

Cuprous Compounds of Acetylene.

II. Dissolved Compounds in Aqueous Chloride Solutions

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Several solid cuprous compounds can be prepared by passing acetylene into solutions containing cuprous chloride complexes. Dissolved compounds are also formed, as demonstrated by the fact that the solution contains a quantity of acetylene larger than can be attributed to the "physical" solubility. The concentration of such compounds, *e. g.* at 1 atm acetylene pressure, often corresponds to a considerable portion of the copper present.

We have undertaken the investigation of these dissolved compounds for two reasons mainly:

a) probably the dissolved compounds give a somewhat simpler illustration of the chemical relations of acetylene to monovalent copper than do the solid compounds, where complicated lattice forces interfere,

b) to the reactivity of the dissolved acetylene compounds can be traced the catalytic effect of some cuprous salt solutions in the aliphatic polymerization of acetylene (synthesis of monovinylacetylene according to Nieuwland ¹) and in addition reactions as *e. g.* the addition of hydrogen cyanide (preparation of acrylonitrile with Nieuwland's catalyst according to Kurtz ²).

The solid compounds are of two main types, *viz.* addition compounds where acetylene retains both hydrogen atoms, and *acetylidic* compounds where copper is substituted for the hydrogen atoms. Our own experiments ³ confirm this classification found in earlier literature ^{1, 4-6}, although some substances previously have been placed in the wrong group, due to incomplete analyses. We have tried to find out whether this grouping into addition and acetylidic compounds holds for the dissolved species also. The composition of the dissolved compounds must however be treated as a separate problem, avoiding presumptions of similarities with the solid ones.

Earlier literature gives only scant information on dissolved acetylene-copper compounds.

The first to observe a dissolved compound was Manchot⁶ who found reason to suggest the composition C_2H_2CuCl . By absorption measurements on mixtures of cuprous chloride and hydrochloric acid he observed that the maximum amount of acetylene chemically held is 1 mole per mole of cuprous chloride, and concluded that this system represents an equilibrium, displaced towards a complete conversion into C_2H_2CuCl . He seems to believe also in the existence of the dissolved compound $C_2H_2(CuCl)_2$.

Manchot's experiments indicate the existence of a compound with the molar ratio acetylene : copper = $n : n$. The value of n remains unknown, as does the chlorine content, which latter problem Manchot never discusses. Strictly interpreted the experiments do not even prove that the compound is of addition type.

Also Tzuyrikh and Ginsburg⁷ have entered upon the question of dissolved copper-acetylene compounds in a paper dealing mainly with the solid yellow compound formed in cuprous chloride-ammonium chloride solutions. They assume that the dissolved compound is of the same composition as the solid one, and suggest an equilibrium reaction formula giving a qualitative explanation of some effects observed. As earlier mentioned³ they have however misidentified the solid compound, which is actually an acetylidic and not an addition compound.

In a later paper Chal'tykyan⁸ rather speculatively deals with the equilibria of the dissolved compounds and their catalytic activity. He regards them all as acetylidic, mainly asymmetrical, and omits simple addition compounds entirely.

TWO TYPES OF DISSOLVED COMPOUNDS

A solution of cuprous chloride in strong hydrochloric acid absorbs acetylene without colour change, whereas solutions containing cuprous chloride and alkali chloride turn intensely yellow. (Earlier literature, especially Manchot⁵, gives the impression that a yellow colouration occurs in solutions with a high content of hydrochloric acid also. We assume that what actually has been observed is only the yellow colour characteristic of Cu^{II} in strong hydrochloric acid.) Thus there exist at least one colourless and one yellow compound, possibly several of each kind. The circumstance that the yellow compound forms in neutral but not in strongly acid solutions makes it probable that this compound is acetylidic.

From the introductory experiments given in Fig. 1 is evident that the total concentration of acetylene absorbed is independent of the hydrogen ion concentration when the acetylene pressure, the cuprous chloride concentration, and also the total concentration of potassium and hydrogen chlorides (KCl predominating) are kept constant. The ionic strength is constant, or approximately constant, at a given concentration of cuprous chloride, and the concentration of the varied component (H^+) is a fairly small part (max. 10 %) of the total electrolytic content. Existing dissolved compounds will then have approximately constant activity coefficients. Thus a variation of the hydrogen ion

