

Dr. N. Pier's  
files.

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W. Sternberg  
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High Pressure Experiments  
Lu 558

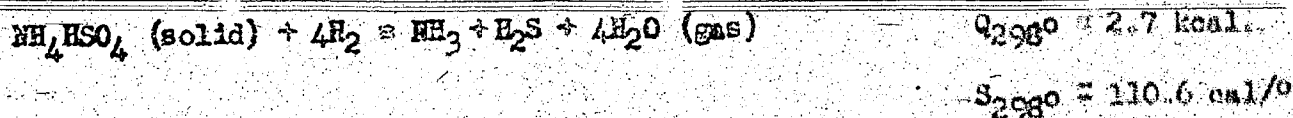
November 17, 1942.

EQUILIBRIUM DURING THE REDUCTION OF NH<sub>4</sub>HSO<sub>4</sub> OR  
CaSO<sub>4</sub> UNDER HYDROGENATION CONDITIONS IN THE LIQUID  
PHASE CONVERTER.

Dr. Urban's experiments (Scholven) have shown, that the addition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> reduces the danger of settling in the liquid phase converters; there have been found however some corrosion phenomena under the Scholven hydrogenation conditions which have been attributed to the presence of sulfuric acid. No such corrosion phenomena could be observed in experiments with Rhenish brown coal in 10 liter converters with the addition of ammonium sulfate, nor has any sulfate been found in the products. In order to decide whether the conditions for the reduction of the sulfate were different because of the higher partial pressure of H<sub>2</sub> in the 10 li. converter (700 against 300 atm.) than in the Scholven method, a computation is made of the reduction equilibrium, namely for NH<sub>4</sub>HSO<sub>4</sub> formed from (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> by splitting off NH<sub>3</sub> above 350°, and which does not undergo any additional decomposition, and the CaSO<sub>4</sub> formed by interaction with the lime contained in the coal.

The following data are available:

Reaction I:



Because of the absence of suitable experimental data, the entropy  $S_{2980}$  of NH<sub>4</sub>HSO<sub>4</sub> is here estimated in analogy to similar salts to be about 40 cal/°. Using Ulich's approximation formula, we get then for the equilibrium constant at the temperature of 450° C, on which our computations will be based:

$$\log K_p = \log \frac{P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} \times P_{\text{H}_2\text{O}}^4}{P_{\text{H}_2}^4} = \frac{2700}{4.57 \times 723} + \frac{110.6}{4.57} \times 0.82 + 24.2 = 25$$

Equilibrium therefore will be on the side of the hydrogenated products under all circumstances; a change in the value of entropy will introduce no changes here.

The reduction of gypsum is another reaction considered possible.

Reaction II:



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$$\log K_p = \log \frac{P_{H_2O}^4}{P_{H_2}} = \frac{3900}{4.59 \times 723} + \frac{43.4}{4.57} = 1.18 + 9.5 = 10.68$$

$$\frac{P_{H_2O}}{P_{H_2}} = 4.7 \times 10^2 *$$

In this case, the equilibrium is reached only when the H<sub>2</sub>O partial pressure becomes about 500 times higher than the partial pressure of H<sub>2</sub>. H<sub>2</sub> actually is always present in large excess, and the reduction will be practically complete. Considered thermodynamically, all sulfates formed upon the addition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> will in all probability be very unstable under the conditions existing in the liquid phase converters.

signed v. Kuffling

\*It would be necessary to consider in more accurate calculations, that the specific heat of the steam increases more with increasing temperature, than that of H<sub>2</sub>, and that more accurate calculations would indicate an equilibrium still further on the side of the hydrogenated compounds.

/rkp