

ABSORPTION OF PHOSPHINE IN AQUEOUS SOLUTIONS OF SODIUM HYPOCHLORITE AND SULPHURIC ACID

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Abstract—The kinetics of absorption of phosphine in aqueous solutions of sodium hypochlorite and sulphuric acid was studied in a stirred cell and a stirred contactor. The reaction of phosphine with aqueous solutions of sodium hypochlorite was found to be first order with respect to phosphine and hypochlorite. The effect of pH on the second order rate constant was also investigated. The value of the second order rate constant was found to vary from 230 to 77,000 l/g mole sec at 28°C in the pH range of 12.95–9.40.

The reaction of phosphine with aqueous solutions of sulphuric acid, in the range of concentrations of 80 to 92% by weight, was also found to be first order with respect to phosphine. The value of the pseudo first order rate constant was found to be in the range of 3×10^6 – 64×10^6 sec⁻¹ at 28°C. Copper sulphate was found to be an effective catalyst in sulphuric acid solutions.

INTRODUCTION

Commercial acetylene produced from calcium carbide invariably contains a significant amount of phosphine. Further the effluent gases from electrothermal phosphorus plants are also reported to contain some phosphine. The removal of phosphine from the above gases is normally accomplished by scrubbing the gas with aqueous solutions of sodium hypochlorite or sulphuric acid. There is scanty information in the literature on the kinetics of absorption of phosphine in the above solutions.

Lawless and Searle [1] have studied the kinetics of the homogeneous reaction between phosphine and sodium hypochlorite at different pH values using the stopped flow method. They have covered a limited range of pH. There is apparently no information in the published literature on the kinetics of the absorption of phosphine in aqueous solutions of sulphuric acid. Sluzovskaya *et al* [2] have reported that copper sulphate acts as a catalyst for the reaction of phosphine with sulphuric acid. This is reported to accelerate the oxidation of absorbed species to phosphoric acid. It is, however, clear from the available information that the reaction between phosphine and aqueous sodium hypochlorite and sulphuric acid are relatively very fast and diffusional factors are likely to be important. In view of the above it was thought desirable to study the kinetics of absorption of phosphine, which is very sparingly soluble in water, in aqueous solutions of sodium hypochlorite and sulphuric acid over a wide range of operating conditions of industrial relevance.

EXPERIMENTAL

The kinetics of absorption of phosphine in aqueous solutions of sulphuric acid upto a concentration of 85% w/w and sodium hypochlorite at pH values of 12.40 and 12.95 was studied in a stirred cell. The design of the cell was the same as that used by Jhaveri and Sharma [3]. The area of contact in the cell was 80 cm². The stirrer was provided with three impellers, one for stirring the liquid surface and the other two in the gas phase to ensure complete mixing in the gas phase. The cell was immersed in a constant temperature water bath maintained at 28°C.

The absorption of phosphine in aqueous solutions of sodium hypochlorite at pH values of 9.40, 10.20, 10.40 and 11.70 was studied in a stirred contactor as the values of the rate constant at lower pH were expected to be relatively very high. The stirred contactor was provided with independent stirrers for the gas and liquid phases. The area of contact in the contactor was 85 cm². The top plate and the gas side stirrer were made of stainless steel while the bottom plate and the liquid side stirrer were made of perspex to avoid corrosion. The absorption of phosphine in aqueous solutions of sulphuric acid above a concentration of 85% w/w was also studied in the stirred contactor as it was expected that some gas side resistance may be present at higher concentrations of the acid in the stirred cell. The top and bottom plates and both the stirrers in the gas and liquid side were made of stainless steel. The design of the contactor was the same as that used by Sridharan and Sharma [4].

Phosphine gas was generated by reacting zinc phosphide with sulphuric acid and collected in an aspirator by the displacement of water. A layer of paraffin oil was maintained over water to prevent the absorption of phosphine in water.

Aqueous solutions of sodium hypochlorite were prepared by passing chlorine in aqueous solutions of sodium hydroxide of predetermined strength. The hypochlorite solution was analysed by liberating iodine from an acidified solution of potassium iodide and titrating the liberated iodine with standard sodium thiosulfate. The pH of the solutions was varied from 9.0 to 13.0. The ionic strength of the solution was maintained constant by the addition of analar sodium chloride.

