EFFECT OF WATER VAPOUR ON THE EQUILIBRIUM BETWEEN CaO AND COS IN COAL GAS

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The effectiveness of calcium oxide in the removal of carbonyl sulfide from coal gas is estimated by thermochemical computations. It is assumed that the gas phase composition is determined by the equilibria of the reactions of water vapour with calcium sulfide and carbonyl sulfide and by the water–gas-shift reaction. The proposed relationships can be employed in engineering considerations and calculations.
Key words: Coal gas desulfurization; Calcium oxide; Carbonyl sulfide; Equilibrium concentrations; Environmental chemistry; Waste gases treatment.

It appears that developments in coal gasification and gas turbine technology will lead to a more efficient production of electricity. Combined cycle systems, using both the gas and steam turbines, offer a significantly higher power efficiency compared with traditional systems.

Downstream requirements (*e.g.*, protection of the gas turbine) and environmental regulations dictate that the raw coal gas produced by a coal gasifier must be cleaned before further use. Aside from a number of impurities such as dust, nitrous compounds, heavy and alkali metal compounds, the raw coal gas contains sulfur mainly in the form of hydrogen sulfide and carbonyl sulfide.

Commercial desulfurization processes are usually based on liquid scrubbing at or below ambient temperatures. This results in a reduction of thermal efficiency as well as in the need for the expensive waste water treatment. In order to attain the maximum thermal efficiency, the coal gas should be desulfurized at temperatures approaching those at which it leaves the gasifier.

In addition to regenerable solid mixed-metal sorbents, recent efforts in hot-gas desulfurization have focused on calcium-based sorbents[1,2] (*e.g.*, lime, limestone and dolomite). Calcium compounds have a considerable

potential because of their utility under both oxidizing[3,4] and reducing conditions and because of their low cost. In a once-through system, spent sorbents need to be converted into a form that is chemically stable after disposal in landfills. The regeneration process reduces the sorbent needs and solid waste handling. However, there are difficulties in completing the regeneration and a decrease in solid reactivity with sulfidation/regeneration cycles[5].

The results of thermodynamic screening of different solids for the high-temperature desulfurization presented by Westmoreland and Harrison[6] show a high affinity of calcium to sulfur. While thermodynamic constraints have been explored in sorption of H_2S on CaO and $CaCO_3$ (refs[7,8]), little is known about equilibrium concentrations in the system CaO–COS.

The aim of this study is to predict the equilibrium constraints for sorption of carbonyl sulfide on calcium oxide in a reducing atmosphere of coal gas.

**THEORETICAL**

Principal Reactions

At high temperatures, carbonyl sulfide rapidly combines with calcium oxide according to the reaction

$$CaO\ (s) + COS\ (g) \rightleftharpoons CaS\ (s) + CO_2\ (g)$$

$$\Delta H^0_{298} = -93.22\ \text{kJ mol}^{-1}\ . \tag{1}$$
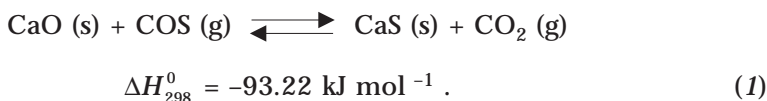
Since the content of water vapour in coal gas is of the order of 10^1 vol.%, we believe that the tendency of calcium sulfide to hydrolyze cannot be neglected

$$CaS\ (s) + H_2O\ (g) \rightleftharpoons CaO\ (s) + H_2S\ (g)$$

$$\Delta H^0_{298} = +59.44\ \text{kJ mol}^{-1}\ . \tag{1a}$$
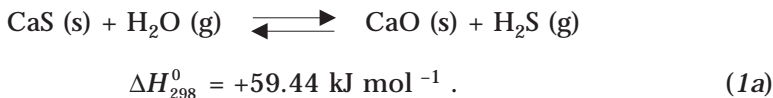
Moreover, one should realize that calcium oxide can also act as a catalyst for the hydrolysis of carbonyl sulfide

$$COS\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2S\ (g)$$

$$\Delta H^0_{298} = -33.77\ \text{kJ mol}^{-1}\ . \tag{2}$$
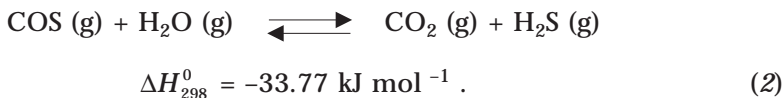
It should be also remembered that carbon monoxide, as one of the main constituents of coal gas, can undergo oxidation to carbonyl sulfide

