

*The Electrochemistry of Solutions of Hydrogen Chloride in Acetone:
the Cell $H_2|HCl|Ag, AgCl$.*

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A study has been made at 25° of the cell $H_2|HCl|Ag, AgCl$, pure acetone being used as solvent. Reproducible e.m.f.s were obtained which vary with the concentration of hydrogen chloride in a way which indicates that hydrogen chloride is a very weak acid in this solvent. Evidence is presented that its dissociation constant is about 10^{-8} . On this basis the standard potential of the silver-silver chloride electrode in acetone is about -0.53 v (cf. $+0.2222$ v in water). The solubility of silver chloride in acetone being taken as 4×10^{-18} mole/l., this leads to a standard potential of the silver electrode of about $+0.50$ v (cf. $+0.798$ v in water).

THE literature on the electrochemistry of non-aqueous solutions is extensive, but the majority of papers deal with conductivity measurements. Little work has been concerned with e.m.f. determinations and few cells without liquid junction have been investigated. The cell $H_2|HCl|Ag, AgCl$ has been studied, the following solvents being used: methanol (Nonhebel and Hartley, *Phil. Mag.*, 1925, **50**, 729), ethanol (Woolcock and Hartley, *ibid.*, 1928, **5**, 1133), dioxan + water (Harned, Walker, and Calmon, *J. Amer. Chem. Soc.*, 1939, **61**, 44), glycerol + water (Lucasse, *Z. physikal. Chem.*, 1926, **121**, 254), acetone + water (Izmailov and Zabara, *J. Phys. Chem. U.S.S.R.*, 1946, **20**, 165), and glacial acetic acid (Heston and Hall, *J. Amer. Chem. Soc.*, 1934, **56**, 1462). In the last two investigations quinhydrone and chloranil electrodes, respectively, were used in place of the H_2 -Pt electrode. There is no report of measurements of this cell when pure acetone is used as solvent.

A study of metal-metal halide electrodes in acetone solutions has been made by Ulich and Spiegel (*Z. physikal. Chem.*, 1936, **177**, A, 103), who report that most of them give irreproducible and unstable potentials. They explain this by supposing that complex ions of the type $M_mCl_n^{(n-m)-}$ are formed: qualitative support for this comes from the observation that the solubilities of silver and mercury halides in acetone are increased by the addition of lithium halide. In our experience, however, silver-silver chloride electrodes when prepared carefully behave satisfactorily in acetone.

Nature of Hydrogen Chloride + Acetone Solutions.—Evidence regarding the state of hydrogen chloride in acetone is conflicting. The early conductivity work of Sackur (*Ber.*, 1902, **27**, 326) suggests that hydrogen chloride behaves as a strong electrolyte, and the same conclusion is reached by Braude (*J.*, 1948, 1971) on the basis of spectrophotometric measurements of the "acidity function" in acetone. On the other hand, conductivity measurements carried out by Ross Kane (Thesis, Oxford, 1929; cf. *Ann. Reports*, 1930, **27**, 344) indicated that hydrogen chloride behaves as a very weak acid

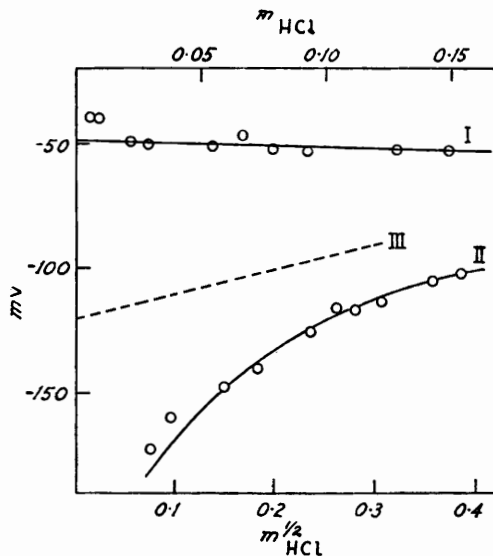
($K_a \sim 10^{-8}$) in acetone. His results were not, however, very reproducible and the work was not published in full. Some preliminary measurements by Mackor (personal communication) confirm the difficulty of obtaining reproducible results, but indicate a dissociation constant of 10^{-6} ; Mackor also suggests that his results may indicate the dimerization of hydrogen chloride in acetone. Recent conductivity measurements by Dr. M. J. Sparnaay in this laboratory confirm that hydrogen chloride does not behave as a simple acid in acetone, but that other equilibria are involved. Nevertheless, the ionic concentrations in the solution correspond approximately to those which would be derived from a weak acid of K_a in the range 10^{-8} to 10^{-7} .

An independent value may be obtained by studying the solubility of silver chloride in hydrogen chloride + acetone. The complexity constant* (K_c) for the reaction $AgCl + Cl^- \rightleftharpoons AgCl_2^-$ is given by Mackor (*Rec. Trav. chim.*, 1951, **70**, 457) as about 5, so that if hydrogen chloride were completely dissociated, silver chloride would be very

Curve I, $E + \frac{RT}{F} \ln m_{HCl}$ against m_{HCl} .

