

Silver Compounds of Acetylene

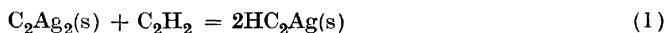
III. The Equilibrium Constant of the Formation of Silver Carbide from Acetylene

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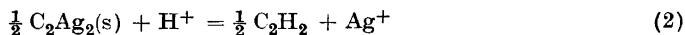
The formation of symmetric silver carbide, $\text{AgC} \equiv \text{CAg}$, from acetylene and Ag^+ with liberation of H^+ is a reversible reaction. By use of strong complex formers with Ag^+ like thiourea or cyanide the carbide can be dissolved, regenerating the equivalent amount of acetylene.

The asymmetric form $\text{HC} \equiv \text{CAg}$ may exist as an intermediate product at the formation or breaking down of symmetric silver carbide, but is not stable at 25°C and moderate acetylene pressure. No formation of the asymmetric carbide can be shown even at an acetylene pressure of 7 atm. If it exists at all the acetylene pressure necessary for its formation at 25°C according to



must exceed 7 atm.

The equilibrium can thus be formulated



The thermodynamic equilibrium constant can be defined as

$$K = a_{\text{Ag}^+} \cdot P_{\text{C}_2\text{H}_2}^{1/2} / a_{\text{H}^+} \quad \text{or} \quad (3)$$

$$\text{p}K = \text{pAg} - \text{pH} + \frac{1}{2} \text{p}P_{\text{C}_2\text{H}_2} \quad (3)$$

The activity of solid silver carbide is taken as unity for $a_{\text{C}_2\text{Ag}_2}$; $P_{\text{C}_2\text{H}_2}$ is measured in atm.

From simple experiments on splitting and formation of carbide the interval wherein the constant must lie can be roughly determined. The silver carbide is completely split by 0.1 M hydrochloric acid (pAg ca 9 and pH ca 1) regenerating acetylene ($pP_{\text{C}_2\text{H}_2}$ ca. 0) which shows that pK must be less than 8. When passing acetylene ($pP_{\text{C}_2\text{H}_2}$ ca. 0) through an aqueous solution of 0.01 M silver perchlorate in 0.1 M perchloric acid (pH ca 1) silver carbide precipitates and the silver content in the solution is eventually depressed to 10^{-4} — 10^{-5} (pAg 4 — 5), as estimated by a potentiometric titration with 10^{-4} M potassium iodide. This gives a lower limit for pK of ca 3. Since pK is larger than 3 the constant can be determined by direct chemical analysis only in systems of high hydrogen ion activity. An analytical method might be used, working with suitable competing complex formers, and would be advantageous if the constants of the complex formers were easily determined. But we have not been able to find a complex former giving a mixture where the silver ions are about equally shared between the two systems. The connection between pAg and pH demanded by the acetylene equilibrium, and the fact that few anions are permissible also considerably limits the choice.

A potentiometric method seems à priori suitable; the H^+ - and Ag^+ -activities being in no way extreme. Several conditions must however be fulfilled: rather quick occurrence of the equilibrium, absence of disturbing side-reactions (*e.g.* some reaction involving a redox process) *etc.* The immediate purpose of our experiments was to find out whether such a method could be used. The three variables to be measured and the experimental conditions generally have therefore been varied over rather a wide range, partly to check that there is a covariation according to the equilibrium formula set up, partly to select the conditions best suited for an accurate determination of the constant. On the whole the results of these experimental variations are satisfactory. There can be no doubt that the measurements actually refer to the equilibrium formulated. In spite of some disturbances, the origin of which is not quite clear, but which are to be discussed, the mean value

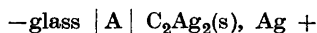
$$pK = 3.46 \text{ at } 25^\circ \text{C}$$

seems to be of satisfactory accuracy and, for the present, sufficient for our investigations. It might however be possible to determine the constant with greater precision.

DISCUSSION OF THE EXPERIMENTAL CONDITIONS

The three quantities required for the calculation of the thermodynamic constant are all *directly measurable*. pAg can be measured potentiometrically as can pH (by means of the glass electrode; in this system hardly any other H/H⁺-electrode could be used). $P_{\text{C}_2\text{H}_2}$ is the partial pressure of acetylene in a gas mixture in equilibrium with the liquid. None of the activities need be computed from an analytically determined concentration; no activity coefficient need be estimated or kept constant.

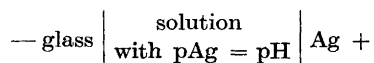
It is also advantageous that only the difference (pAg-pH) enters into the calculation of p*K*. This difference should be obtained directly from the potential between a glass and a silver electrode immersed in the same solution, *i.e.* in a cell *without liquid junction*,



where A is a solution in equilibrium with solid silver carbide and with a gas mixture of known acetylene partial pressure. The potential of this cell can be used for the calculation of (pAg — pH) from

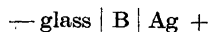
$$E = E^\circ - \frac{\ln 10 RT}{F} (\text{pAg} - \text{pH}) \quad (4)$$

where E° is the standard potential of the electrode couple, *i.e.* the potential of the cell



Even when using a third electrode as a reference in order to get absolute values for the variables pAg and pH, the diffusion potential to the reference electrode will be eliminated in the calculation of p*K*.

