Item #20
## Calculations and Experiments on the Chemical Equilibrium of the Claus-process

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At the request of Dr. Braus it has been tried by computation and experimentation to obtain numerical data of the equilibrium of the reaction: $2H_2S + SO_2 = 2H_2O + 3S$
Aim of the investigations was to determine whether the deposition of sulfur and water from the gas to be converted influences the equilibriu and the quantity of the recoverable sulfur. It has been tried to determine the equilibrium by computation and experiment.

I.   The computation of the equilibrium
The numerical determination of the constants of equilibrium in the technically interesting range of temperatures was carried out:
1. from the free energies of formation of the reacting substances at 25°C.
2. from measured data of the constant of equilibrium according to investigations of Lewis and Randall (Journ. Amer. Chem. Soc. 40, 362, 1918). In both cases the transformation to the interesting temperature was performed graphically and numerically. By doing this it could be shown that the graphical method could be applied to a narrow temperature range even with a simplified assumption that the heat formation is independent of the temperature. For the computation of the constant of equilibrium and for the following evaluation of the results it is advisable to distinguish between the following reactions:

$$2H_2S \ (g) + SO_2 \ (g) = 3S \ (L) + 2H_2O \ (g) \text{ and}$$

$$2H_2S \ (g) + SO_2 \ (g) = \frac{3}{V} S_V \ (g) + 2H_2O \ (g) +)$$
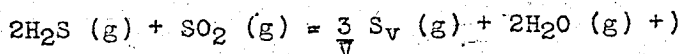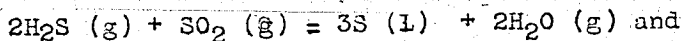
+) (g) and (l) indicate either the gaseous or liquid phase, ⩘ designates the equilibrium-liquid of the two sulfur-modifications. This difference disappears at the boiling point of the sulfur. The following table #1 contains the thermal data upon which the computation are based. The data have been extracted from the following books: International critical tables, Vol. 7,
Landolt Boernstein and Lewis Randall, Thermodynamics, page 559,
The vapor pressure and the molecular weight of the sulfur vapors (Table #2) originate from a publication of Treyner and Schupp (Z. phys. chem. 68, 129 (1910)
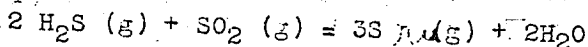
Table 1

	Heat content Cal/mol	Free energy Cal/mol	Molecular heat P.
H_2S (g)	-4,800	-7,840	8.44
			$8.81-0.0019T:0.0000022T^2$
SO_2 (g)	-70,940	-69,660	8.95
H_2O (g)	-57,840	-54,507	$7.0 + 0.0071T-0.00000186T^2$
	+300	+93	8.44
			$8.81-0.0019T + 0.00000222T^2$
			= 6.9
S_2 (g)	+29,690	+18,280	5.4 + 0.005T
S_6 (g)	+22,600	+11,900	6.50 + 0.0010T
S_8 (g)	+20,000	+10,000	
	0	0	5.37
			4.12 + .0047 T

Table 2

t°C.	T (°K)	p(mmHg)	(average atom-number)
100	373	0.0085	7.77
125	398	9.053	-
150	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	27.0	-
300	573	48.0	7.26
325	598	77.0	-
350	623	128.0	7.05
400	673	378.0	6.80
450	723	828.0	6.71

Equilibrium of the reaction

$2 H_2S$ (g) + SO_2 (g) = $3S$ (g) + $2H_2O$

According to the table F_{298} = 23,285 cal.

Applying the formula $\Delta F = -RT \ln K$
The constant of equilibrium = K_{298} = 8.7×10^{-18} I.

(whereby the constant of equilibrium was computed from the partial pressures)
For the computation of the constant at 580°K according to the Gibbs-Helmholtz equation $\dfrac{d \ln K}{dt} = \dfrac{\Delta H}{RT^2}$

          II

For the negative heat formation the reaction is carried out at a chosen temperature
$\Delta H = \Delta H_{298} + \Delta C_p \times (T-298.2)$ III

The equations II and III are combined and integrated
$\log. \dfrac{K_{298}}{K_t} = \Delta H_{298}y - \Delta C_p Z$ I'

Whereby

$$Y = \frac{298.2-T}{4.5787 \times 298.2T} \qquad \text{and}$$

$$Z = 2.982Y - \frac{1}{R} \log \frac{298.2}{T}$$

(R = Molec. gas constant)

For the numerical computation the figures of the functions (?) and S from the tables were employed.

