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K. M. Allal, J. C. Dolignier, G. Martin. Determination of Thermodynamical Data of Calcium Hydroxichloride. Revue de l'Institut Français du Pétrole, 1997, 52 (3), pp.361-368. 10.2516/ogst:1997046 . hal-02079115

TECHNICAL NOTE

DETERMINATION OF THERMODYNAMICAL DATA OF CALCIUM HYDROXICHLORIDE

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DÉTERMINATION DES DONNÉES THERMODYNAMIQUES DE L'HYDROXYCHLORURE DE CALCIUM

La réaction de l'acide chlorhydrique avec des adsorbants alcalins tels que la chaux au niveau de stations d'incinération entraîne la formation de chlorure ainsi que de l'hydroxychlorure de calcium. Une étude thermodynamique des différentes réactions mises en jeu dans le procédé de déchloruration serait nécessaire, afin de montrer qu'un tel produit serait théoriquement susceptible d'être formé. Cependant, les données thermodynamiques de CaClOH permettant de mener à bien une telle étude ne sont pas disponibles dans la littérature. Par conséquent, une méthode permettant de prédire ces données a été développée dans ce présent travail. Des valeurs d'énergie de Gibbs et d'entropie de formation de CaClOH prédites par cette méthode à différentes températures ont été comparées à celles déterminées à l'aide du modèle de Mostafa, et des résultats satisfaisants ont été obtenus.

DETERMINATION OF THERMODYNAMICAL DATA OF CALCIUM HYDROXICHLORIDE

The reaction of hydrochloric acid with dry alkaline sorbents such as hydrated lime in the incineration units leads to the formation of not only calcium chloride but calcium hydroxichloride as well. A thermodynamic study of the chemical reactions involved in the dechlorination process is required in order to show if such a product is theoretically possible to be formed. However, the data of CaClOH necessary to carry out such a study are not available in the literature. Hence, a method of predicting these data is developed in the present work. Predicted values of Gibbs energy and entropy of formation of CaClOH at different temperatures are compared to values calculated by Mostafa's model and satisfactory results were obtained.

DETERMINACIÓN DE LOS DATOS TERMODINÁMICOS DEL HIDROXICLORURO DE CALCIO

La reacción del ácido clorhídrico con adsorbentes alcalinos, como, por ejemplo, la cal, a nivel de las estaciones de incineración provoca la formación de cloruro, así como de hidroxicloruro de calcio. Un estudio termodinámico de las diversas reacciones que intervienen en el procedimiento de descloruración serían necesarias con objeto de demostrar que semejante producto sería susceptible de formación. No obstante, los datos termodinámicos de CaClOH que permitan llevar a buen término semejante estudio no se encuentran disponibles en la literatura. Por consiguiente, se ha desarrollado con motivo del presente trabajo, un método que permite predecir tales datos. Los valores se energía de Gibbs y de entropía de formación de CaClOH predecidos por este método con distintas temperaturas, se han comparado con aquellos determinados mediante el modelo de Mostafa, habiéndose obtenido así resultados satisfactorios.

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INTRODUCTION

It is nowadays frequent to use incineration processes as an alternative to land filling of municipal solid waste. In spite of the obvious advantages such as a significant volume reduction and the energy recovery, such a technology involves aerial releases of acid gases which are very harmful for the environment. Among the most important ones is hydrochloric acid, formed during combustion of PVC. The need for a purification step is therefore compulsory.

A way to reduce the HCl contents in the flue gases is by reaction with dry, fine alkaline sorbents such as calcium hydroxide [1] and [2]. The reaction mechanism of the dechlorination process remains however not fairly well known. As a matter of fact, in some previous works [3, 4, 5], calcium chloride was identified as being the only reaction product formed as shown by reaction 1.

