

## THERMODYNAMIC ANALYSIS OF A FLUIDIZED BED COMBUSTOR

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## ABSTRACT

In the analysis of fluidized bed combustion performance, it is very important to understand the thermodynamic constraints imposed by the chemical reactions involved. The results of the current thermodynamic analysis identify reactions which are likely to occur and those which are unlikely to occur. Twenty reactions involving flue gas components, limestone, dolomite and NaCl additives were studied. The standard heat of formation and the standard Gibbs free energy of formation of various chemical species were calculated at temperatures between 295 and 1273 K. The thermodynamic analysis indicates that for typical fluidized combustor operating conditions (850°C, 1 atm), limestone and dolomite decompose completely and that all the SO<sub>2</sub> can theoretically be removed by reaction with CaO in the combustor. The analysis also indicates that chemical reactions cannot account for the improvement of the performance of limestone or dolomite when NaCl, a sulfur-capture enhancing additive, is introduced into the combustor.

## NOMENCLATURE

$a_i$	Activity coefficient of species $i$ .
$a_{j,i}$	Reaction coefficient matrix.
$A_i, B_i, C_i, D_i$	Heat capacity coefficients (cal g <sup>-1</sup> mol <sup>-1</sup> K <sup>-1</sup> ).
$C_{pi}$	Heat capacity of species, $i$ (cal g <sup>-1</sup> mol <sup>-1</sup> K <sup>-1</sup> ).
$G_i$	Partial molar Gibbs free energy of species $i$ (kcal g <sup>-1</sup> mol <sup>-1</sup> ).
$\Delta G^0$	Standard Gibbs free energy change of reaction (kcal g <sup>-1</sup> mol <sup>-1</sup> ).
$\Delta G_f^0$	Standard Gibbs free energy of formation (kcal g <sup>-1</sup> mol <sup>-1</sup> ).

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$\Delta H^0$	Standard heat of reaction (kcal g <sup>-1</sup> mol <sup>-1</sup> ).
$\Delta H_f^0$	Standard heat of formation (kcal g <sup>-1</sup> mol <sup>-1</sup> ).
$J_{a,in}$	Inlet activity ratio.
$K_a$	Equilibrium constant.
$n_i$	Number of moles of species i.
$n_T$	Total number of moles of gaseous components.
$Q_i$	Number of species i.
$R$	Ideal gas constant (cal g <sup>-1</sup> mol <sup>-1</sup> K <sup>-1</sup> ).
$T$	Temperature (K).
$v_i$	Stoichiometric coefficient.

## INTRODUCTION

One of the advantages of the fluidized bed combustion of coal is the ability to reduce the emission of both sulfur and nitrogen oxides. Limestone, CaCO<sub>3</sub>, or dolomite, CaMg(CO<sub>3</sub>)<sub>2</sub>, are fed as sorbents along with the coal into the combustion zone, and the sulfur oxides formed during the burning of the coal react with the sorbents, thereby removing SO<sub>2</sub> from the combustion gas. The initial reaction of the sorbents when fed into the bed is calcination, the loss of CO<sub>2</sub>. The calcined products then react with sulfur oxides to form sulfate products. The utilization of CaO is only 40–70%. This limit is due to steric limitations of the CaSO<sub>4</sub> [1,2] produced which blocks the pores of the calcined lime and prevents further reaction. In order to reduce raw limestone requirements, methods to increase the capacity of the sorbents have been studied [3,4]. Experiments conducted by Pope, Evans and Robbins, Inc. [5] demonstrated that the addition of crystalline NaCl to the fluidized bed combustor increased the capacity of limestone to reduce sulfur oxide emission. Experiments performed at the Argonne National Laboratory [4] have shown that other salts, notably CaCl<sub>2</sub> and MgCl<sub>2</sub> in concentrations of less than 0.5 mol%, are also capable of improving the performance of either limestone or dolomite. Since this improvement in calcium utilization could be very important economically, the effect of NaCl on reaction equilibria was studied.

The present thermodynamic analysis was conducted to develop an understanding of the possible reactions of sulfur oxides with sorbents and the effects of salts such as NaCl on the reactions. Possible reactions of the sorbents in a flue gas atmosphere were considered, and the reactions of NaCl with both flue gas and sorbent materials were studied. The study has been divided into groups of related reactions:

- Calcination reactions.

- Sulfation reactions.

- Reactions of NaCl(g) with sorbents.

- Reactions of NaCl(g) with sorbents and flue gas.

