

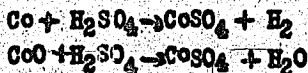
Determination of the Free Metal-Content in Catalysts

(Acid-vacuum method)

API-TOM Reel 48, Frames 744-749

1) General

The reduction of the Co catalysts is generally not carried to completion. Therefore, there is found aside from metallic Co, still unreduced oxide and carbonate. The determination of the portion of reduced metal rests on the following reaction:



On dissolving in acid, the oxide forms water. Only the reduced metal, on treatment with  $\text{H}_2\text{SO}_4$ , forms an equivalent amount of hydrogen, which is measured. Through determination of the total amount of cobalt used it is possible to calculate the portion of reduced metal.

In the practical carrying out of this determination, various possibilities for errors should be watched for:

- a) Nitrogen to be used for transfer of the catalyst is to be tested for oxygen. Even small amounts of oxygen in nitrogen can cause a noticeable oxidation of the catalyst after longer contact.
- b) Saturated catalysts have usually come in contact with air. They are then no longer to be brought in contact with hydrogen, i.e. for the rinsing of vessels. For then a strong heating takes place, while the oxygen of the air attached to the catalyst burns with the hydrogen. This causes the possibility of a further reduction.
- c) The hydrogen adsorbed on the catalyst has to be previously sucked off in vacuo, since otherwise the reduction values found are too high. In order to remove all but small remnants of oxygen it is sufficient to suck for 1-2 minutes with the full vacuum of a water aspirator pump. In cases of saturated catalysts it is further necessary to heat, since at times the saturating oil prevents the sucking off of the hydrogen.
- d) Hydrochloric acid should not be used for the examination of the catalyst since it sometimes contains chlorine which combines with a corresponding amount of Co-metal without formation of  $\text{H}_2$ .

2) Apparatus

The apparatus is to be seen on the enclosed sketch. (Frames 749)  
The stoppering of the reaction flask can be accomplished with ground-glass or with rubber stoppers.

### 3) Filling

Into the reaction flask one fills an amount of catalyst to contain appr. 0.5 - 0.6 g Co.

- a) Unsaturated catalyst is brought into the reaction flask with constant addition of hydrogen into the reaction flask through the sidearm and simultaneous passing of hydrogen through the storage vessel from which the catalyst is to be transferred. Then the apparatus is put together and 20-30 cc of 50% sulfuric acid is put into the dropping funnel. The stream of hydrogen is cut off by means of a clamp and simultaneously the hydrogen in the flask is sucked off as completely as possible through the 3-way stopcock by means of a water aspirator pump. Particularly it should be seen to it that the apparatus is completely tight.
- b) Catalyst saturated with oil can be brought into the clean and dry reaction flask as such. Then the air is replaced by oxygen-free nitrogen. The flask is put into a bowl of boiling water and sucked for about 15 minutes with the aid of a water aspirator pump. It is better yet to heat in a hollowed aluminum block at 200° for five minutes during the sucking. The heating of the catalyst is necessary in order to be able to suck off the hydrogen adsorbed on the catalyst. The aluminum block is removed and the flask is cooled.
- c) With CO<sub>2</sub>-saturated catalyst one proceeds as under 3a.

### 4) Dissolving

The connection between the reaction flask and the gas burette is completed by turning the 3-way stopcock. The check-valve prohibits the backflow of the sealing water from the gas burette. Then one slowly adds the sulfuric acid to the catalyst, being careful not to let any gas escape or air seep in through the dropping funnel. Depending on the type of catalyst, there immediately evolves a sufficient amount of gas to close the check-valve; otherwise one heats carefully with a small burner. The gas evolved rises in the gas burette by replacement of the sealing water. The adjustment vessel had best stand low, so that even a slight gas pressure can open the check-valve. One heats until the gas-evolution is completed and the steam formed has driven over all the gas in the burette.

The flame is removed and the 3-way stopcock turned so that the reaction flask is in contact with the outside air. Gas volume, temperature, and barometer are read. The contents of the reaction flask is transferred quantitatively to a flask, diluted, heated until all the cobalt sulfate is dissolved, and after being brought to room temperature is filtered by suction to separate the kieselguhr and the thorium sulfate. The cobalt content is then determined by the following method:

### 5) Determination of the Cobalt

- a) The indirect method of determining the amount of cobalt by

\* Stopcock with an outlet through the end of the key.

weighing of the kieselguhr, leads to completely unsatisfactory values which do not always correspond to the composition of the catalyst.

b) The titration method with cyanide does not lead to exact values either, since in this definite concentrations have to be kept and the endpoint is difficult to recognize.

c) The titration method with soda lye gives perfect values in the absence of impurities which have a pH value similar to that of cobalt.

d) The photometric method is the quickest. With filtered solutions that are completely clear it gives values which are accurate enough. (Filter cold!)

e) The electrolytic method gives perfect results.

### 6) Determination of the hydrogen

In the volume of gas obtained, it is best to determine the percentage of hydrogen in an Orsat-apparatus attached to the rest of the apparatus. Since the constituents which are present aside from the hydrogen do not affect this determination, one can simply burn the hydrogen over copper oxide at 290° by the known method. It is superfluous to cool the small steel tube with copper oxide between determinations. From 5-7 determinations can be made without oxidizing or cooling.

### 7) Calculation

58.9 g Co give 22.40 l H<sub>2</sub>.

1 g Co give 380 cc H<sub>2</sub>

Then if y cc of H<sub>2</sub> are developed from x g of total cobalt,

$$\text{Cobalt value (\%)} = \frac{y \cdot 100}{x \cdot 380}$$

### 8) Example

One catalyst gives: .150 cc gas at 20° and 762 mm pressure  
Under normal conditions: .162 cc gas at 0° and 760 mm pressure  
The analysis shows: 96.9% H<sub>2</sub>

~~Obtained: 157 cc H<sub>2</sub>~~  
0.590 g Co photometrically

$$\text{Cobalt value (\%)} = \frac{157 \cdot 100}{0.590 \cdot 380} = 70\% \text{ metal}$$

9) Accuracy

With accurate determinations of cobalt, the limit of error amounts to 2-3 units of the reduction value in either direction.

/s/ Roelen

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