It seems that the reaction mechanism is more complex. Gullet *et al.* [6] were able to identify the presence of other solid phases in the reaction products, in particular calcium hydroxichloride. This compound was in fact detected as soon as 1990 by Kosnyrev [7] when mixing hydrated lime with hydrated calcium chloride. Jozewicz *et al.* [8] have shown afterwards that calcium hydroxide can react with calcium chloride, and have finally proposed the following reaction mechanism:

$$\begin{gathered}Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2\,H_2O\\ \Delta H_f^{298} = -\,25.787 \text{ kcal/mol}\end{gathered} \qquad (1)$$

$$\begin{gathered}Ca(OH)_2 + HCl \rightarrow CaClOH + H_2O\\ \Delta H_f^{298} = -\,17.754 \text{ kcal/mol}\end{gathered} \qquad (2)$$

$$\begin{gathered}Ca(OH)_2 + CaCl_2 \rightarrow 2\,CaClOH\\ \Delta H_f^{298} = -\,9.725 \text{ kcal/mol}\end{gathered} \qquad (3)$$

For a complete representation, the formation of calcium chloride from calcium hydroxichloride is added to the reaction mechanism:

$$\begin{gathered}CaClOH + HCl \rightarrow CaCl_2 + H_2O\\ \Delta H_f^{298} = -\,8.029 \text{ kcal/mol}\end{gathered} \qquad (4)$$

It is therefore important to identify accurately the reaction product because it influences the ratio Ca/Cl, which determines the amount of Ca-based sorbents to be used in the dechlorination process. So a thermodynamic study of the above mentioned reactions is required. The data necessary to carry out such a study are however not available in the literature. In the present work, a method to predict them is therefore proposed. It is important to mention also that all these reactions happen at atmospheric pressure and that all the calcium based substances, namelly, $Ca(OH)_2$, $CaCl_2$ and CaClOH are in a solid state whereas H_2O and HCl are in a gas state. Note that reactions 1 to 4 are not independent and that, for instance, reaction 1 is the sum of reactions 2 and 4.

1 DEVELOPMENT OF THE METHOD

The same approach as Kosnyrev [9], but taking into consideration in the present study the effects of the temperature, is proposed to evaluate the free enthalpy of formation of the earth alkali hydroxichloride compounds and particularly calcium hydroxichloride.

The aim hence is to relate the Gibbs energy of formation to the enthalpy of formation. Values of ΔG_f versus ΔH_f for $MeCl_2$ and $Me(OH)_2$, where Me stands for Be, Mg, Ca, Sr, and Ba, are plotted at different temperatures, and the results are shown in Figures 1 and 2 respectively. It can be seen that a linear relation is obtained in both cases.

$$\Delta G^{T}_{f,MeCl_2} = a_1(T)\Delta H^{T}_{f,MeCl_2} + b_1(T) \qquad (5)$$

$$\Delta G^{T}_{f,Me(OH)_2} = a_2(T)\cdot\Delta H^{T}_{f,Me(OH)_2} + b_2(T) \qquad (6)$$

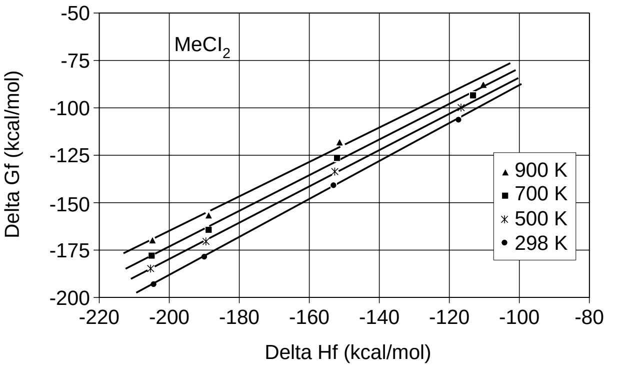

Figure 1

Gibbs energy of formation of $MeCl_2$ compounds as a function of the enthalpy of formation and the temperature.

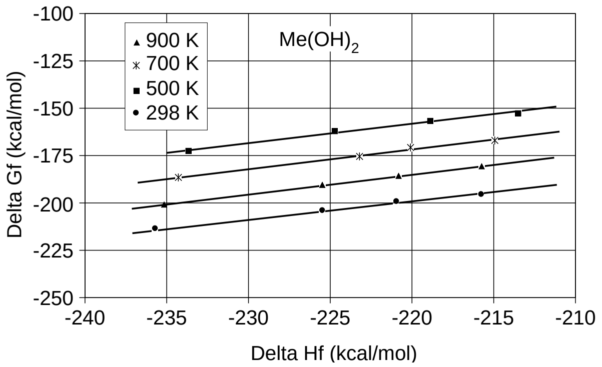

Figure 2

Gibbs energy of formation of $Me(OH)_2$ compounds as a function of the enthalpy of formation and the temperature.