TABLE 1  
Chemical reactions studied (1 atm, 850°C)

Reaction	$\Delta G^0$ , kcal g <sup>-1</sup> mol <sup>-1</sup>	$k_a$	$J_{a,in}$
R1 CaCO <sub>3</sub> (s) → CaO(s) + CO <sub>2</sub> (g)	1.138	0.60	0.139
R2 MgCO <sub>3</sub> (s) → MgO(s) + CO <sub>2</sub> (g)	-21.523	1.54 × 10 <sup>4</sup>	0.139
R3 CaMg(CO <sub>3</sub> ) <sub>2</sub> → CaCO <sub>3</sub> (s) + MgO(s) + CO <sub>2</sub> (g)	-19.493	6.21 × 10 <sup>3</sup>	0.139
R4 CaO(s) + SO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → CaSO <sub>4</sub> (s)	-45.618	7.54 × 10 <sup>8</sup>	2.81 × 10 <sup>3</sup>
R5 CaO(s) + SO <sub>3</sub> (g) → CaSO <sub>4</sub> (s)	-47.078	1.45 × 10 <sup>9</sup>	
R6 CaO(s) + SO <sub>2</sub> (g) → CaSO <sub>3</sub> (s)	-12.390	2.58 × 10 <sup>2</sup>	5.26 × 10 <sup>2</sup>
R7 CaSO <sub>3</sub> (s) + $\frac{1}{2}$ O <sub>2</sub> (g) → CaSO <sub>4</sub> (s)	-33.228	2.93 × 10 <sup>6</sup>	5.35
R8 MgO(s) + SO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → MgSO <sub>4</sub> (s)	-17.543	2.59 × 10 <sup>3</sup>	2.81 × 10 <sup>3</sup>
R9 MgO(s) + SO <sub>3</sub> (g) → MgSO <sub>4</sub> (s)	-9.399	6.75	
R10 2 NaCl(g) + CaCO <sub>3</sub> (s) → Na <sub>2</sub> CO <sub>3</sub> (l) + CaCl <sub>2</sub> (l)	-8.294	41.1	2.77 × 10 <sup>9</sup>
R11 2 NaCl(g) + CaMg(CO <sub>3</sub> ) <sub>2</sub> (s) → Na <sub>2</sub> CO <sub>3</sub> (l) + MgCl <sub>2</sub> (l) + CaCO <sub>3</sub> (s)	-5.993	14.7	2.77 × 10 <sup>9</sup>
R12 2 NaCl(g) + CaO(s) → Na <sub>2</sub> O(s) + CaCl <sub>2</sub> (l)	26.733	6.28 × 10 <sup>-6</sup>	2.77 × 10 <sup>9</sup>
R13 2 NaCl(g) + CaSO <sub>4</sub> (s) → Na <sub>2</sub> SO <sub>4</sub> (s) + CaCl <sub>2</sub> (l)	-28.867	4.15 × 10 <sup>5</sup>	2.77 × 10 <sup>9</sup>
R14 2 NaCl(g) + CaCO <sub>3</sub> (s) + H <sub>2</sub> O(g) → Na <sub>2</sub> CO <sub>3</sub> (l) + CaO(s) + 2 HCl(g)	13.858	2.01 × 10 <sup>-3</sup>	0.0
R15 2 NaCl(g) + CaCO <sub>3</sub> (s) + SO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → Na <sub>2</sub> SO <sub>4</sub> (s) + CaCl <sub>2</sub> (l) + CO <sub>2</sub> (g)	-68.134	1.82 × 10 <sup>13</sup>	1.82 × 10 <sup>12</sup>
R16 2 NaCl(g) + CaO(s) + H <sub>2</sub> O(g) → NaOH(l) + CaCl <sub>2</sub> (l)	-6.470	18.20	4.86 × 10 <sup>10</sup>
R17 2 NaCl(g) + CaO(s) + SO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → Na <sub>2</sub> SO <sub>4</sub> (s) + CaCl <sub>2</sub> (l)	-71.854	9.62 × 10 <sup>13</sup>	1.08 × 10 <sup>12</sup>
R18 2 NaCl(g) + CaSO <sub>4</sub> (s) + H <sub>2</sub> O(g) → Na <sub>2</sub> SO <sub>4</sub> + CaO(s) + 2 HCl(g)	-6.949	22.5	0.0
R19 CaO(s) + 2 NO <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → Ca(NO <sub>3</sub> ) <sub>2</sub> (l)	20.04	1.26 × 10 <sup>-4</sup>	7.91 × 10 <sup>5</sup>
R20 CaO(s) + 2 NO(g) + $\frac{1}{2}$ O <sub>2</sub> (g) → Ca(NO <sub>3</sub> ) <sub>2</sub> (l)	33.25	3.38 × 10 <sup>-7</sup>	

Reactions of sorbents with nitrogen oxides.

The thermodynamic functions calculated are the standard heat of reaction,  $\Delta H^0$ , the standard Gibbs free energy of reaction,  $\Delta G^0$ , and the equilibrium constant,  $K_a$ . These functions were computed at 50° intervals from 200 to 1000°C. The equilibrium concentrations of the gaseous products were also determined from the thermodynamic functions. Although the kinetic or physical limitations of the system have not been considered, the calculations permit analysis of the maximum possible extent of reaction.

The reactions studied in this work are listed in Table 1, and these form a fundamental set of reactions for the fluidized bed combustor. Chemical reaction equations and their associated  $\Delta H^0$  and  $\Delta G^0$  can easily be obtained from the thermodynamic functions of formation of the compounds involved in the reaction scheme. The data in this paper, therefore, also provide a basis for studying additional reactions. A thermodynamic analysis of a typical fluidized bed combustor operating at 850°C, 1 atm and 18% excess air was carried out. This demonstrates the utility of a thermodynamic analysis and allows the formation of certain conclusions regarding the likelihood of the various chemical reactions considered.

