

# Essential Factors in Removing Carbonyl Sulfide from Coal Gas with Lime and Limestone

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High-temperature processes for desulfurization of coal gas are receiving considerable attention. Carbonyl sulfide sorption on lime/limestone is discussed with respect to thermodynamics. Theoretical minimum equilibrium concentrations of carbonyl sulfide are derived as functions of temperature, pressure, and carbon dioxide content in the coal gas.

Current commercial processes for desulfurization of coal gases traditionally involve wet scrubbing and, consequently, operate below 120°C [1]. Such low-temperature processes are based on chemical solvent absorption and physical solvent absorption that require cooling the resulting gases.

The development of new technologies for power generation aims at producing energy that costs less than that produced by other competitive methods and complies with the accepted environmental standards [2]. New attractive systems include *e.g.* pressurized coal gasification technology to produce fuel gas for gas turbines in combined cycle generations (*e.g.* Integrated Gasification Combined Cycle and Topping Cycle).

In general, the process of coal gasification produces gaseous products rich in carbon monoxide, hydrogen, and nitrogen (air-blown gasification) with smaller quantities of steam and carbon dioxide. The sulfur present in coal is converted mainly to hydrogen sulfide and, in a lesser, but significant, extent, to carbonyl sulfide. Of course, the occurrence of other sulfur species, such as elemental diatomic sulfur (S<sub>2</sub>) and carbon sulfide cannot be ruled out. It is also because of their corrosive nature, why these pollutants must be removed from the coal gas before it is further processed.

High-temperature desulfurization of coal gas (above 500°C) employs a noncatalytic gas-solid reaction. The process uses solid sorbents, such as oxides of metals (*e.g.* iron, zinc, manganese, and vanadium and limestones or dolomites [3–5]). Hot gas desulfurization has some economic and technical advantages over low-temperature techniques that make it a promising way of gas cleaning. Mainly because of their relatively low cost, calcium-based sorbents (*e.g.* limestones and dolomites) are viable candidates for sulfur-capturing

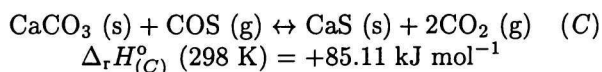
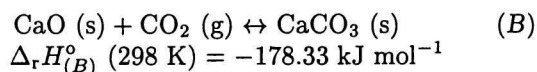
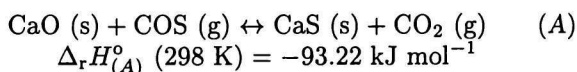
agents in an *in situ* coal gasification-desulfurization process.

While some thermodynamic data on the reaction between calcium oxide and hydrogen sulfide can be found in the literature (*e.g.* [6–8]), little is available for the reaction between calcium oxide or calcium carbonate and carbonyl sulfide. The aim of this study is to define and explore the influence of the operation conditions on the limits of limestone and lime to capture carbonyl sulfide in coal gas. Systematic thermochemical computations, based on sound but limited theoretical considerations and some experimental data, were performed. We believe that the presented findings suggest the operation conditions most likely to result in optimum for carbonyl sulfide fixation by limestone and lime.

## THEORETICAL

### Equilibria in the System COS—CO<sub>2</sub>—CaO

In the three-component system, consisting of gaseous carbonyl sulfide, carbon dioxide, and solid calcium oxide, three reactions (C) = (A) – (B) can occur as follows



The solid phases are assumed to be in the pure

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state and the solid activities are taken as unity in this approach [9–11]. When considering which reactions are thermodynamically feasible, three situations can occur.

If the dissociation pressure of calcium carbonate is lower than the partial pressure of carbon dioxide in the gas phase, the reaction (B) is entirely shifted to the right-hand side and, therefore, calcium oxide cannot occur in the system. Only calcium carbonate and calcium sulfide are present in the system and as follows from the Gibbs phase rule, this region is bivariant. Since calcium oxide is not present in the reaction system, the reactions (A) and (B) cannot take place. Thus, the partial pressure of carbonyl sulfide in this region is governed by the equilibrium of the reaction (C) and we can express it as

$$\ln\{p(\text{COS})\} = \frac{\Delta_r G_{(C)}^\circ}{RT} + 2 \ln\{p(\text{CO}_2)\} \quad (1)$$

where  $\Delta_r G_{(C)}^\circ$  is the standard Gibbs energy of reaction (C). The partial pressures  $p(\text{COS})$  and  $p(\text{CO}_2)$  in eqn (1) as those in the whole work are given in kPa.

