

THE CHEMICAL EQUILIBRIUM IN THE CLAUS PROCESS

Calculations and experiments were carried out to obtain data on the equilibrium of the reaction $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$. The purpose of the investigation was to determine how deposition of sulphur and condensation of water from the unreacted gas would affect the position of the equilibrium and thereby the amount of sulphur to be obtained.

1. Calculation of the equilibrium.

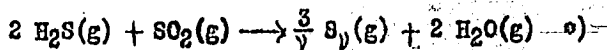
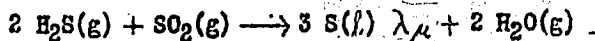
The calculation of the equilibrium constant in the temperature region of technical importance was carried out:

a. From the free energy of formation of the reactants at 25°C., and

b. From the experimental data given in a paper by Lewis and Randall (J. A. C. S. 40, 332, (1918)).

In both cases the conversion to the temperature desired was carried out graphically and algebraically. It could be shown that the graphical conversion can be used for a limited temperature region by assuming a heat of reaction which is independent of the temperature.

In the calculation of the equilibrium constant and the evaluation of the results, it is advantageous to distinguish between the two following reactions:



This difference obviously disappears at the boiling point of sulphur.

The following Table 1 gives the thermal data used in the calculations. The data of the International Critical Tables, volume 7, besides those of Landolt-Börnstein and Lewis and Randall, "Thermodynamics", were used. The vapor pressure and the molecular weight of the sulphur vapor (see Table 2) were taken from the paper by Preuner and Schupp (Z. Phys. Chem. 68, 129, (1910)).

*) (g) and (l) refer to the gaseous and liquid phase. λ_{μ} refers to the equilibrium liquid of the two S modifications.

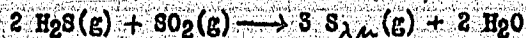
Table 1

	<u>Heat Content</u> cal/mol	<u>Free Energy</u> cal/mol	<u>Molecular Heat Capacity</u> C_p
$H_2S(g)$	-4800	-7840	8.44 $8.81 - 0.0019T + 0.0000022T^2$
$SO_2(g)$	-70940	-69660	8.95 $7.0 + 0.0071T - 0.00000186T^2$
$H_2O(g)$	-57840	-54507	8.44 $8.81 - 0.0019T + 0.0000022T^2$
$H_2O(l)$	+300	+93	$\nu_i = 6.9$ $\sim 5.4 + 0.005T$
$S_2(g)$	+29690	+18280	$6.50 + 0.0010T$
$S_6(g)$	+22600	+11900	
$S_8(g)$	+20000	+10000	

Table 2

<u>t(°C)</u>	<u>T(°K)</u>	<u>p(mmHg.)</u>	<u>ν (average number of atoms)</u>
100	373	0.0085	7.77
125	398	0.053	-
160	423	0.23	7.65
175	448	0.70	-
200	473	2.26	7.52
225	498	4.6	-
250	523	12.0	7.40
275	548	27	-
300	573	48	7.26
325	598	77	-
350	623	128	7.06
400	673	378	6.80
450	723	828	6.71

Equilibrium of the reaction:



According to the data of the tables, ΔF_{298} is equal to 23,285 cal from which it follows according to the equation $\Delta F = -RT \ln K$, that the equilibrium constant is $K_{298} = 8.7 \times 10^{-18}$. *) (1)

For the calculation of the constant at 580° K according to the Gibbs-Helmholtz equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (2)$$

the negative heat of reaction at a given temperature is introduced

$$\Delta H = \Delta H_{298} + \Delta C_p(T-298.2) \quad (3) \text{ and}$$

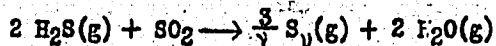
the equations 1, 2 and 3 are combined and integrated. It follows then

$$\log \frac{K_{298}}{K_T} = \Delta H_{298} y - \Delta C_p z \quad (4) \quad \text{where } y = \frac{298.2 - T}{4.5787 \cdot 298.2T} \quad (5) \quad \text{and}$$

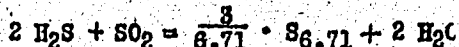
$$z = 298.2y - \frac{1}{R} \log \frac{298.2}{T} \quad (**) \quad (6)$$

For numerical calculations the tabulated values of the functions x and y were used which are given in the appendix of Lewis and Randall's book "Thermodynamics". According to the above calculations the equilibrium constant K_{580} is equal to 23.8, whereas the conversion of the experimental data of Lewis and Randall gives K_{580} equal to 23.5.