It was obtained $K_{580} = 23.8$ whereas from Lewis and Randalls determination the value $K_{580} = 23.5$ can be computed.

The constant of equilibrium of the reaction

$2H_2S$ (g) + SO_2 = $\frac{3}{V} S_{v(g)}$ + $2H_2O$ (g) has been computed from the constant of equilibrium which was determined by Lewis and Randall. At its boiling point the sulfur has an average atom number $V = 6.71$. (Compare table 2)

The preceding equation can therefore be written:

$2H_2S + SO_2 = \frac{3}{6.71} S_{6.71} + 2H_2O$
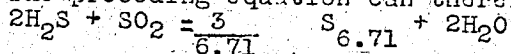
and the determined constant (By Lewis and Randall) can be written

$$K_{718} = \frac{(H_2S)^2 \times (SO_2)}{(H_2O)^2 \times (S_v)^{3/v}}$$

whereby at the boiling point of the sulfur $(S_v)^{3/v}$ becomes = 1.
At chosen temperatures the constant of equilibrium with gaseous sulfur (?) can be computed from that of the equilibrium with liquid sulfur according to the following equation:

$$K_T^* = \frac{K_T}{(S_V)^{3/v}} \qquad\qquad\qquad VII$$

whereby (S_V) equals the partial pressure at the corresponding temperature. $K_{580} = 4.66$
The graphical transformation of the constant of equilibrium was performed by means of a diagram, in which $-R \ln K$ was plotted against the reciprocal value of the absolute temperature. Assume the applicability of equation II and a constant ΔH there exists a linear connection between the quantities plotted on the axis of the diagram

II. Determination of the equilibrium

The experimental investigation of the equilibrium at temperatures substantially below the boiling point of the sulfur must create difficulties because the absorption of the sulfur vapors to be expected is responsible for an incorrect determination of its concentration in the gas phase and results in erroneous results. Therefore static methods for the determination of the equilibrium cannot be employed.
If the equilibrium is determined in a gas flow a catalyst cannot be dispensed with. But it is very difficult to secure a complete reaction and a proper measurement of the temperatures. If a catalyst is applied, the true reaction temperatures are at or near its active

places. With a comparatively small reactor such a temperature cannot be measured and since the reaction is exothermic the reaction temperature is not identical with the average temperature in the furnace.

If a flowing gas stream is applied, the gas concentration at which the determination is carried out is very limited; the upper limit is the concentration at which precipitation of liquid sulfur occurs, which spoils the catalyst; the lower limit is the conc. below which the catalyst does not work or works but unsatisfactorily. Under the present condition it was possible to investigate gases with a sulfur content ranging from 1-10%. Approximately 40% water vapor was added.

The test kilns were partly equipped with electrical heating or, in order to maintain a perfectly uniform temperature a bath of boiling anthracene (324°C.) was employed. During the performance of the tests the charge of the catalyst was as low as $\frac{1}{4}$ to 1/20 of the normal charge. (500 liters of gas per hour per liter catalyst). Before beginning with the determinations proper the catalyst was operated with the gas mixture to be tested for a longer period of time until a stationary condition had been reached with respect to the gases and vapors which were absorbed by the catalyst. The analysis before and after the catalyst was carried out by absorbing H_2S and SO_2 by iodine solution whereby the volume of the gas to be analyzed was depending on the sulfur content of the gas. The constant of equilibrium can be computed from the analytical data as follows:

$$K = \frac{\dfrac{1(a-a') + (b-b^2)}{V} \quad \dfrac{3}{V} \quad a-a' + d}{a'^2 \times b'}$$

whereby a is the partial pressure of H_2S in atm.
  b " " " "   " " SO_2 " "
  d " " "   "   " H_2O " "

a' and b' are the corresponding values after the reaction. The expression (a-a') + (b-b') can be replaced by c-c', whereby c or c' respect. indicates the total sulfur.