A third advantage is that the standardization of this system, *i.e.* finding E° for a given glass electrode, is very easy to perform. Measurements of the potential E^s of the cell



where B is an equimolar solution of nitric acid and silver nitrate of total concentration c , show that the potential varies but slightly with c ; the reason for this being naturally that the deviation from the standard potential depends only on the rather insignificant difference between the activity coefficients

of silver and hydrogen ions in the same solution. It is easy to extrapolate to $c = 0$, where $E^o = E^s$.

An introductory discussion of foreseen experimental difficulties is justified since the procedure has partly been evolved from such a discussion.

The use of pH-buffered solutions can be supposed to be advantageous; experiments also have proved this. Buffer substances and concentrations can be chosen at will as regards their influence on the activity coefficients as the activities are directly measured. Anions forming insoluble complex salts, *e.g.* of the type $C_2Ag_2 \cdot AgAn$, must however be avoided. An analytical check of the composition of the solid phase may become misleading, as a stoichiometrically complete transformation of an insoluble complex salt into silver carbide and vice versa is a very slow process. To decide whether silver carbide or a complex salt is the stable solid phase one should know the constants that, according to formulas (3) and (4) in a previous publication¹, characterize the system in the presence of a given anion. But we cannot start with the knowledge of any such system; on the contrary the determination of the silver carbide — acetylene equilibrium is a primary task in such an investigation. It is certain only that *perchlorate* can be regarded as an innocuous anion. This has been proved by the solubility determinations¹ where silver carbide has been shown to be the solid phase in the presence of silver perchlorate of concentrations up to 2 *M*. The possibility that solid complex perchlorates form in the present system is even less. Such a conclusion can be drawn from just the qualitative validity of the formulas referred to. To be safe we have tried to limit our experiments to perchlorate systems. Some experiments with acetate ion present have however given acceptable results.

Identical activity of the silver carbide samples used in the different experiments must be assumed when calculating the equilibrium constant. Even though the identification of the solid phase as silver carbide is certain, the presupposition of constant activity arouses some doubt. The particles of silver carbide are so small that there is a risk that variations in size may cause change in activity. In order to trace such variations silver carbide has been prepared in different ways. No reliable information has been acquired concerning activity variations of importance, still, it might be such variations that limit the accuracy of the measurements. In one case only, a phenomenon appears that may indicate a formation of silver carbide of distinctly different activity: if potentiometer measurements are carried out in such yellow solutions as result from passing acetylene into very dilute silver perchlorate in the absence of other salts,¹ p. 108 values are obtained (not very constant) that indicate a much higher silver carbide activity. Still, we find that such measurements, even though they might be of importance when investigating the nature of

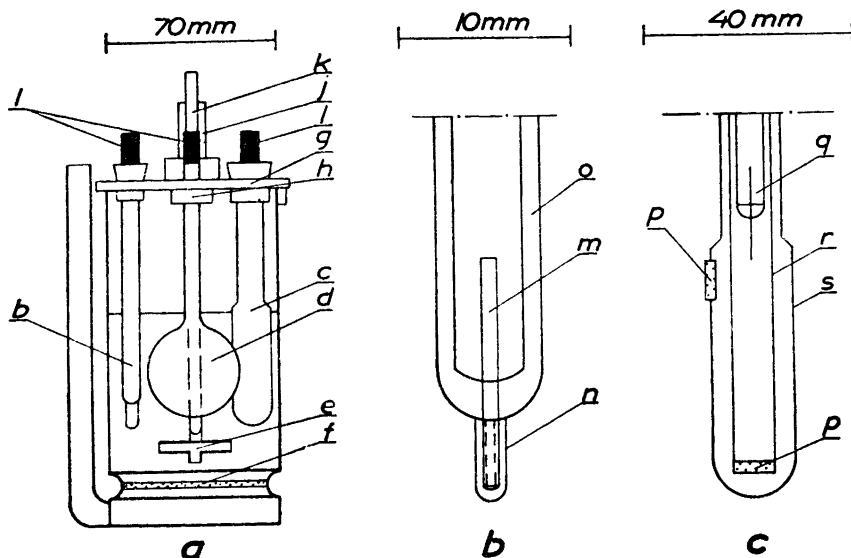


Fig. 1. Apparatus: a Vessel; b Silver electrode; c Reference electrode; d Glass electrode; e Stirrer; f Fritted disk Pyrex M or C; g Lid of plexiglas; h Holder for glass electrode; j K. P. G. bearing; k Shaft of stirrer; l Jackets; m Pt-wire 1 mm Ø, projecting part thread-cut; n Silver sponge; o Jena Normal glass; p Fritted disk Jena G 5|3; q Ag|AgCl-electrode according to Brown; r Internal tube 0.01-M NaCl, 2-M NaClO₄; s External tube, 2-M NaClO₄.

the «yellow modification», are here irrelevant. Among the experiments described below there is none where the yellow modification was present, except as an unstable intermediate product in the formation of «normal» silver carbide. — Finally it should be remarked that in the potentiometric experiments no inconvenient transformation of the silver carbide occurs, such as that which necessitated repeated addition of fresh silver carbide in the solubility determinations.¹, p. 113

Apart from the risk of non-reproducible activity of the solid silver carbide the low silver ion activity seems to be the main difficulty of the measurements. Even at pH=1 and an acetylene pressure of 1 atm. p_{Ag} is 4.5 and then increases linearly with pH. In the determination of the solubility products of several insoluble silver salts a common experience seems to be that satisfactory results have been achievable only when using silver electrodes covered, generally by electrolysis, with the silver salt. This method would be advantageous also in our case, especially as it is conceivable that certain disturbances, caused by possible impurities in the continuously introduced acetylene or by some side-

reaction, would be eliminated. We have succeeded in making silver/silver carbide electrodes by electrolysis at a low current density in an ammoniacal solution saturated with acetylene, but these electrodes have not given reproducible potentials.

