Studies on Arsenic Trichloride as a Solvent

III.   Potentiometric Acid-base Titrations in AsCl$_3$

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Potentiometric titrations have been carried out in AsCl$_3$ solutions
using Ag, AgCl electrodes. The idea of a Cl$^-$ ion concentration govern-
ing the acid-base processes has been confirmed by these measurements.

In the preceding paper [1] the importance of potentiometric measurements of
pCl in AsCl$_3$ solutions was pointed out and the use of Ag, AgCl-electrodes
was suggested. This paper will deal with the possibilities of measuring large
pCl changes in potentiometric acid-base titrations in AsCl$_3$. The definition
acid + Cl$^-$ = base leads to the use of the following concentration cell:

$$\text{Ag, AgCl} \mid \text{Cl}^- \ (C_1) \parallel \text{Cl}^- \ (C_2) \mid \text{Ag, AgCl}$$

Titrations have been carried out with the acid FeCl$_3$ against the bases
(CH$_3$)$_4$NCl, C$_5$H$_5$N, (C$_2$H$_5$)$_2$NH and with the base (CH$_3$)$_4$NCl against the acids
FeCl$_3$ and SbCl$_5$.

A comparison with a conductometric titration has also been made.

EXPERIMENTAL

C h e m i c a l s u s e d. Commercial AsCl$_3$ was purified by two distillations at a
final boiling point of 229° C. The conductance of the distilled AsCl$_3$ was measured in the
part A of the receiver (Fig. 1). (The instrument used was a Philips Philoskop, type GM
4140, and the measurements were performed at a frequency of 1 000 p/s.) As long as the
conductance was considered to be too high the liquid was poured out through K to B.
When the purity was satisfactory the liquid was permitted to pass through the syphon
S to C. Table 1 shows the results of one such distillation. The fractions following 7 gave
the same conductance and were all collected in the flask C. The conductance was constant
after 12 hours. The lowest value [2] previously measured in AsCl$_3$ seems to be 1.4—1.6 · 10^{-7}
ohm^{-1} cm^{-1} at 0° C. Our value obtained at + 19° C is considerably lower, although the
conductance of AsCl$_3$ has a positive temperature coefficient [2].

The other chemicals were all purified by standard methods, with particular care to
keep them dry.

E l e c t r o d e s. The Ag, AgCl electrodes were made according to Brown [3]. Before
use they were left in ethyl ether for 24 hours and then heated to 130° C during one hour.

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The design of the cell is shown in Fig. 2 a. The reference electrode R is filled with a solution of $(CH_3)_4NCl$ in $AsCl_3$. The carefully ground-in stopper at J still permits an equilibrium potential to be obtained. Emf was measured with a vacuum tube voltmeter (*Ermi*).

Apparatus. Preliminary experiments showed that it was most unsatisfactory to use stopcocks in the apparatus because of the creeping out of the $AsCl_3$ solution and because of chemical reactions with every available type of grease. A special titration apparatus was therefore designed to avoid stopcocks or any contact between solution and greased parts (Fig. 2 a and b). The reagent solution is passed from the vessel V into the U-tube system consisting of tubes A and B. The addition of reagent to the solution in K takes place in the following way. The whole apparatus, Fig. 2 a, is tilted clockwise in the plane of the paper. The buret is then turned around S so that the solution will rise in A. The solution will begin to flow from A to C at about 90° rotation and the bent tip at T will then point downwards allowing a drop-wise addition of solution. (The amount of solution in A—B must be such that it can be completely transferred to A.) The apparatus could readily be manipulated in such a way that the solution in C would flow back into A—B. By means of a calibrated scale attached to A—B volume readings were taken before and after the addition of solution through C. During the conductometric titration a conductance cell (of the same shape as shown in Fig. 1) replaces the electrode system.

Results. The results are summarized in Table 2 and Figures 3—5.

DISCUSSION OF THE RESULTS

The ionic character of the reactions studied here has previously been established by conductometric titrations [4]. The fact that the potentiometric titrations give as satisfactory results as indicated by Table 2 shows further,

Table 1.