Curve II, $E + \frac{2RT}{F} \ln m_{HCl}$ against $m_{HCl}^{\frac{1}{2}}$.

Curve III, Theoretical slope of curve II at infinite dilution.



soluble in hydrogen chloride + acetone: this is not so. Hydrogen chloride being assumed to be a weak acid in acetone, the solubility of silver chloride is given, approximately, by the equation

$$m_{AgCl_2^-} = \{[K_c^2/(K_c + 1)]m_{HCl}K_a\}^{\frac{1}{2}} \dots \dots \dots (1)$$

where m_{HCl} is the stoichiometric (initial) concentration of hydrogen chloride.

A number of experiments were carried out in an attempt to determine $m_{AgCl_2^-}$. In these, crystals of silver chloride were sealed in tubes containing hydrogen chloride + acetone of known strength (about $N/10$) and rotated in a thermostat at 25° for several days. The ampoules were then opened, and a sample of the solution diluted with an equal volume of conductivity water. The formation of an opalescence, and the eventual coagulation of the precipitate, was followed in a Hilger Spekker Absorptiometer. Calibration experiments were carried out by adding known volumes of 0.01N-silver nitrate solution to solutions of hydrogen chloride in 50% acetone + water. In all cases the opalescence increased to a maximum and then declined linearly with time. The observations were not easily reproducible, for the opalescence produced in the solubility determinations gave optical densities of the order of only 0.05. These were matched in calibration runs in which the silver-ion concentration was about 3×10^{-5} . From these experiments we conclude that the solubility of silver chloride in 0.1M-hydrogen chloride in

* The complexity constant is defined as the equilibrium constant for the formation of a complex ion.

acetone is $3.0 \pm 1.0 \times 10^{-5}$. It was found also that some reaction occurred in the solution in the course of several days at 25°, leading to a slight yellow coloration and the development of a characteristic odour. Equilibration for less than 48 hr., however, gave an undetectable quantity of silver ion in the solution. Despite the large experimental uncertainty of these measurements, they indicate that the order of magnitude of the acid dissociation constant of hydrogen chloride in acetone is between 10^{-8} and 10^{-9} .

The Cell $\text{H}_2|\text{HCl}|\text{Ag}, \text{AgCl}$ in Acetone.—The e.m.f. of this cell is given by

$$E = E^0 - (2RT/F) \ln \alpha m_{\text{HCl}} \gamma_{\pm} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where α is the degree of dissociation, m_{HCl} the stoichiometric molality of hydrogen chloride, and γ_{\pm} the mean activity coefficient of the ions. On introduction of the dissociation constant

$$K_a = m_{\text{HCl}} [\alpha^2/(1 - \alpha)] \gamma_{\pm}^2 / \gamma_{\text{HCl}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

eqn. (2) becomes

$$E + \frac{RT}{F} \ln m_{\text{HCl}} = E^0 - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln (1 - \alpha) - \frac{RT}{F} \ln \gamma_{\text{HCl}} \quad . \quad . \quad . \quad (4)$$

Since K_a is very small, $(1 - \alpha)$ can be set equal to unity at the concentrations studied, so that

$$E + \frac{RT}{F} \ln m_{\text{HCl}} = E^0 - \frac{RT}{F} \ln K_a - \frac{RT}{F} \ln \gamma_{\text{HCl}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Since $\ln \gamma_{\text{HCl}}$ will probably vary linearly with m_{HCl} in dilute solution, we might expect a graph of $E' = E + (RT/F) \ln m_{\text{HCl}}$ against m_{HCl} to be linear. The intercept gives $E^0 - (RT/F) \ln K_a$ and the variation of γ_{HCl} with m_{HCl} can be deduced from the slope. If K_a is known, E^0 can then be evaluated.

EXPERIMENTAL

Materials.—Acetone, purified through the bisulphite compound, was kept over solid potassium permanganate for several days and fractionally distilled in an efficient column (about 40 theoretical plates). Water is the main impurity and can be removed satisfactorily only by careful distillation, since the use of strong dehydrating agents tends to lead to condensation reactions. The purest acetone has been reported (Lannung, *Z. physikal. Chem.*, 1932, **161**, 255; cf. Kraus and Reynolds, *J. Amer. Chem. Soc.*, 1948, **70**, 1709) to have a conductivity of 10^{-10} ohm⁻¹ cm. at 20°; that used in the present work varied from batch to batch in the range $3-5 \times 10^{-9}$ ohm⁻¹ cm.

Hydrogen chloride solutions in acetone were prepared by passing dry hydrogen chloride into acetone. The hydrogen chloride was made from dry, bromine-free sodium chloride and concentrated "AnalaR" sulphuric acid, and was passed through a trap at -70° and through anhydrous magnesium perchlorate before entering the acetone. The acetone + hydrogen chloride solution was analysed by weighing out a portion and pouring it into aqueous silver nitrate. The mixture was boiled gently for about $\frac{1}{2}$ hr. and left for 3-4 days to ensure complete precipitation of the silver chloride, which was then collected in a sintered-glass crucible and weighed. Analyses were made both of the freshly prepared solution and of the solution at the end of the run. These usually agreed well.