In the experiments therefore metallic silver electrodes (of »thermal» type) have been used exclusively. The vessel is so constructed that the solid silver carbide can be dispersed with as violent agitation as its explosive tendency permits. Unfortunately only a comparatively small quantity of silver carbide can be used in each experiment*.

EXPERIMENTAL PROCEDURE

The vessel consists of a Pyrex cylinder, $h = 150$ mm, $d = 70$ mm, shaped as in Fig. 1. Gas can be introduced either through the fritted disk in the bottom or through a glass tube (not shown on fig.) passing through the lid and ending just above the surface of the liquid. Several silver electrodes can be introduced. The stirrer consists of a T-tube of 6 mm glass. Precipitate and liquid are drawn from the bottom of the vessel and then thrown out through the horizontal arms. The stirrer is driven through a flexible shaft by a motor so shielded that stirring can go on while measuring. The vessel is immersed in an oil-thermostat where the temperature is $25.00^\circ\text{C} \pm 0.05$.

Glass electrodes of a relatively low resistance (not over 1 megohm) have been used in order to reduce the risk of leakage currents, which is large in this type of experiment where a gas saturated with water-vapour flows through the apparatus. After checks against the hydrogen electrode two slightly different Hartmann & Braun electrodes were selected; one (I) with standard acetate buffer + 0.01 *M* KCl and with Ag/AgCl electrode according to Brown²; the other (II) delivered complete with built-in calomel electrode. On the stem of the glass electrode is cemented a ring of plexiglas which can be screwed on to the lid of the vessel.

Silver electrodes are constructed according to Fig. 1 with a threaded platinum rod carrying the silver sponge. We have found these preferable to Brester's³ spiral type, being more easily covered with an even, complete, and practically crack-free silver sponge. This gives a faster exchange of the solution at the electrode surface, and equilibrium is attained more rapidly. The silver plating and the thermal reduction of silver oxide paste is performed according to Brester's directions. Moderate variations in electrolysis, heating, and cooling do not seem to influence the reproducibility, which is checked by measuring mutual potential differences in 0.001 *M* and 0.1 *M* silver perchlorate. The potentiometer used has a sensitivity of 0.01 mV. The reproducibility of the electrodes, even from different groups, has as a rule been better than ± 0.1 mV and in several cases ± 0.01 mV. Electrodes differing more than 0.1 mV from the average were rejected. We have thus found a remarkable reproducibility but we have not studied more closely the requirements.

* Wet silver carbide is said not to explode on grinding, but we have convincing experience to the contrary.

Reference electrode (see Fig. 1) consists of an Ag/AgCl-electrode² with 2*M* sodium perchlorate in the salt bridge; a rather unsatisfactory arrangement considering the diffusion potential, but contamination by some foreign anion must be avoided. Calibration of the system glass electrode — reference electrode has been performed in the usual manner with buffer solutions, without any greater demand for precision, as only an approximate value of the pH is required.

Potentiometer. Vacuum-tube potentiometer: Radiometer, Copenhagen, Type PHM 3 d, adjusted against Eppley standard cell and calibrated over the measuring range against a compensation bridge NC Jensen, Copenhagen, giving an accuracy of ± 0.2 mV.

Gases and gas mixtures. Acetylene of fair purity has been delivered in cylinders with normal filling (AGA) but without acetone. Nitrogen of commercial quality, in some cases freed from oxygen⁴ (No difference in the results has been observed.) For the preparation of gas mixtures of known composition two methods have been used:

(a) Filling acetylene cylinders with an acetylene-nitrogen mixture, the composition checked through analyses. The method is not suited for accurate procedure as the reversible sorption of acetylene in the filling causes a continuous increase in the acetylene content of the gas when emptying the cylinder. The acetylene percentage must be checked before and after each experiment.

(b) Arranging a constant and accurately measured flow of acetylene and nitrogen resp., which are mixed and passed into the vessel. For this purpose a special technique of high precision has been devised, a more detailed description of which will be given elsewhere.

Chemicals. The solid silver carbide and the silver perchlorate have been prepared in the manner already described¹. Other chemicals of analytical purity.

Procedure of standardization. All standardizations and checks have been performed in the vessel (except the checking of the silver electrodes mentioned) mounted as in the determinations of the acetylene equilibrium. The working conditions of the glass electrode are thus identical in both cases. For the same reason a stream of gas (nitrogen) of approximately the same speed as in the real experiments has been passed through the solution during the standardizations. In this way the atmosphere around the glass electrode is kept at approximately constant humidity.