The equilibrium constant for the reaction



was calculated from the equilibrium constant determined by Lewis and Randall. At the boiling point of sulphur, the sulphur has an average number of atoms of 6.71 according to the measurements of Preuner and Schupp (compare Table 2). The preceding equation should, therefore, be written as follows:



and the constant measured by Lewis and Randall can also be written as follows:

$$K_{718} = \frac{[\text{H}_2\text{S}]^2 [\text{SO}_2]}{[\text{H}_2\text{O}]^2 [\text{S}_y]^{3/y}}$$

in which at the boiling point of the sulphur the term $[\text{S}_y]^{3/y}$ becomes 1. At any

*) The equilibrium constant is defined as the equilibrium constant calculated from the partial pressures.

***) R is the molar gas constant.

given temperature the equilibrium constant for gaseous sulphur follows from the equation

$$K_T = \frac{K_p}{[S_p]^{3/2}} \quad (7)$$

where the partial pressure of the sulphur vapor at the temperature chosen should be substituted for $[S_p]$. According to the above equations K_{580} was found to be - 4.66.

The graphical conversion of the equilibrium constant can be carried out from a diagram in which $-R \ln K$ is plotted against the reciprocal value of the absolute temperature. Assuming the validity of equation 2 and assuming further that ΔH is constant, a linear relation exists between the terms plotted on the ordinates of the diagram.

Measurement of the Equilibrium

The experimental investigation of the equilibrium at temperatures which lay considerably below the boiling point of sulphur was difficult insofar as the adsorption of the sulphur vapors, which was to be expected, would lead to erroneous values for the sulphur concentration in the gas phase and thereby to erroneous final results. Static methods for the measurement of the equilibrium, therefore, had to be eliminated from the start.

In measurements of the equilibrium in flowing gas, however, a catalyst could not be omitted and this resulted in a certain doubt whether the reaction had gone to completion and also gave difficulty in the measurement of the temperature. (In the reaction with catalyst, the reaction temperature would necessarily have to be the temperature on or near the active centers. This temperature is very difficult to determine experimentally in a comparatively small reactor and since the reaction is strongly exothermic the temperature is certainly not identical with the actually measured average temperature in the reactor space.)

In the experimental measurements on flowing gas, the gas concentrations at which the measurements could be carried out were considerably limited; the upper limit was given by the concentration at which separation of liquid sulphur would take place causing inactivation of the catalyst, whereas the lower limit was given by the concentration below which the catalyst is not any longer or not uniformly active. Actually, gases containing 1 - 10% total sulphur were investigated and up to 40% steam was added.

Some of the reactors were heated electrically, while some were immersed in a bath of boiling technical anthracene in order to obtain better temperature control. The space velocity in these experiments was only 1/4 to less than 1/20 of the practical space velocity (600 liters of gas per hour and liter of catalyst).

Prior to the experiments the catalyst was used for some time with the gas mixture to be investigated until conditions with respect to the vapors and gases adsorbed by the catalyst had become constant. Analysis of the gas before and after it had passed the catalyst was carried out as usual by absorption of H_2S and SO_2 in iodine solution.

The equilibrium constant is calculated from the analytical data according to

$$K = \frac{\left[\frac{(a-a^1)}{y} + \frac{(b-b^1)}{y} \right]^{3/2} [a-a^1 + \kappa]}{[a^1]^2 [b]} \quad (8)$$

In this equation "a" means partial pressure of H₂S in atmospheres; "b" - partial pressure of SO₂ in atmospheres; "c" - partial pressure of water in atmospheres. a¹ and b¹ signify the corresponding values according to the reaction. The expression (a-a¹) + (b-b¹) can be replaced by (c-c¹) where c or c¹ refers to the total sulphur.