A measured quantity of sodium hypochlorite solution was taken in the apparatus. The cell was flushed with nitrogen to displace air. Nitrogen rather than oxygen should be used as phosphine burns spontaneously in the presence of air. After flushing, phosphine of the desired composition was passed for a suitable length of time. Then the stirrer was started and a run was taken. The gas flow rate was measured using a soap film meter. The duration of a run was 10–20 min. After each run, the cell

was again flushed with nitrogen to avoid the contact of phosphine with air. The phosphine gas concentration was determined volumetrically in an Orsat apparatus with potassium permanganate as the absorbent. The rate of absorption was measured by analysing the liquid sample at the end of each experiment. Different concentrations of sodium hypochlorite at pH values of 9.40, 10.20, 10.40, 11.70, 12.40 and 12.95 were taken and the concentration of phosphine was varied from 2 to 20% v/v. The measured values of the specific rate of absorption along with other pertinent data are reported in Table 1.

In the experiments for the absorption of phosphine in sulphuric acid, a measured quantity of sulphuric acid was taken in the cell. The system was flushed with nitrogen to remove air and after flushing a run was taken in the same manner as in the case of sodium hypochlorite solutions. At the end of 10 min, a sample of the outgoing gas was collected and analysed for its phosphine content. The specific rate of absorption was calculated by analysing the phosphine content of the inlet and outlet gas streams. The gas flow rate was maintained at a prefixed value in the range of 10–20 cm³/sec. Different concentrations of sulphuric acid were taken and at each concentration, the partial pressure of phosphine was varied. The measured values of the specific rate of absorption along with the other pertinent data are reported in Table 2. To find out

the catalytic effect of copper sulphate on the specific rate of absorption, different concentrations of sulphuric acid were taken and 0.5% by weight of copper sulphate was added. At each concentration of sulphuric acid, the partial pressure of phosphine was varied.

SOLUBILITY OF PHOSPHINE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID AND SODIUM HYPOCHLORITE

The solubility of phosphine in water at 28°C has been reported by Weston to be 7.77×10^{-6} moles/cm³ atm [5]. Since the reactions between dissolved phosphine and sodium hypochlorite and sulphuric acid are very fast, the physical solubility of phosphine in these solutions cannot be determined analytically. The solubility of phosphine in aqueous solutions was estimated from the following equation

$$\log \left[\frac{A_w}{A^*} \right] = K_s I \quad (1)$$

where,

$$K_s = i_+ + i_- + i_x \quad (2)$$

The ionic strength of the aqueous solutions was calculated

Table 1 Absorption of phosphine in aqueous solutions of sodium hypochlorite at 28°C

| No | Apparatus used | Ionic strength ion/l | pH | Concentration of NaOCl $B_0 \times 10^3$ mole/cm ³ | $R_A \times 10^7$ mole/cm ² sec atm | Rate constant k_2 1/mole sec |
|----|----------------|----------------------|-------|---|--|--------------------------------|
| 1 | A | 1.5 | 12.95 | 0.386 | 2.17 | 234 |
| 2 | A | 1.5 | 12.95 | 0.633 | 2.80 | 240 |
| 3 | A | 1.5 | 12.40 | 0.104 | 1.71 | 526 |
| 4 | A | 1.5 | 12.40 | 0.199 | 2.47 | 575 |
| 5 | A | 1.5 | 12.40 | 0.394 | 3.54 | 598 |
| 6 | B | 1.9 | 11.70 | 0.245 | 4.31 | 1865 |
| 7 | B | 1.5 | 10.40 | 0.218 | 12.50 | 13400 |
| 8 | B | 1.5 | 10.20 | 0.218 | 15.20 | 19500 |
| 9 | B | 2.3 | 10.20 | 0.218 | 11.93 | 17750 |
| 10 | B | 1.5 | 9.40 | 0.351 | 38.30 | 76600 |