In the determination of E° for the system



the vessel is charged with 200 ml of water and measured amounts are added of a stock solution which is 1.00 *M* both in silver nitrate and nitric acid, the equimolarity of which has been checked by careful analyses. The volume is adjusted to ca. 200 ml after every addition. E° must be determined in connection with every experiment as the potential of the glass electrode slowly changes.

The procedure for the investigation of the acetylene equilibrium is apparent from the discussion of the results in the following section. The measurements have been carried out in diffuse electric light, strong day-light seems unfavourable. The composition of the solution was usually altered by adding 10 ml of liquid and after mixing again removing 10 ml, thus keeping the volume constant at ca 200 ml. The gas flow rate was about 350 ml/min.

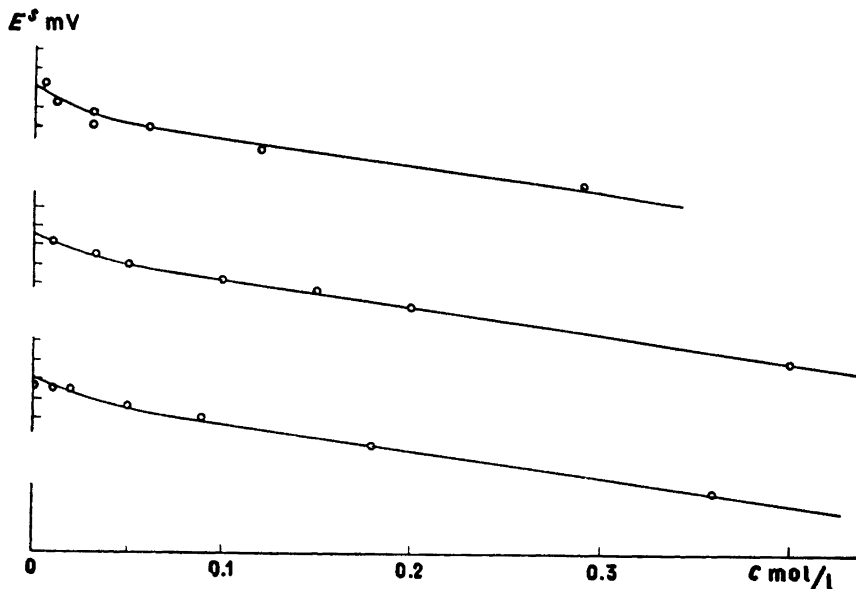
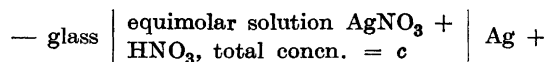


Fig. 2. Determination of E° for the system — glass | liquid | Ag +.

STANDARDIZATIONS AND CHECKS.

Determination of E° . The potential E^s of the cell



varies but slightly with the concentration c , as is demonstrated in Fig. 2, giving the results of three typical experiments. (The E -axis units are mV, positive direction upwards.)

For every point the relation

$$E^s = E^\circ + \frac{\ln 10 RT}{F} (\log f_{\text{Ag}} - \log f_{\text{H}}) \quad (5)$$

should hold. The observed relationship $E^s = F(c)$ should thus express the influence of the concentration on the difference $(\log f_{\text{Ag}} - \log f_{\text{H}})$. With decreasing c both terms tend to zero; but the difference can be neglected where the single terms are still comparatively large. The circumstances thus favour an extrapolation to $c = 0$ where $E^s = E^\circ$.

The experiments show — as demonstrated by the figure — that E^0 is a linear function of the concentration when this exceeds ca. 0.05 M . (The deviation from the linear relationship in the interval $0.05 < c < 0.4 M$ is in no case greater than the experimental error ± 0.2 mV.) At concentrations below 0.05 M the curve shows some deviation from the straight line. The measurements become less reproducible at low concentrations; isolated points falling outside the curve connecting the others and the bent part of the curve having a somewhat different shape in different experiments. So far we have interpreted this poor reproducibility as the result of accidental disturbances. To avoid these difficulties we have used the following procedure at each standardization: the straight line is produced to the E -axis and the value thus obtained is increased by 0.7 mV, this being the mean, from several experiments, of the difference between the intercepts on the E -axis of the produced straight line and the curve. The method has the advantage that the determinations are based on well reproducible measurements in the linear interval. A possible error in the value 0.7 mV — hardly, however, more than some tenths of a mV — would appear with the same effect in all experiments.

It is interesting to note that $(\log f_{\text{Ag}} - \log f_{\text{H}})$ varies linearly with the concentration (within the range $0.05 < c < 0.4 M$)

$$\log f_{\text{Ag}} - \log f_{\text{H}} = f_{\pm\text{AgNO}_3} - \log f_{\pm\text{HNO}_3} = -0.25 \times c \quad (6)$$

The assumption, often made⁵, that the individual character of an electrolyte can be accounted for by a linear c -term in the function $\log f = F(c)$ seems fully justified in this particular case*. However, the dependence on the concentration is so small that a minor deviation from a linear relationship would hardly be perceptible in spite of the advantage that $(\log f_{\text{Ag}} - \log f_{\text{H}})$ is measured directly. A further discussion of these problems is beyond the scope of this article.