The following Table 3 gives the comparison of the results obtained by calculations and the experimental results. The experimental data and their average show in general good agreement with the calculated values.

Table 3

T	Calculated		Exptl. Determined		Exptl. Conditions
	From ΔF	From K_{718}	Mean Value	Individual Measurements	
298	78.1	80.0			
580	23.8	23.5			
718				12.87	
298	63.7				
580	21.3	21.3	22.1	21.2 20.9 24.7	A
580		21.3	18.8	19.3 18.8 18.4	B
523		26.0	24.0	(23.0) (24.5) (24.7)	C
597		20.0	19.8	20.4 20.5 18.8 19.5 19.6	D

In the series of experiments termed A, an electrically heated reactor was used, the space velocity was about 1/4 of that used in the plant, the total

If, instead of the partial pressure volume percents are used for a, b, and c, the result has to be multiplied by 100^(1- α) or 1.168 has to be added to the logarithm of the constant.

sulphur of the gas was varied between 8 and 0.5% and the gas contained about 40% of water vapor.

Series B was carried out under the same conditions, except that no water was added and the total sulphur varied between 7 - 10%. The steam in the tail gas is calculated with the assumption that the feed gas was saturated with steam at 25°C.

Series C refers to experimental results obtained in tests with newly developed catalyst. The temperature was 250°C. As it was to be expected, the reaction did not go to completion because of the high space velocity. The constant found is somewhat low but under consideration of the somewhat changed conditions it is in agreement with the other values.

Series D was obtained at 325°C, without the addition of steam and at an extremely low space velocity. The total sulphur in the gas fed to the catalyst was about 10%.

On comparison of the data it appears as if the equilibrium would be reached easier in the presence of steam. This fact would be in agreement with some theories on the mechanism of the catalytic action.

As to the accuracy in the determination of the equilibrium constant, it must be emphasized that the figure behind the decimal point is somewhat uncertain. The apparently good agreement of some of the calculated values with the experimental values and the extent of the deviation makes it appear as if the accuracy were greater, but it must be considered that a number of experiments giving deviating results were not used because of their comparatively large error. It was not always possible to find a reason for the deviation.

Evaluation of the Data

For the calculation of the equilibrium it is best to use the values for the constant given in Figure 1. Constant K^* or K should be used, dependent on the form of the sulphur, gaseous or liquid. When the figure found for the experimental temperature is divided by 4.579, the Brigg logarithm is obtained and from this K can be found. If this K value is used in equation 8, the concentration desired can be calculated for the given initial concentration. However, since the number of atoms of sulphur is not a whole number, the equation becomes transcendental. In order to facilitate evaluation a diagram was drawn in which the amount of H_2S and SO_2 can be directly obtained. The diagram has been constructed with the assumption that the crude gas contains 10% $H_2S + SO_2$ in the stoichiometric ratio.

Curves are given for the equilibrium with liquid and with gaseous sulphur; furthermore, curves for various water contents in the feed gas. Whether the sulphur will be obtained as gas or in the form of a liquid can be calculated from the concentration in the feed gas and the temperature according to the data in Table 1 (vapor pressure of sulphur and number of atoms). For a gas with 10% H_2S and SO_2 in the stoichiometric ratio the actual vapor pressure of sulphur as compared to the vapor pressure which would exist if the gas would react quantitatively is given in Table 4.

