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RETRIEVAL OF THERMODYNAMIC PROPERTIES OF $M(OH)_2$ (M = Mn, Ni AND Cd) PHASES FROM HYDROTHERMAL PHASE EQUILIBRIA OF MO—H_2O SYSTEMS

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The standard thermodynamic properties of $M(OH)_2$ (M = Mn, Ni and Cd) solid phases have been retrieved using a graphical approach based on the already reported P *vs.* T curves obtained from hydrothermal studies of MO—H_2O systems. This approach avoids the use of heat capacity effects. The values retrieved by this modified approach are in good agreement with the calorimetric values.

Several approaches have been suggested in the recent past [1–8] for the estimation of thermodynamic properties of geochemically important mineral reactions simulated in the laboratory by a hydrothermal technique. However, most of the thermodynamic data on mineral phases are derived from direct calorimetric measurements, and an exhaustive compilation of the data has been presented by Robie and Waldbaum [9]. Of late, a hydrothermal crystal growth technique has attracted the attention of material researchers for the production of homogeneous materials of high purity required for the desired physicochemical properties. Most of the approaches proposed to estimate the thermodynamic properties depend on the accurate heat capacity data of all the phases involved in the equilibrium reactions. Quite often, however, the heat capacity data of the resulting phases are not reported and they are sometimes not reliable. Moreover, there is a dearth of data on the heat capacity behaviour of various metal oxides, hydroxides and oxyhydroxides over a wide range of temperatures. Therefore, it becomes imperative to evolve suitable methods for estimation of the thermodynamic properties of the various solid phases obtained during the phase equilibria studies, without recourse to heat capacity effects. The use of the Clapeyron equation to estimate the thermodynamic properties from hydrothermal phase equilibria studies is also

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fraught with limitations, as the volume change of a reaction involving a gas phase is influenced markedly by pressure changes. This marked dependence of the volume change of a reaction on pressure is seen in some dehydration equilibria, where the shape of the dehydration line is strongly curved in the low-pressure regions. Nevertheless, the Clapeyron equation can still be used with reasonable accuracy for systems which involve no gas phase reactions, or those which tend to show a nearly linear relationship over a wide P *vs.* T range.

In the present paper, the authors illustrate a modified graphical approach to retrieve the standard thermodynamic properties of M(OH)$_2$ phases from dehydration equilibria, without recourse to the heat capacity data of the phases involved. This approach is based on the methods proposed by Fisher and Zen [4] and Chatterjee [7].

Experimental results

The reported hydrothermal phase equilibria diagrams for the systems MnO—H$_2$O [10], NiO—H$_2$O [11] and CdO—H$_2$O [12] are reproduced in Figs 1–3. The observed phases, M(OH)$_2$ and MO indicate stability even under relatively low P *vs.* T conditions.

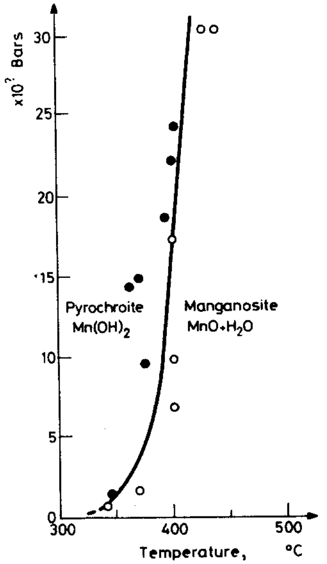

Fig. 1 System MnO—H$_2$O (C. Klingsberg and R. Roy [10])

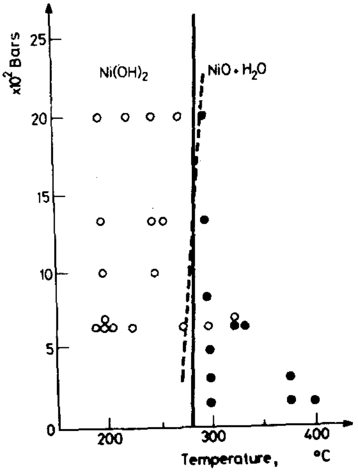

Fig. 2 System NiO—H_2O (Micheal A. Aia [11])

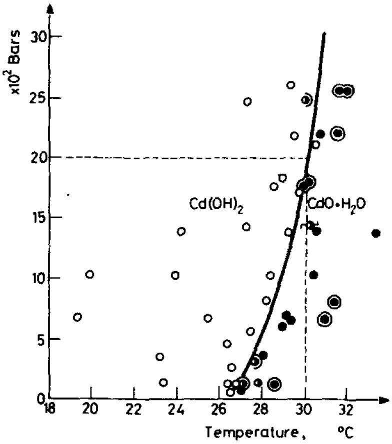

Fig. 3 System CdO—H_2O (L. S. Dentglasser and R. Roy [12])

Thermodynamic relations

General considerations: Various approaches employed to extract standard thermodynamic data from hydrothermal phase equilibria studies differ only in their rearrangement and the choice of standard states, although these approaches lead to internally consistent results. The approach suggested by Fisher and Zen [4], involving the vapour phase in the retrieval equations, will be considered for the present purpose.