Check of $dE/d(pAg-pH)$ for the cell —glass | solution | Ag + can, within a limited range, be performed by the same dilution technique as has been described for the determination of E^0 . If the solution consists of a mixture of silver nitrate and nitric acid in the molar proportion 1 : 100 one gets a potential decreasing linearly with c (= the total concentration). The slope is practically identical with that of the determinations of E^0 . In such an ex-

* At the computation of this expression (6) the incomplete dissociation of the nitric acid ought to be taken into consideration. A recalculation using the value of Redlich⁶ for the dissociation constant gives but a minor contribution to the linear c -term, about one tenth of the mentioned factor-0.25 and of the same sign.

periment the extrapolated potential for $c = 0$ was -3.2 mV; a standardization performed on the same occasion gave $E^{\circ} = +116.0$. Thus

$$dE/d(\text{pAg-pH}) = 59.6$$

which corresponds well with the theoretical value 59.16 at 25°C .

Calibration of the glass electrode and determination of its potential against the hydrogen electrode, E^{g} has been performed by direct comparison between glass and hydrogen electrodes by the method of MacInnes and Belcher⁷ and has given the following results.

Table 1. Determination of E^{g} for two glass electrodes. (The E^{g} -values corrected to 1 atm. hydrogen pressure.)

Solution	pH	E^{g}	
		Glass I	Glass II
HCl 0.24 M	0.7	565.2	719.0
HAc 0.1 M, NaAc 0.1 M	4.6	564.8	719.2
$\text{Na}_2\text{B}_4\text{O}_7$ 0.05 M	9.2	566.2	735.8

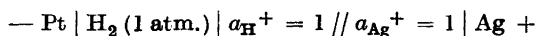
It is evident that the E^{g} slightly varies with the pH. A considerable deviation appears only at pH 9 for glass II, which has quite a large alkali error. Between pH 7 and 1 constancy of ± 0.3 mV can be counted on.

The E^{g} -values of the glass electrodes change somewhat with their aging but so slowly that errors need not be feared; standardizations are made in connection with every series of measurements. The variations in E° are parallel.

As a further check we have computed the standard potential of silver from

$$E^{\circ}_{\text{Ag}} = E^{\circ} + E_{\text{g}}$$

giving the potential for the cell



where the sign// represents a hypothetical electrolyte contact without diffusion potential. In an experiment where E° and E^{g} were determined on the same day we got

$$E^{\circ}_{\text{Ag}} = +801 \text{ mV}$$

in fair agreement with the best values in literature⁸ which lie within 799.2—800.2 mV.

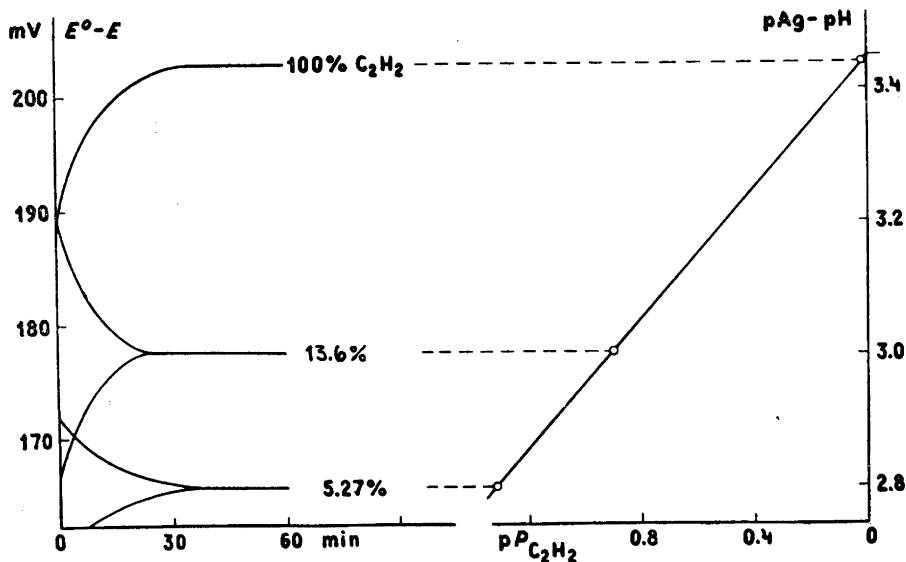
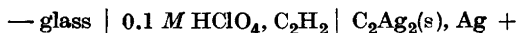


Fig. 3. Variation of $P_{C_2H_2}$ at pH ca. 1.

It should be pointed out that the procedure devised for the determination of the standard potential of silver is founded on measurements in a cell without liquid junction — therein differing from earlier determinations. In spite of the limited accuracy of the glass electrode the procedure is of a certain interest and could possibly be developed into a good means for the determination of the standard potential of silver.

RESULTS

Fig. 3 shows the result of an experiment where the acetylene pressure in the cell



is varied between 0.05—1 atm. The potential responds rather swiftly to a change in the acetylene pressure and establishes itself at a given value, reproducible for each pressure. As shown by the time curves, identical values appear whether the acetylene pressure is adjusted from above or from below, thus proving a true equilibrium. The shape of these curves naturally depends upon the gas flow rate, particularly in the beginning. A rough estimate shows that the time necessary for the establishment of equilibrium is longer than the

time required for alteration of the concentration of acetylene dissolved in the liquid.