#### METHODS OF CALCULATION

##### *Calculation of $\Delta H^0$ , $\Delta G^0$ and $K_a$*

A chemical reaction between substances,  $Q_i$ , may be written as



where  $v_i$  denotes the stoichiometric coefficients and is positive for products and negative for reactants. The standard free energy change of a reaction at temperature  $T$ ,  $\Delta G^0$ , is the sum of the free energies of formation of the products in their standard states minus the free energies of formation of the reactants in their standard states.

$$\Delta G^0 = \sum v_i (\Delta G_f^0)_i \quad (2)$$

where  $(\Delta G_f^0)_i$  is the standard free energy of formation of species  $i$  at the reaction temperature. The standard heat of reaction,  $\Delta H^0$ , is given by a similar expression.

$$\Delta H^0 = \sum v_i (\Delta H_f^0)_i \quad (3)$$

where  $(\Delta H_f^0)_i$  is the standard heat of formation for species  $i$ .

The following expression relates the equilibrium constant,  $K_a$ , to the standard free energy change of a reaction,  $\Delta G^0$ .

$$RT \ln K_a = -\Delta G^0 \quad (4)$$

and

$$K_a = \prod_{i=1}^Q a_i^{v_i} \quad (5)$$

where  $a_i$  is the activity of component  $i$  in the equilibrium mixture.

*Calculation of  $(\Delta H_f^0)_i$  and  $(\Delta G_f^0)_i$*

The standard heat of formation and Gibbs free energy of formation are usually compiled at a reference temperature of 298.15 K. It is possible to calculate the thermodynamic functions at other temperatures, if heat capacity and latent heats of transition data are available for the species constituting the formation reaction. Heat capacity data for most substances are well represented by an equation of the form

$$C_{pi} = A_i + B_i T + C_i/T^2 + D_i T^2 \quad (6)$$

where  $C_{pi}$  is the heat capacity of species  $i$  at temperature  $T$  and  $A_i$ ,  $B_i$ ,  $C_i$ ,  $D_i$  are empirical constants.

The standard heat of formation is related to the heat capacities of the reactants and products by the following expression.

$$\int d(\Delta H_f^0)_i = \int \sum v_i C_{pi} dT \quad (7)$$

Integration of eqn. (7) between temperatures  $T_1$  and  $T_2$  leads to the following expression.

$$\begin{aligned} (\Delta H_f^0)_{i,T_2} - (\Delta H_f^0)_{i,T_1} = & \Delta A_i (T_2 - T_1) + \Delta B_i (T_2^2 - T_1^2)/2 \\ & - C_i (1/T_2 - 1/T_1) + D_i (T_2^3 - T_1^3)/3 \end{aligned} \quad (8)$$

where  $\Delta A_i = \sum v_i A_i$  and  $\Delta B_i$ ,  $\Delta C_i$  and  $\Delta D_i$  are given by similar expressions.

Most of the formation reactions studied have phase transitions of one or more of the products or reactants. At a transition temperature, a latent heat of transition,  $\Delta H_{trans}$ , exists, but the Gibbs free energy change of transition is zero, a necessary condition of phase equilibria. It is therefore necessary to add the latent heat of transition to the calculated heat of reaction. In addition, phase changes usually result in changes in the heat capacities of either reactants or products. This is also taken into consideration in the calculation procedure.

The Gibbs free energy of formation at a temperature,  $T$ , is found by integration of the following equation

$$\int \frac{d(\Delta G_f^0)_i}{T} = - \int \frac{(\Delta H_f^0)_i}{T^2} dT \quad (9)$$

Substitution of eqn. (7) for  $(\Delta H_f^0)_i$  in eqn. (9) and integrating between

TABLE 2  
Estimated inlet gas composition to combustor

Component	Volume (%)
N <sub>2</sub>	76.45
CO <sub>2</sub>	13.90
H <sub>2</sub> O	5.70
O <sub>2</sub>	3.50
SO <sub>2</sub>	0.19
NO <sub>2</sub>	0.26

temperatures  $T_1$  and  $T_2$  leads to eqn. (10).

$$\begin{aligned} \frac{(\Delta G_f^0)_{i,T_2}}{T_2} = & \frac{(\Delta G_f^0)_{i,T_1}}{T_1} + \frac{(\Delta H_f^0)_{i,T_1}}{T_1} - \Delta A_i \ln \frac{T_2}{T_1} \\ & - (\Delta B_i/2)(T_2 - T_1)/2 - (\Delta C_i/2)(1/T_2^2 - 1/T_1^2) \\ & - (\Delta D_i/6)(T_2^2 - T_1^2) \end{aligned} \quad (10)$$

At a phase transition, there is no change in  $\Delta G_f^0$ , but heat capacities of some of the species may change resulting in changes in either  $\Delta A_i$ ,  $\Delta B_i$ ,  $\Delta C_i$  or  $\Delta D_i$ .

