HEATS OF DECOMPOSITION AND EQUILIBRIUM DISSOCIATION PRESSURES OF THE MAGNESIAN AND CALCAREOUS COMPOUNDS IN DESULFURIZATION TECHNOLOGIES

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In processes for flue gas cleanup, several magnesian and calcareous compounds occur either as parent sorbent materials or as reaction products. Very simple predictive expressions are proposed for estimating the decomposition heats and dissociation pressures of hydroxide, carbonate, sulfite and sulfate of magnesium and calcium at different temperatures. The developed relationships are based on the thermochemical data and experimental results taken from the literature.

Dry sorption of sulfur dioxide on a variety sorbents is a viable alternative for desulfurization of flue gas generated by combustion of the fossil fuels. From the standpoint of overall process economy, magnesian and calcareous compounds are cheap materials that can also be used in nonregenerative technologies for flue gas cleanup[1]. Whereas sulfations of calcium oxide and magnesium oxide in flue gas are simple reactions at temperatures as high as 700 – 950 °C (refs[2 – 4]), such reactions are little understood when the sorption takes place at temperatures below 600 °C (refs[5,6]). The first principles of chemical thermodynamics provide a sound basis for considerations of the occurring reactions at various temperatures and how far they will proceed in reaching equilibrium.

This brief note is a sequel to a recent study of ours[7] on the thermal stability of some magnesian and calcareous compounds. The previous work[7] also reports results of the thermogravimetric analyses (TGA) for common magnesian and calcareous materials. This paper is aimed at providing simple predictive relationships which can easily be employed in the engineering considerations and calculations.

Dissociation Reactions

Magnesium and calcium hydroxides, carbonates, sulfites and sulfates dissociate by heating according to the reactions

$$M(OH)_2\,(s) \;=\; MO\,(s) + H_2O\,(g) \qquad (A)$$

$$MCO_3\,(s) \;=\; MO\,(s) + CO_2\,(g) \qquad (B)$$

$$MSO_3\,(s) \;=\; MO\,(s) + SO_2\,(g) \qquad (C)$$

$$MSO_4\,(s) \;=\; MO\,(s) + SO_2\,(g) + 1/2\,O_2\,(g)\,, \qquad (D)$$

where M denotes magnesium or calcium.

It should be noted that the disproportionation reactions usually accompanying the thermal decomposition of sulfites are not assumed in this work. Since low pressures are considered in this study, the assumption of ideal gas behaviour of all gaseous components is quite feasible. Further details on the description of chemical equilibria of the reactions (*A*) – (*D*) can be found in previous work[7].

Heats of Decomposition

The standard changes of enthalpy of the reactions (*A*) – (*D*) are usually expressed as functions of temperature by the series

$$\Delta H^0(T) \;=\; aT + bT^2 + cT^3 + dT^{-1} + eT\,. \qquad (1)$$

The values of the coefficients in Eq. (*1*) deduced from the tabulated thermochemical data (ref.[7]) are summarized in Table I. The range of temperatures given in this table follows from that of the C_P-data employed. The values of the dissociation heats of the individual compounds at 25 °C are also summarized in Table I.

It has been found that the five-constant relationship (*1*) can be approximated by a simple quadratic equation

$$\Delta\overline{H}^0(T) \;=\; k_1 + k_2T + k_3T^2\,. \qquad (2)$$

The constants for Eq. (*2*) were sought in a temperature range of interest so as to minimize the sum of squared errors, Q_1, defined by

$$Q_1 \;=\; \sum_{j=1}^{n} (\Delta H_j^0 - \Delta\overline{H}_j^0)^2\,, \qquad (3)$$

where ΔH^0 and $\Delta\overline{H}^0$ are the predictions of Eqs (*1*) and (*2*), respectively. The number of data points, n, was n = 100 and these points were equally spaced in the temperature range of interest. The resulting coefficients k_1, k_2 and k_3 for the respective compounds are given in Table II. Quality of the fit is documented using the standard deviation, s_1, as a statistical measure

$$s_1 = (Q_1/n)^{1/2} . \qquad (4)$$

As can be seen from Tables I and II, the three-constant equation (*2*) approximates the predictions of Eq. (*1*) very well.

