

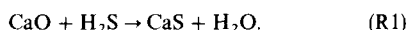


## The adsorption of H<sub>2</sub>S on sulphided limestone

(First received 6 January 1995; revised manuscript received 9 May 1995; accepted 25 May 1995)

### 1. INTRODUCTION

Because of its low price and its favourable thermodynamic features calcined limestone (i.e. CaO) is a candidate sorbent for both non-regenerative and regenerative desulphurization of coal gas. To enable the design of an absorber in which coal gas is desulphurized with calcined limestone, the kinetics of reaction (R1) should be known:



These have been studied by many investigators, a.o. by Westmoreland *et al.* (1977), Borgwardt *et al.* (1984), Abbasian *et al.* (1993) and Heesink and Van Swaaij (1995). Nevertheless, there is no consensus yet about the sulphidation mechanism. Borgwardt *et al.* (1984) state that a non-porous product layer is formed and that solid-state diffusion of H<sub>2</sub>S through the sulphided product layer (i.e. CaS) towards the unreacted CaO is rate determining. However, Heesink and Van Swaaij (1995) suggest that the product layer remains porous and that reaction at the surface of the unreacted CaO determines the rate of sulphidation.

When a non-porous product layer is formed upon sulphidation, the overall sulphidation rate would be proportional to the concentration of adsorbed H<sub>2</sub>S at the surface of the product layer which consists of sulphided limestone. Assuming that the adsorption equilibrium remains established, the apparent reaction order in H<sub>2</sub>S would thus be determined by the absorption behaviour of H<sub>2</sub>S on sulphided limestone. However, if the product layer remains porous and reaction at the surface of the unreacted CaO would be rate determining, the reaction order would be determined by the adsorption behaviour of H<sub>2</sub>S on unreacted CaO.

To gain a better insight in the sulphidation mechanism, in this study the adsorption behaviour of H<sub>2</sub>S on sulphided limestone was examined. If a non-porous product layer is formed upon sulphidation, the experimental results of Heesink and Van Swaaij (1995), showing a reaction order of 0.5 in H<sub>2</sub>S at temperatures between 500 and 700°C and H<sub>2</sub>S pressures varying from 50 to 12,000 Pa (see Fig. 1), should be confirmed by the outcome of the adsorption measurements. If not, a porous product layer is most probably formed and the rate of sulphidation is determined by reaction at the unreacted CaO surface.

### 2. EXPERIMENTAL

Adsorption isotherms were determined according to the transient response method, i.e. by measuring the breakthrough of H<sub>2</sub>S at the outlet of a packed bed of sulphided limestone particles. The applied experimental set-up is shown in Fig. 2. The packed-bed reactor (PBR) consisted of a quartz tube with a diameter of 3.5 cm and a length of 80 cm, which was heated by two ovens (type Heraeus RO 4/25) placed in series. The first oven, covering 40 cm of the

PBR, was used to preheat the gas. The second oven enclosed the bed of sulphided limestone which had a length of 30 cm. Preheat zone and bed were separated by a gas distributor made of sintered quartz. The thermocouple needed for temperature control was placed in between the inner wall of the second oven and the outer wall of the PBR and not inside the bed to avoid any H<sub>2</sub>S adsorbing at the thermocouple. Before experiments were started the axial temperature profile inside the bed was measured. The maximum temperature deviation was found to be no more than 5°C.

With the help of electronic mass flow controllers a mixture of 4 vol% H<sub>2</sub> and balance helium was composed. Before leading the mixture through the PBR, it was first sent through a bed of BASF R3-11 catalyst to remove traces of O<sub>2</sub> possibly present in the applied gases. In this way gradual oxidation of CaS towards CaSO<sub>4</sub> was prevented. Either H<sub>2</sub>S or Ar was added stepwise to the gas mixture to measure breakthrough behaviour. Whereas Ar was added before the catalyst bed, H<sub>2</sub>S was supplied behind the bed to avoid poisoning of the catalyst. All gases were taken from bottles. Part of the PBR effluent was sent to a Varian 920 thermal conductivity detector (TCD) for analysis. The TCD was connected to a computer for data acquisition.