Apparatus used A—Stirred cell, Volume of aqueous solution = 200 cm³ Speed of stirring = 60 rev/min B—Stirred contactor, Volume of aqueous solution = 600 cm³ Speed of stirring = 175 rev/min

Table 2 Absorption of phosphine in aqueous solutions of sulphuric acid at 28°C

| No | Apparatus used | Concentration of H ₂ SO ₄ % w/w | Concentration of H ₂ SO ₄ mole/l | Acidity function [-Ho] | $R_A \times 10^6$ moles/cm ² sec atm | Rate constant $k_1 \times 10^{-6}$ sec ⁻¹ |
|----|----------------|---|--|------------------------|---|--|
| 1 | A | 79.70 | 14.06 | 7.47 | 0.96 | 3.1 |
| 2 | A | 82.40 | 14.78 | 7.90 | 1.46 | 6.1 |
| 3 | A | 83.25 | 15.00 | 8.03 | 1.92 | 9.6 |
| 4 | A | 84.40 | 15.29 | 8.20 | 3.25 | 22.4 |
| 5 | A | 85.55 | 15.62 | 8.38 | 4.27 | 29.8 |
| 6 | B | 88.50 | 16.37 | 8.82 | 7.76 | 44.3 |
| 7 | B | 92.93 | 17.23 | 9.36 | 17.70 | 64.0 |

Apparatus used A—Stirred cell, Volume of aqueous solution = 170 cm³ Speed of stirring = 40 rev/min B—Stirred contactor, Volume of aqueous solution = 600 cm³ Speed of stirring = 175 rev/min

from the following expression

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (3)$$

where C_i is the concentration of ion of valency Z_i . The second dissociation of sulphuric acid (namely, $\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$) is known to be negligibly small in the range of the concentration of acid used in this work. Further it is reported that in the range of sulphuric acid concentration employed, even the first dissociation to H^+ and HSO_4^- does not occur completely [6]. The ionic strength of the acid solution would, therefore, be numerically equal to the molarity of the acid dissociated, in the range of acid concentration covered in this work.

The contribution of various species to the value of K_s was taken from the reported values in the literature [7]. The contribution of phosphine to the value of K_s was calculated from the value of K_s reported by Weston for sodium chloride solution, the contribution of HSO_4^- ion was calculated from the values of the solubility of sulphur dioxide in sulphuric acid reported by Sankholkar [8]. It has been assumed that for the entire range of sulphuric acid concentration covered in this work eqn (1) holds.

DIFFUSIVITY OF PHOSPHINE IN AQUEOUS SOLUTIONS OF SULPHURIC ACID

The diffusivity of phosphine in water at 28°C was calculated by Wilke-Chang correlation and found to be $2.05 \times 10^{-5} \text{ cm}^2/\text{sec}$. The diffusivity of phosphine in aqueous solutions of sulphuric acid, in the range of acid concentrations employed in this study, cannot be experimentally determined since the reaction of dissolved phosphine in the acid is very fast. It is not reasonable to estimate the value of the diffusivity from the familiar Wilke-Chang correlation, because of relatively large variation in the viscosity (almost 25 fold). Sankholkar has measured the diffusivity of sulphur dioxide in aqueous solutions of sulphuric acid of 72.4 and 81.8% (w/w) by absorption in a laminar liquid jet. The following equation was found to hold

$$\frac{D\mu^{0.68}}{T} = \text{Constant} \quad (4)$$

The above correlation was used for the calculation of the diffusivity of phosphine in aqueous solutions of sulphuric acid. The relevant viscosity data are available in the literature [9].

The diffusivity of phosphine in aqueous solutions of hypochlorite was estimated from the Wilke-Chang equation as here the maximum variation in the viscosity was found to be 20%.