In the second region the dissociation pressure of calcium carbonate is higher than the partial pressure of carbon dioxide in the gas phase, so that the equilibrium of reaction (B) is quantitatively shifted to the left-hand side. Therefore, calcium carbonate cannot occur in the reaction system. Only calcium oxide and calcium sulfide are present in the solid phase and this region is bivariant from the standpoint of thermodynamics. Reactions (B) and (C) cannot take place and the partial pressure of carbonyl sulfide is given by the equilibrium of reaction (A). The equilibrium partial pressure of carbonyl sulfide in the system is given by eqn (2)

$$\ln\{p(\text{COS})\} = \frac{\Delta_r G_{(A)}^\circ}{RT} + \ln\{p(\text{CO}_2)\} \quad (2)$$

where  $\Delta_r G_{(A)}^\circ$  is the standard Gibbs energy of reaction (A).

The third situation occurs when the dissociation pressure of carbon dioxide is exactly equal to the partial pressure of carbon dioxide present in the system. Calcium carbonate, calcium oxide, and calcium sulfide can exist and all three reactions (A), (B), and (C) have to be considered. The Gibbs phase rule indicates the system is univariant in this situation. As can be seen, the above equations (reactions) are not independent. Reaction (A) is equivalent to the sum of reaction (B) and reaction (C):  $(A) = (B) + (C)$ . The partial pressure of carbonyl sulfide in this situation is given by eqn (1) or (2) with the constraint on temperature of the system expressed by eqn (3)

$$T_{(B)} = \frac{\Delta_r G_{(B)}^\circ}{R \ln\{p(\text{CO}_2)\}} \quad (3)$$

where  $\Delta_r G_{(B)}^\circ$  is the standard Gibbs energy of reaction (B). The relationship (3) predicts the temperature above which reaction (A) occurs and below which reaction (C) takes place. In other words, eqn (3) specifies the temperature above which the carbonation of calcium oxide cannot take place and below which carbon dioxide can combine with calcium oxide and, thus, can interfere with the sorption of carbonyl sulfide. It should be noted in eqns (1) and (2), the presence of acidic carbon dioxide inherently increases the fugacity of the acidic species of interest (carbonyl sulfide) in the reaction with basic calcium oxide.

## RESULTS AND DISCUSSION

### Dissociation Pressure of Calcium Carbonate – Comparison of Theory with Experiment

The thermodynamic data employed in this work were obtained from the compendium of *Barin* [12]. We believe that this collection of thermochemical properties provides, like the JANAF tables and the U.S. Bureau of Mines Bulletins, the best possible data.

The Gibbs energy of reaction (B) was deduced from the tabulated data at different temperatures and correlated by means of the very simple linear relationship as a function of temperature

$$\Delta_r G_{(B)}^\circ = +149.97 \text{ kJ mol}^{-1} \text{K}^{-1} \cdot T - 174480 \text{ kJ mol}^{-1} \quad (4)$$

for  $T \in \langle 300 \text{ K}, 1200 \text{ K} \rangle$ .

The standard state of a substance throughout this work is its pure form in a defined state of aggregation (ideal gas or crystalline solid) at a pressure of 100 kPa and a specified temperature.

Since the activity of the solid phase is assumed to be unity, we can express the equilibrium dissociation pressure of calcium carbonate as follows

$$\log\{p(\text{CO}_2)\} = -\frac{9113.76 \text{ K}}{T} + 9.83351 \quad (5)$$

$T \in \langle 300 \text{ K}, 1200 \text{ K} \rangle$

Alternatively, the equilibrium decomposition temperature,  $T_{(B)}$ , defined by eqn (3), can be expressed from eqn (5).

In order to verify eqn (5), we compared its predictions with the experimental measurements given in the literature [13]. Fig. 1 presents the measured dissociation pressures of calcium carbonate at different temperatures. As can be seen the experimental results compare quite well with the predictions of the entirely theoretical relationship (5).