A computer program was developed to calculate  $\Delta G_f^0$  and  $\Delta H_f^0$  between 298.15 and 1273 K. The data utilized for the calculations were obtained from refs. 1 and 6-9, and some of these data are presented in Tables 2 and 3.

TABLE 3  
Equilibrium concentrations in a fluidized bed combustor (1 atm, 850°C)

Chemical Species	Sorbent (mol)		
	None	CaCO <sub>3</sub>	CaMg(CO <sub>3</sub> ) <sub>2</sub>
CO <sub>2</sub>	13.90	14.09	14.28
CO	$1.8 \times 10^{-7}$	$1.9 \times 10^{-7}$	$2.1 \times 10^{-7}$
SO <sub>3</sub>	$1.9 \times 10^{-2}$	$7.0 \times 10^{-8}$	$7.0 \times 10^{-8}$
SO <sub>2</sub>	$1.71 \times 10^{-1}$	$6.8 \times 10^{-7}$	$6.5 \times 10^{-7}$
O <sub>2</sub>	3.75	3.40	3.40
H <sub>2</sub> O	5.70	5.70	5.70
NO <sub>2</sub>	$5 \times 10^{-5}$	$5 \times 10^{-5}$	$5 \times 10^{-5}$
NO	$5 \times 10^{-5}$	$5 \times 10^{-3}$	$5 \times 10^{-3}$
N <sub>2</sub>	76.58	76.58	76.45
CaCO <sub>3</sub>		0.0	0.0
CaO		$1.45 \times 10^{-7}$	$1.45 \times 10^{-7}$
CaSO <sub>4</sub>		$1.9 \times 10^{-1}$	$1.9 \times 10^{-1}$
CaMg(CO <sub>3</sub> ) <sub>2</sub>			0.0
MgSO <sub>4</sub>			0.0
MgO			$1.9 \times 10^{-1}$

<sup>a</sup> Molar ratio Ca/S = 1:1.

### Calculation of Equilibrium Concentration

The thermodynamic functions obtained above were then used to calculate the equilibrium composition for a given set of chemical species. Systems of equations for determining the equilibrium composition can be based on either (a) the use of equilibrium constants or (b) the use of a minimum thermodynamic potential. The latter approach was used and the calculations were based on a method first proposed by White et al. [10] and later extended to heterogeneous mixtures by Boynton [11].

Assuming we have a system consisting of  $Q$  components, the first  $S$  components being insoluble solids and containing  $n_i$  moles of component  $i$ , the total Gibbs free energy of the system,  $G$ , is given by the sum of the partial molar Gibbs free energy for each component,  $\bar{G}_i$ .

$$G = \sum_{i=1}^Q n_i \bar{G}_i = \sum_{i=1}^S n_i \frac{(\Delta G_f^0)_i}{RT} + \sum_{i=S+1}^Q n_i \frac{(\Delta G_f^0)_i}{RT} + \ln \frac{n_i}{n_T}$$

For an ideal gas state,  $n_T$  is the sum of moles of all gaseous components.

The atoms present are chosen as the independent components of the system, and a conservation of atomic species leads to the following expression.

$$b_j = \sum_{i=1}^Q a_{j,i} n_i \quad (1 < j < E) \quad (12)$$

where  $E$  is the number of atomic species and  $a_{j,i}$  is the number of  $j$  atoms in component  $i$ .

Assuming an approximate solution,  $n_i^K$ , the calculation procedure provides an improved solution,  $n_i^{K+1}$ . The Gibbs free energy is replaced by a quadratic approximation at the  $K$ th iteration.

$$F^{K+1} = \frac{G^{K+1}}{RT} = F^K + \sum_{i=1}^Q (n_i^{K+1} - n_i^K) (\partial F^K / \partial n_i) + 1/2 \sum_{i=1}^Q \sum_{l=1}^Q (n_i^{K+1} - n_i^K) (n_l^{K+1} - n_l^K) (\partial^2 F^K / \partial n_i \partial n_l) \quad (13)$$

The mass balance constraint is incorporated into the solution by means of Lagrangian multipliers.

$$\theta^{K+1} = F^{K+1} + \sum_{j=1}^E \bar{\Lambda}_j \left( b_j - \sum_{i=1}^Q a_{j,i} n_i^{K+1} \right) \quad (14)$$

$\theta = F$  for all values of  $F$ , and a minimum in  $\theta$  corresponds to a minimum in  $F$ . At equilibrium, the total Gibbs free energy is a minimum, and the partial derivative for each component must vanish.

$$\frac{\partial F}{\partial n_i} = \frac{\partial \theta}{\partial n_i} = 0 \quad 1 \leq i \leq Q \quad (15)$$

The combination of the above equations leads to the following set of linear equations [12].