TABLE I
Coefficients in the correlation $\Delta H^0(T) = aT + bT^2 + cT^3 + dT^{-1} + e$ for different compounds

Compound	a	$b \,.\, 10^3$	$c \,.\, 10^6$	$d \,.\, 10^{-5}$	e	ΔT^a K	ΔH^0_{298} kJ mol^{-1}
$Mg(OH)_2$	29.22	-47.23	0.0	6.196	74 471	550	81.06
$Ca(OH)_2$	-10.59	7.913	0.0	-6.531	113 930	750	109.28
$MgCO_3$	8.834	-20.72	0.0	-2.680	117 790	750	117.68
$CaCO_3$	-11.56	-4.187	0.0	-23.95	189 780	1 200	177.93
$MgSO_3$	14.82	-26.71	6.607	7.586	141 773	850	146.54
$CaSO_3$	28.68	-30.29	0.0	-0.0335	217 897	1 200	223.74
$MgSO_4$	23.29	-36.35	6.607	5.242	374 098	1 200	379.74
$CaSO_4$	37.15	-39.93	0.0	-2.378	493 850	1 370	500.57

[a] Temperature range from 298 K to K.

TABLE II
Coefficients in the approximate relationship $\Delta\overline{H}^0(T) = k_1 + k_2T + k_3T^2$ for different compounds

Compound	k_1	k_2	k_3	s_1 kJ mol^{-1}	$\Delta\overline{H}^0_{298}$ kJ mol^{-1}
$Mg(OH)_2$	78.656	20.1456	-0.0408949	0.0162	81.03
$Ca(OH)_2$	110 055	-3.41558	0.00373356	0.0338	109.37
$MgCO_3$	116 199	11.7808	-0.0224375	0.0140	117.72
$CaCO_3$	177 660	6.64289	-0.0124821	0.2310	178.53
$MgSO_3$	147 478	-0.288724	-0.00995425	0.0176	146.51
$CaSO_3$	217 881	28.7012	-0.0302981	0.0009	223.74
$MgSO_4$	379 411	7.21205	-0.0183272	0.1293	379.93
$CaSO_4$	492 890	38.1909	-0.0402536	0.0419	500.70

Equilibrium Pressures of Gaseous Components

The dissociation of hydroxides, carbonates and sulfites is given by the equilibrium pressures, P, of water vapour, carbon dioxide and sulfur dioxide, respectively, as follows from the reactions (*A*) – (*C*), (see ref.[7]). Since sulfur dioxide and oxygen evolve in reactions (*D*), the dissociation equilibrium of sulfates is given by the term $P_{SO_2} P_{O_2}^{1/2}$. The equilibrium dissociation pressures of hydroxides, carbonates and sulfites can be described as functions of temperature by the relationship[7]

$$\ln P = A \ln T + BT + CT^{-2} + DT^2 + ET^{-1} + F . \tag{5}$$

In case of sulfates, the term $\ln (P_{SO_2} P_{O_2}^{1/2})$ occurs on the left-hand side of Eq. (5) instead of $\ln P$.

The numerical coefficients in Eq. (5) were evaluated from the tabulated thermochemical data and from the experimental findings[7]. Their values are summarized in Table III for the respective magnesium and calcareous compounds. In order to avoid tedious manipulating with such lengthy relationships, the predictions of Eq. (5) were approximated by the much simpler equation

$$\ln \overline{P} = (-K_1/T) + K_2 . \tag{6}$$

The constants K_1 and K_2 for Eq. (*6*) were chosen, similarly as for Eq. (*2*), so as to minimize the sum of squared errors, Q_2, introduced as

$$Q_2 = \sum_{j=1}^{n} (\ln P_j - \ln \overline{P}_j)^2 , \tag{7}$$

TABLE III
Coefficients in the correlations $\ln P(T) = A \ln T + BT + CT^{-2} + DT^2 + ET^{-1} + F$ for hydroxides, carbonates and sulfites and $\ln (P_{SO_2} P_{O_2}^{1/2}) = A \ln T + BT + CT^{-2} + DT^2 + ET^{-1} + F$ for sulfates