If the values of the partial pressure a, b, and c are replaced by percent by volume, the obtained result must be multiplied by 100 (1-3) or 1.1680 must be added to the logarithm of the constant. $\dfrac{}{V}$

The following table 3 represents a comparison of the results obtained by measurement with those obtained by calculation. The means values of the measured results are in accord with the computed ones. The following explanations must be made:
An electrically heated furnace was employed for the tests listed under A. The catalyst charge was $\frac{1}{4}$ of the usual amount; the total sulfur content of the gases varied between 8 and 0.5% and the gas contained 40% water vapors. Test run "B" was carried out under the same conditions as before but without an addition of water vapor. The total sulfur content of the gas was 7-10%. The content of water vapor present in the final gas was computed under the assumption that the crude gas was saturated with water vapor at 25°C.

Test run "C" comprises experiments which were obtained by the application of newly developed catalysts. The temperature was 250°C. As can be easily expected, due to the high output, the reaction was not complete. The obtained constant is a little too low but taking into consideration the remarks made before, it fits well into the curve

Test run "D" was carried out at 324°C, without addition of water vapor and with an extremely low output of the catalyst. The total sulfur content before the catalyst was about 10%.

Table 3

T	T	From $\triangle$ F	From K_{718}	Mean value	Measured	Test run
-R ln K	298	78.1	80.0			
	580	23.8	23.5			
-R ln K*	718					
-R ln K*	298	63.7			12.87	
	580	-21.3	21.3	22.1	21.2	A
	530				20.9	
	580				24.7	
	580		21.3	18.8	19.3	B
	580				18.8	
	523				18.4	
	523		26.0	24.0	(23.0)	C
	523				(24.5)	
	597				(24.7)	
	597		20.0	19.8	20.4	D
	597				20.5	
	597				18.8	
	597				19.5	
					19.6	

In comparing the test runs apparently the equilibrium is reached more easily if water vapor is present. Such a fact is in accordance with some modern reflections upon the action of a catalyst. With respect to the precision of the determination of the constant of equilibrium it must be said that the figure following the decimal point of the value -R ln K is not quite certain.