Fraction no.	Spec. cond. ohm^{-1} cm^{-1}
1	$5.7 \cdot 10^{-6}$
2	$1.8 \cdot 10^{-6}$
3	$1.0 \cdot 10^{-6}$
4	$5.6 \cdot 10^{-7}$
5	$2.8 \cdot 10^{-7}$
6	$1.2 \cdot 10^{-7}$
7	$1.0 \cdot 10^{-7}$

Table 2.

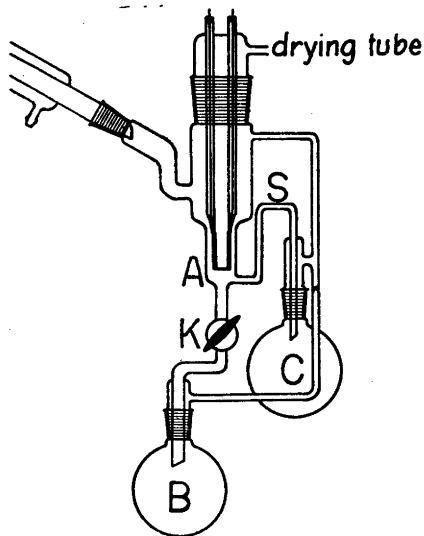| Solution in K		End.-point (ml)		Solution in V		Fig. no.
Solute	mmole solute / 1 000 g $AsCl_3$	Calc.	Found	Solute	mmole solute / 1 000 g $AsCl_3$	
$(CH_3)_4NCl$	0.21	2.55	2.56	$FeCl_3$	1.4	3 a
C_5H_5N	0.50	6.36	6.54	$FeCl_3$	1.4	3 b
$(C_2H_5)_2NH$	0.3	2.2	2.34	$FeCl_3$	1.4	3 c
$FeCl_3$	0.26	2.69	2.68	$(CH_3)_4NCl$	1.7	4 a
$SbCl_5$	0.47	2.96	3.01	$(CH_3)_4NCl$	1.7	4 b
$(CH_3)_4NCl$	0.29	4.38	4.39	$FeCl_3$	1.4	5

Fig. 1. Reception part of the apparatus used for purification of AsCl₃ by distillation.
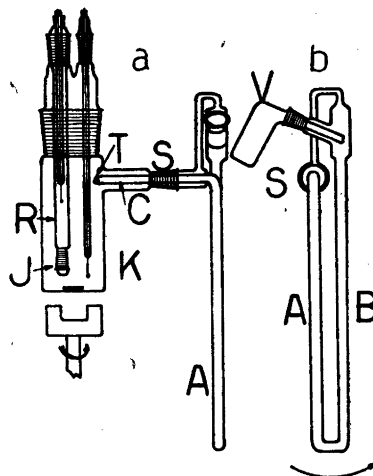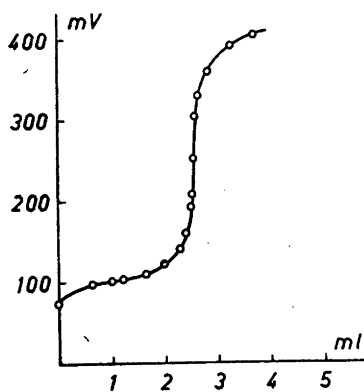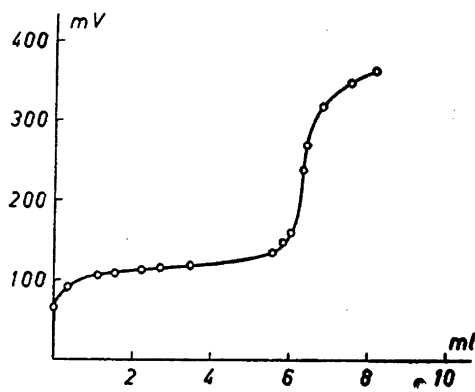
Fig. 2 a. Titration apparatus.
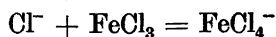b. Perpendicular view of the buret.

a   b

Fig. a. b. Potentiometric titration curves (see Table 2).