$$\sum_{l=1}^E r_{j,l} \bar{\Lambda}_l + \sum_{i=1}^S a_{j,i} n_i^{K+1} + n_T^{K+1} \left[ \sum_{i=S+1}^Q a_{j,i} (n_i^K / n_T^K) \right] \\ = b_j + \sum_{i=S+1}^Q a_{j,i} n_i^K \left[ (\Delta G_f^0)_i / RT + \ln(n_i^K / n_T^K) \right] \quad 1 < j < E \quad (16)$$

$$\text{(where } r_{j,l} = \sum_{L=S+1}^Q a_{j,i} a_{l,i} n_i^K \text{)}$$

$$\sum_{j=1}^E \bar{\Lambda}_j a_{j,i} = \frac{(\Delta G_f^0)_i}{RT} \quad 1 < i < S \quad (15)$$

$$\sum_{j=1}^M \bar{\Lambda}_j b_j = \sum_{i=1}^S n_i^K \frac{(\Delta G_f^0)_i}{RT} + \sum_{i=S+1}^Q n_i^K \left[ \frac{(\Delta G_f^0)_i}{RT} + \ln(n_i^K / n_T^K) \right] \quad (16)$$

The solution of the above set of equations results in the  $K+1$  iteration values of the solid concentration (moles) directly and can be used to obtain the  $K+1$  iteration values of the gaseous mole numbers. The convergence of this method is not guaranteed unless care is taken to ensure that new mole numbers are all positive. It is also necessary to ensure that the minimum is not passed,  $(\partial\theta/\partial n_i < 0)$ , and to start the calculation procedure with a fair approximation to ensure the convergence of the scheme.

TABLE 4

Thermodynamic properties of important compounds at 1 atm, 298.15 K [6–9]

Compound	$\Delta G_f^0$	$\Delta H_f^0$	$C_{pi}$			
			$A_i$	$B_i \times 10^3$	$C_i \times 10^{-5}$	$D_i \times 10^6$
CaCO <sub>3</sub> (s)	-269.80	-288.46	24.98	5.24	-6.20	0.0
CaMg(CO <sub>3</sub> )(s)	-517.10	-556.0	37.33	19.24	-5.16	0.0
CaO(s)	-144.37	-151.79	11.86	1.08	-1.66	0.0
CaSO <sub>3</sub> (s)	-260.0	-279.0	15.22	22.40	0.0	0.0
CaSO <sub>4</sub> (s)	-315.93	-342.76	16.78	23.60	0.0	0.0
MgCO <sub>3</sub> (s)	-241.90	-261.9	18.62	13.80	-4.16	0.0
MgO(s)	-136.10	-143.81	11.707	0.751	-2.734	0.0
MgSO <sub>4</sub> (s)	-279.80	-307.1	25.439	11.06	-5.234	0.0
Na <sub>2</sub> O(s)	-90.609	-99.90	15.826	10.484	-1.944	-3.367
NaCl(g)	-48.117	-43.36	8.923	0.176	-0.379	0.0
CO <sub>2</sub> (g)	-94.254	-94.051	10.55	2.16	-2.04	0.0
SO <sub>2</sub> (g)	-71.748	-70.944	10.38	2.54	-1.42	0.0
CO(g)	-32.781	-26.416	6.79	0.98	-0.11	0.0
NO(g)	20.719	21.570	7.03	0.92	-0.140	0.0
NO <sub>2</sub> (g)	12.390	8.041	10.07	2.28	-1.67	0.0
H <sub>2</sub> O(g)	-54.634	-57.796	7.17	2.56	0.08	0.0
SO <sub>3</sub> (g)	-88.690	-94.580	13.658	6.536	-3.086	-1.847



A computer program was developed to use the above procedure to calculate the equilibrium composition for a given set of components at a specified temperature. The program was written in FORTRAN and the calculations performed on a Univac 1108 computer. In calculating the equilibrium and outlet gas concentration from the combustor, it was assumed that flue gas of a composition given in Table 4 entered the combustor. In addition it was assumed that solid or liquid products and reactants were pure components with activities equal to unity. The Rivesville fluidized bed combustor demonstration plant operates at a temperature of 850°C and 18% excess air [13]. The combination of these conditions with the analysis of Arkwright coal [14] led to the flue gas analysis given in Table 4, based on the assumption that all the fuel carbon, sulfur and nitrogen oxidized to  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{NO}_2$ , respectively.

## RESULTS AND DISCUSSION

The calculated standard free energy of formation,  $\Delta G_f^0$ , of the various chemical species are presented in graphical form in Figs. 1 and 2 for the