MECHANISM OF REACTION

Reaction between phosphine and hypochlorite

Lawless and Searle have reported that phosphine is oxidized to hypophosphorus acid when absorbed in aqueous solutions of sodium hypochlorite



But in the present study, it was found that phosphine is oxidized to phosphoric acid instead of hypophosphorus acid. The stoichiometric factor for phosphine with sodium hypochlorite was determined by absorbing a known volume of phosphine in sodium hypochlorite solution of a known concentration. The following reaction is believed to take place



Dennis and O'Brien [10] have also reported that phosphine is oxidized to phosphoric acid when absorbed in sodium hypochlorite. They have also reported that the rate of absorption of phosphine was strongly dependent on the pH of the solution. Further in the patent literature it has been pointed out that the oxidation goes to phosphoric acid [11].

Reaction between phosphine and sulphuric acid

In the reaction of phosphine with aqueous solutions of sulphuric acid, phosphine is oxidized to phosphoric acid and sulphuric acid is reduced to hydrogen sulphide. Hydrogen sulphide in the acid medium and in the presence of some oxidizing agent will be oxidized to elemental sulphur [12]. In the present study the same phenomenon was observed and elemental sulphur was precipitated. The concentration of sulphuric acid has a very large effect on the rate of absorption of phosphine.

RESULTS AND DISCUSSION

Absorption of phosphine in aqueous solutions of sodium hypochlorite

Preliminary experiments at pH values of 12.40 and 12.95 were carried out in the stirred cell at different speeds of stirring (40–80 rev/min). The specific rate of absorption was found to be independent of the speed of stirring showing that the hydrodynamic factors are not important. The enhancement factor $[R_A/A \cdot k_L]$ was found to be very much greater than 3 and much less than $[B_0/ZA^*]$ thus confirming that the reaction falls in fast pseudo m th order reaction regime. For experiments in the stirred contactor at pH values of 9.40, 10.20, 10.40 and 11.70, the speed of stirring was varied from 150 to 250 rev/min. Here also the specific rate of absorption was found to be independent of the speed of stirring. The gas side stirrer speed was varied from 700 to 1200 rev/min and the specific rate remained practically constant indicating the gas-side resistance was absent. Further the enhancement factor was found to be very much greater than 3 and much less than $[B_0/ZA^*]$. This confirms that the reaction falls in fast pseudo m th order reaction regime.

For a reaction falling in the fast pseudo m th order reaction regime, the specific rate of absorption is given by the following equation

$$R_A = [A^*] \sqrt{\left(\frac{2}{m+1} D_A k_{mn} [A^*]^{m-1} [B_0]^m\right)} \quad (7)$$

where, R_A = Specific rate of absorption, mole/cm² sec, $[A^*]$ = Solubility of the solute in the electrolyte solution, mole/cm³, D_A = Diffusivity of the dissolved gas in the

liquid, cm^2/sec , $k_m = (m + n)$ th order reaction rate constant, $(\text{cm}^3/\text{mole})^{m+n-1} \text{sec}^{-1}$, $[B_0]$ = Concentration of the non-volatile reactant, mole/cm^3 , m = Order of the reaction with respect to the gas, and n = Order of the reaction with respect to the non-volatile reactant

Further experiments were carried out in the stirred cell at a speed of stirring of 60 rev/min and in the stirred contactor at 175 rev/min. The speed of the gas-side stirrer of the stirred contactor was kept at 900 rev/min. The effect of the partial pressure of phosphine on the specific rate of absorption is shown in Fig 1 from which it is clear that the specific rate of absorption varies linearly with the partial pressure of phosphine, indicating that the reaction is first order with respect to phosphine. A plot of $[R_A/A^*]^2$ against the concentration of sodium hypochlorite is shown in Fig 2 which indicates that the specific rate of absorption increases as square root of the concentration of sodium hypochlorite. This indicates that the reaction is first order with respect to sodium hypochlorite. The values of the second order reaction rate constant were found to be 236, 564, 1865, 13380, 18530 and

76600 $\text{l}/\text{mole sec}$ at pH values of 12.95, 12.40, 11.70, 10.40, 10.20 and 9.40 respectively at 28°C . The following equation holds

$$\log k_2 = 11.398 - 0.697 \text{ pH} \quad (8)$$

The strong influence of pH on the reaction rate constant can perhaps be attributed to the fact that the per cent of total chlorine in sodium hypochlorite solutions present as undissociated hypochlorous acid varies exponentially with pH [13] and apparently the active species are reported to be HOCl.

