosite or Mn in calcite may be near the equilibrium values for the disordered case.

It appears the from this study of existing phase equilibrium work which includes constraints from natural occurences and lower temperature hydrothermal experiments, that the mixing behaviour of the system $CaCO_3-MnCO_3$ can well be approximated by an asymmetrical mixing model outside the range of short and long range order.

This fact may be of considerable importance to deduce mixing models for other rhombohedral carbonatic systems where the high temperature of disorder of the dolomite-type phase makes it difficult to calculate the activities for the disordered case over larger P−T−X ranges.

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