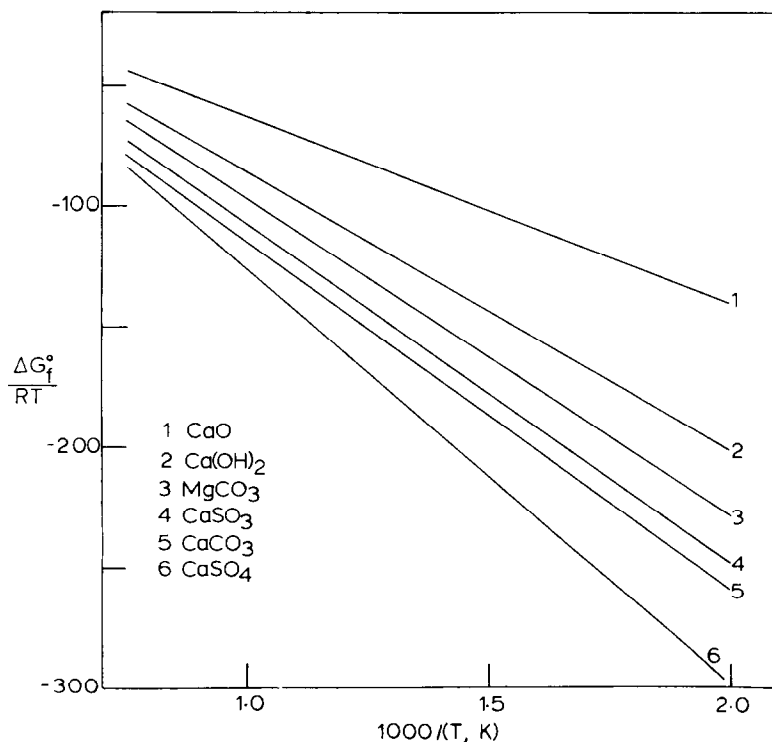


Fig. 1. Standard Gibbs free energy of formation for some compounds in the solid state.

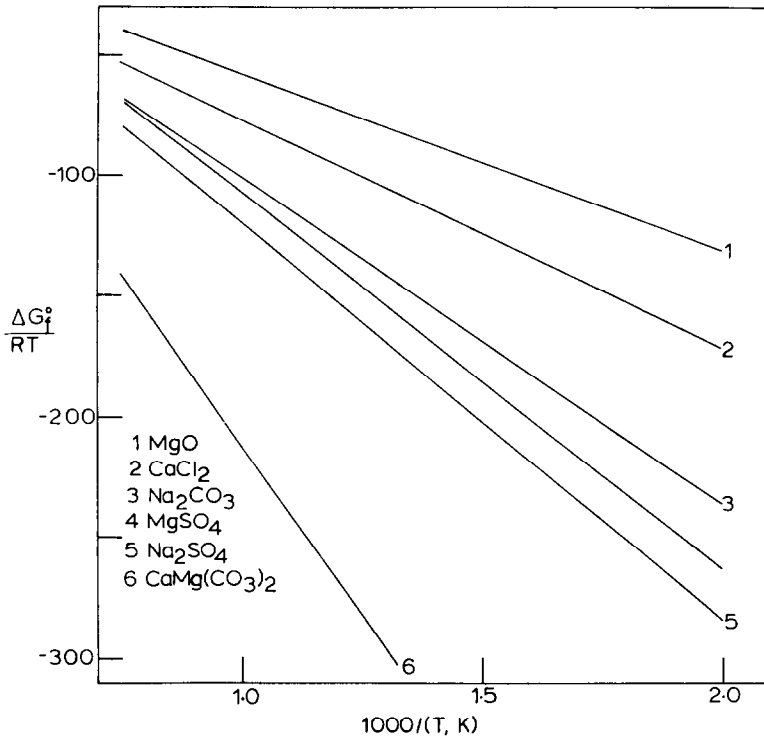


Fig. 2. Standard Gibbs free energy of formation for some compounds in the solid state.

solid species and in Figs. 3 and 4 for the gaseous species. In Figs. 1–4 the group ( $\Delta G_f^0/RT$ ) is plotted against ( $1000/T$ ). A straight line can be drawn through most of the data points, indicating that the standard heat of reaction is nearly constant. The various chemical reactions studied are listed in Table 1 along with values of the free energy change and the equilibrium constant at 850°C. This temperature is representative of most fluidized bed-coal combustion operations. A large negative value of  $\Delta G^0$  is equivalent to a large equilibrium constant and high conversion. Conversely, a large positive value of  $\Delta G^0$  is equivalent to a low equilibrium constant and a low conversion. The direction in which a reaction will proceed depends on the inlet concentration, and if the inlet activity ratio,  $J_{a,in}$ , is less than  $K_a$ , the reaction will proceed in the direction written. The inlet activity ratio is given by

$$J_{a,in} = \prod_{i=1}^Q (a_i)_{in}^{\alpha_i} \quad (17)$$

The calculated equilibrium concentration of the gases leaving the combustor are given in Table 4. The table gives the outlet (equilibrium) concentration when the feed to the combustor is a mixture of flue gases, a mixture of flue gases and limestone and a mixture of flue gases and dolomite.