Lawless and Searle have reported a value of the second order rate constant of 267 $\text{l}/\text{mole sec}$ at a pH of 13.0 at 21.5°C . The value of the second order rate constant obtained in this work was 236 $\text{l}/\text{mole sec}$ at a pH of 12.95 at 28°C .

From a practical point of view it would, therefore, be desirable to work at lower pH values in the range of 9 to 10 consistent with the other desirable features from the plant operation point of view (e.g. corrosion behaviour).

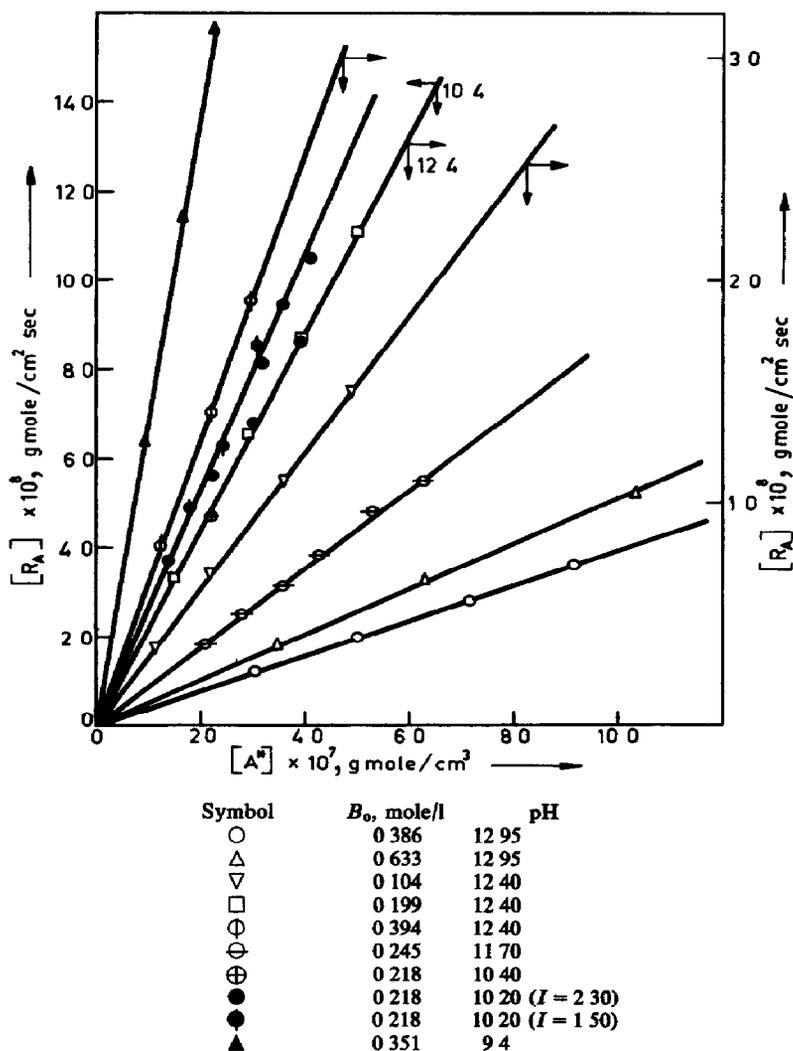


Fig 1 Effect of the partial pressure of phosphine on the specific rate of absorption in aqueous solutions of sodium hypochlorite in the stirred cell and the stirred contactor at 28°C