Because the values of the ionic radius of OH-, 0.168 nm [10] and Cl-, 0.181 nm [11] are very close, one can expect a regular variation of the thermodynamic characteristics in the series hydroxide, hydroxichloride and chloride of earth alkali respectively. Since MeClOH is an intermediate compound between $MeCl_2$ and $Me(OH)_2$ (substitution of Cl- by OH-), one can as previously relate ΔG_f to ΔH_f linearly:

$$\Delta G^T_{f,MeClOH} = a(T) \cdot \Delta H^T_{f,MeClOH} + b(T) \qquad (7)$$

where

$$a(T) = \frac{a_1(T) + a_2(T)}{2} \qquad (8)$$

$$b(T) = \frac{b_1(T) + b_2(T)}{2} \qquad (9)$$

and $\Delta H^T_{f,MeClOH}$, the enthalpy of formation of the considered earth alkali hydroxichloride at a given temperature. The values of a and b of the earth alkali hydroxichloride reported in Table 1 have been calculated from equation (8) and (9) respectively.

TABLE 1

Temperature effect on the coefficient a and b

T (K)	a	b (kcal/mol)
298.15	1.010	18.429
400	1.016	25.423
500	1.023	32.323
600	1.036	40.525
700	1.019	42.036
800	0.993	41.932
900	0.975	43.3144
1000	0.935	39.081

2 DISCUSSION

To validate and strengthen this approach, the predicted values of the free enthalpy of formation of magnesium hydroxichloride have been compared to those mentioned in the literature. Table 2 shows that the calculated values are in good agreement with those reported in the Janaf's tables.

TABLE 2

Comparison between the predicted and the literature values of the Gibbs energy as a function of the temperature for MgOHCl

T (K)	$\Delta H_{f.literature}$ (kcal/mol)	$\Delta G_{f.literature}$ (kcal/mol)	$\Delta G_{f.predicted}$ (kcal/mol)
298.15	-191.199	-174.773	-174.68
400	-191.080	-169.313	-168.840
500	-190.868	-163.893	-163.271
600	-190.555	-158.526	-157.563
700	-190.140	-153.219	-152.804
800	-189.623	-147.979	-147.933
900	-189.006	-142.809	-143.114
1000	-190.346	-137.544	-139.691

The determination of the Gibbs energy of formation of calcium hydroxichloride from equation (7) requires the knowledge of the enthalpy of formation. It has been thought that it would be interesting to evaluate it from our own measurements and compare it with the values reported in the literature. So it is necessary to prepare a given amount of this compound in order to carry out these measurements.

2.1 Preparation

A solid mixture containing 80% (mol) $Ca(OH)_2$ and 20% (mol) $CaCl_2{\cdot}2H_2O$ was first prepared and then analysed by X-ray diffraction. Figure 3 shows that the same phases as the ones mentioned in a previous work [8] were detected, namely, calcium hydroxide and calcium hydroxichloride. This result suggests that CaClOH is formed when $Ca(OH)_2$ and $CaCl_2{\cdot}2H_2O$ are contacted according to:

$$Ca(OH)_2 + CaCl_2{\cdot}2H_2O \rightarrow 2\ CaClOH{\cdot}2H_2O \qquad (10)$$

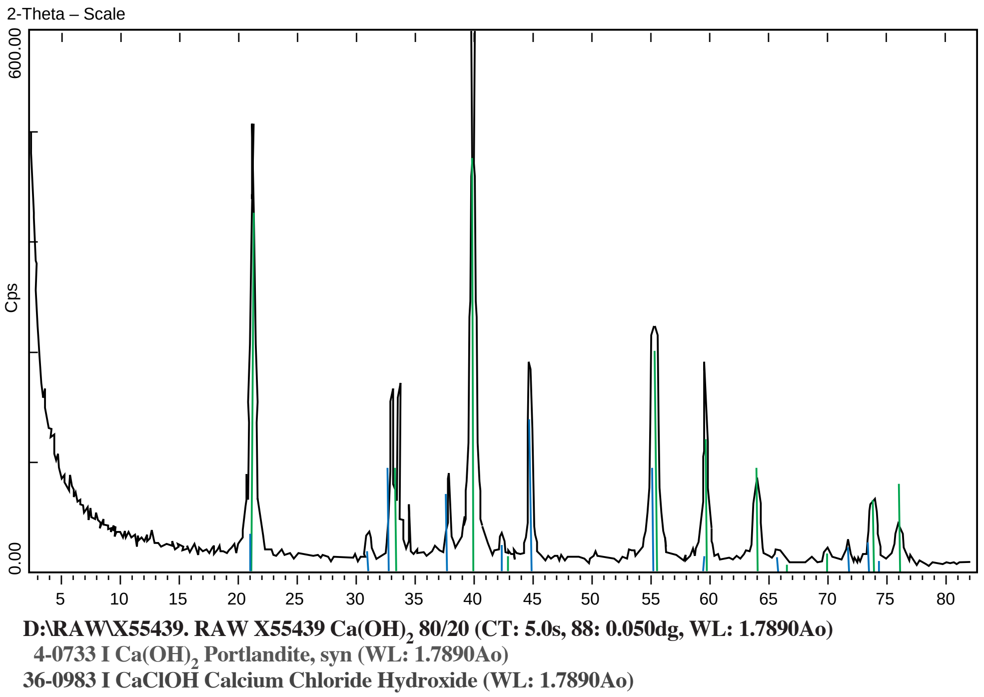

Figure 3

X-ray diffraction spectrum of a 80% $Ca(OH)_2$- 20% $CaCl_2{\cdot}2H_2O$ sample.

2.2 Determination of ΔH_f

A few mg of this physical mixture were analysed afterwards by thermogravimetry (TGA), and the thermogram obtained has shown a series of weight losses, as illustrated in Figure 4.

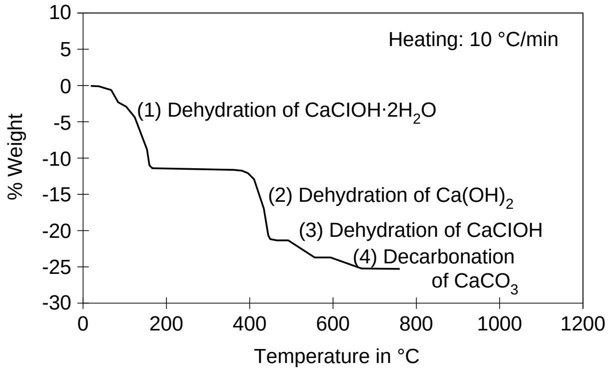

Figure 4

TGA scan thermogram of a sample containing 70% Ca(OH)2 and 30% $CACl_2{\cdot}2H_2O$.

The mass balance suggests that the first weight loss corresponds to the dehydration of the hydrated calcium hydroxichloride according to:

$$2\ CaClOH{\cdot}2H_2O \rightarrow 2\ CaClOH + 2\ H_2 \qquad (11)$$

the second loss, to the dehydration of the remaining $Ca(OH)_2$ according to:

$$Ca(OH)_2 \rightarrow CaO + H_2O \qquad (12)$$

the third, to the dehydration of CaClOH as:

$$2\ CaClOH \rightarrow CaO{\cdot}CaCl_2 + H_2O \qquad (13)$$

and the fourth, to the decarbonation of $CaCO_3$ initially present in the mixture,

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (14)$$

A differential scan calorimetry (DSC) was performed simultaneously to the TGA, and the results are shown in Figure 5.

It can be seen that each of the above mentioned reactions, corresponds an endothermic peak, the area of which is related to the reaction enthalpy. So a graphical integration of the peak corresponding to reaction 13 between 479 and 564°C has given a value of ΔH_R equal to 23.718 kcal/mol. One can therefore deduce the enthalpy of formation of calcium hydroxichloride from the following equation:

$$\Delta H^{T}_{f,CaClOH} = \frac{(\Delta H^{T}_{f,CaO\cdot CaCl2} + \Delta H^{T}_{f,H2O} - \Delta H^{T}_{R})}{2} \qquad (15)$$

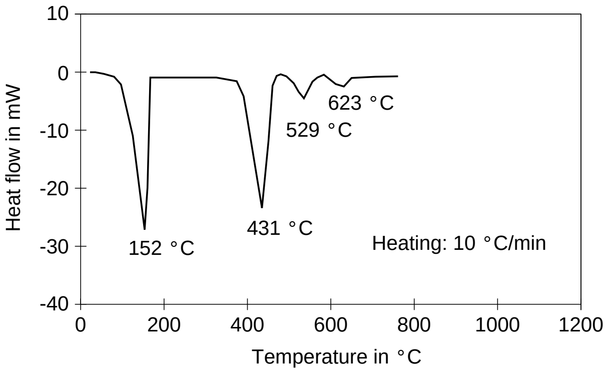

Figure 5

Differential scan calorimetry of a sample containing 70% Ca(OH)2 and 30% $CaCl_2{\cdot}2H_2O$.