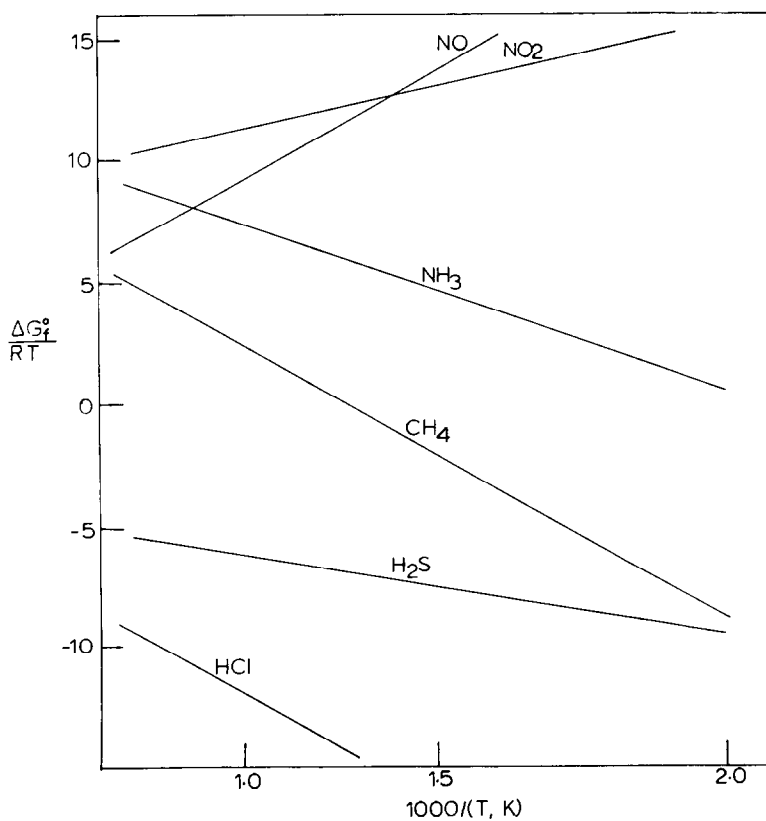


Fig. 3. Variation of Gibbs free energy with temperature for some compounds in the gaseous state.

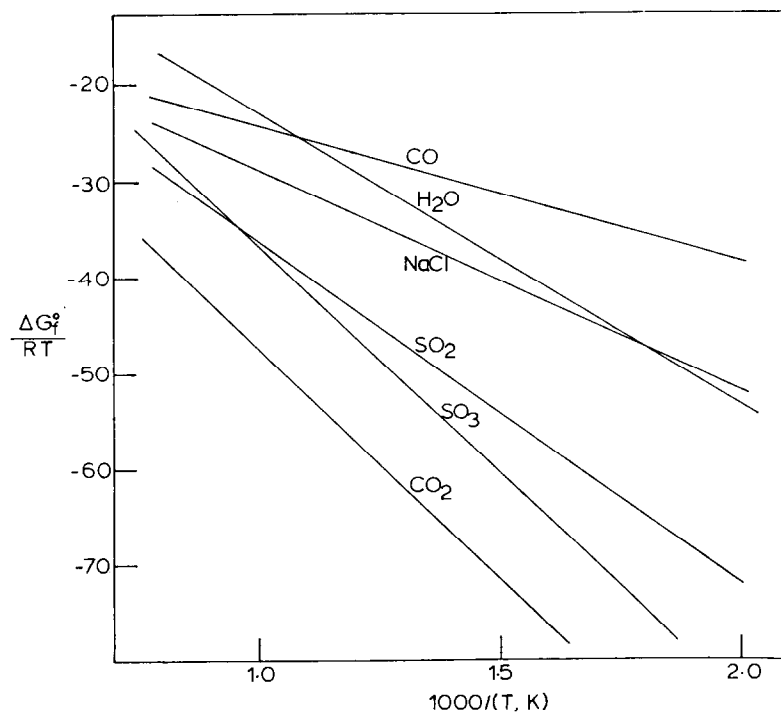


Fig. 4. Variation of Gibbs free energy with temperature for some compounds in the gaseous state.

TABLE 5

Latent heat of transition and heat capacity polynomials of chemical species with phase transitions

Chemical Species	Transition temperature (K)	Latent heat (kcal g <sup>-1</sup> mol <sup>-1</sup> )	Heat capacity C <sub>pi</sub> (cal g <sup>-1</sup> mol <sup>-1</sup> K)				Temperature range (K)
			A <sub>i</sub>	B <sub>i</sub> × 10 <sup>3</sup>	C <sub>i</sub> × 10 <sup>-5</sup>	D <sub>i</sub> × 10 <sup>6</sup>	
CaCl <sub>2</sub>	1045	6.80	17.18	3.04	-0.6	0.0	298-1045
			24.70	0.0	0.0	0.0	1045-2273
NaCl	1074	6.73	10.98	3.9	0.0	0.0	298-1074
			18.586	-1.8	0.0	0.0	1074-1500
Na <sub>2</sub> CO <sub>3</sub>	723	0.165	2.633	58.236	5.854	0.0	298-723
	1123	7.09	11.97	30.85	0.0	0.0	723-1123
NaOH	568	1.52	45.30	0.0	0.0	0.0	1123-2000
			17.15	-26.5	0.0	56.35	298-568
			20.55	0.0	0.0	0.0	268-593
			21.38	-1.4	0.0	0.0	593-900
Na <sub>2</sub> SO <sub>4</sub>	522	2.584	20.00	0.0	0.0	0.0	900-1663
			19.676	36.893	0.0	0.0	298-522
			34.668	13.049	0.0	0.0	522-980
			34.102	14.176	0.0	0.0	980-1157
	1157	5.50	47.180	0.0	0.0	0.0	1157-2000

### Calcination reactions

The initial reaction of the sorbents in the fluidized bed is calcination, the loss of CO<sub>2</sub>. Reactions R1 to R3 are the calcination reactions for three potential sorbents. ΔG<sup>0</sup> for reaction R1 is positive and negative for reactions R2 and R3. Although G<sup>0</sup> is positive for R1, this reaction proceeds since J<sub>a,in</sub> is less than K<sub>a</sub>, and the inlet partial pressure of CO<sub>2</sub> (0.139 atm) is less than the equilibrium partial pressure of CO<sub>2</sub> for R1 (0.623 atm). Under typical fluidizing conditions reactions R1-R3 should proceed to completion and result in complete disassociation of the sorbents.