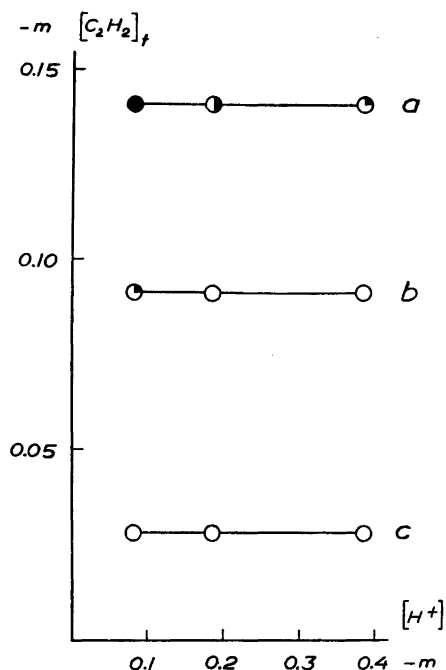


Fig. 1. Acetylene absorption and colour; dependence on hydrogen ion concentration; 1 atm and 20° C. KCl + HCl: 4.00 m.

a) 0.50 m, b) 0.30 m, and c) 0.00 m cuprous chloride

- denotes strong yellow colour
- ◐ » medium » »
- ◑ » faint » »
- no visible coloration

concentration should give information on the existence of protolytic equilibria. The assumption that the acetylene absorption corresponds to equilibrium reactions has been confirmed: it is easy to state that the acetylene absorption is reversible, and that a rapid and reproducible shift in the equilibrium occurs when the pressure is altered. The total concentration measured (curves a and b) partly consists of "physically" dissolved acetylene. Presumably this contribution closely equals the acetylene absorption in the blank (curve c) where cuprous chloride is absent. But even if this should not be exactly true it is evident that the concentration of acetylene bound to Cu^{I} is independent of the hydrogen ion concentration.

But the colour of the solution is markedly changed, the yellow colouration rapidly fading with increasing acidity. Extinction measurements³ in a similar

system have shown that the extinction depends on the hydrogen ion concentration as could be expected for an *acetylidic* compound.

The experiments of Fig. 1 indicate that the yellow compound, even in intensely coloured solutions, occurs only in a low concentration, and that the main part of the chemically combined acetylene is present as a colourless compound whose concentration is independent of the hydrogen ion concentration, and thus must be of *addition* type. The yellow compound has a very high molar extinction³ which supports the assumption that its concentration is small.

The concentration of hydrochloric acid has been varied only within 0.1–0.4 m. An appreciably lower concentration than 0.1 m is not feasible as a solid acetylidic compound precipitates. Measurements at higher acidity show a slowly increasing gas absorption. The solutions remain colourless however, and it seems most improbable that a new kind of acetylidic compounds could form in a stronger acid. The conclusion primarily valid for the interval in Fig. 1, that addition compounds predominate, can certainly be generalized to hold also for solutions of higher acidity. In the following we can therefore assume that measurements of the total acetylene absorption can be utilized for determination of the total concentration of addition compounds, at least when the solution is acid and colourless.

In *op. cit.*³ we have stated that the yellow acetylidic compound of these systems is an anion of the composition $C_2(CuCl)_n^{2-}$, where n is a high number, probably 8. This compound will not be dealt with any further here, the main subject of this paper being the colourless addition compounds and their equilibria.

1. Introduction

a) Symbols

P_A	Acetylene pressure in atm
$[C_2H_2]_t$	Total concentration of dissolved acetylene
$[C_2H_2]_{Cu}$	Concentration of Cu^I -bound acetylene
$\pi_A = P_A(1 - [C_2H_2]_{Cu}/CuCl_t)$	
α	Absorption coefficient in moles/1 000 g water \times atm
$CuCl_t$	Total concentration of cuprous chloride
$\{CuCl\}$	Activity of cuprous chloride. Standard state: solid substance
S	Solubility of cuprous chloride (acetylene absent)
HCl_t	Total concentration of hydrochloric acid
K	Thermodynamic equilibrium constant
γ	Molal activity coefficient

All concentrations are given in m, *e. g.* moles/1 000 g of water.

b) *Survey.* The primary aim of the experiments was to establish *empirical relations* for the reversible acetylene absorption in acid solutions of cuprous chloride and a dissociating chloride. Secondly we tried to decide what conclusions could be drawn as to the *composition* of the addition complexes.

Most measurements have been carried out in solutions with hydrochloric acid, this yielding a system with the minimum number of components. For a comparison are included some experiments with alkali chlorides, a small amount of acid being added to suppress the formation of acetylidic compounds. Through absorption measurements in a manometric apparatus according to Fig. 7, the relation between total concentration of acetylene absorbed and the partial pressure was first determined. The concentration of copper-bound acetylene then results by subtraction of the estimated contribution of "physical" solubility. Under d) in this section this assumption is discussed in detail.

We presume that no solid acetylene compounds form and that disturbances from catalytic reactions can be corrected for. These premises are discussed further under e) and f).

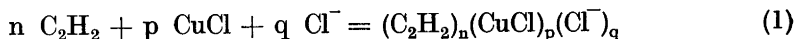
The absorption is measured either in a homogenous system or in a system in equilibrium with solid cuprous chloride. In the first case, if the inorganic components are CuCl, HCl and H₂O, the concentration of complex-bound acetylene can be determined as a function of the three variables P_A , HCl_t and $CuCl_t$. When solid cuprous chloride is present the variables P_A and HCl_t are sufficient.