Technique.—The silver-silver chloride electrodes consisted of an intimate mixture of precipitated silver and silver chloride as recommended by Brønsted (*Kgl. Danske Vidensk. Selsk.*, 1920, **3**, No. 9) and by Güntelberg (*Z. physikal. Chem.*, 1926, **123**, 199). Great care was taken to remove bromide impurities because of their serious effect on the potential of this electrode. The hydrogen electrodes were 1 cm.² platinized platinum plates. Preliminary work by Mr. D. S. Brown in this laboratory had shown that hydrogen electrodes produce no detectable reduction of acetone to isopropyl alcohol during bubbling of hydrogen for 24 hr.

The cell was essentially similar to that described by Güntelberg and contained duplicate sets of electrodes. The solution in the silver-silver chloride electrode compartment was deoxygenated with oxygen-free nitrogen; this is very important because of the high solubility of oxygen in acetone and the effect of this gas on the potential of the electrode. Hydrogen from a cylinder was purified by passage over heated copper, then over soda-lime and through a

liquid-air trap. Gases were brought into equilibrium with the cell solutions by means of pre-saturators; to be effective these had to be of large volume ($5 \times$ the volume of the solution in the cell).

Because of the high resistance of the cell, an electrometer valve detector similar to that described by Greville and Maclagan (*Trans. Faraday Soc.*, 1931, 27, 210) was used in conjunction with a Tinsley Type 4025 potentiometer. All leads were of coaxial-screened cable. E.m.f.s could be read to better than 0.1 mv. The cell was kept in a screened air-thermostat maintained at $25^\circ \pm 0.1^\circ$.

Before each run the cell and pre-saturators were washed several times with distilled water, then conductivity water and finally acetone. They were then dried for 36 hr. at 120° . Filling with solution was carried out by means of an apparatus which reduced contact between the solutions and air to a minimum. The electrodes reached equilibrium in 6–12 hr. and the e.m.f.s remained constant to within 0.5 mv for at least several hours. Equilibrium was always approached from lower values of the e.m.f., the hydrogen electrode becoming steadily more negative relative to the silver–silver chloride electrode.

As mentioned above, a slow reaction takes place between hydrogen chloride and acetone. Some preliminary unpublished work by Fletcher, Ogston, and Gatty (1934) (personal communication from Dr. A. G. Ogston) suggests that in 0.1*N*-solution at room temperature the reaction is approximately of first order with a half-life of some 350 hr. The constancy and reproducibility of the e.m.f.'s obtained in our work indicate that this reaction does not seriously affect the results, provided that freshly prepared solutions are employed.

Results.—The results are summarized in the Table and $E' = E + (RT/F) \ln m_{HCl}$ is plotted against m_{HCl} in Curve I. Apart from the two points at concentrations below 0.01*m* the points lie, to within 2–3 mv, on the straight line $E'(v) = -0.049 - 0.02 m_{HCl}$.

E.M.F. of the cell $H_2|HCl|Ag, AgCl$ *in pure acetone at* 25° ($p_{H_2} = 1$ atm.).

(Sign of e.m.f. is that of the right-hand electrode.)

m_{HCl}	0.0056	0.0090	0.0219	0.0290	0.055	0.067	0.079	0.093	0.128	0.149
E (mv)	+93.8	+81.1	+48.3	+39.2	+22.6	+22.6	+12.6	+7.2	-0.1	-4.6
$E + (RT/F) \ln m_{HCl}$ (mv)	-39.4	-39.4	-49.8	-50.9	-51.8	-46.7	-52.4	-53.2	-52.9	-53.5

This is in accordance with the predictions of eqn. (5). If hydrogen chloride were a strong electrolyte in acetone a graph of $E + (2RT/F) \ln m_{HCl}$ against $m_{HCl}^{\frac{1}{2}}$ should approach linearity at small concentrations and have a slope of 0.094. As shown in Curve II, this is not so. If we assume the dissociation constant of hydrogen chloride in acetone to be about 10^{-8} , we obtain for the standard potential of the silver–silver chloride electrode in acetone $E^0_{Ag, AgCl} = -0.53$ v, compared with +0.2222 v in water.

Using Mackor's value (personal communication) for the solubility product of silver chloride in acetone, *viz.*, $L = 4 \times 10^{-18}$, we obtain for the standard potential of the silver electrode in acetone $E^0_{Ag} = +0.50$ v, compared with +0.798 v in water. Silver is therefore much less "noble" in acetone than in water.

The slope of curve I should be $(2.303RT/F) \log \gamma_{HCl}$, which leads to $\log \gamma_{HCl} = 0.3m$. We do not know of any other estimates of the activity coefficient of hydrogen chloride in acetone with which to compare this value.

The above estimates of standard potentials are, of course, dependent upon the accuracy of the rough value of 10^{-8} for K_a , and of Mackor's determination of the solubility of silver chloride in acetone.

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