The connection between the values for $(pAg - pH)$ and the corresponding values for $pP_{C_2H_2}$ (calculated from the acetylene content of the gas, the total pressure and the partial pressure of the water vapour) is demonstrated in the right part of the diagram, showing that the variables are correlated as demanded by the formula

$$pK = pAg - pH + \frac{1}{2} pP_{C_2H_2}$$

The slope $d(pAg - pH)/dpP_{C_2H_2}$ for the straight line is -0.49_3 , in good agreement with the theoretical value $-\frac{1}{2}$. A more accurate value for the slope requires a variation of the acetylene pressure over a wider range. But it is difficult to prepare a gas mixture with an acetylene content below 1% while maintaining the necessary relative accuracy.

The numerical values of pK calculated from the three measuring points are: 3.465, 3.462, and 3.452. In an isolated experiment of this type the pK -value is reproducible within 0.01 units. Divergencies between series at different pH are however often considerably larger.

Experiments at pH greater than 2 frequently give unsatisfactory results. The most obvious trouble is that the equilibrium potential is often very slowly established. In some cases it has been impossible to get a constant value within reasonable time (3—4 h). Evidently such a drawn-out procedure is in itself a disadvantage. Several experiments give the impression that it is possible to differentiate between, on the one hand, the time curve corresponding to the establishment of the acetylene — silver carbide equilibrium, and on the other hand a still slower drift of the potential corresponding to an accumulation of impurities or some similar disturbance. It is all the same impossible to make a correction giving the «true» potential. As a rule values from experiments where a comparatively stable potential is reached only after a long time are obviously faulty. We have however thinned our material only by rejecting experiments not giving a constant potential within 1—1½ h. In the table some rejected values, in brackets, are given as examples.

We have not been able to explain the disturbances satisfactorily. The following observations though, contain some suggestions:

(a) At a pH lower than 2 disturbances are insignificant. But in neutral or alkaline solution they occur almost regularly; especially striking if the pH is raised during the course of an experiment by the addition of a base. In order to get satisfactory results in such solutions the experiment must be

Table 2. Determination of pK at different pH .

Measurements a, b, etc. under one number have been performed in sequence, pH -changes effected by addition to the solution.

The pH and composition of the solution are approximately stated. $P_{C_2H_2}$ has been calculated from the acetylene content of the gas, the total pressure and the partial pressure of water vapor (ev. + ammonia). Where two values for ($E^\circ - E$) are given these correspond to an attainment of the equilibrium from opposite directions according to Fig. 3. Brackets design potentials of unsatisfactory constancy.

No.	Addition of solid C_2Ag_2	Solution mol/l	pH	$P_{C_2H_2}$ atm.	$E^\circ - E$ millivolt	pK
13 a	2 millimole	0.01 $HClO_4$	2.1	0.579	196.5	3.44
b	»	0.05 $HClO_4$	1.5	»	196.2	3.44
c	»	0.35 $HClO_4$	1.1	»	198.4	3.47
d	»	ca 0.01 $HClO_4$ + 0.34 NH_4ClO_4	1.7	»	198.3	3.47
					198.8	3.48
					198.8	3.48
					197.5	3.46
					197.5	3.46
10	—	0.01 $AgClO_4$ + 0.1 $HClO_4$	1.3	0.0674	170.4	3.47
					169.7	3.46
9 a	2 millimole	0.05 NH_3 + 0.05 NH_4ClO_4 + 0.10 NH_4Ac	9.0	0.230	192.7	3.58
(Ag_1)	»	do	»	»	189.8	3.53
(Ag_2)	»	do	»	»	(201)	(3.72)
					(195)	(3.64)
b	»	0.05 HAc + 0.05 NH_4Ac + 0.15 NH_4ClO_4	4.7	»	188.1	3.49
(Ag_1)	»	do	»	»	186.1	3.47
(Ag_2)	»	do	»	»	(190)	(3.57)
					(188)	(3.52)
c	»	0.2 NH_4ClO_4 + 0.05 $HClO_4$ + 0.1 HAc	1.2	»	186.7	3.48
(Ag_1)	»	do	»	»	186.7	3.48
(Ag_2)	»	do	»	»	186.7	3.48
8 a	»	0.05 $HClO_4$	1.5	0.190	182.5	3.44
b	»	0.35 $HClO_4$	1.0	»	182.1	3.44
c	»	2.7 $HClO_4$	0.5	»	183.5	3.46
					182.7	3.45
					(185)	(3.49)
					183.8	3.46
7 a	»	0.06 HAc + 0.01 $NaAc$ + 0.04 $NaClO_4$	4.0	0.968	(200)	(3.39)
b	»	do	»	0.164	181.8	3.46
c	»	0.01 $HClO_4$ + 0.1 HAc + 0.1 $NaClO_4$	1.4	0.968	206.3	3.49
d	»	do	»	0.164	183.8	3.50

No.	Addition of solid C_2Ag_2	Solution mol/l	pH	$P_{C_2H_2}$ atm.	$E^\circ - E$ millivolt	pK
6 a	2 millimole	0.1 $HClO_4$	1.3	0.155	181.3 180.9	3.47 3.46
b	»	0.1 $NaClO_4$ + 0.1 HAc	2.1	»	178.6 177.6	3.41 3.43
c	»	0.1 $NaClO_4$ + 0.05 NaAc + 0.05 HAc	3.6	»	(145)	(2.82)
5 a	»	0.01 $HClO_4$	2.1	0.145	179.4 180.4	3.45 3.47
b	»	0.1 $HClO_4$	1.3	»	180.4 180.4	3.47 3.47
c	»	ca 0.01 $HClO_4$ + 0.1 NH_4ClO_4	2.0	»	178.4 178.3	3.43 3.43
3 a	»	0.1 $HClO_4$	1.3	0.0499	166.4 166.4	3.47 3.47
b	»	do	»	0.127	178.3 178.3	3.46 3.46
c	»	do	»	0.953	203.5 203.5	3.45 3.45

performed by dissolution or precipitation of silver carbide at the intended or higher pH.