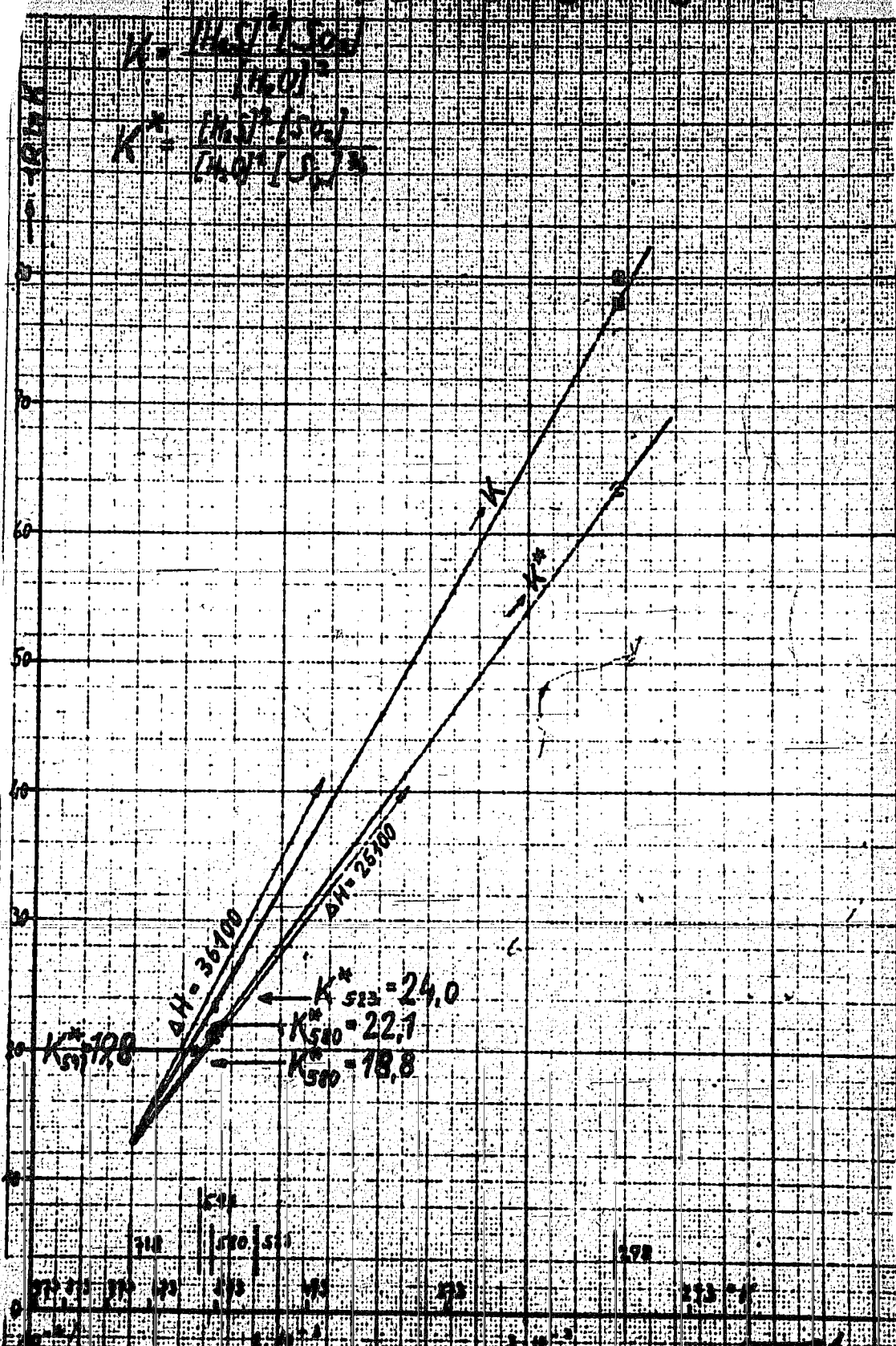
Table 4

10% H₂S + SO₂
gives the following
vapor pressure of
S (mm. Hg.)

Vapor pressure of
S (mm. Hg.)

<u>°C.</u>	<u>S (mm. Hg.)</u>	<u>Vapor pressure of S (mm. Hg.)</u>
150	9.95	0.23
175	10.20	0.70
200	10.35	2.26
250	10.6	12
300	10.7	48
350	11.0	128