The experimental procedure was as follows. First the bed was heated up while purging with a gas mixture containing 4 vol% H<sub>2</sub> in He. The applied H<sub>2</sub> concentration agrees with the concentration that was used by Heesink and Van Swaaij (1995) when measuring sulphidation kinetics. The flow rate was fixed at 250 ml (STP) min<sup>-1</sup>. Once the desired temperature had been reached, Ar was instantaneously added to the gas stream. At the same time the collection of TCD data was started. After the TCD outlet signal had stabilized, the set-point for the argon mass flow controller was increased instantaneously resulting in a new breakthrough curve "on top" of the previous one. By performing this procedure several times a series of breakthrough curves was obtained. This procedure was then repeated with H<sub>2</sub>S instead of Ar applying equal partial pressures. Breakthrough curves of Ar and H<sub>2</sub>S were also measured with an empty PBR. These curves were used to correct for the difference between the residence times of Ar and H<sub>2</sub>S (note that H<sub>2</sub>S was added further downstream than Ar) and for possible adsorption of H<sub>2</sub>S at the internal surface of the lines and the PBR. The raw TCD data were transformed into breakthrough curves by the help of a spreadsheet program. A typical result is shown in Fig. 3. The areas limited by the breakthrough curves of H<sub>2</sub>S and Ar, which are a measure of the (incremental) amount of H<sub>2</sub>S adsorbed by the bed, were calculated numerically. By adding up the areas that were subsequently obtained in one series, adsorption isotherms could be obtained. At the end of an experiment, the bed was purged with the He-H<sub>2</sub> mixture while heating to a higher temperature (typically 800°C) to ensure that all adsorbed H<sub>2</sub>S was removed before a new experiment was started. Once further heating

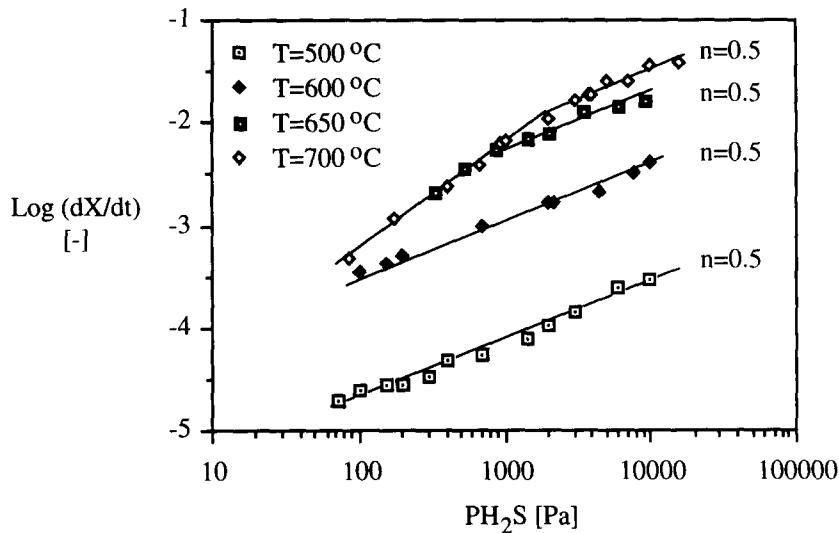


Fig. 1. Order plots obtained by Heesink and Van Swaaij (1995) for the sulphidation of calcined Wülfrath limestone with  $\text{H}_2\text{S}$  at 500, 600, 650 and 700°C (conversion rates calculated at a sulphidation extent of 30%).