$$CO\ (g) + H_2S\ (g) \rightleftarrows COS\ (g) + H_2\ (g)$$

$$\Delta H^0_{298} = -7.36\ \text{kJ mol}^{-1}\ . \tag{3}$$
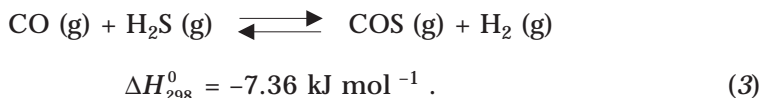
Apparently, the summation of reactions (*2*) and (*3*) leads to the water–gas-shift reaction (WGS):

$$CO\ (g) + H_2O\ (g) \rightleftarrows CO_2\ (g) + H_2\ (g)$$

$$\Delta H^0_{298} = -41.14\ \text{kJ mol}^{-1}\ . \tag{3a}$$
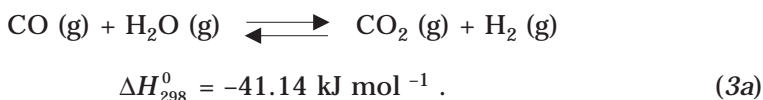
In general, it is the initial C : H : O ratio in the feed to the gasifier and the equilibrium of the WGS reaction (*3a*) at a given temperature that determine the content of the main components in coal gas. Clearly, other reactions such as the heterogeneous Boudouard reaction

$$C\ (s) + CO_2\ (g) \rightleftarrows 2\ CO\ (g)$$

$$\Delta H^0_{298} = +172.42\ \text{kJ mol}^{-1} \tag{3b}$$
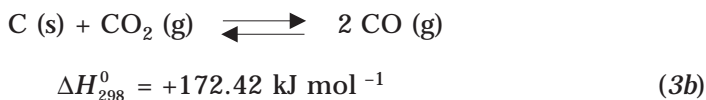
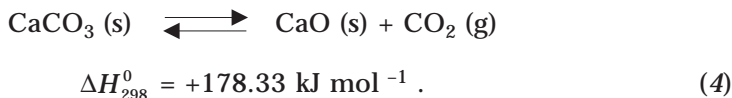should be also considered in the gasification process itself.

Although thermal decomposition of hydrogen sulfide into diatomic sulfur (S_2) and hydrogen can occur at high temperatures, findings in the literature indicate that the amounts of S_2 in coal gas are much smaller than those of COS (ref.[9]).

Coal gas also contains smaller, but significant amounts of carbon dioxide ($\approx 10^0$ vol.%) which can compete in reacting with carbonyl sulfide if the sorption takes place at lower temperatures. Therefore, the above considerations implicitly assume that sorption of carbonyl sulfide occurs at temperatures just equal to or higher than the decomposition (calcination) temperature T_d of calcium carbonate (limestone). Under such conditions (*i.e.*, $T \geq T_d$), the partial pressure of carbonyl sulfide is not increased by the presence of carbon dioxide.

RESULTS AND DISCUSSION

Decomposition Temperature of Calcium Carbonate

At a given partial pressure of carbon dioxide, calcium carbonate undergoes decomposiiton if the temperature is sufficiently high:

$$CaCO_3 \text{ (s)} \quad \rightleftharpoons \quad CaO \text{ (s)} + CO_2 \text{ (g)}$$

$$\Delta H_{298}^0 = +178.33 \text{ kJ mol}^{-1} . \tag{4}$$

The decomposition temperature of a compound (T_d) is generally defined as a temperature at which the pressure of the released gas is equal to the pressure of the surrounding atmosphere.

Experimental measurements on the equilibrium dissociation pressure of calcium carbonate were found in the literature[10,11]. A simple least-square procedure was employed, and the measured data were fitted in this work to the regression relationship

$$\log P_{CO_2, d} = -8\,689.1/T + 9.4181$$

$$T \in \langle 820 \text{ K}, 1\,500 \text{ K} \rangle . \tag{5}$$

In order to investigate the agreement between the experiment embodied in Eq. (*5*) and the thermodynamic predictions, thermochemical properties compiled by Knacke *et al.*[12] and Barin[13] were employed. These collections of thermodynamic data were also employed in all the gas–solid equilibria considered in this work. The standard changes in the Gibbs energy ΔG_4^0 were deduced for reaction (*4*) from the tabulated data at different temperatures and regressed here by means of a very simple linear relationship as a function of temperature

$$\Delta G_4^0 = +149.97\,T - 174\,480$$

$$T \in \langle 300 \text{ K}, 1\,200 \text{ K} \rangle . \tag{6}$$

It is assumed that the gaseous components exhibit the ideal behaviour and the activities of reactants in the solid state are taken as unity throughout this work. Then, we can express the equilibrium dissociation pressure of calcium carbonate from Eq. (*6*) as

$$\log P_{CO_2, d} = -9\,113.8/T + 9.8335 . \tag{7}$$

The experimental data as well as the predictions of Eqs (*5*) and (*7*) are shown in Fig. 1. It is apparent that the experimental results are in a very good agreement not only with the regression formula (*5*), but also with the predictions of the derived relationship (*7*).

