Thermochimica Acta, 194 (1992) 149–153
Elsevier Science Publishers B.V., Amsterdam

Thermodynamic analysis of a fluidized-bed combustor

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(Received 8 April 1991)

Abstract

A paper previously published in this journal (Thermochim. Acta, 75 (1984) 9) analyzed the thermodynamics of reactions involved in the capture of sulfur by calcium carbonate in fluidized-bed combustors. It is shown here that the earlier paper contained several fundamental errors, and consequently many of the results presented were incorrect. For this work a model of the system was developed that allowed for investigation of a wider range of temperatures and pressures and included the effect of vapor-phase non-ideality. Using this model a corrected thermodynamic analysis was performed and the scope of the previous study was extended to cover a range of operating conditions. The analysis shows that sulfur capture is primarily by reaction of SO_2 with CaO formed from calcined limestone. For typical fluidized-bed combustor conditions of 850 °C, 1 atm, sulfur is removed to a level of 0.003 ppm, while at pressures typical of pressurized fluidized-bed combustors (20 atm) the equilibrium sulfur concentration in the gas phase is 0.0003 ppm. There are pitfalls in applying the results of equilibrium predictions to actual performance.

NOMENCLATURE

A_i, B_i, C_i, D_i	Heat capacity coefficients of species *i* (cal mol^{-1} K^{-1})
C_{pi}	Heat capacity of species *i* (cal mol^{-1} K^{-1})
$\Delta G_f^{\ominus}$	Standard Gibbs free energy of formation (kcal mol^{-1})
$\Delta G^{\ominus}$	Standard Gibbs free energy change of reaction (kcal mol^{-1})
$\Delta H_f^{\ominus}$	Standard heat of formation (kcal mol^{-1})
$\Delta H^{\ominus}$	Standard heat of reaction (kcal mol^{-1})
R	Ideal gas constant (kcal mol^{-1} K^{-1})
T	Temperature (K)
ν_i	Stoichiometric coefficient

INTRODUCTION

Several technologies for burning coal are currently under investigation as methods for controlling emissions of sulfur and nitrogen oxides from power generation plants. Many of these involve the addition of sorbents to the zone in which the coal is combusted. Because of the large number of species that may be present in the combustion zone, determination of the

0040-6031/92/$05.00

important reactions and calculation of the equilibrium composition are non-trivial problems. It is, however, highly desirable to know the equilibrium distribution of certain species, particularly sulfur, that we wish to remove in the solid phase. Several such thermodynamic analyses have therefore been undertaken for different types of combustor, including those of Denloye et al. [1] and Whitney et al. [2]. The paper published by Denloye et al. [1] contains a very serious error that causes their quantitative results to be inaccurate. This and several other shortcomings are corrected in the following analysis.

SOURCE OF ERROR

Denloye et al. [1] considered twenty reactions that might occur in a fluidized-bed combustor. They presented their results in the form of plots of the Gibbs free energy of formation of 24 species against temperature (data that are available in many good thermochemical data sources, e.g. Barin and Knacke [3]). While studying their paper it came to our attention that a fundamental mistake had been made in deriving the equations used to calculate the Gibbs free energy.

Denloye et al. [1] state correctly that the heat of reaction for reaction j is given by

$$\Delta H_j^{\ominus} = \sum \nu_i \left(\Delta H_f^{\ominus}\right)_i \tag{1}$$

and, because

$$\int \mathrm{d}\left(\Delta H_f^{\ominus}\right)_i = \int C_{pi}\, \mathrm{d}T \tag{2}$$

where

$$C_{pi} = A_i + B_i T + C_i/T^2 + D_i T^2 \tag{3}$$

we can write

$$\int \mathrm{d}\left(\Delta H_j^{\ominus}\right) = \int \sum \nu_i C_{pi}\, \mathrm{d}T \tag{4}$$

which we believe is the expression intended by Denloye et al.'s eqn. (7). They integrate this correctly; however, they then misstate the Gibbs–Helmholtz equation (their eqn. 9), which should read

$$\int \mathrm{d}\left(\frac{\Delta G_{fi}^{\ominus}}{T}\right) = -\int \frac{\left(\Delta H_f^{\ominus}\right)_i}{T^2}\, \mathrm{d}T \tag{5}$$

by making an error in the left-hand term so that it reads

$$\int \frac{\mathrm{d}\left(\Delta G_{fi}^{\ominus}\right)}{T} = -\int \frac{\left(\Delta H_f^{\ominus}\right)_i}{T^2}\, \mathrm{d}T$$