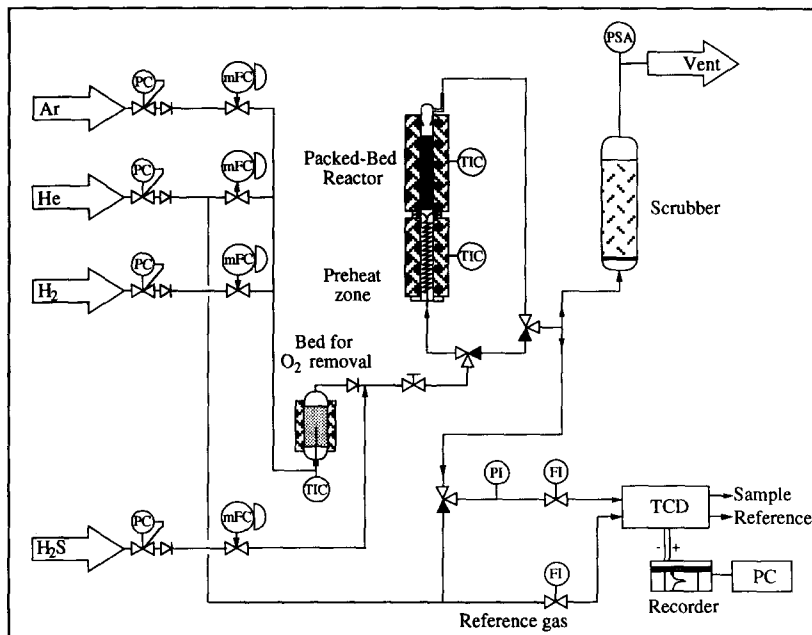


Fig. 2. A simplified flowsheet of the applied experimental set-up.

did not result in any TCD response, all  $\text{H}_2\text{S}$  was assumed to be desorbed.

All PBR experiments were performed with a single batch of 250 g sulphided limestone from the German quarry at Wülfrath which was also used for the sulphidation study performed by Heesink and Van Swaaij (1995). Particles with a diameter ranging from 0.5 to 1.4 mm were applied. Table 1 gives the composition of the applied limestone in raw, calcined and sulphided form. Calcination as well as sulphidation of the limestone were carried out beforehand in a separate bubbling fluidized-bed reactor. Calcination was performed by heating up to 850°C while fluidizing with  $\text{N}_2$  and was stopped after about 2.5 h when no  $\text{CO}_2$  was detected in

the reactor effluent anymore. Sulphidation was subsequently carried out at 600°C with a gas mixture consisting of 2 vol%  $\text{H}_2\text{S}$  and 4 vol%  $\text{H}_2$  in  $\text{N}_2$  which was first led through an  $\text{O}_2$ -removing catalyst bed. The  $\text{H}_2\text{S}$  content of the reactor effluent was continuously measured by incinerating a small fraction of the off-gases and measuring the produced amount of  $\text{SO}_2$  by means of infrared analysis. Sulphidation was stopped after approximately 4 h when no  $\text{H}_2\text{S}$  was absorbed anymore. After cooling, 250 g of the sulphided material was transferred to the PBR. About 1 g was used for mercury porosimetric measurement. The specific surface area of the sulphided material was determined at  $9.2 \text{ m}^2 \text{ g}^{-1}$ . To ensure that the adsorption measurements would not be affected by

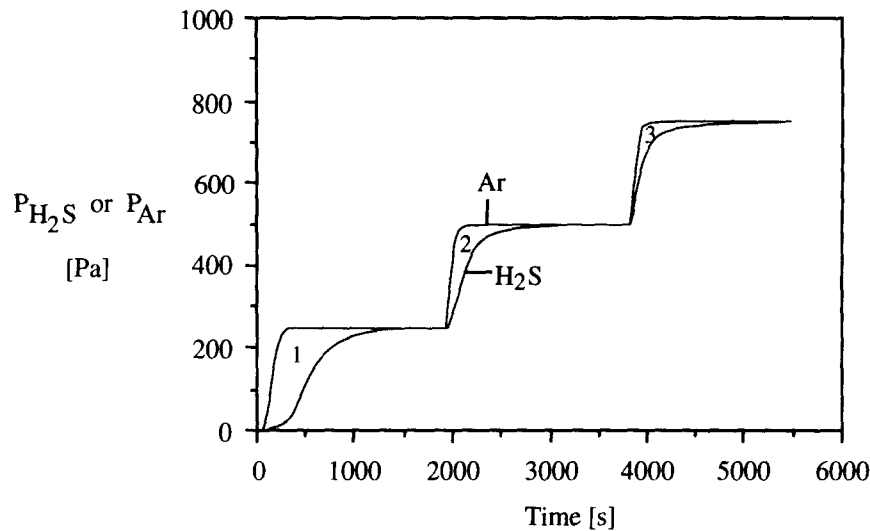


Fig. 3. Demonstration of the applied method to determine adsorption isotherms. The areas enclosed by the breakthrough curves of H<sub>2</sub>S and Ar are a measure of the adsorbed amount of H<sub>2</sub>S: area 1 is a measure of the amount adsorbed at an H<sub>2</sub>S pressure of 250 Pa; the sum of areas 1 and 2 is a measure of the adsorbed amount at an H<sub>2</sub>S pressure of 500 Pa, etc.