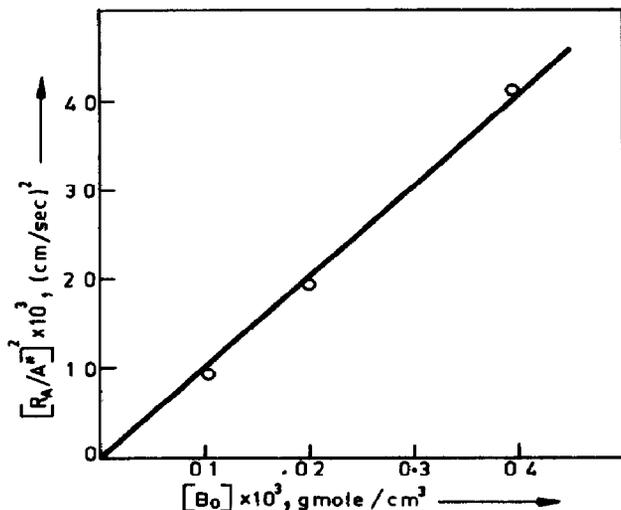


Fig 2 Effect of the concentration of sodium hypochlorite on the specific rate of absorption of phosphine in the stirred cell at 28°C pH = 12.40 $[A^*] = 4.0 \times 10^{-7}$ mole/cm³ Volume of aqueous solution = 200 cm³ Speed of stirring = 60 rev/min Ionic strength = 1.50 g ion/l

Absorption of phosphine in aqueous solutions of sulphuric acid

Some preliminary experiments with acid concentrations upto 85% w/w were carried out at different speeds of stirring (30–80 rev/min) in the stirred cell. The specific rate of absorption was found to be independent of the speed of stirring indicating that the hydrodynamic factors are not important. Further the enhancement factor $[R_A/A^*k_L]$ was found to be very much greater than 3 and much less than $[B_0/ZA^*]$ indicating that the reaction falls in fast pseudo m th order reaction regime. Further experiments were carried out at a speed of stirring of 40 rev/min. The experiments with acid concentrations above 85% w/w were carried out in the stirred contactor at a liquid stirrer speed of 175 rev/min. The gas side stirrer speed was kept at 1200 rev/min. Here also the enhancement factor $[R_A/A^*k_L]$ was found to be very much greater than 3 and much less than $[B_0/ZA^*]$ indicating that the reaction falls in fast pseudo m th order reaction regime.

The effect of the partial pressure of phosphine on the specific rate of absorption is shown in Fig 3 from which it is clear that the specific rate of absorption increases linearly with the concentration of phosphine. The values of the pseudo first order rate constant were calculated for different concentrations of sulphuric acid and are reported in Table 2. There was a substantial increase in the specific rate of absorption due to the presence of copper sulphate.

It is reasonable to correlate the values of the rate constant in aqueous solutions of sulphuric acid with the acidity function, H_0 . The values of the acidity function, H_0 , for different concentrations of sulphuric acid have been reported by Liler [9]. It is more rational to correlate the rate constant data for concentrations of sulphuric acid upto 85% and above 85% by weight separately as the behaviour of the sulphuric acid changes at about 84.50% and then the sulphuric acid becomes the solvent and water

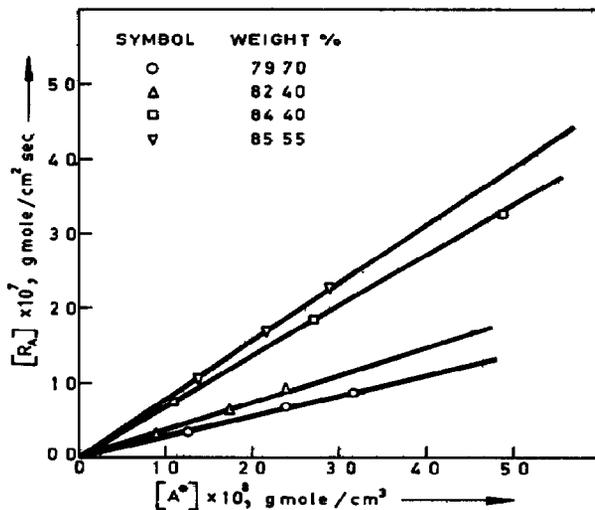


Fig 3 Effect of the partial pressure of phosphine on the specific rate of absorption in aqueous solutions of sulphuric acid in the stirred cell at 28°C. Volume of aqueous solution = 170 cm³ Speed of stirring = 40 rev/min

the solute (84.5% w/w corresponds to the mole fraction of sulphuric acid of 0.5). The experimental data were fitted by the least square method (Fig 4) and the following equations hold

$$\text{Upto 85\% acid,} \quad \log k_1 = 1.129[-H_0] - 2.009 \quad (9)$$

$$\text{Above 85\% acid,} \quad \log k_1 = 0.381[-H_0] + 4.253 \quad (10)$$

[The data pertaining to sulphuric acid solutions containing copper sulphate as a catalyst can also be correlated by similar equations.]