The relationship (*7*) derived above provides the decomposition temperature of calcium carbonate t_d as high as 891 °C. This predicted value is quite close to the handbook values of 898 (ref.[11]) and 882 °C (ref.[14]). Therefore, we believe that our findings above also document that the data tabulated in refs[12,13] are well-founded and can be employed in our engineering considerations.

Equilibrium of the Reaction of Carbonyl Sulfide with Calcium Oxide

We believe that the reactions (*1a*), (*2*) and (*3a*) constitute a well-founded basis for estimating equilibrium concentrations of carbonyl sulfide in coal gas in contact with calcium oxide.

Apparently, there are six gaseous species (COS, CO, CO_2, H_2, H_2O and H_2S) in the system, and we have three constrains given by the simultaneous equilibria of the respective reactions (*1a*), (*2*) and (*3a*).

Following the common thermodynamic principles, we can express the equilibrium partial pressure of carbonyl sulfide in the system as follows:

$$P_{COS} = (K_{1a}K_{3a}/K_2)\,(P_{H_2O}\,P_{CO}/P_{H_2}) \,. \tag{8}$$

The standard changes of the Gibbs energy for reactions (*1a*), (*2*) and (*3a*) were deduced from the tabulated data[13] at different temperatures and re-
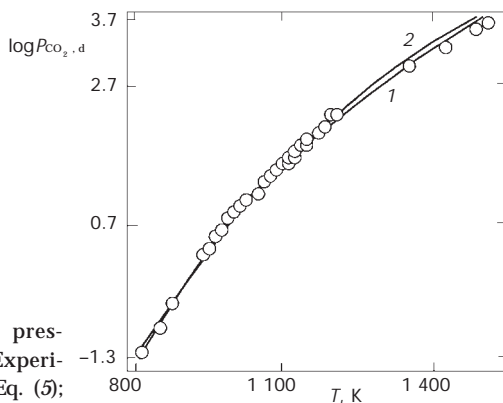

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Measured and predicted dissociation pressures of calcium carbonate $P_{CO_2,d}$. ○ Experimental values (ref.[10]); *1* predictions of Eq. (*5*); *2* predictions of Eq. (*7*)

gressed in this work by means of a very simple linear relationship as a function of temperature

$$\Delta G_i^0 = a_i T + b_i$$

$$T \in \langle 900 \text{ K}, 1\,400 \text{ K} \rangle . \tag{9}$$

The subscript *i* refers herein to the reactions (*1a*), (*2*) and (*3a*), respectively.

The resulting coefficients a_i and b_i for the respective reactions are given in Table I. Equation (*9*) can be rewritten in terms of the quantities K_i (K_{1a}, K_2 and K_{3a}) as follows:

$$\ln K_i = A_i/T + B_i . \tag{10}$$

Numerical coefficients A_i and B_i are summarized in Table II. As shown above, while reaction (*1a*) is moderately endothermic, reactions (*2*) and

TABLE I
Regression coefficients in the equation $\Delta G_i^0 = a_i T + b_i$ for different reactions

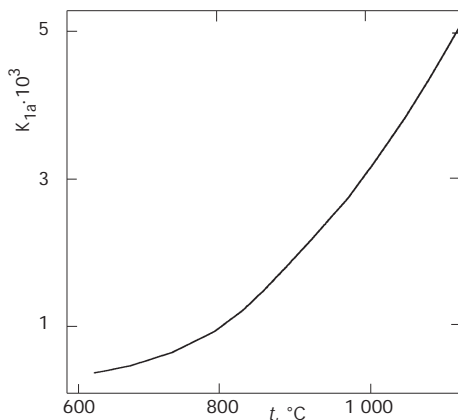| Coefficient	Reaction		
	(*1a*)	(*2*)	(*3a*)
a_i	$3.5400 . 10^{-4}$	$2.5300 . 10^{-3}$	$3.0642 . 10^{-2}$
b_i	60.970	−34.140	−33.657

Units of ΔG_i^0, a_i, b_i see Symbols.