A value of $\Delta H_{f,CaClOH}$ equal to – 218.409 kcal/mol has been found. This result agrees fairly well with the literature since a value of – 217.700 kcal/mol was given by Kosnyrev [9].

In addition to this, a sample of $Ca(OH)_2$ exposed to HCl stream in a drop tube furnace was prepared for X-ray diffraction (XRD) analysis. The operating conditions were 250°C reaction temperature and 1000 ppm HCl.

It appears from the XRD spectrum represented in Figure 6, that no calcium chloride is formed since the only phase containing chloride detected, is calcium hydroxichloride. Now that the enthalpy of formation has been evaluated, one can use the proposed method to determine the thermodynamic data of CaClOH.

Table 3 gives these data at different temperatures. It is important to note that the specific heat Cp is given as a function of the temperature by means of Mostafa's model [12], which uses a group contribution technique. It is expressed as:

$$C_p = \sum_j n_j \Delta_{a,j} + \left(\sum_j n_j \Delta_{b,j} \cdot 10^{-3}\right) \cdot T + \left(\sum_j n_j \Delta_{c,j} \cdot 10^{6}\right) \cdot T^{-2} + \left(\sum_j n_j \Delta_{d,j} \cdot 10^{-6}\right) \cdot T^{2} \qquad (16)$$

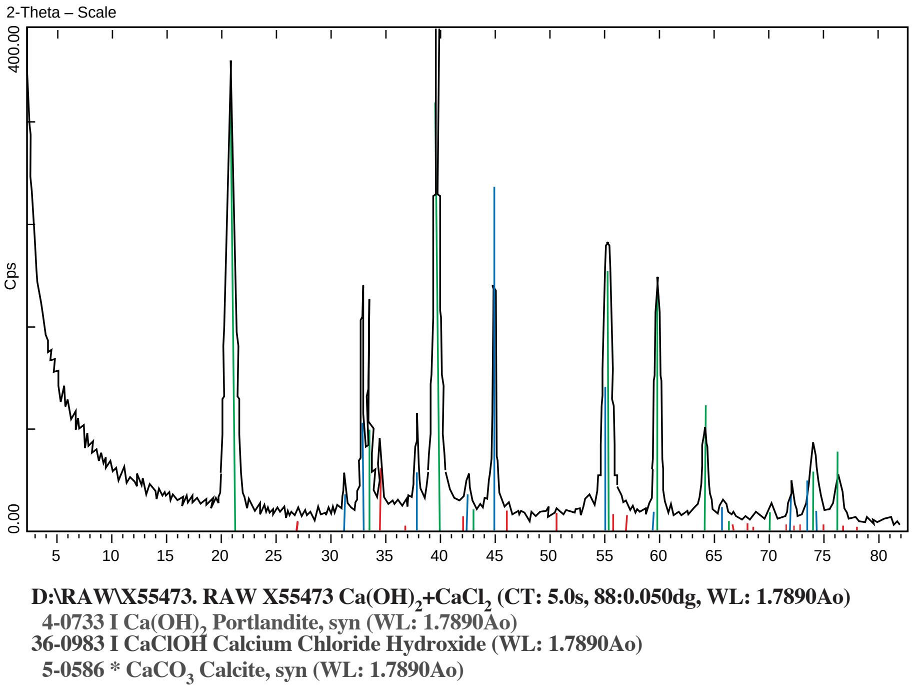

Figure 6

X-ray diffraction spectrum a $Ca(OH)_2$ sample exposed to a HCl gas stream.