Table 1. Chemical composition of the applied Wülfrath limestone in raw, calcined and sulphided form (in wt%)

Component	Raw	Calcined <sup>†</sup>	Sulphided <sup>†</sup>
CaCO <sub>3</sub>	97.20	—	—
MgCO <sub>3</sub>	0.90	—	—
CaO	—	95.90	—
CaS	—	—	98.33
MgO	—	0.76	0.61
Si	0.54	0.95	0.76
Fe	0.09	0.16	0.13
Al	0.06	0.11	0.09
K	0.03	0.06	0.05
Sr	0.03	0.06	0.05

<sup>†</sup>Calculated from the composition of raw limestone assuming complete calcination and sulphidation.

sulphidation of CaO traces, that possibly remained after sulphidation in the fluidized-bed reactor, the bed material was further sulphided in the PBR by leading through a gas mixture consisting of 2 vol% H<sub>2</sub>S, 4 vol% H<sub>2</sub> and balance He while maintaining the PBR at a temperature of 700°C. After some 2 h the H<sub>2</sub>S concentration in the effluent was found to stabilize at the adjusted value of 2 vol% and sulphidation was concluded to be complete.

### 3. RESULTS AND DISCUSSION

Figure 4 shows the raw results of the adsorption experiments. The given values of the surface concentration,  $\sigma$ , were calculated on the basis of the initial surface area of the sulphided limestone which was 9.2 m<sup>2</sup> g<sup>-1</sup>. However, mercury porosimetric measurement did show that the bed material had suffered from sintering during its one week stay in the PBR, resulting in a specific surface area of 4.9 m<sup>2</sup> g<sup>-1</sup> after completion of the last experiment. It is however reasonable to assume that the specific surface area did not change dramatically during the measurement of a single isotherm which took about 4 h. Therefore, the obtained results can be used to predict the apparent reaction order in H<sub>2</sub>S if a non-

porous product layer would be formed upon sulphidation. In that case the rate of sulphidation would be proportional to the H<sub>2</sub>S concentration at the surface of the sulphided product layer

$$\frac{dX}{dt} \equiv \sigma \equiv P_{H_2S}^n \quad (1)$$

Table 2 shows the best-fit values of  $n$  as derived from the data depicted in Fig. 4 together with the corresponding 95% probability ranges. Although there is quite some scatter in these data all values of  $n$  are significantly lower than 0.5 which is the reaction order in H<sub>2</sub>S as observed by Heesink and Van Swaaij (1995)

In order to determine the enthalpy and entropy of adsorption the raw adsorption data were interpreted assuming Langmuir adsorption, both with and without dissociation of the adsorbed H<sub>2</sub>S molecules. When no dissociation occurs the following equation applies:

$$\frac{1}{\sigma} = \frac{1}{\sigma_m} + \frac{1}{\sigma_m b P_{H_2S}} \quad (2)$$

where  $\sigma$  represents the actual surface concentration of H<sub>2</sub>S (in mol m<sup>-2</sup>),  $\sigma_m$  the maximum surface concentration (when all sites are occupied) and  $b$  the Langmuir adsorption constant defined as

$$b = \exp\left(\frac{\Delta S_{ads}^0}{R}\right) \exp\left(\frac{-\Delta H_{ads}^0}{RT}\right) \quad (3)$$

where  $\Delta S_{ads}^0$  and  $\Delta H_{ads}^0$ , respectively, represent the difference between the entropies and the difference between the enthalpies of adsorbed H<sub>2</sub>S and ideally gaseous H<sub>2</sub>S. In general, these values do not depend much on the temperature and are therefore assumed to be constant in the relevant temperature range (450–700°C). The value of  $-\Delta H_{ads}^0$  is also referred to as heat of adsorption,  $Q_{ads}$ . When the H<sub>2</sub>S molecules dissociate upon adsorption,  $\sigma$  can be calculated from

$$\frac{1}{\sigma} = \frac{1}{\sigma_m} + \frac{1}{\sigma_m \sqrt{b P_{H_2S}}}. \quad (4)$$