FIG. 2
Dependence of $K_{1a} = P_{H_2S}/P_{H_2O}$ temperature predicted by Eq. (*10*) for reaction (*1a*)

(*3a*) are rather weakly exothermic. Consequently, K_{1a} increases with increasing temperature as can be seen in Fig. 2. The opposite trends are exhibited by K_2 and K_{3a} in Figs 3 and 4. The overall influence of temperature on the term $K_{1a}K_{3a}/K_2$ is illustrated in Fig. 5. Then the combination of Eqs (*8*) and (*10*) makes it possible to predict the equilibrium partial pressure of carbonyl sulfide in contact with calcium oxide as a function of temperature and partial pressures of water vapour, carbon monoxide and hydrogen.

Equation (*8*) can be rewritten with the aid of Eqs (*10*) in terms of the equilibrium mole fractions of the respective gaseous components into the form

$$\ln y_{COS} = -7\,391.2/T - 3.4237 + \ln (y_{H_2O}\,y_{CO}/y_{H_2}\ . \tag{11}$$

It should be noted that the equilibrium levels of COS in contact with calcium oxide are influenced by concentrations of water vapour, carbon mon-

TABLE II
Coefficients in the relationship $\ln K_i = A_i/T + B_i$ for different reactions

Coefficient	Reaction		
	(*1a*)	(*2*)	(*3a*)
A_i	−7 333.1	4 106.1	4 048.0
B_i	−0.04258	−0.30429	−3.6854

Units of A_i, B_i see Symbols.
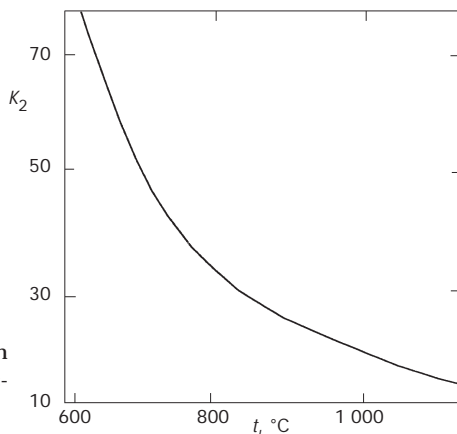
FIG. 3
Dependence of $K_2 = P_{CO_2}\,P_{H_2S}/(P_{COS}\,P_{H_2O})$ on temperature predicted by Eq. (*10*) for reaction (*2*)

oxide and hydrogen in coal gas. On the other hand, they are not affected by the total pressure in the system provided the assumption of ideal behaviour remains feasible.

Curve *1* in Fig. 6 gives the equilibrium concentrations of carbonyl sulfide over calcium oxide in coal gas containing 10 vol.% of water vapour and carbon monoxide and hydrogen in a volume ratio of 1.2. It is evident that even at temperatures as high as 1 100 °C, it is possible to remove about 98% carbonyl sulfide from coal gas. At lower temperatures, equilibrium concentrations of carbonyl sulfide are lower, approaching the 1 ppm level (essentially complete removal of COS) at about 600 °C. However, the sulfidation reaction proceeds more slowly and carbon dioxide can also be sorbed at such lower temperatures.
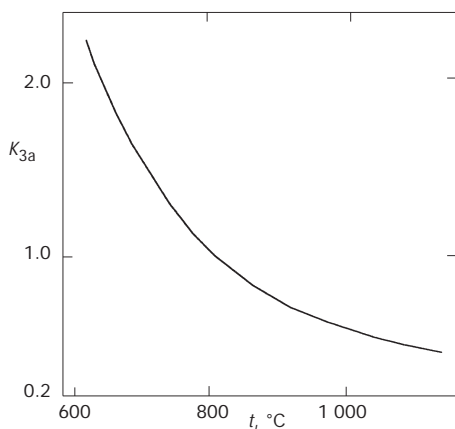

Fig. 4
Dependence of $K_{3a} = P_{CO_2} P_{H_2}/(P_{CO} P_{H_2O})$ on temperature predicted by Eq. (*10*) for reaction (*3a*)
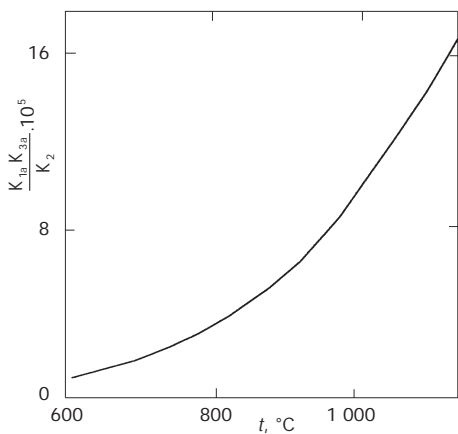

Fig. 5
Overall influence of temperature on $K_{1a}K_{3a}/K_2$

Curve *2* in Fig. 6 shows the equilibrium concentrations of carbonyl sulfide if only reaction (*1*) is considered

$$\ln y_{COS} = -11\ 391.6/T + 0.22274 + \ln y_{CO_2} \ . \tag{12}$$

Although there are some noticable differences in Eqs (*11*) and (*12*), the differences between their predictions for a typical coal gas are not dramatic as shown in Fig. 6 and Table III.