### Sulfation reactions

SO<sub>2</sub> capture can proceed by two alternate paths. The first path is the capture of SO<sub>2</sub> or SO<sub>3</sub> leading to CaSO<sub>4</sub> by reaction R4 or R5. The second path is the capture of SO<sub>2</sub> to form CaSO<sub>3</sub>, R6 followed by R7, to form sulfation products. Reactions R4-R7 all have large negative values of ΔG<sup>0</sup> which is indicative of high equilibrium conversions. J<sub>a,in</sub> is less than K<sub>a</sub> for reaction R4 which therefore proceeds in the forward direction. Under the assumed conditions in the combustor, reaction R6 will not proceed in the forward direction and calcium sulfite will not be formed. Reaction R7 is thermodynamically feasible and if calcium sulfite is introduced into the bed,

it would be converted to  $\text{CaSO}_4$ .  $\text{MgO}$  can be converted to  $\text{MgSO}_4$  by reactions R8 and R9. Both reactions are feasible but the very low inlet concentrations of  $\text{SO}_2$  and  $\text{SO}_3$  will prevent the forward reaction and the formation of  $\text{MgSO}_4$ .

The equilibrium concentration of the gases leaving the combustor at  $850^\circ\text{C}$  is given in Table 4 for a system consisting of inlet flue gases and limestone or dolomite with a  $\text{Ca/S}$  molar ratio of 1:1. The calculations show that both limestone and dolomite decompose completely and that  $\text{CaO}$  is responsible for over 99% conversion of  $\text{SO}_2$  to  $\text{CaSO}_4$ .  $\text{MgO}$  does not react with  $\text{SO}_2$  under the assumed conditions in the combustor.

#### *Reactions of $\text{NaCl}(\text{g})$ with sorbents*

$\text{NaCl}$  has a melting point of  $801^\circ\text{C}$  and at  $850^\circ\text{C}$ , it will be present in the combustor either in the liquid and vapor phases or in the vapor phase only. The vapor pressure of  $\text{NaCl}$  at  $850^\circ\text{C}$  was calculated to be  $1.013 \times 10^{-3}$  atm by using an expression given by Barin and Knacke [6]. Assuming a molar  $\text{Na/Ca}$  feed ratio of 50:1 (representative of  $\text{NaCl}$  dosage into fluidized bed combustors) all the  $\text{NaCl}$  introduced will vaporize since the resulting partial pressure of  $\text{NaCl}$  will be less than the prevailing pressure, and  $\text{NaCl}$  will be present only in the vapor phase. The reactions of  $\text{NaCl}(\text{g})$  with the sorbents is studied in reactions R10–R13. Reactions R10, R11 and R13 all have a large negative free energy change and would be feasible except for the very low inlet activity of  $\text{NaCl}$ . Under the conditions in the combustor, none of these reactions will proceed in the forward direction.

#### *Reactions of $\text{NaCl}(\text{g})$ with sorbents and flue gases*

Vapor phase  $\text{NaCl}$  and flue gas components are potential reactants with sorbents. Possible reactions that could occur are analyzed in reactions R14–R18. Reactions R15 and R17 have large negative values of  $\Delta G^0$  and could proceed in the combustor.

#### *Reactions of sorbents with oxides of nitrogen*

The possibility of the reduction of  $\text{NO}_x$  emission from the combustor by the reaction of the sorbent materials with nitrous oxides was also studied.  $\Delta G^0$  for reactions R19 and R20 are large and positive. In addition,  $J_{a,\text{in}}$  is less than  $K_a$  and none of the reactions will proceed under the given conditions.

## CONCLUSIONS

(1) The capture of  $\text{SO}_2$  in the fluidized bed by limestone and dolomite is most likely by direct formation of calcium sulfate in reaction R4, which

results in equilibrium conversion greater than 99%. Due to equilibrium considerations, the formation of  $\text{CaSO}_3$  either as a product or an intermediate is unlikely.

(2)  $\text{MgO}$  does not contribute to the capture of  $\text{SO}_2$  in the atmospheric fluidized bed combustor.

(3) For the reactions studied, little driving force exists for the direct reaction of  $\text{NaCl(g)}$  with the sorbents or with the sorbents and flue gases.

(4) Under the conditions assumed in this study (1 atm,  $850^\circ\text{C}$ ) nitrogen oxides do not react with any sorbent materials.

(5) Chemical reactions cannot account for the improvement in the performance of limestone when  $\text{NaCl}$  (1 mol%) is introduced along with it into the combustor. Rather, some other phenomenon must be responsible.

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