TABLE 3

Predicted thermodynamical data of calcium hydroxichloride

T (K)	Cp (cal/mol.K)	ΔH_f (kcal/mol)	ΔG_f (kcal/mol)	ΔS_f (kcal/mol)
298.15	18.240	-217.700	-201.448	-54.509
400	20.186	-214.761	-192.773	-54.967
500	21.523	-215.598	-188.234	-54.708
600	22.641	-215.587	-182.823	-54.606
700	23.656	-215.348	-177.404	-54.206
800	24.619	-215.003	-171.660	-54.180
900	25.552	-214.594	-165.916	-54.088
1000	26.468	-214.317	-161.137	-52.999

where nj is the number of groups of j^{th} type in a single compound, and $\Delta_{i,j}$ the group contribution for i of the j^{th} ionic, atomic or ligand molecule group. Substituting the values of $\Delta_{i,j}$ for CaClOH, given in Table 4, into equation (10) leads to:

$$C_{p,CaClOH} = 18.181 + 8.345.10^{-3}T + 0.216 \cdot 10^{6} T^{-2} + 0.166 \cdot 10^{-6} T^{2} \text{ (cal/mol.K)} \tag{17}$$

TABLE 4

Group contribution involved in equation (17)
for the prediction of the specific heat of calcium hydroxide

Group	nj	Δa,j	Δb,j	Δc,j	Δd,j
Ca++	1	4.897	-1.489	-0.006	-0.770
Cl-	1	6.366	2.482	-0.060	0.157
OH-	1	6.918	7.352	-0.150	0.779

The values of the enthalpy of formation reported in Table 2 are determined from the widely known relation given by (13), expressing the enthapy as a function of the specific heats. In the case of CaClOH formation, the specific heat variation is expressed as:

$$\Delta C_p = C_{p,CaClOH} - C_{p,Ca} - 0.5\left(C_{p,O_2} + C_{p,H_2} + C_{p,Cl_2}\right) \tag{18}$$

The values of the entropy given in Table 2 were deduced when equalizing equation (7) with the following relation:

$$\Delta G_f^T = \Delta H_f^T - T \cdot \Delta S_f^T \tag{19}$$

hence,

$$\Delta S_f^T = \frac{\Delta H_f^T[1 - a(T)] - b(T)}{T} \tag{20}$$

Figure 7 shows a comparison between the values of ΔS_f determined from the proposed model represented by equation (20) and those predicted when substituting equation (18) into the following relation:

$$\Delta S_f^T = \Delta S_f^{298} + \int_{298}^{T} \frac{\Delta C_p}{T} \cdot dT \tag{21}$$

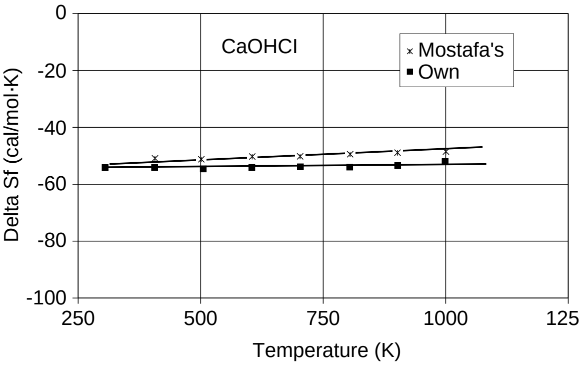

Figure 7

Comparison between predicted values of DS_f versus the temperature.

It can be seen that a fairly good agreement is obtained, particularly at low temperature. Similarly, a comparison between the values of the Gibbs energy estimated by the proposed method (equation (7)) and those determined by the known thermodynamic relation expressing the Gibbs energy as a function of the specific heats and the temperature, are presented in Figure 8. Here too, a good agreement is obtained. Note that the use of Mostafa's model is necessary to determine the value of ΔCp.

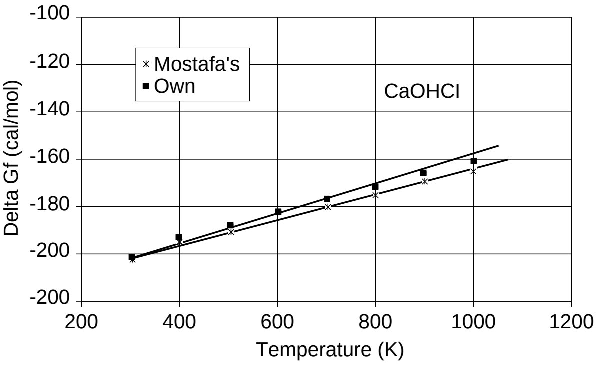

Figure 8

Comparison between predicted values of DG_f versus the temperature.