The raw adsorption data were evaluated by fitting the results

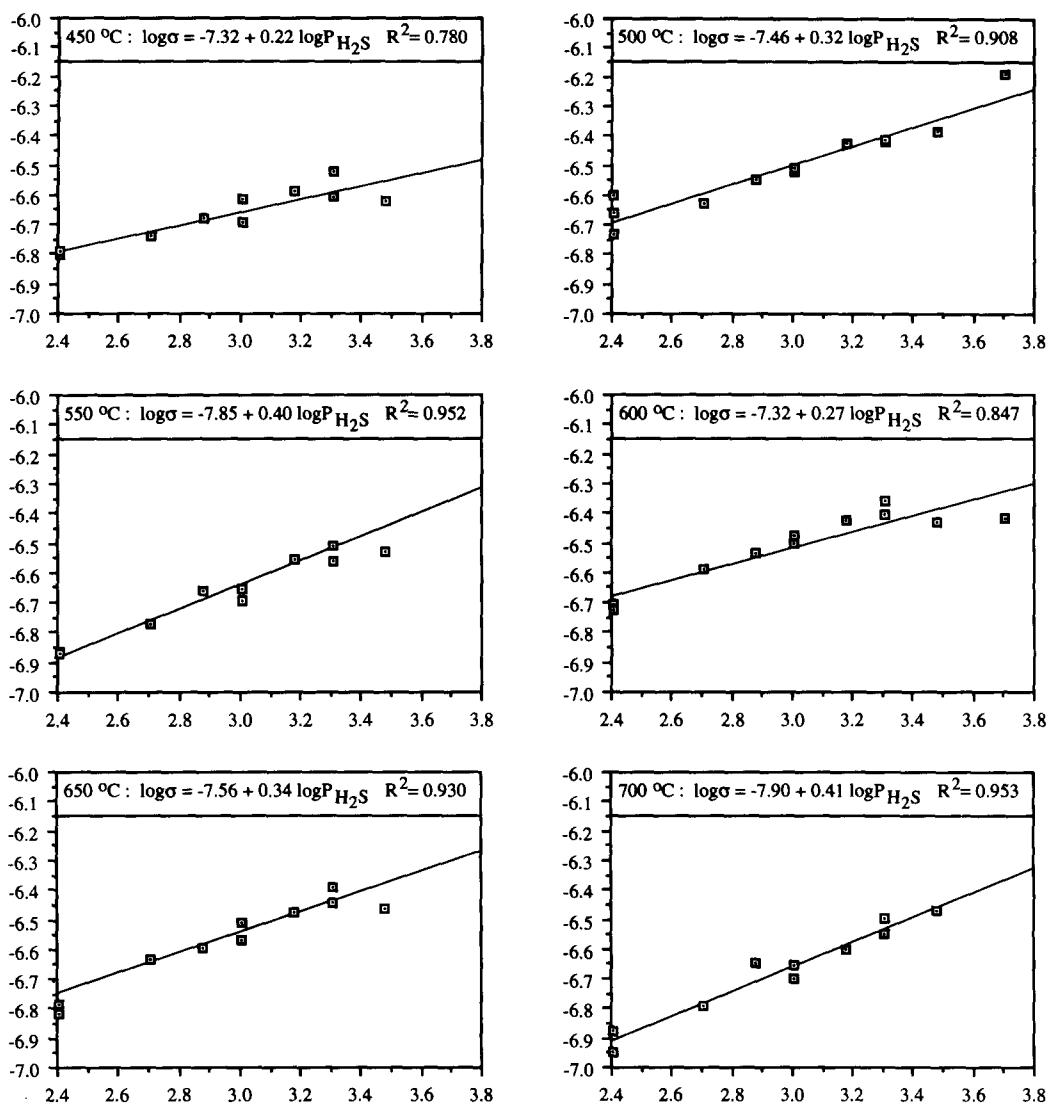


Fig. 4. Measured isotherms for the adsorption of  $\text{H}_2\text{S}$  on sulphided Wulfrath limestone; (horizontal axis)  $\log P_{\text{H}_2\text{S}}$  (Pa); (vertical axis)  $\log \sigma$  ( $\text{mol m}^{-2}$ ).