It is apparent that thermodynamic computations do not suffice for detailed engineering considerations. Any practical application must also include, *e.g.* the reaction kinetics, complex phenomena such as the sintering of calcium oxide at high temperatures and a number of technology requirements and needs.

TABLE III
Equilibrium COS removal[a] (%) from coal gas with calcium oxide

Reaction(s)	Temperature, K					
	900	1 000	1 100	1 200	1 300	1 400
(*1a*), (*2*), (*3a*)[b]	99.89	99.76	99.54	99.20	98.70	98.01
(*1*)[c]	99.96	99.86	99.60	99.06	98..04	96.34

[a] Related to the inlet mole fraction, $c_{COS} = 1 \cdot 10^{-3}$. [b] Estimated for $y_{CO}/y_{H_2} = 1.2$ and $y_{H_2O} = 0.10$. [c] Estimated for $y_{CO_2} = 0.10$.
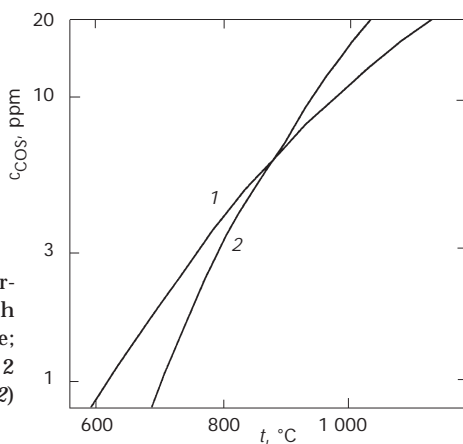

FIG. 6
Computed equilibrium concentration of carbonyl sulfide c_{COS} in coal gas in contact with calcium oxide as a function of temperature; predictions of Eq. (*11*) for $(y_{CO}/y_{H_2}) = 1.2$ and $y_{H_2O} = 0.10$ (*1*); predictions of Eq. (*12*) for $y_{CO_2} = 0.10$ (*2*)

CONCLUSIONS

Carbonyl sulfide exhibits high affinity to calcium oxide.

The 10 ppm level of carbonyl sulfide can still be attained at about 900 °C. Its equilibrium concentration is adversely influenced by the presence of water vapour and the ratio of concentrations of carbon monoxide and hydrogen in coal gas.

Good agreement between the predicted and measured equilibrium dissociation pressures of calcium carbonate suggests that the presented results are based upon sound (but limited) considerations and data.

SYMBOLS

a_i	fitted constant in Eq. (*9*), kJ mol^{-1} K^{-1}
A_i	fitted constant in Eq. (*10*), K
b_i	fitted constant in Eq. (*9*), kJ mol^{-1}
B_i	fitted constant in Eq. (*10*)
c_{cos}	volume concentration of carbonyl sulfide, ppm
ΔG_i^0	standard change of the Gibbs energy of reaction (*i*), kJ mol^{-1}
ΔH_{298}^0	standard heat of reaction at 298 K, kJ mol^{-1}
K_i	quantity given by Eq. (*10*)
K_{1a}	$= P_{H_2S}/P_{H_2O}$, quantity in Eq. (*8*)
K_2	$= P_{CO_2} P_{H_2S}/(P_{COS} P_{H_2O})$, quantity in Eq. (8)
K_{3a}	$= P_{CO_2} P_{H_2}/(P_{CO} P_{H_2O})$, quantity in Eq. (8)
P_j	partial pressure of gaseous component *j* at equilibrium, kPa
$P_{CO_2,d}$	equilibrium dissociation pressure of CO_2, kPa
t	temperature, °C
t_d	decomposition temperature of $CaCO_3$ defined in the text, °C
T	thermodynamic temperature, K
T_d	decomposition temperature of $CaCO_3$ defined in the text, K
y_j	mole fraction of gaseous component *j*

Subscripts

i	denotes reaction (*1a*), (*2*) and (*3a*), respectively
j	denotes the gaseous component COS, CO_2, CO, H_2S, H_2O and H_2, respectively

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