Similarly as at eqn (4), a simple least-square procedure was employed in correlating the measured data. The resulting, best-fit constants are given in the equation below

$$\log\{p(\text{CO}_2)\} = -\frac{8689.10 \text{ K}}{T} + 9.41810 \quad (6)$$

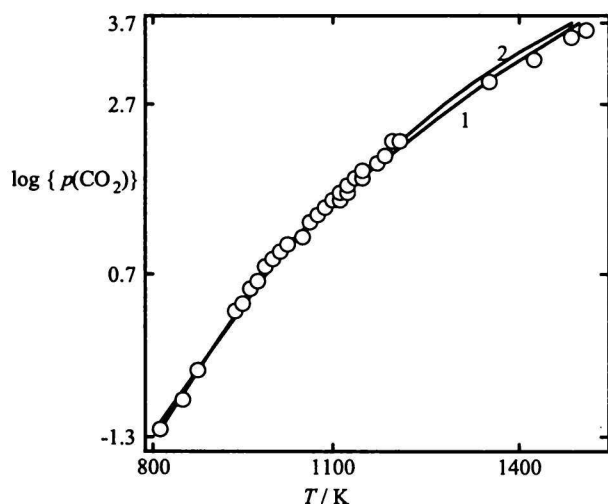


Fig. 1. Measured and predicted dissociation pressures of calcium carbonate:  $\circ$  experimental data points [13]; solid curve 1: predictions of empirical eqn (6); solid curve 2: predictions of theoretical eqn (5) based on the thermodynamic data taken from *Barin* [12].

$$T \in \langle 820 \text{ K}, 1500 \text{ K} \rangle$$

The predictions of eqn (6) are also compared with the original, experimental data points in Fig. 1. The results shown in this figure indicate very good agreement between the theoretical eqn (5) and the empirical eqn (6).

The decomposition temperature of a compound,  $t_{\text{decomp}}$ , is defined as the temperature at which the partial pressure of a gaseous product is equal to the pressure of the surrounding atmosphere. The theoretical relationship (5) leads to  $t_{\text{decomp}}$  ( $p(\text{CO}_2) = 101.325 \text{ kPa}$ ) as large as  $891^\circ\text{C}$ . This prediction compares very well with handbook values of  $882^\circ\text{C}$  [14] and  $898^\circ\text{C}$  [15]. We believe that also our above findings document that the data tabulated in *Barin* [12] are well-founded.

### Reaction of Carbonyl Sulfide with Calcium Carbonate

As discussed above, calcium carbonate can occur in the system at temperatures lower than those given by eqn (5) (or eqn (6)), *i.e.* at

$$T < \frac{9113.76 \text{ K}}{9.83351 - \log\{p(\text{CO}_2)\}} \quad (7)$$

Consequently, reaction (C) is likely to take place at such temperatures. The Gibbs energy of this reaction has been calculated from the data of *Barin* [12] at different temperatures and correlated by means of a simple linear relationship

$$\Delta_r G_{(C)}^\circ = 79196.6 \text{ kJ mol}^{-1} - 147.057 \text{ kJ mol}^{-1} \text{ K}^{-1} \cdot T \quad (8)$$

$$T \in \langle 300 \text{ K}, 1300 \text{ K} \rangle$$

Having in mind common relations among the thermodynamic quantities, we can describe the equilibrium state of reaction (C) as follows

$$\log\{p(\text{COS})\} = 2 \log\{p(\text{CO}_2)\} + \frac{4136.74 \text{ K}}{T} - 9.68109 \quad (9)$$

$$T < T_{(B)}$$

or

$$\log y(\text{COS}) = \log\{p\} + 2 \log y(\text{CO}_2) + \frac{4136.74 \text{ K}}{T} - 9.68109 \quad (10)$$

$$T < T_{(B)}$$

As can be seen in eqn (10), the equilibrium concentration of carbonyl sulfide is inherently increased by the operation (total) pressure within the system and by the presence of carbon dioxide in the gas phase.

Analogously to the above procedure, the standard Gibbs energy of reaction (A) has been expressed as

$$\Delta_r G_{(A)}^\circ = 1.85192 \text{ kJ mol}^{-1} \text{ K}^{-1} \cdot T - 94714.5 \text{ kJ mol}^{-1} \quad (11)$$

$$T \in \langle 600 \text{ K}, 1600 \text{ K} \rangle$$

Eqn (11) can be further rewritten either in terms of the partial pressures

$$\log\{p(\text{COS})\} = \log\{p(\text{CO}_2)\} + 0.096733 - \frac{4947.3 \text{ K}}{T} \quad (12)$$

$$T > T_{(B)}$$

or in terms of the mole fractions of carbonyl sulfide and carbon dioxide

$$\log y(\text{COS}) = \log y(\text{CO}_2) + 0.096733 - \frac{4947.3 \text{ K}}{T} \quad (13)$$

$$T > T_{(B)}$$

Again, the presence of carbon dioxide increases the fugacity of carbonyl sulfide. However, the adverse effect of carbon dioxide is not so strong as in previous case, *i.e.* when  $T < T_{(B)}$ .