The dehydration reaction in the $M(OH)_2$ systems can be represented as

$$M(OH)_2 \rightarrow MO + H_2O \tag{1}$$

If P_e and T_e represent the equilibrium pressure and temperature on a univariant curve, the fundamental equation for the condition of equilibrium is

$$\Delta G_{r(Te,Pe)} = \Delta G_{f,s(Te,Pe)} + \Delta G_{f,H_2O(Te,Pe)} = 0 \tag{2}$$

where $\Delta G_{r(Te,Pe)}$ is the Gibbs free energy of the reaction at T_e and P_e, while $\Delta G_{f,s}$ is the free energy of formation for the solids only and is equal to $\Delta G_{f,MO} - \Delta G_{f,M(OH)_2}$. The free energy change in any closed system, homogeneous or heterogeneous, is

$$\Delta G = V\,dP - S\,dT.$$

Introducing standard free energies for one mole of each phase:

$$\begin{gathered}\Delta G^0_{f,s} + \Delta G^0_{f,H_2O} - \int_{298}^{T_e} \Delta S_{f,r(T_e,P_e)}^{(T)dT} + \\ + \int_{1}^{P_e} \Delta V_{f,r}(P)\,dP = 0\end{gathered} \tag{3}$$

where subscripts r refer to dehydration equilibria as a whole. Further, the entropy and volume changes of the reaction can be identified as

$$\Delta S_{f,r}(T) = \Delta S_{f,s}(T) + \Delta S_{f,H_2O}(T)$$

$$\Delta V_{f,r}(T) = \Delta V_{f,s}(P) + \Delta V_{f,H_2O}(P)$$

Defining

$$\Delta S_{f,s} = S_{f,MO} - S_{f,M(OH)_2} + S_{f,H_2} + \tfrac{1}{2} S_{f,O_2}$$

and $\Delta V_{f,s} = V_{f,MO} - V_{f,M(OH)_2}$, and substituting these results into Eq. (3), we get

$$\begin{gathered}\Delta G^0_{f,s} + \Delta G^0_{f,H_2O} - \int_{298}^{T_e} \Delta S_{f,s}(T)\,dT - \int_{298}^{T_e} S_{f,H_2O}(T)\,dT \\ + \int_{1}^{P_e} \Delta V_s(P)\,dP + \int_{1}^{P_e} V_{H_2O}(P)\,dP = 0\end{gathered} \tag{4}$$

The evaluation of integrals involving H_2O in the above equation has been simplified by Fisher and Zen [4] through the incorporation of a free energy function $G^*_{H_2O(Te,Pe)}$.

If the volume change of the solid phases ΔV_s is considered to be independent of pressure, then the volume integral of the solid phases can be approximated to $(P_e - 1)\,\Delta V_s$. Thus, Eq. (4) simplifies to

$$\Delta G^0_{f,s} - \int_{298}^{T_e} \Delta S_{f,s}(T)\,dT + (P_e - 1)\,\Delta V_s + G^*_{H_2O(Te,Pe)} = 0 \tag{5}$$

However, the use of Eq. (5) for every point-by-point retrieval requires a prior knowledge of the heat capacity changes of the solid phases over the range of experimental temperatures. Since $\Delta S_{f,s}$ is a slowly varying function of temperature in most dehydration reactions, it is recommended by many [8] to replace the entropy integral in Eq. (5) by $\Delta S_{f,s}(T-298)$, where T is the experimental temperature in degrees Kelvin. Thus, neglecting the heat capacity effects, Chatterjee [7] has suggested a graphical method for the estimation of $\Delta H^0_{f,s}$ and $\Delta S^0_{f,s}$, which makes use of the following approximation:

$$\Delta G^0_{f,s} - \int_{298}^{T_e} \Delta S_{f,s}(T)\,\mathrm{d}T = \Delta G^0_{f,s(T_e)} \simeq \Delta H^0_{f,s} - T_e \Delta S_{f,s}$$

Introducing this in Eq. (5), we get

$$\Delta H^0_{f,s} - T_e \Delta S_{f,s} + (P_e - 1)\Delta V_s + G^*_{H_2O(T_e,P_e)} = 0$$

Note that $\Delta H^0_{f,s}$ and $\Delta S_{f,s}$ correspond to 298 K and 1 bar. The above equation can be arranged as

$$(P_e - 1)\Delta V_s + G^*_{H_2O(T_e,P_e)} = T_e \Delta S_{f,s} - \Delta H^0_{f,s} \tag{6}$$

Equation (6) suggests that straight line behaviour should be observed when the left-hand side is plotted against temperature, and the intercept should yield $-\Delta H^0_{f,s}$, while the slope should correspond to $\Delta S_{f,s}$.