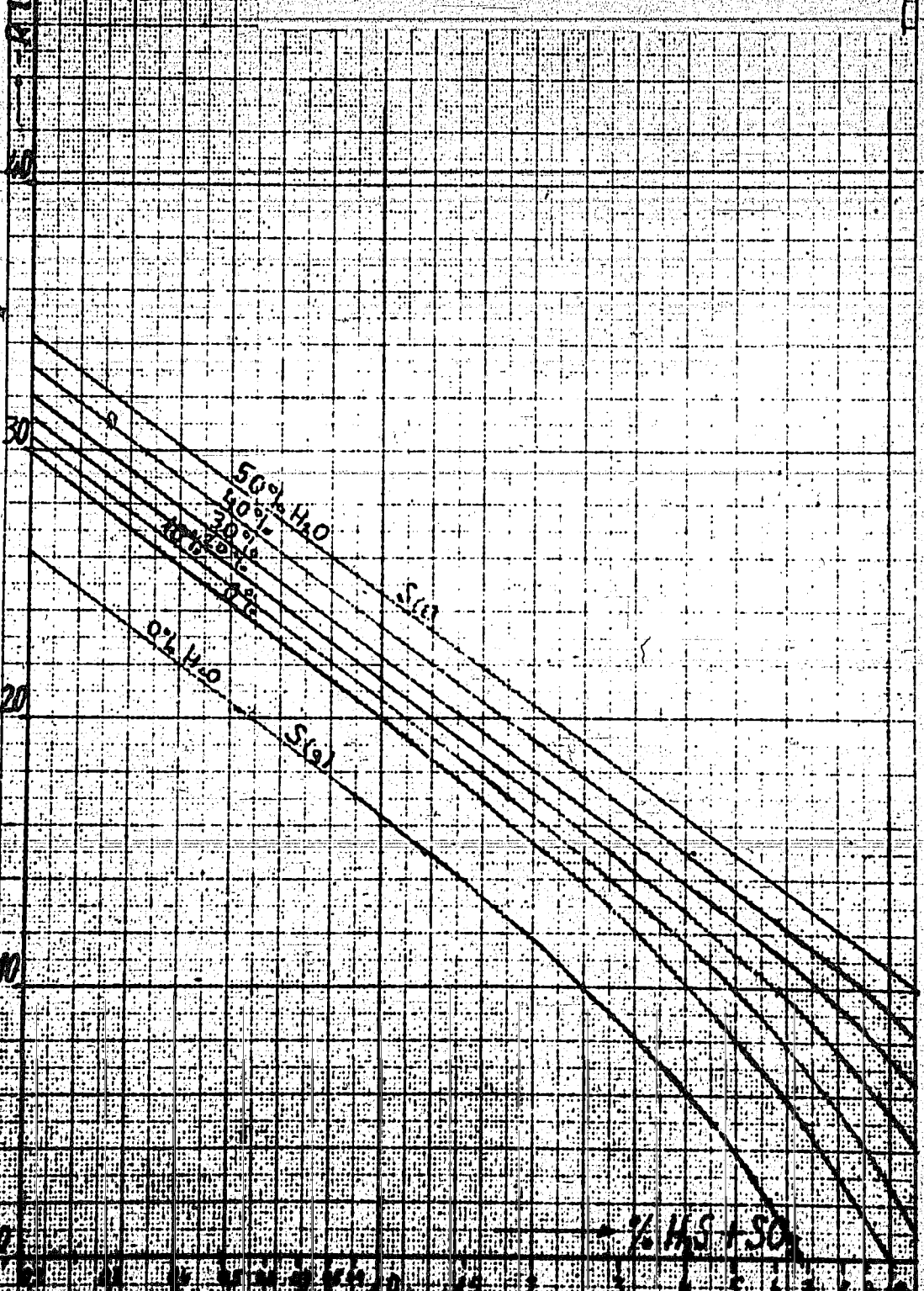
TEMPERATURE COEFFICIENT OF THE EQUILIBRIUM CONSTANT



Arminsherk Merseburg
 Institute of Chemistry

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RELATION OF SO₂ AND H₂S CONCENTRATION IN THE TAIL GAS AND
 THE EQUILIBRIUM CONSTANT AT A CONCENTRATION OF 10% H₂S AND SO₂
 IN THE RAW GAS



Ammoniakwerk Merseburg
 Gesellschaft für chemische Industrie
 Leipzig (1950)

Di. Oelrichs

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