It is apparent that the curves defined by eqns (9) and (12) or by eqns (10) and (13) intersect at a point the coordinates of which are determined by the equilibrium state of reaction (B), *i.e.* by a given partial pressure of carbon dioxide and by the corresponding temperature. Taking the predictions of eqns (9) and (12) (or eqns (10) and (13)) as equal, we get for the dissociation pressure of calcium carbonate

$$\log\{p(\text{CO}_2)\} = -\frac{9084.04 \text{ K}}{T} + 9.77782 \quad (14)$$

If we compare this relationship with eqns (5) and (6), we can see that the values of the constants in eqn (14) lie between those appearing in eqns (5) and (6). The decomposition temperature,  $t_{\text{decomp}}$ , at which  $p(\text{CO}_2) = 101.32 \text{ kPa}$ , predicted by eqn (14) is as large

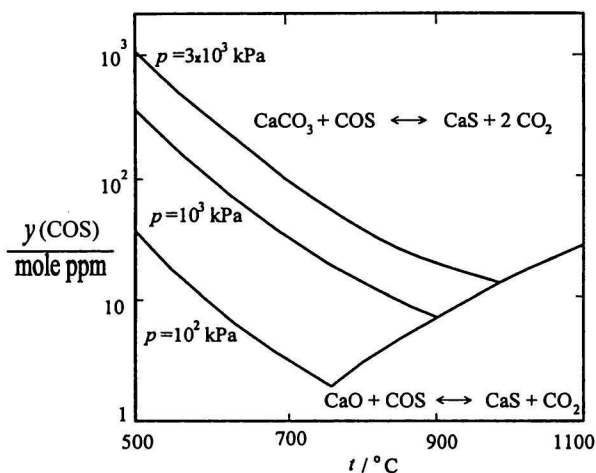


Fig. 2. Calculated equilibrium concentration of COS in coal gas in contact with CaO/CaCO<sub>3</sub> as a function of the temperature and the total operation pressure for the gas containing 10 vol. % CO<sub>2</sub>.

as 896°C. This prediction is close to handbook values of 882°C [14] and 898°C [15]. Also this finding indicates that the final relationships (9), (10), (12), and (13) are consistent.

Graphical forms of the equilibrium eqns (10) and (13) are presented in Fig. 2. As can be seen, carbonyl sulfide has strong affinity to calcium oxide. However, the fugacity (*i.e.* partial pressure) of carbonyl sulfide is increased by the presence of carbon dioxide at temperatures below the decomposition temperature of calcium carbonate. The lowest level of carbonyl sulfide thermodynamically possible in coal gas in contact with lime (limestone) occurs at the decomposition temperature of calcium carbonate. This quantity is only a function of the partial pressure of carbon dioxide and can be predicted from eqn (5) or (6) or (14).

The extremal course of the curves in Fig. 2 follows from a simple fact that reaction (A) is exothermic ( $\Delta_r H_{(A)}^{\circ}(298\text{ K}) = -93.2\text{ kJ mol}^{-1}$ ), whereas reaction (C) is endothermic ( $\Delta_r H_{(C)}^{\circ}(298\text{ K}) = +85.1\text{ kJ mol}^{-1}$ ).

