

CALCULATION OF THE ABSORPTION OF CARBON MONOXIDE IN A COPPER FORMIATE-CARBONATE SOLUTION

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Introduction

The carbon monoxide content of synthesis gas greatly influences the activity of the catalyst used in ammonia synthesis. Carbon monoxide is a potent catalyst poison, hence its removal from synthesis gas is the most important and at the same time most complicated problem in the purification of the gases of the ammonia industry. The complication lies in the fact that 0.005 per cent carbon monoxide is sufficient to reduce significantly the activity of the catalyst.

Industrial processes based on adsorption and absorption, respectively, have been worked out for the removal of the impurities. Especially the absorption processes have been widely accepted, and absorption by copper salt (formiate and carbonate) solutions has gained the greatest significance.

Of the different methods to calculate the absorption of carbon monoxide in copper formiate D. W. Krevelen's is the best [1].

His equation is essentially suited for the description of the investigated absorption process, but as in industrial practice the composition of the solution and the pressure above the solution is different and there are also other gases present, the equation in its original form does not describe the process with sufficient accuracy.

The aim of the present paper is to bring Krevelen's equation to a form in which it should be applicable for the calculation of industrial processes.

A description of the absorption apparatus is given, followed by the detailed discussion of the differences between industrial conditions and the conditions under which the cited authors have carried out their experiments (I) and the influence of these differences on absorption (II). An equation describing absorption is proposed and its validity discussed (III).

Apparatus

The screwed on lid of a 2 litre steel autoclave tested at 250 atm. pressure, carried in one of its holes a manometer extending into the gas space of the vessel and a joint provided with a valve, and in its other hole a Y joint reaching

into the liquid in the autoclave. One branch of the Y joint was connected to a manometer and a reducing valve, the other to a valve (Fig. 1).

The autoclave was filled with about 500 ml of the absorbent solution and closed. Valves 1 and 2 were opened and gas was introduced till the pressure as indicated by manometer I (desired value of the pressure) was equal to the pressure shown by the manometer II (the actual pressure in the gas space). Valve 1 was closed and the autoclave shaken by a shaking machine provided

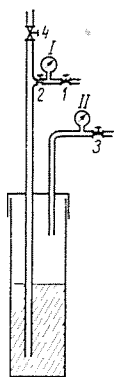


Fig. 1

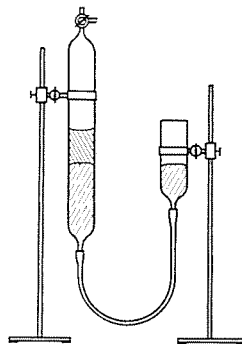


Fig. 2

with thermostat. The introduction of the gas was repeated till no further decrease in pressure (absorption of gas) could be observed.

In the second part of the experiment the quantity of the dissolved gas was determined with a gasburette (Fig. 2). The burette was filled with mercury and its three-way stop-cock was joined to the tube which reached into the liquid of the absorption vessel. The valve was opened and by adjusting the three-way stop-cock part of the fluid was let out, whereby the air entrapped between the valve and the stop-cock was removed, and the other part of the solution was let into the burette.

Under the influence of the pressure difference gas was liberated which occupied the upper section of the burette, above the absorbing solution. The system was allowed to stand for a some time, the mercury levels adjusted and the volume of liquid and gas read off. The results were reduced to 1 atmosphere and 0° C, taking into consideration the solubility of gases at 1 atmosphere.

Deviations from Krevelen's experimental conditions

Table I shows the compositions of some solutions used in industrial absorption, and the compositions of the solutions used by Krevelen and Larson.

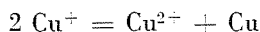
As can be seen, there are the following more important differences between solutions N^{os}. 1 to 7 and N^{os}. 8 to 9:

Table 1
Composition of the solution

N ^o .	Concentration of components g/l.					Reference
	Cu ⁺	Cu ²⁺	NH ₃	HCOOH	CO ₂	
1.	135.5	15.5	144	58.2	93.7	(2)
2.	122.8	16.1	151.5	80.5	85	
3.	107.2	14.1	173.2	61	66	
4.	100.4	13.1	125	54	58.5	
5.	103.0	33.0	152	121.5	45.5	our solution
6.	112.8	37.9	160	86.9	81	
7.	124.6	18.4	153	62.1	43.6	(3)
8.	59.7	1.3	119	77.4	—	(4)
9.	50.8	—	76	61.7	—	(1)

1. The industrial solutions contain a significant quantity of copper (II) ions, while solution N^o. 9 contains no copper (II) ions and solution N^o. 8 hardly any. Solutions used in industrial absorption contain copper (II) ions for the following reasons:

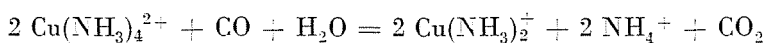
During the regeneration of the solution metallic copper may precipitate according to the



endotherm reaction. At the comparatively high temperatures (70° to 80 °C) used for regeneration this may result in the occlusion of the tube. The copper (II) ions are added to prevent disproportionation.