Retrieval exercise for the CdO—H_2O system as an illustration

Equation (6) has been successfully employed [8] to retrieve the standard thermodynamic properties of the following mineral reaction:

$$\text{pyrophyllite} = \text{andalusite} + 3\,\text{quartz} + H_2O$$

However, only a few isobaric reversal brackets have been used in this retrieval exercise.

If every point on the well-behaved P *vs.* T curve of a dehydration reaction is considered to represent true equilibrium values of pressure and temperature, then Eq. (6) should give a straight line passing through all such points. Conversely, if the use of Eq. (6) results in a well-defined straight line with the satisfactory retrieval of standard thermodynamic properties of any one of the solid phases, then this should be compelling evidence of the reliability of the experimental P *vs.* T curve. This argument is demonstrated in the NiO—H_2O system, where the true equilibrium boundary is indicated with dotted lines (Fig. 2). The values so retrieved along this P *vs.* T line are in better agreement with the reported values than those obtained from the reported [11] curve.

For the reaction $Cd(OH)_2 = CdO + H_2O$:

$$\Delta V_s = V_{CdO} - V_{Cd(OH)_2} = -14.981 \text{ cm}^3$$

The molar volumes of CdO and $Cd(OH)_2$ are taken from the tables [9, 13] and the quantity $(P_e - 1)\Delta V_s$ is calculated from the experimental P *vs.* T curve reported by Glasser and Roy [12]. The function $G^*_{H_2O(T_e, P_3)}$ is obtained from the tables provided by Fisher and Zen [4] by interpolating to the required P *vs.* T values. When plotted against the experimental temperatures, the results yield a straight line with a slope of 189.54 J deg^{-1} mol^{-1} and an intercept of -302.71 kJ mol^{-1}. The enthalpy ($\Delta H_{f,s}$) and entropy ($\Delta S_{f,s}$) values retrieved in this way are used to calculate the standard heat of formation and entropy of formation of the hydroxide phase, i.e. $Cd(OH)_2$. The same procedure is adopted to retrieve the standard values of other hydroxide phases, namely $Ni(OH)_2$ and $Mn(OH)_2$. The plots of $G^*_{H_2O} + \Delta V_s(P_e - 1)$ vs. equilibrium temperatures (T_e) are shown in Figs 4–6, for the MnO—H_2O, NiO—H_2O and CdO—H_2O systems, respectively. All the relevant data are presented in Table 1.

Estimation of ΔG^0_f for $Cd(OH)_2$

Rearranging Eq. (5) for the reaction $Cd(OH)_2 = CdO + H_2O$, we obtain

$$\Delta G^0_{f,Cd(OH)_2} = \Delta G^0_{f,CdO} - \Delta S_{f,s}\Delta T + (P_e - 1)\Delta V + G^*_{H_2O(T_e, P_e)} \qquad (7)$$

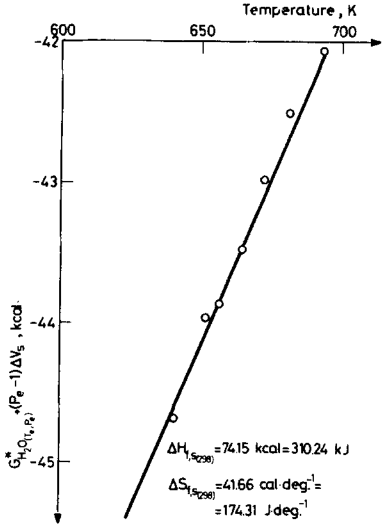

Fig. 4 Retrieved thermodynamic properties for $Mn(OH)_2$ from the reported [10] Mn(OH), system

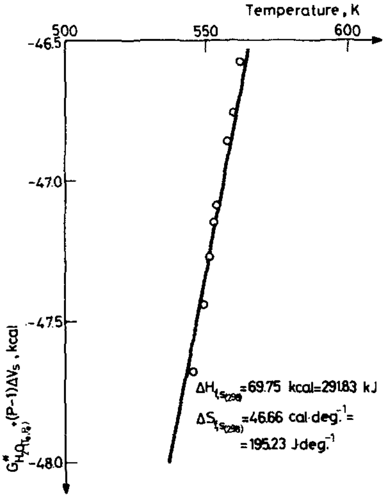

Fig. 5 Retrieved thermodynamic properties for $Ni(OH)_2$ from the reported [11] $Ni(OH)_2$ system