Finally they substitute the equation for $\Delta H^{\ominus}$ as a function of T to obtain an integrated form of the Gibbs–Helmholtz equation giving $\Delta G^{\ominus}$ as a function of ΔC_p (where $\Delta C_{\mathrm{pi}} = \Sigma \nu_i C_{pi}$). Whether as a result of accumulated errors or fresh mistakes, their integration of this equation (their eqn. (10)) contains no fewer than four inaccuracies and should read

$$\frac{(\Delta G^{\ominus})_{T_2}}{T_2} = \frac{(\Delta G^{\ominus})_{T_1}}{T_1} + \frac{(\Delta H^{\ominus})_{T_2}}{T_2} - \frac{(\Delta H^{\ominus})_{T_1}}{T_1} - \Delta A \ln\left(\frac{T_2}{T_1}\right) - \Delta B(T_2 - T_1) - \frac{\Delta C}{2}\left(\frac{1}{T_1^2} - \frac{1}{T_2^2}\right) - \frac{\Delta D}{2}(T_2^2 - T_1^2) \qquad (6)$$

A longer, but more convenient, form is given in eqn. 7

$$\begin{aligned}\frac{(\Delta G^{\ominus})_{T_2}}{T_2} &= \frac{(\Delta G^{\ominus})_{T_1}}{T_1} + (\Delta H^{\ominus})_{T_1}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) - \Delta A \ln\left(\frac{T_2}{T_1}\right) + \Delta A T_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ &\quad - \frac{\Delta B}{2}(T_2 - T_1) + \frac{\Delta B T_1^2}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\Delta C}{2}\left(\frac{1}{T_1^2} - \frac{1}{T_2^2}\right) \\ &\quad - \frac{\Delta C}{T_1}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) - \frac{\Delta D}{6}(T_2^2 - T_1^2) + \frac{\Delta D T_1^3}{3}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (7)\end{aligned}$$

To assess whether the incorrect equations were actually used in deriving the results presented by Denloye et al., their calculations were repeated

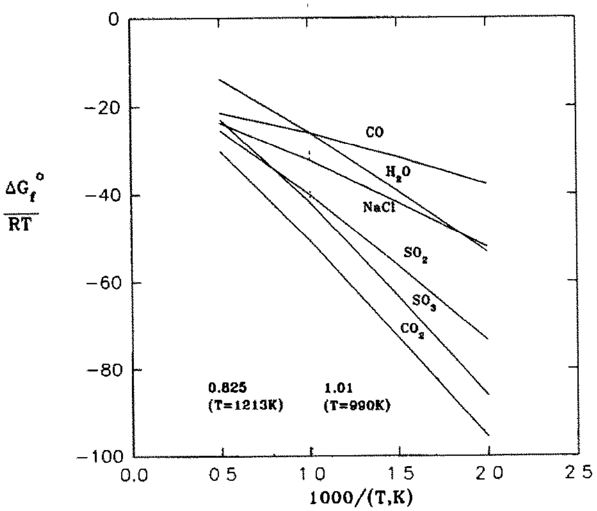

Fig. 1. Variation of Gibbs free energy of formation of gas phase compounds with temperature (corrected version of figure 4 in the paper by Denloye et al. [1]).

using their data and the correct formulae. Figure 1 shows a corrected plot of Denloye et al's figure 4 that clearly illustrates the quantitative difference. The plots appear qualitatively similar, since not all terms in Denloye et al.'s equation were wrong; however, if one examines the intersection of the lines for SO_2 and SO_3 the intersection should be at $1000/T = 0.825$ (rather than the Denloye et al. value of 0.95) and for CO and H_2O the intersection should be at $1000/T = 1.01$ (cf. 1.08). As noted earlier, information on $\Delta G_f^{\ominus}$ versus T for different species can be obtained from any reliable source of thermochemical data. The stated purpose of Denloye et al. was to calculate the equilibrium composition in the fluidized bed combustor. At no point in their paper were such results presented; in fact, the table that is supposed to contain the results (their table 4) is actually a list of thermodynamic properties. The calculations described below supply this information.