Compound	A	$B \cdot 10^3$	$C \cdot 10^{-5}$	$D \cdot 10^6$	E	F	t_{decomp}, °C
$Mg(OH)_2$	3.514	-5.680	-0.3726	0.0	-8 957	-0.2103	360
$Ca(OH)_2$	-1.274	0.9517	0.3928	0.0	-13 703	29.1768	540
$MgCO_3$	1.062	-2.492	0.1612	0.0	-14 167	18.2457	480
$CaCO_3$	-1.390	-0.5036	1.440	0.0	-22 825	34.4161	898
$MgSO_3$	1.782	-3.212	-0.4562	0.3973	-17 051	15.3292	570
$CaSO_3$	3.449	-3.643	0.00201	0.0	-26 207	5.4955	980
$MgSO_4$	2.801	-4.372	-0.3152	0.3973	-44 994	23.0057	1 135
$CaSO_4$	4.468	-4.802	0.1430	0.0	-59 397	12.3054	1 650

where P_j and $\overline{P}_j$ are the predictions of Eqs (*5*) and (*6*), respectively. Symbol *n* denotes the number of data points equally spaced in a temperature range of interest. Similarly as in the case of Eq. (*3*), the number of data points was $n = 100$. The resulting constants and the standard deviations

$$s_2 = (Q_2/n)^{1/2} \tag{8}$$

are given for the respective reactions in Table IV. The agreement between Eqs (*5*) and (*6*) is good excepting calcium sulfate for which Eq. (*5*) should be preferred.

A useful parameter related to the thermal stability of a compound, which is capable of evolving the gaseous product/products, is the decomposition temperature. It is defined as a temperature at which the pressure of the released gas/gases, is equal to the pressure of the surrounding atmosphere that is generally taken to be 101.325 kPa. Combining this definition with the reaction stoichiometry indicates that in case of sulfates, the term $(P_{SO_2} P_{O_2}^{1/2})$ amounts to 392.6 $(\text{kPa})^{3/2}$ at the atmospheric pressure (101.325 kPa) at $T = T_{\text{decomp}}$.

As can be seen from Tables III and IV, the differences in t_{decomp} predicted by Eqs (*5*) and (*6*) are practically negligible except for calcium sulfate. Nevertheless, this difference appears to be acceptable in light of the differences in experimental results reported in the literature. For example, the measured results of Halstead and Moore[8] and those of Matsuda et al.[9] lead to the values of the decomposition temperature for calcium hydroxide equal 505 °C and 604 °C, respectively. It corresponds to a well-established fact that the reactivity of solids considerably varies with a number of factors such as the crystallinity, minute impurities and origin of the given material.

TABLE IV

Coefficients in the approximate relationships $\ln \overline{P}(T) = (-K_1/T) + K_2$ for hydroxides, carbonates and sulfites and $\ln \overline{(P_{SO_2} P_{O_2}^{1/2})} = (-K_1/T) + K_2$ for sulfates

Compound	K_1	K_2	s_2	t_{decomp}, °C
$Mg(OH)_2$	9 500	19.6727	0.0507	358
$Ca(OH)_2$	13 154	20.7960	0.0031	540
$MgCO_3$	13 886	23.0623	0.0532	480
$CaCO_3$	20 961	22.5705	0.0440	894
$MgSO_3$	17 193	25.0016	0.0541	570
$CaSO_3$	26 325	25.6979	0.1025	976
$MgSO_4$	44 642	37.9030	0.1026	1 125
$CaSO_4$	57 936	36.6387	0.3405	1 616

It can be concluded that at temperatures of interest, the proposed correlations (*2*) and (*6*) make it possible to predict the heats of decomposition and the dissociation pressures, respectively, with reasonable accuracy. In contrast to the more rigorous relationships (*1*) and (*5*), the expressions developed can be solved for temperature without resorting to iteration techniques. They include only three and two fitted constants, respectively. With respect to their simplicity, they can easily be employed in engineering computations and considerations.

SYMBOLS

C_p	heat capacity, J mol^{-1} K^{-1}
ΔH^0	standard heat of decomposition, J mol^{-1}
ΔH^0_{298}	standard heat of decomposition at 298 K, J mol^{-1}
$\Delta \overline{H}^0$	standard heat of decomposition predicted by Eq. (*2*)
$\Delta \overline{H}^0_{298}$	standard heat of decomposition at 298 K predicted by Eq. (*2*)
$k_1 - k_3$	fitted constants defined in Eq. (*2*)
K_1, K_2	fitted constants defined in Eq. (*6*)
n	number of data points used in evaluating constants
P	equilibrium pressure of a gaseous component, kPa
$\overline{P}$	equilibrium pressure of a gaseous component predicted by Eq. (*6*), kPa
Q_1	sum of squared errors defined in Eq. (*3*)
Q_2	sum of squared errors defined in Eq. (*7*)
s_1	standard deviation defined in Eq. (*4*)
s_2	standard deviation defined in Eq. (*8*)
T	temperature, K
T_{decomp}	decomposition temperature defined in the text, K
t_{decomp}	decomposition temperature, °C

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