III. Evaluation of the figures

If the equilibrium must be computed the values necessary for the computation should be taken from diagram 1. Depending on whether the formed sulfur shall be obtained gaseous or liquid the constant K* or K respect. should be applied. By dividing the observed figure through 4.579 the Briggian logarithm is obtained and consequently K. By inserting the K-value into equation VIII permits the computation of the desired concentrations from the known initial concentrations. Due to the fractional apparent atom number of the sulfur a transcenés dental equation is obtained. In order to facilitate the evaluation of a diagram was drawn from which the volume of $H_2S + SO_2$ can be directly extracted. The diagram was computed assuming that the initial gas contains 10% $H_2S + SO_2$ in the proper stoichiometric proportions. Curves have been provided covering the equilibrium with liquid and gaseous sulfur, in addition the curves show the influence of various amounts of water vapors present in the initial gas. Whether the sulfur will be obtained in the gaseous or liquid phase can be computed from table 2 which contains the vapor pressure and the atom figures of the sulfur. Provided a gas contains 10% $H_2S + SO_2$ in the proper stoichiometric proportion table 4 represents the actual vapor pressure of the sulfur in comparison with that vapor pressure which would occur
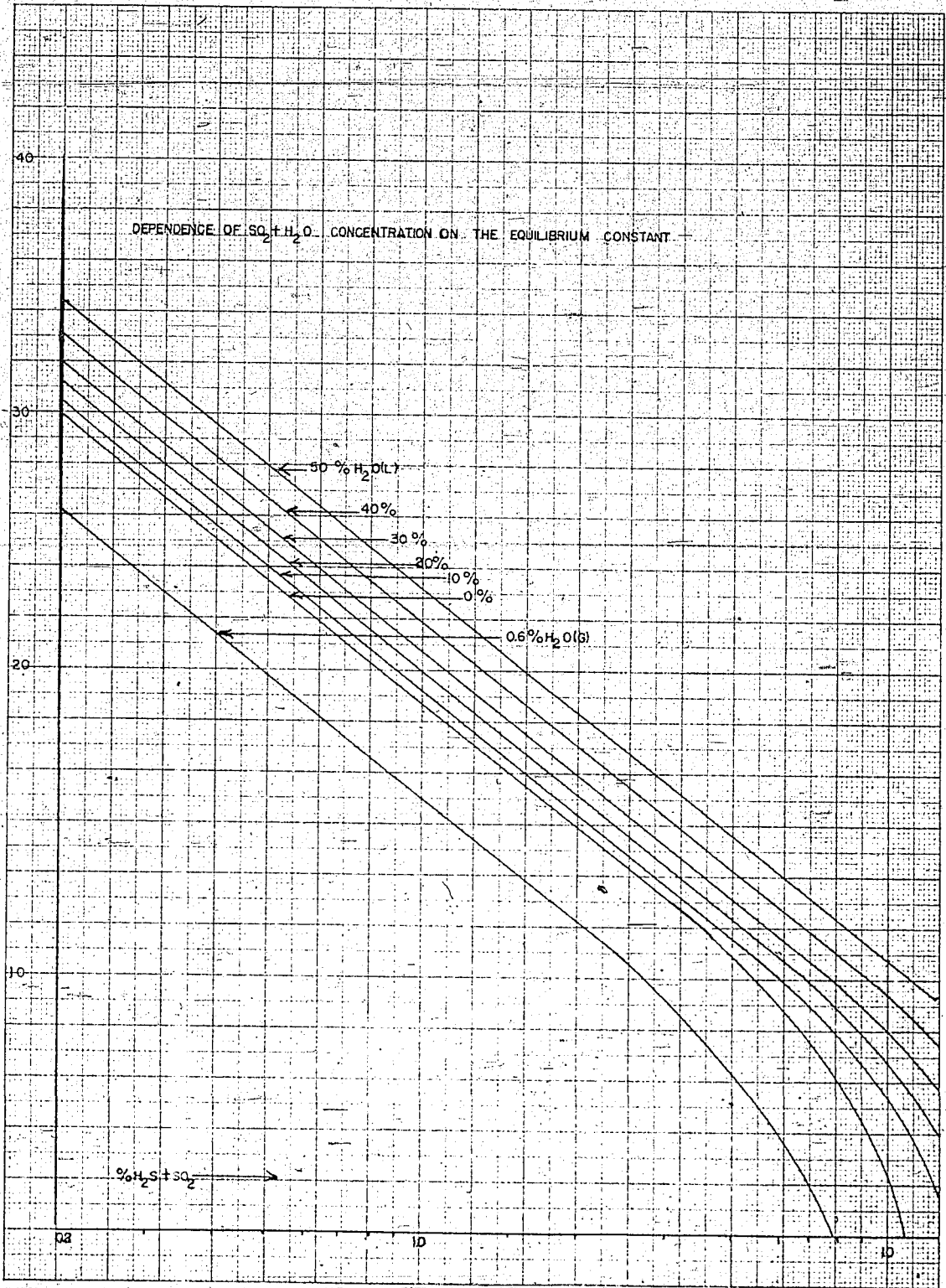
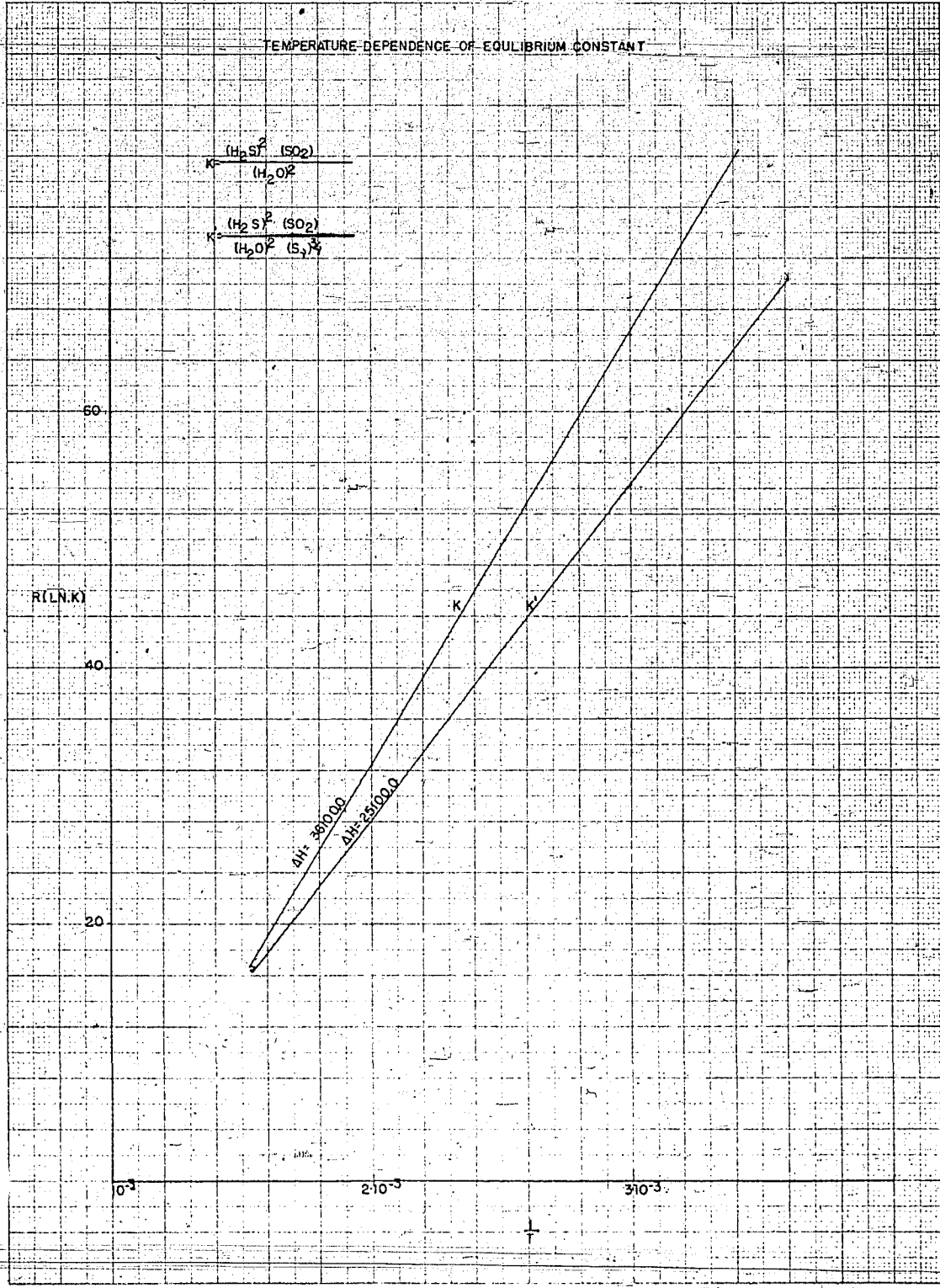if no condensation takes place and if a complete reaction is obtained.

Table 4

°C.	10% H_2S + SO_2 will yield mm-Hg;pressure of the sulfur	Sulfur vapor pressure mm. Hg
150	9.95	0.23
175	10.20	0.70
200	10.35	2.26
250	10.50	12.00
300	10.70	48.00
350	11.00	128.00

IV. Summary

The constants of equilibrium of the claus-kiln reaction and their dependence on temperature have been determined by computation and experiment. Methods for the graphical computation of the equilibrium for some important cases are presented. The equilibrium is influenced according to the law of mass action and by the presence of H_2O and sulfur.

DEPENDENCE OF SO₂+H₂O CONCENTRATION ON THE EQUILIBRIUM CONSTANT

50 % H₂O(L)
40%
30 %
20%
10 %
0%
0.6%H₂O(G)

% H₂S + SO₂

TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT

$$K = \frac{(H_2S)^2\,(SO_2)}{(H_2O)^2}$$

$$K = \frac{(H_2S)^2\,(SO_2)}{(H_2O)^2\,(S_2)^{\frac{3}{2}}}$$