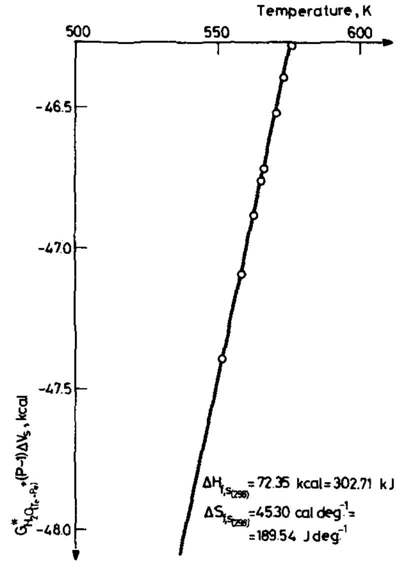

Fig. 6 Retrieved thermodynamic properties for $Cd(OH)_2$ from the reported [12] $CdO—H_2O$ system

Considering 2 kbar and 300° as the true equilibrium pressure and temperature, as confirmed from the retrieval exercise, then $\Delta P = 1.999$ kbar and $\Delta T = 275$ K. Interpolation from the Fisher and Zen [4] tables gives $G^*_{H_2O(T_e,P_e)} = -192.205$ kJ (kcal converted into kJ). Further, substituting $\Delta S_{f,s} = 189.54$ J deg^{-1} mol^{-1} (as

Table 1 Comparison of retrieved standard thermodynamic properties of $M(OH)_2$ phases with those reported from calorimetric studies

Solid phase	Retrieved data	Reported data	Reference
$Mn(OH)_2$	ΔH^0_f kJ mol^{-1} -695.38	-693.71	[13]
	ΔG^0_f kJ mol^{-1} -608.14	-610.45	[13]
		-614.46	[14]
		-602.08	[14]
	S^0_f J deg^{-1} mol^{-1} 115.81	101.67	[14]
		94.14	[14]
		88.28	[13]
$Ni(OH)_2$	ΔH^0_f kJ mol^{-1} -531.58	-529.69	[13]
	ΔG^0_f kJ mol^{-1} -458.44	-447.27	[13]
		-445.85	[14]
	S^0_f J deg^{-1} mol^{-1} 73.18	87.86	[13]
		56.48	[14]
$Cd(OH)_2$	ΔH^0_f kJ mol^{-1} -560.87	-560.66	[13]
	ΔG^0_f kJ mol^{-1} -475.80	-473.63	[13]
		-471.75	[14]
		-474.30	[14]
		-472.75	[14]
	S^0_f J deg^{-1} mol^{-1} 95.69	96.23	[13]
		99.16	[14]
		89.96	[14]

obtained from our retrieval exercise) and taking $\Delta G^0_{f,\mathrm{CdO}} = -228.45$ kJ mol^{-1} from the reported data [13], Eq. (7) gives the standard free energy of formation of $Cd(OH)_2$ as -475.805 kJ mol^{-1}. A similar exercise is repeated to calculate the standard free energies of formation of other hydroxide phases, and the data are given in Table 1.

The enthalpy of dehydration of $Cd(OH)_2$ is also measured by DTA in order to make a comparison with the retrieved values. $Cd(OH)_2$ decomposes at ~230° and the measured enthalpy is 31.63 kJ mol^{-1}. The calculated enthalpy at ~230° obtained by incorporating the reported C_p values of CdO, H_2O [9] and $Cd(OH)_2$ [14] into Kirchoff's equation, is 26.44 kJ mol^{-1}. This observed discrepancy of 5.19 kJ mol^{-1} could only be attributed to the reported C_p value of $Cd(OH)_2$.

Conclusion

From the retrieval exercise, it is evident that whenever accurate hydrothermal data are available on an equilibrium involving well-defined phases, even with minimum thermochemical data it is possible to calculate the standard thermodynamic properties of one or more solid phases with accuracies comparable to those of calorimetric data. The simplicity of the approach is that it makes no reference to the heat capacity effects.

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Zusammenfassung — Basierend auf unlängst beschriebenen, aus hydrothermischen Untersuchungen von $MO—H_2O$ Systemen gewonnenen $p-T$ Kurven wurden mittels einer graphischen Näherung die thermodynamischen Standardeigenschaften von $M(OH)_2$ Festphasen (M = Mn, Ni und Cd) bestimmt. Dieses Verfahren umgeht den Gebrauch von Wärmekapazitätseffekten. Die durch dieses modifizierte Verfahren erhaltenen Werte stehen in guter Übereinstimmung mit den kalorimetrischen Werten.

Резюме — На основе графической зависимости давление-температура, полученной при гидротермическом изучении систем $MO—H_2O$, исправлены стандартные термодинамические характеристики твердых гидроокисей $M(OH)_2$, где M = марганец, никель и кадмий. Такое графическое приближение исключает использование эффектов теплоемкости. Полученные таким методом исправленные значения хорошо согласуются с калориметрическими данными.