(b) If the acetylene pressure is altered during the course of a slow change in the potential, the latter is quickly displaced by an amount fairly well corresponding to the alteration. Afterwards the potential again slowly drifts in the same direction, with practically the same speed as before.

(c) The slow establishment of the potential is associated with some process on the surface of the silver electrode. If, when the potential has become tolerably steady, still another silver electrode is introduced, it is quite a while before this second electrode shows the same potential as the first. Two simultaneously introduced silver electrodes sometimes require unequal times before they show the same potential, although they seem identical according to checks and standardizations. In some cases a residual difference was observed, but disappeared when the pH was reduced to a value below 2 (see Table 2, expt. 9).

Although impurities in the acetylene can be suspected as a source of error we have not been able to get any definite effect either by scrubbing the gas with various absorbents, or by changing the gas flow rate. (Naturally the partial pressure adjusts itself more speedily when the flow rate is higher.)

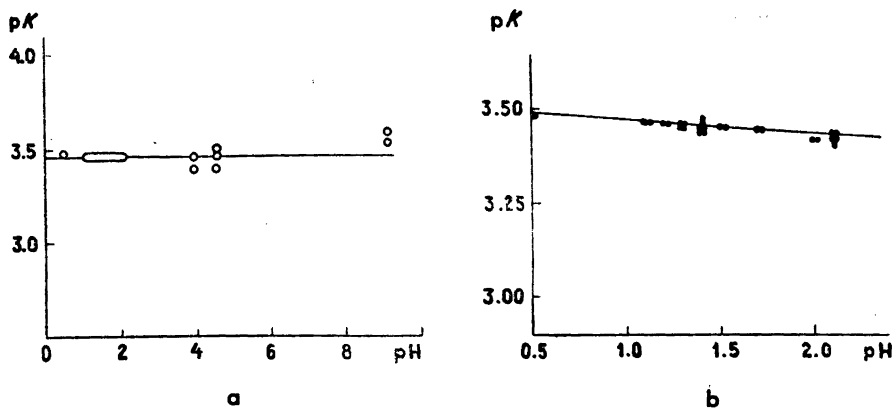


Fig. 4. Values for pK .

Nor has any phenomenon been observed indicating an «over-activity» of acetylene when dispersed in fine bubbles.

Computations of the equilibrium constant should thus be based on measurements performed at a pH less than 2. Isolated experiments with tolerably constant potentials at a higher pH are however satisfactory for the conclusion that pK , according to the equilibrium formula, is in fact independent of pH. Cf. Fig. 4 a where the computed pK values are plotted against pH.

But also results from experiments in acid medium give rise to some doubts. All the measurements within the range considered in Fig. 4 b (pH between 0.5 and 2.2) give pK values between 3.4 and 3.5, but there is a certain trend towards higher values at lower pH. Thus it is not permissible to calculate a mean on the assumption that the variations are caused by incidental measuring errors. The mean value of the equilibrium constant

$$pK = 3.46 \text{ at } 25^\circ \text{C}$$

may therefore be somewhat uncertain in the second decimal place.

THERMODYNAMIC DATA FOR THE REACTION SILVER CARBIDE
→ ACETYLENE

An estimation of the change in enthalpy⁹ from the equilibrium constant $pK = 3.46$ gives



If the standard potential of silver at 25° C is assumed to be + 800 mV we get for the reaction



and then, for the non-ionic reaction, can be calculated

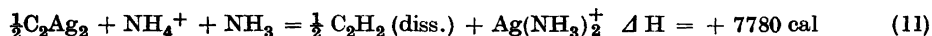


Thermodynamically the conditions for a reduction of silver carbide are favourable, corresponding to the equilibrium constant

$$K = P_{\text{C}_2\text{H}_2}/P_{\text{H}_2} = 10^{20.1} \quad (10)$$

Two measurements from literature can be used for the calculation of the heat of reaction.

(a) Berthelot and Delépine¹⁰ made calorimetric measurements at the precipitation of silver carbide from an aqueous solution of acetylene + an aqueous solution of silver nitrate with excess ammonia and got



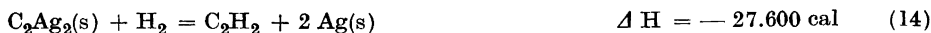
A utilization of Berthelot's results for the computation of ΔH of reactions (7) or (9) demands supplementary heat data. Berthelot's own calculations give, using somewhat different nomenclature



The use of newer values for the data necessary for the recalculation give a difference albeit rather small. The uncertainty of Berthelot's primary determination is however too large to justify such a recalculation. For an estimation of the heat of the non-ionic reaction from the value given above the ΔH -value must be known for $\text{Ag}^+ \rightarrow \text{Ag(s)}$. The most reliable seems to be Lingane's¹¹ determination of the temperature coefficient of the standard silver electrode (dE/dT) at 25° C = 0.967 mV/degree. Together with (8) this gives



From (12) and (13) we get



(b) Stadler¹² gives a value for the heat of explosion of silver carbide, as measured in a detonation bomb.