that the Ag, AgCl electrode behaves at least roughly as a pCl electrode. There is thus reason to speak of a Cl⁻ concentration in the AsCl₃ solution and to write, e.g., the reaction between $(CH_3)_4NCl$ and $FeCl_3$ as

$$Cl^- + FeCl_3 = FeCl_4^-$$

The existence of an ionic product and of a scale of acid and base strength follows from the confirmation of the existence of a Cl⁻-concentration. The former may be best studied by conductometric methods [5].
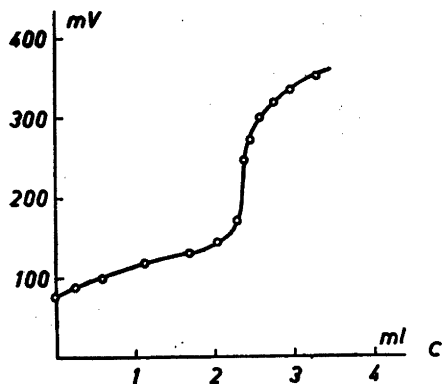
Fig. 3 c. Potentiometric titration curves
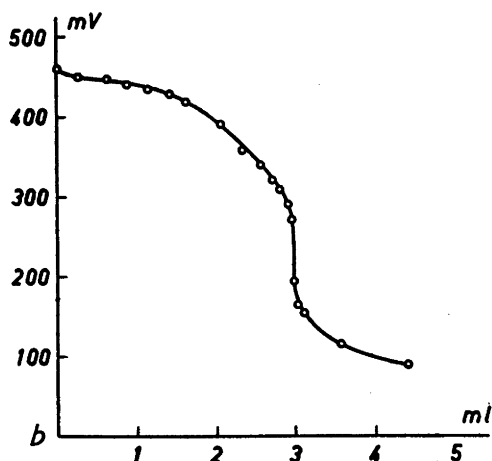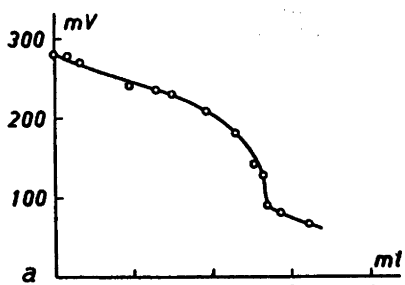(see Table 2).
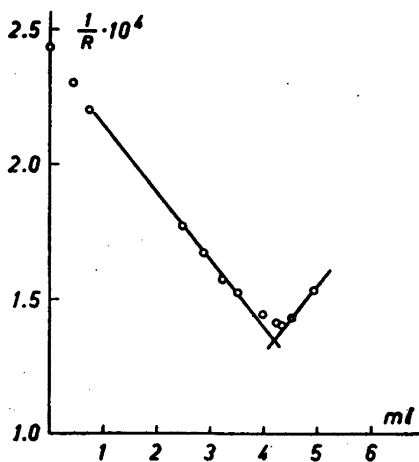

Fig. 4. Potentiometric titration curves (see Table 2).

Fig. 5. Conductometric titration curve
(see Table 2).

A maximum value can be obtained for the product $K = C_{AsCl_2}^{+} \cdot C_{AsCl_4}^{-}$ if we assume that the liquid junction potential can be neglected and that $(CH_3)_4NCl$ as well as $SbCl_5$ are strong electrolytes in $AsCl_3$. We obtain from Fig. 4 b

$$\tfrac{1}{2}\ pk = \frac{460-215}{60} - \log\ C_{SbCl_5},$$

giving $pk > 15$ and $C_{AsCl_2}^{+} \cdot C_{AsCl_4}^{-} < 10^{-15}$.

We cannot hope to come further with the potentiometric methods without elaborate experiments and extended theoretical calculations. There are different reasons to expect difficult problems:

1. The unknown liquid junction potential.
2. The unknown degree of dissociation of the acid and base solutions in $AsCl_3$.
3. The unknown acid-base behavior and solubility product of the slightly soluble AgCl in $AsCl_3$.
4. The difficulties involved in determining the activity factors in solvents with low dielectric constants.

These problems are too complex to give much hope of a very accurate treatment. We intend, however, to explore further the possible usefulness of the potentiometric methods for studying ionic reactions in $AsCl_3$ and other solvents.

REFERENCES

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4. Gutmann, V. *Z. anorg. Chem.* **266** (1951) 331.
5. Gutmann, V. *Monatsh.* **85** (1954) 491.