Table 2. Best-fit values of  $n$  for the adsorption of  $\text{H}_2\text{S}$  on sulphided Wulfrath limestone together with the 95% probability ranges

Temperature (°C)	$n$ (dimensionless)
450	$0.22 \pm 0.07$
500	$0.32 \pm 0.07$
550	$0.40 \pm 0.06$
600	$0.27 \pm 0.07$
650	$0.34 \pm 0.07$
700	$0.41 \pm 0.07$

Table 3. Correlation between experimental data and data predicted on basis of Langmuir-type adsorption

Temperature (°C)	$R^2$ Langmuir (dimensionless)	$R^2$ Langmuir with dissociation (dimensionless)
450	0.861	0.881
500	0.783	0.863
550	0.941	0.969
600	0.739	0.750
650	0.970	0.960
700	0.926	0.947
Average	0.870	0.895

with eqs (2) and (4). The correlation between the experimental results and those predicted on the basis of the two adsorption isotherms is given in Table 3. Overall, the best fits are obtained by assuming dissociative Langmuir adsorption though the differences are quite small. Fragments possibly formed by dissociation are H and HS (Anderson, 1971).

Table 4 summarizes the best fit values of  $\sigma_m$  and  $b$  as obtained on the basis of eq. (4). Due to sintering as well as experimental errors the values of  $\sigma_m$  vary somewhat but typically amount to  $1 \mu\text{mol m}^{-2}$ . This value compares reasonably with the value of  $0.14 \mu\text{mol m}^{-2}$  that Thomas and

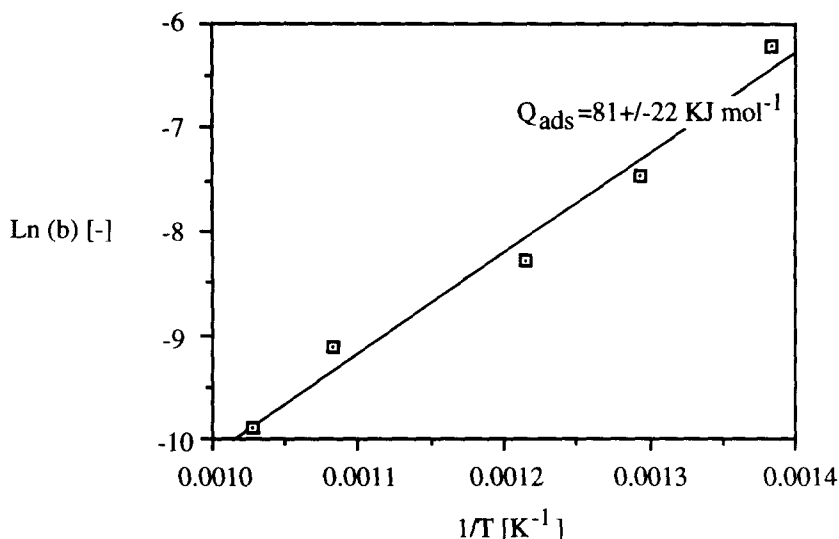


Fig. 5. Arrhenius plot of the Langmuir adsorption constant  $b$  for the system  $\text{H}_2\text{S}$ -sulphided Wülfraath limestone; dissociative Langmuir adsorption assumed.  $Q_{\text{ads}}(95\%) = 81 \pm 22 \text{ kJ mol}^{-1}$ .