2. Solutions N^{os}. 1 to 7 have a high carbonate content. Solutions N^{os}. 8 and 9 are carbonate free.

During regeneration the copper (II) ion content of the solution oxidizes part of the carbon monoxide liberated by desorption, according to the following reaction:



Only part of the carbon monoxide can be removed by heating, thus there is always more or less carbonate in the solution.

There are also some important differences between the conditions under which absorption was carried out by the authors mentioned and by us. These differences are summed up in Table 2 they are the following:

Table 2
Factors influencing absorption

No.	Pressure atm	Carbon monoxide content		Temperature °C
		input %	output %	
1.	125	3.5	0.002	25
2.	110	2.6	0.003	18—21
3.	1	100	—	20

1. Partial pressure of carbon monoxide is considerably higher in our experiments than used by KREVELEN at all.

2. Absorption did not take place under isobar conditions. The pressure of carbon monoxide was reduced as a consequence of absorption and approached zero at the end of the process.

3. Instead of pure carbon monoxide a mixture of nitrogen, hydrogen and carbon monoxide was absorbed in our experiments.

Influence of the discrepancies on the calculation

In KREVELEN's paper the following equations are used to describe absorption:

$$C_{\text{eq}} = \frac{m}{(m-1)(mB-A)p} \quad (1)$$

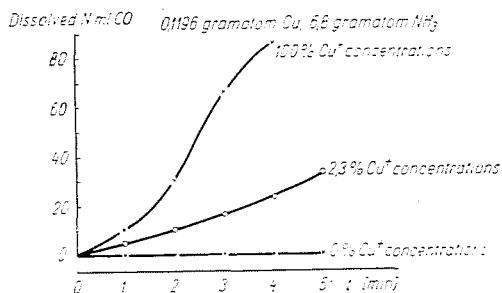
i. e.

$$\log_{10} C_{\text{eq}} = \frac{13\,500}{2.3 RT} - 0.04 I - 9.830$$

This latter equation is valid for copper formiate solutions only.

The effect of copper (II) ions on absorption.

MÖLLER [5] has shown that the solution of copper (II)₂ ions does not absorb measurable quantities of carbon monoxide at room temperature. (Graph. 1).



Graph 1. Absorption as a function of time at various

This statement was supported by the experiments carried out by EGALON [6]. Thus in the calculation of the absorption, the effect of the copper (II) ions can be considered as of some neutral constituent of the solution.

The effect of the carbonate content of the solution

Copper (I) diamine carbonate complex is an active component in the absorption process with an absorption differing from that of the formiate. Some measurements were carried out to determine the absorption capacity

Table 3
Composition of the solutions grammole/litre

Ions	1	2	3
Cu ⁺	1.59	1.75	1.75
Cu ²⁺	0.36	0.40	0.40
CO ₂	2.07	2.42	2.42
NH ₃	11.30	9.41	10.30
NH ₃ (free) .	4.85	2.02	2.91

Table 4

Nº.	I	T	C _{eq}
1.	4.56	290	0.94
		305	0.34
		283	1.48
2.	7.65	293	0.60
		303	0.37
3.	7.65	283	1.41
		293	0.56
		303	0.35

of this compound. Tables 3 and 4 show the solutions used for the tests and the results obtained. From these data the equilibrium constant can be calculated by the following equation:

$$\log_{10} C_{\text{eq}} = \frac{11\,900}{2.3 RT} - 0.04 I - 8.660$$

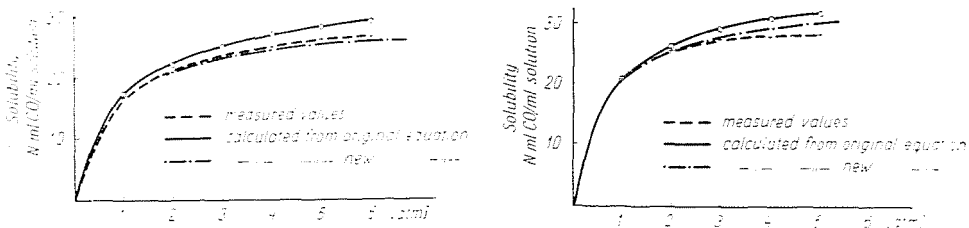
Owing to the difference in the absorption capacity of the two constituents, an average equilibrium constant, depending on the composition of the solution, must be used in the calculations. Assuming that during the absorption in the formiate and carbonate solution, the formiate and carbonate ions act upon each other only as some foreign ions, the copper carbonate content can be accounted for by calculating that quantity of formiate which is equivalent with it as far as absorption capacity is concerned and in the calculations the solution is considered as if consisting of formiate only. Thus:

$$A = A_{\text{formiate}} + A_{\text{carbonate}} \frac{m_{\text{carbonate}}}{m_{\text{formiate}}}$$

where the two m values refer to solutions of identical temperature and identical composition (containing instead of copper formiate copper carbonate) above which the partial pressure of carbon monoxide is also identical. In order to calculate the m value the values corresponding to the investigated absorption have to be substituted. For the determination of the A values the copper carbonate and copper formiate content of the solution must be known. If these are known, the effect of the carbonate content can be accounted for.

Accounting for the effect of increased pressure

In industrial absorption the partial pressure of carbon monoxide ranges 3 to 5 atm. In this pressure interval absorption does not longer follow Henry's law. From our measurements far more accurate results might be obtained by supposing that absorption is proportional not to the first, but to the 4/5th power of the pressure (see Graphs 2 and 3). The solutions tested were the solu-



Graphs 2—3. Absorption as a function of pressure at $T = 293^{\circ}$

tions Nos. 2 and 3 in Table 3. The carbon monoxide concentration of the solution can be calculated from the following formula:

$$[\text{CO}] = H p^{4/5} \quad (2)$$

The Henry coefficient of Equ. 2 can be calculated as follows

$$[CO] = H p = \frac{g_{co}/M_{co}}{g_{co}/M_{co} + 100/\bar{M}_{sol}} \quad (3)$$

The average molecular weight of the solution is obtained

$$\bar{M}_{solution} = \frac{\sum_{i=1}^n c_i M_i}{\sum_{i=1}^n M_i} = 0.497 D + 0.369 A + 0.064 B + 0.068 E \quad (4)$$

The following relationship exists between the quantities g_{co} and V :

$$g_{co} = 100 \frac{q_{co}}{q_{solution}} V \approx \frac{125}{q_{solution}} V \quad (5)$$

Thus the task consists in the determination of the absorption capacity corresponding to small pressures, i.e. of the linear equation describing the initial section of the $V = V p$ curve. Rearrangement of Krevelen's equation results in

$$\frac{1}{m} = \frac{1}{0.5 + \frac{A}{2B} + \frac{1}{2B C_{eq} p} + \left[\left(0.5 + \frac{A}{2B} + \frac{1}{2B C_{eq} p} \right)^2 - \frac{A}{B} \right]}$$

and

$$\frac{V}{V_{max}} = \frac{1/m}{1/m_{min}}$$

Taking into consideration that

$$m_{min} = 1$$

the following result is obtained:

$$V = V_{max} \frac{1}{0.5 + \frac{A}{2B} + \frac{1}{2B C_{eq} p} + \left[\left(0.5 + \frac{A}{2B} + \frac{1}{2B C_{eq} p} \right)^2 - \frac{A}{B} \right]}$$

If $p \rightarrow 0$, then

$$\lim_{p \rightarrow 0} V = V_{max} B C_{eq} p$$

and

$$V_{max} = 22.41 A$$

thus

$$\lim_{p \rightarrow 0} V = 22.41 A B C_{eq} p$$

From Eqs. 3, 4, 5 and 6 it follows that

$$H = \frac{100 ABC_{eq} / Q_{solution}}{100 \frac{AB C_{eq} P}{Q_{sol.}} + \frac{201}{D} + \frac{271}{A} + \frac{1560}{B} + \frac{1470}{E}}$$

Let us suppose that $p = 0.1$ atm, where linearity is still a very good approximation. In this case the member containing p in the denominator is negligible and the equation takes the following form:

$$H = \frac{ABC_{eq}}{Q_{solution}} \times (0.497 D + 0.369 A + 0.064 B + 0.068 E) \quad (7)$$

Accounting for anisobar conditions

The carbon monoxide content of the gas passing through the absorption tower (thus the partial pressure of carbon monoxide) decreases, thus absorption cannot be considered as an isobar absorption, and not the initial pressure, but the momentary (equilibrium) pressure must be substituted into the Krevelen equation. Thus the carbon monoxide concentration in the solution is:

$$[CO] = Hp^{1/2} - \frac{A}{m} \quad (8)$$

The effect of nitrogen and hydrogen on absorption

The gas to be purified contains mainly hydrogen and nitrogen (some gas compositions are given in Table 5). Other gases are present only in relatively small quantities and we have found that under the experimental conditions used, they are absorbed only to a small degree, so that their effect can be neglected.