From Stadler's result we obtain directly, using the most reliable (according to Parks and Huffmann¹³) value for acetylene's heat of formation



the following value for the change in enthalpy in the non-ionic reaction

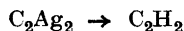


and by application of (14) we get for the ionic reaction



The difference between the values which can be calculated from Berthelot's — (12) and (14) and Stadler's — (18) resp. (17) — determinations is thus considerable. Only two further quantities are required when using Stadler's values but the result appears as a relatively small difference between the large heats of formation of silver carbide and acetylene. For the present Stadler's value is to be preferred.

For the reaction

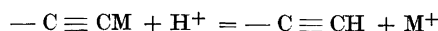


the following thermodynamic data are thus available

Reaction	ΔG° cal	ΔH cal	ΔS° cal/degree
$\frac{1}{2} \text{ C}_2\text{Ag}_2(\text{s}) + \text{H}^+ = \frac{1}{2} \text{ C}_2\text{H}_2(\text{g}) + \text{Ag}^+$	+ 4.720	+ 17.400	+ 42.6
$\text{C}_2\text{Ag}_2(\text{s}) + \text{H}_2 = \text{C}_2\text{H}_2(\text{g}) + 2 \text{ Ag(s)}$	- 27.400	- 15.400	+ 40.3

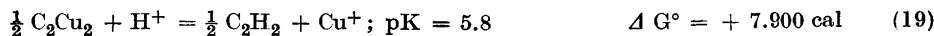
COMPARISON WITH OTHER ACETYLIDES

The potentiometric method for determining equilibrium constants for reactions of the type



offers a possibility of comparing the stabilities of different acetylides.

Experiments in progress on the system cuprous carbide — acetylene have given the preliminary result



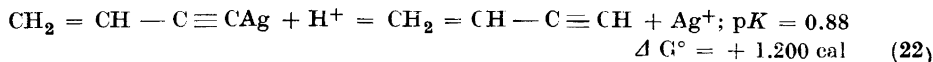
and for the non-ionic reaction



When comparing with the corresponding value for silver carbide it is evident that the cuprous carbide is essentially more stable



If the procedure described is to be used for a comparison between acetylene and monoacetylenes, $\text{RC}\equiv\text{CH}$, it must be limited to such monoacetylenes as can be handled in the gaseous state, or at least have a considerable vapour pressure at 25°C. A determination of pK for butenyne gave

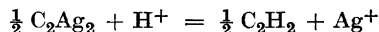


(As in the case of acetylene the activity of the hydrocarbon is measured in atmospheres. Gaseous butenyne is near enough ideal to render this acceptable.) Thus the silver compound of butenyne is considerably easier to split than silver carbide. In a 0.5 M silver perchlorate solution saturated with butenyne silver, which, like silver carbide, forms soluble complexes with silver ions, a considerable butenyne pressure can be shown after the addition of acid, whilst such breaking down of silver carbide is not to be observed with ordinary methods.

It is conceivable that all monoacetylenes have pK -values, which, like that for butenyne, are considerably lower than for acetylene. The conjugated system $\text{C} = \text{C} - \text{C}\equiv\text{C}$ whose resonance must diminish the tendency to acetylide formation, and on the whole the acetylenic character of the terminal hydrogen atom, is however specific for butenyne. A utilization of the experimentally determinable pK -values for an evaluation of the «acidity» of the CH -bond in $\text{RC}\equiv\text{CH}$ -compounds, and a systematic investigation of the effect of different substituents, R , would be of great interest. The definition of the standard conditions (e.g. 1 atm. pressure for the hydrocarbons, resp. solid state for the acetylide) involves however an inescapable arbitrariness.

SUMMARY

1. For the determination of the equilibrium constant of the reaction



a potentiometer method has been devised, based on measurement of the potential in a cell without liquid junction: — glass | A | $\text{C}_2\text{Ag}_2(\text{s})$, Ag^+ , where A is a solution in equilibrium with solid silver carbide and with a gas mixture of known acetylene pressure. A simple method for the determination of the standard

potential of the electrode couple is given. By using perchlorate, which, under the conditions prevailing, does not form insoluble complex salts with silver carbide, it has been possible to perform the experiments over a wide pH-range

2. Only in acid solution are the values well reproducible, giving the mean

$$pK = pAg - pH + \frac{1}{2} pP_{C_2H_2} = 3.46 \text{ at } 25^\circ \text{C}$$

(acetylene activity measured in atm.)

3. The thermodynamic constants (ΔG° , ΔH and ΔS°) have been calculated for the formulated reaction and for the non-ionic reduction of silver carbide to acetylene.

4. The possibility of using a pK -value, obtained by this method for characterization of various acetylene compounds of the type $RC \equiv CH$ has been discussed. The pK -value of butenyne is only 0.88; the difference from acetylene is supposedly dependent on the conjugated system $C=C-C \equiv C$ of butenyne.

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