It has been found that the standard enthalpies of the reactions (A)—(C) can be described by a simple quadratic equation

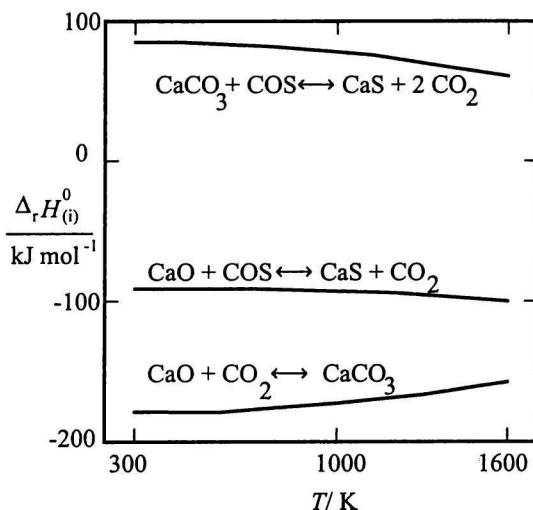


Fig. 3. Standard enthalpies of reactions (A), (B), and (C) at different temperatures.

$$\Delta_r H_{(i)}^{\circ}(T) = k_{(i),1} + k_{(i),2} \cdot T + k_{(i),3} \cdot T^2 \quad (15)$$

The numerical coefficients for the respective reactions are given in Table 1. Different effects of temperature on the corresponding standard reaction enthalpies are seen in Fig. 3.

It is evident that the equilibrium concentrations change rapidly with change in temperature. As can be seen in Fig. 2, a carbonyl sulfide level of 10 mole ppm occurs at about 900°C ( $p(\text{CO}_2) = 100\text{ kPa}$ ). This corresponds to a fractional carbonyl sulfide removal of 0.99, when the raw coal gas with 0.1 vol. % COS is assumed.

In comparison with hydrogen sulfide, carbonyl sulfide exhibits higher affinity to calcium oxide/calcium carbonate. For example, an H<sub>2</sub>S level of 100 mole ppm will be in equilibrium with CaO under similar conditions [16].

## CONCLUSION

Though not extensive, the experimental data support the predictions of the proposed relationships.

Carbonyl sulfide exhibits strong affinity to calcium oxide. Its equilibrium partial pressure in the sys-

Table 1. Coefficients in the Relationship  $\Delta_r H_{(i)}^{\circ}(T) = k_{(i),1} + k_{(i),2} \cdot T + k_{(i),3} \cdot T^2$  for Reactions (A), (B), and (C);  $T \in (298\text{ K}, 1600\text{ K})$

Reaction (i)	$k_{(i),1}$	$k_{(i),2}$	$k_{(i),3}$	$\Delta_r H_{(i)}^{\circ}(298\text{ K})$
	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup> K <sup>-1</sup>	kJ mol <sup>-1</sup> K <sup>-2</sup>	kJ mol <sup>-1</sup>
(A)	-92.0521	-3.26130 · 10 <sup>-3</sup>	+4.53050 · 10 <sup>-7</sup>	-93.22
(B)	-179.6206	+2.99497 · 10 <sup>-3</sup>	+6.81403 · 10 <sup>-6</sup>	-178.33
(C)	+87.5685	-6.25627 · 10 <sup>-3</sup>	-6.36098 · 10 <sup>-6</sup>	+85.11

tem COS—CO<sub>2</sub>—CaO is a nonmonotonous function of temperature at a given partial pressure of carbon dioxide. The lowest level of carbonyl sulfide thermodynamically feasible in the gas phase in contact with calcium carbonate occurs at the decomposition temperature of calcium carbonate.

The proposed relationships are based on sound, but simplified considerations. They predict the influence of temperature, overall pressure, and presence of carbon dioxide on the ability of calcium oxide/calcium carbonate to capture carbonyl sulfide in coal gas. We believe that these equations can be employed in engineering considerations and calculations.

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### SYMBOLS

$\Delta_r G_{(i)}^\circ$	standard Gibbs energy of reaction $i$	J mol <sup>-1</sup>
$\Delta_r H_{(i)}^\circ$	standard enthalpy of reaction $i$	
	at 298 K	kJ mol <sup>-1</sup>
$\ln x$	base-e (Napierian) logarithm of $x = 2.30259 \log x$	
$\log x$	base-ten (Briggsian) logarithm of $x = 0.434294 \ln x$	
ppm	parts per million	
$p$	operation (total) pressure	kPa
$p(\text{COS})$	partial pressure of carbonyl sulfide	kPa
$p(\text{CO}_2)$	partial pressure of carbon dioxide	kPa
$R$	ideal gas-law constant = 8.31441	
		J (mol K) <sup>-1</sup>
$t$	Celsius temperature	°C
$T$	thermodynamic temperature	K
$y(\text{CO}_2)$	mole fraction of carbon dioxide	
$y(\text{COS})$	mole fraction of carbonyl sulfide	

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