According to the established theories $\log k_1$ should vary linearly with H_0 but in this work the slope of the plot of $\log k_1$ against $[-H_0]$ was found to be 1.129. This difference is perhaps due to the uncertainties associated

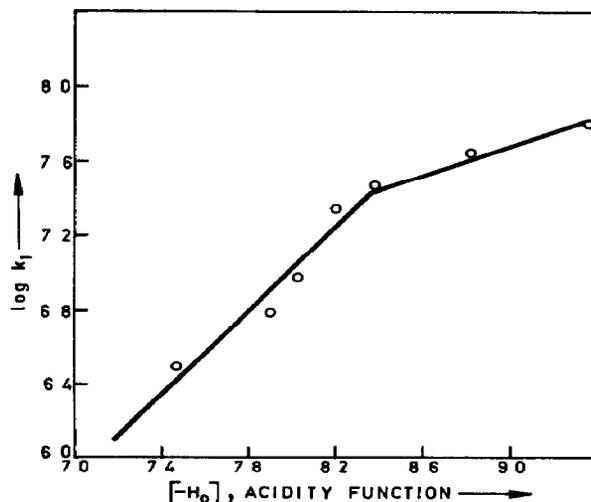


Fig 4 Effect of the acidity function on the reaction rate constant in the absorption of phosphine in aqueous solutions of sulphuric acid at 28°C

with the calculation of k , as a 10% error in the estimated value of solubility would imply a 22% error in the value of the rate constant, and a 10% error in the value of diffusivity would imply an error of 10% in the value of the rate constants

However, a single line can be fitted for the entire range of sulphuric acid concentration covered which gives a slope of 0.726 with a standard deviation of 0.160

CONCLUSIONS

1 The absorption of phosphine in aqueous solutions of sulphuric acid and hypochlorite in the range covered in this work is accompanied by fast pseudo first order reaction. The reaction is also first order with respect to hypochlorite

2 The value of the second order rate constant is a strong function of the pH of the solution in the case of hypochlorite solutions, and the concentration of sulphuric acid in the case of sulphuric acid solutions

3 In the case of hypochlorite solutions, it would be desirable to adopt lower pH of the absorbent (around 9 to 10). It has also been claimed in the patent literature that a pH value of 9.2 would be desirable in industrial practice for the removal of phosphine

4 In the case of sulphuric acid solutions, it would be desirable to use a small amount of copper sulphate as a catalyst for gases containing phosphine which are free from acetylene

From a practical point of view, aqueous solutions of sulphuric acid provide an additional advantage of drying the acetylene gas obtained from calcium carbide. In case in the same plant a caustic chlorine unit is also located, then the outlet sulphuric acid from chlorine drying towers can also perhaps be advantageously employed

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NOTATION

[A_w] solubility of solute in water, mole/cm³
 [A^*] solubility of solute in electrolyte solution, mole/cm³

[B_0] concentration of non-volatile reactant, mole/cm³
 D_A diffusivity of the dissolved gas in the liquid, cm²/sec
 H_0 acidity function of sulphuric acid
 I ionic strength of solution, g ion/l
 k_L liquid side mass transfer coefficient, cm/sec
 k_2 second order reaction rate constant l/mole sec
 k_{mn} ($m+n$)th order reaction rate constant, (cm³/mole) ^{$m+n-1$} sec⁻¹
 $K_s = i_+ + i_- + i_g, l/ion$
 m order of the reaction with respect to the gas
 n order of the reaction with respect to the non-volatile reactant
 R_A specific rate of absorption, mole/cm² sec
 T absolute temperature, °K
 Z number of moles of hypochlorite or sulphuric acid reacting with one mole of phosphine

Greek symbol

μ viscosity of the solution, cp

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