Table 5
Composition of the gas to be absorbed $v\%$

Components	H ₂	N ₂ +A	CO ₂	CH ₄	CO	Ref.
N ^o 1.	69.0	24.0	1.7	0.7	4.6	(7)
N ^o 2.	70.9	22.8	0.2	1.9	4.2	(8)
N ^o 3.	68.6	25.2	0.0	1.9	3.9	(9)

As shown by these graphs the absorption of both gases is so small that they can be discussed as independent, parallel absorptions. The effect of nitrogen

and hydrogen can be accounted for by subtracting from the quantity of the solution the quantity of solution needed for the absorption of nitrogen and hydrogen, i. e. by calculating for the sake of simplicity not with quantities of solutions, but with the quantity of copper in the solution. As the latter is very small, it can be taken as constant (the error thus arising is maximum 0.3%).

$$A_{\text{actual}} \approx 0.985 A \quad (9)$$

The new equation and its application

The new absorption equation derived from eq. 1,2,7,8,9 is the following:

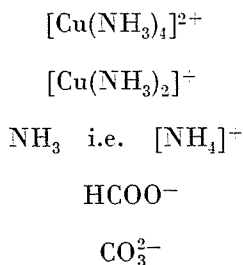
$$C_{\text{eq}} = \frac{(m-1) \left[mB - 0.985 \left(A_f + A_k \frac{m_k}{m_f} \right) \right] + \frac{Bm^2}{\varrho_{\text{sol}}} (0.497 D + 0.369 A + 0.064 B + 0.068 E)}{\frac{Bmp^{1/2}}{\varrho_{\text{sol}}} (m-1) \left[mB - 0.985 \left(A_f + A_k \frac{m_k}{m_f} \right) \right] (0.497 D + 0.369 A + 0.064 B + 0.068 E)}$$

In order to be able to apply the above equation, the method of calculating the values marked with the different letters has to be known.

The calculation of A , D and E follows from their definition, while the value of ϱ_{sol} is obtained by simple measurement.

Calculation of the value of "B"

Analysis carried out by Egalon [10] has shown that copper complex solutions contain bicarbonates only in very small quantities or not at all. Thus the following ions are present in the solution:



Thus the following value is obtained for B :

Scope of the equation

The simultaneous conditions limiting the scope of the equation are:

1. $B > 0$
2. $m > 0$
3. $m > 1$
4. $m > 0.985 \frac{A}{B}$

Beyond these limits $C_{\text{eq}} < 0$, which has no chemical interpretation.

These conditions follow from the reaction equation of absorption, because:

1. Without free ammonia no absorption is possible;
2. An infinitely small quantity of the absorbent cannot absorb gas of finite quantity;
3. In the equation of Krevelen et al. at least one mole of copper salt is needed for the absorption of one mole carbon monoxide;
4. The determining factor of the reaction will always be the reactant component present in the smallest concentration.

Key to symbols

- A = concentration of the copper (I) salt
- B = concentration of free ammonia
- c = concentration
- C_{eq} = equilibrium constant
- D = concentration of copper (II) ions
- E = concentration of water
- g_{CO} = part by weight of carbon monoxide which 100 parts by weight of solution is capable of absorbing
- H = Henry coefficient
- I = ion strength
- m = number of moles of copper (II) salt necessary for the absorption of one mole carbon monoxide
- M = molecular weight
- p = partial pressure of carbon monoxide
- R = universal gas constant
- ρ = density
- T = absolute temperature
- V = the quantity of carbon monoxide in normal ml that one ml solution is capable of absorbing.

Summary

The present paper deals with the calculation of the absorption of carbon monoxide in copper formiate carbonate solution. It was found that the equation of Krevelen is a good basis for the calculation of the absorption, but industrial conditions significantly differ from the conditions on which this equation is based. These differences and their effect on absorption is discussed.

The following conclusions are arrived at:

1. The copper (II) ions behave as passive components from the viewpoint of absorption.

2. Copper carbonate is an active component but its absorption capacity as a function of the temperature is not the same as that of copper formiate.

3. At higher pressures absorption does not follow the law of Henry, but is proportional to the 4/5th power of the partial pressure of carbon monoxide.

4. The Henry coefficient can be determined from the original Krevelen equation for low pressures (0.1 atm).

5. Absorption does not take place under isobar conditions. The quantity and consequently the pressure of carbon monoxide decreases during absorption.

6. The small quantities of nitrogen and hydrogen present in the gas mixture have a slight hindering effect on absorption.

Comparison of the above with Krevelen's postulates gave a new equation for absorption, the scope and way of application of which are given.

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