Table 4. Best-fit values of  $\sigma_m$  and  $b$   $\text{H}_2\text{S}$ -CaS system assuming dissociative Langmuir adsorption

Temperature (°C)	$\sigma_m$ ( $\mu\text{mol m}^{-2}$ )	$b$ ( $\text{Pa}^{-1}$ )
450	0.38	$2.04 \times 10^{-3}$
500	0.75	$5.80 \times 10^{-4}$
550	0.67	$2.55 \times 10^{-4}$
600	0.66	$9.50 \times 10^{-4}$
650	1.13	$1.11 \times 10^{-4}$
700	1.21	$5.02 \times 10^{-5}$

Ullah (1969) measured for the system  $\text{H}_2\text{S}$ -NiS (NiS supported by  $\gamma$ -alumina) at temperatures ranging from 500 to 650°C. The obtained  $b$  values generally obey the demand that they decrease at increasing temperature. Only at 600°C a discrepancy is observed. Figure 5 shows an Arrhenius plot of the obtained  $b$  values. The deviating value obtained at 600°C has not been included. The heat of adsorption,  $Q_{\text{ads}}$ , that can be derived from Fig. 5 amounts to  $81 \pm 22 \text{ kJ mol}^{-1}$ . The given range refers to the 95% probability interval. The average value of  $81 \text{ kJ mol}^{-1}$  compares quite well with the value of  $77 \text{ kJ mol}^{-1}$  reported by Thomas and Ullah (1969) for the  $\text{H}_2\text{S}$ -NiS system.

The observation of a low surface coverage and a relatively high heat of adsorption indicate that the adsorption of  $\text{H}_2\text{S}$  on sulphided limestone belongs to the category of entropically ideal site adsorption as defined by de Boer and Kruyer (1952). Confirmation for this can be obtained by comparing the obtained value of  $\Delta S_{\text{ads}}^\circ$  with the value that is predicted on the basis of the theory of entropically ideal site adsorption. These values, respectively, amount to about  $-167$  and  $-175 \text{ J mol}^{-1} \text{ K}^{-1}$  in the relevant temperature range. In case of entropically ideal mobile adsorption, the adsorbed  $\text{H}_2\text{S}$  would act as a two-dimensional gas and  $\Delta S_{\text{ads}}^\circ$  would amount to about  $-52 \text{ J mol}^{-1} \text{ K}^{-1}$ . It is therefore concluded that the adsorbed  $\text{H}_2\text{S}$  molecules are practically immobile.

#### 4. CONCLUSIONS

If a non-porous product layer is formed during the sulphidation of calcined limestone the reaction order in  $\text{H}_2\text{S}$

would correspond with the value of  $n$  as defined by eq. (1). This value was found to range from  $0.22 \pm 0.07$  at 450°C to  $0.41 \pm 0.07$  at 700°C, whereas Heesink and Van Swaaij (1995) observed a reaction order of 0.5 at all temperatures. We therefore conclude that adsorption of  $\text{H}_2\text{S}$  at the surface of the sulphided product layer is not a relevant step in the sulphidation mechanism. This implies that the product layer remains porous during sulphidation and that reaction at the surface of the unreacted CaO governs the rate of sulphidation.

*Acknowledgements*—This investigation was supported by the Directorate-General XII of the European Communities and the Dutch organizations TNO-IMET and NOVEM BV. The authors also acknowledge J. Nijmeijer and E. J. Ruesink for their assistance in the experimental work.

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#### NOTATION

$b$	Langmuir adsorption constant, $\text{Pa}^{-1}$
$n$	reaction order in $\text{H}_2\text{S}$ , dimensionless
$P_{\text{H}_2\text{S}}$	partial $\text{H}_2\text{S}$ pressure, Pa
$Q_{\text{ads}}$	heat of adsorption ( $= -\Delta H_{\text{ads}}^\circ$ ), $\text{J mol}^{-1}$
$R$	gas constant, $\text{J mol}^{-1} \text{ K}^{-1}$ or correlation coefficient, dimensionless
$t$	time, s
$T$	temperature, K
$X$	sulphidation extent, dimensionless

#### Greek letters

$\Delta H_{\text{ads}}^\circ$	enthalpy difference between gaseous and adsorbed material, $\text{J mol}^{-1}$
$\Delta S_{\text{ads}}^\circ$	entropy difference between gaseous and adsorbed material, $\text{J mol}^{-1} \text{ K}^{-1}$
$\sigma$	surface concentration, $\text{mol m}^{-2}$
$\sigma_m$	maximum surface concentration, $\text{mol m}^{-2}$

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