Now that the thermodynamic data of CaClOH have been evaluated and validated by the above mentioned comparisons, a thermodynamic study of the chemical reactions involved during the dechlorination process could be done.

The effect of temperature on the equilibrium constant K of reactions 1, 2, 3 and 4 is represented in Figure 9. It can be seen first, as far as equilibrium thermodynamics is concerned, that all the reactions involved in the mechanism are possible in the temperature range considered.

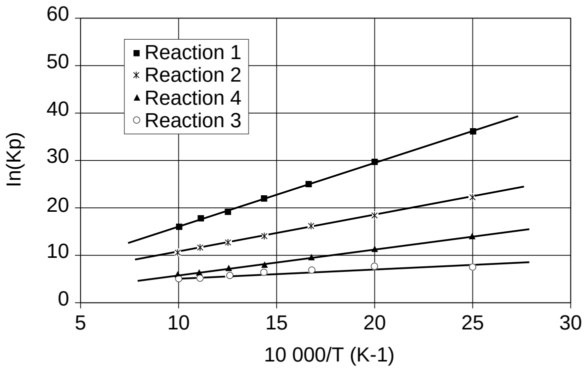

Figure 9

Influence of the temperature on the equilibrum constant.

In addition, a temperature increase leads to a decrease of the equilibrium constant, agreeing therefore with thermodynamic laws since all the considered reactions are exothermic.

The results as presented here give the final equilibrium state of the considered system but no informations about the reaction mechanism. However, the analytical measurements conducted by X-ray diffraction and thermogravimetry seem to indicate that calcium hydroxichloride is actually formed during the dechlorination process according to reactions 2 and 3.

To broaden the range of validity of this proposed method, values of ΔG_f^{298} of other compounds from an other class of elements of the periodic table, for instance the aluminium class, have been calculated.

Table 5 shows, indeed, that the predicted values agree fairly well with the ones mentioned in the literature [14].

TABLE 5

Comparison between the predicted and the literature values of the Gibbs energy of formation of other compounds at 298 K

Compounds	ΔG (literature) (kcal/mol)	ΔG (predicted) (kcal/mol)	% error
AlOOH	-210.59	-214.39	1.80
AlOCl	-175.58	-168.65	3.94
BOOH	-176.37	-173.29	1.75
BOCl	-152.54	-149.75	1.83

CONCLUSION

A method of evaluating the thermodynamical data of the earth alkali hydroxichlorides and in particular CaClOH has been developed in the present work. The predicted values of ΔG_f and ΔS_f have shown to be in good agreement with those either evaluated by other technics or mentioned in the literature. The thermodynamical study of the reactions involved as well as the experimental analysis indicate that, calcium hydroxichloride could be formed during the dechlorination process, and that the formation of calcium chloride seems to be subsequent to the total conversion of calcium hydroxide into calcium hydroxichloride.

NOMENCLATURE

a	coefficient in the linear relation for the prediction of ΔG_f of MeClOH
a_1	coefficient in the linear relation for the prediction of ΔG_f of $MeCl_2$
a_2	coefficient in the linear relation for the prediction of ΔG_f of $Me(OH)_2$
b	coefficient in the linear relation for the prediction of ΔG_f of MeClOH in kcal/mol
b_1	coefficient in the linear relation for the prediction of ΔG_f of $MeCl_2$ in kcal/mol
b_2	coefficient in the linear relation for the prediction of ΔG_f of Me(OH) in kcal/mol
Cp	specific heat in cal/(mol·K)
nj	number of groups of the jth type in a single compound being predicted
T	absolute temperature in K

$\Delta a,j$	group contribution for a of the j^{th} ionic, atomic, or ligand molecule group in cal/(mol·K)
$\Delta b,j$	group contribution for b of the j^{th} ionic, atomic, or ligand molecule group in cal/((mol.(K)$_2$)
$\Delta c,j$	group contribution for c of the j^{th} ionic, atomic, or ligand molecule group in cal.K/mol
$\Delta d,j$	group contribution for d of the jth ionic, atomic, or ligand molecule group in cal/(mol.(K)$_3$)
ΔG_f	free enthalpy of formation in kcal/mol
ΔH_f	free enthalpy of formation in kcal/mol
ΔH_R	reaction enthalpy in kcal/mol
ΔS_f	entropy of formation in cal/(mol·K).

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Final manuscript received in March 1997