EQUILIBRIUM CALCULATIONS

The equilibrium compositions of gas and condensed phase species were calculated using an adaptation of a computer code developed by Whitney et al. [2]. The original version inputs an initial number of moles of each species to be considered (thereby providing the basis for the mass balance) along with the temperature and pressure. A set of independent chemical reactions and material balances is then developed and computed to equilibrium using a Newton–Raphson iterative scheme. The upgraded version also incorporates a correction for gas-phase non-ideality, calculating the fugacities of gas-phase species following the method recommended by Prausnitz et al. [4]. This involves calculation of second virial coefficients using the Pitzer–Curl–Tsonopoulos correlation [5].

Because Denloye et al. did not state their assumptions with regard to coal composition, the composition chosen was that of Illinois No. 6 sub-bituminous, a typical mid-western coal. This has a moisture- and ash-free (MAF) composition by weight of 80.61% C, 5.89% H, 1.50% N, 4.64% S, and 7.36% O. The ratio of air to coal was assumed to be 110% of stoichiometric, where stoichiometric air is defined as the amount of air required if CO_2, H_2O, N_2 and SO_2 were the only products of combustion. The ratio of calcium to sulfur was fixed at 1.5 : 1, although any ratio greater than 1 : 1 would give virtually the same sulfur removal. Calculations were performed for two pressures, 1 and 20 atm. The lower pressure is typical of fluidized-bed combustor (FBC) boiler operation, while the higher corresponds to operating a pressurized fluidized-bed combustor (PFBC) followed by a gas turbine. The predicted gas-phase compositions are shown in Table 1. Oxides of nitrogen are also present in trace amounts in the effluent gas, but they were not considered in this analysis.

TABLE 1

Composition of effluent gas from a fluidized-bed combustor

Pressure (atm)	N_2 [a]	O_2 [a]	CO_2 [a]	CO [a]	H_2O [a]	H_2 [a]	SO_2 (ppb)	SO_3 (ppb)
1	0.759	0.017	0.158	2.8E−7	0.067	1.1E−7	34	2.8
20	0.761	0.017	0.156	6.2E−8	0.067	2.4E−8	2.4	0.9

[a] Mole fraction.

These results confirm (not surprisingly) that from equilibrium considerations alone we expect a very effective sorption of SO_2 by CaO under combustor conditions. It should be recognized, however, that these thermodynamic calculations yield no information about the kinetic feasibility of a particular reaction, and are therefore only useful as a method for selecting sulfur control strategies by carrying out preliminary screening of likely sorbents. Within this context it should also be noted that solid-phase species that do not necessarily participate in any sulfur-absorbing reactions themselves can play an important role in sorption if their presence improves the kinetics of reaction of another solid species (e.g. by modifying the solid structure or by providing catalysis). Denloye et al.'s conclusion Number 2 should therefore be more accurately stated as, "When dolomite is added to the atmospheric fluidized-bed combustor, SO_2 is not captured in the form of a magnesium salt".

CONCLUSIONS

(1) Addition of limestone or dolomite to fluidized-bed combustors could remove more than 99.9% of the sulfur present in the coal if the sulfur-absorbing reactions were able to proceed to equilibrium.
(2) Thermodynamic analyses of sulfur absorption in coal combustion systems are a useful method for preliminary screening of likely sorbents, but do not account for kinetic effects, which must ultimately determine the feasibility of any process.
(3) Several errors occurring in a paper previously published on this subject [1] have been described and corrected.

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