A development of these empiric functions leads to the introduction of S (*cf.* above) as a parameter, so that the degree of saturation $CuCl_t/S$ is used as a variable; S being regarded as an empirical function of HCl_t .

The next step is the introduction of the thermodynamic activity $\{CuCl\}$ as a variable instead of $CuCl_t$ or degree of saturation. Here we utilize potentiometric measurements of the relation between the activity and the concentration of cuprous chloride in hydrochloric acid solutions. In some cases the activity is estimated by other means.

Finally the composition of the addition complexes is discussed. We assume the components to be only acetylene, cuprous ion and chloride ion, and neglect possible hydration. For convenience we use the expression $(C_2H_2)_n(CuCl)_p(Cl^-)_q$ as a general formula for an addition compound. The coefficient q may be negative, but the least sum of $p + q$ is zero, denoting a chloride-free cationic compound.

A given complex stays in equilibrium with its components according to



and the corresponding thermodynamic equilibrium constant $K_{n,p,q}$ is defined by

$$[(C_2H_2)_n(CuCl)_p(Cl^-)_q] = K_{n,p,q} \cdot P_A^n \cdot \{CuCl\}^p \cdot [Cl^-]^q \cdot \gamma_{Cl}^q / \gamma_{n,p,q} \quad (2)$$

The acetylene partial pressure has here been accepted as a measure of thermodynamic activity; this assumption is discussed under c).

Mixtures of several complexes with different n,p,q -values may occur. For the total concentration of acetylene in addition complexes holds the formula

$$[C_2H_2]_{Cu} = \sum n \cdot K_{n,p,q} \cdot P_A^n \cdot \{CuCl\}^p \cdot [Cl^-]^q \cdot \gamma_{Cl}^q / \gamma_{n,p,q} \quad (3)$$

By a comparison between this formula and the empiric function

$$[C_2H_2]_{Cu} = f(P_A, \{CuCl\}, HCl_t) \quad (4)$$

we try to determine what terms occur in the sum expression (3) and hence the composition of the complexes present. The experiments were divided into three sections, in each of which one of the three variables P_A , $\{CuCl\}$, and HCl_t was varied while the others were kept constant or allowed to covariate as determined by the experimental conditions.

c) *Acetylene activity and measurement of P_A .* Only a few determinations of acetylene's activity (fugacity), or its deviations from the ideal gas law have been carried out. From the data¹⁰ possible to utilize for a calculation of the activity coefficient (approaching unity as the pressure tends to zero) no more certain conclusion can be drawn than that the activity coefficient at 25° and 1 atm presumably lies within 0.985–0.995. Since the coefficient is uncertain we refrain from corrections. Also, determinations of the physical solubility in water and electrolyte solutions give the impression that correction is unnecessary; Table 1 demonstrates that the absorption coefficient does not vary appreciably with the pressure.

The presence of a minor amount (appr. 0.4 % by volume) of impurities in the acetylene, mainly methane and nitrogen, causes a certain error in the P_A -value. However, it is possible to perform the experiments in such a manner (*cf.* "Apparatus and Procedure") that the relative error in P_A remains constant within each series.

Our conclusion is that the P_A -value, measured as the difference between total and vapour pressures, can be accepted as an activity measure.

d) *Acetylene absorption in water and aqueous electrolyte solutions.* Acetylene is quite soluble in water and electrolyte solutions. Hence there exists in cuprous chloride solutions also a quantity of acetylene not bound to copper. (The term "physical" has been used exclusively to denote this kind of absorption, bearing no assumption as to its nature.) We have assumed that the physical solubility in such systems can be determined by a parallel experiment where the solution has the same content of dissociating chloride as in the main experiment, but

does not contain cuprous chloride. Such an assumption cannot be regarded as generally valid, but for the present experiments no great uncertainty will result.

We take as an example a series (Table 4 b) of measurements on the system 4 m HCl_t and x m CuCl_t. For all values of x we have used the same figure for the physical solubility as that measured at x = 0. If x is low, e.g. 0.1 m or below, this can be immediately accepted. The concentration of inorganic cuprous complexes and of dissolved acetylene compounds is so small, both absolutely and in comparison with HCl_t, that no important effect on the physical absorption of acetylene can arise, even if these complexes should have high molar effects of salting in or out. When x reaches higher values it is possible, that the physical solubility will be altered to some extent. But the total acetylene absorption also increases with x, almost proportionally, and at the maximum value for x, about 0.75 m, the total absorption is more than 10 times higher than the physical solubility. Thus it is not probable that the relative error in the concentration of complex-bound acetylene, calculated as a difference, will increase appreciably with x.

As is evident from Table 1 the physical solubility in water and electrolyte solutions very closely follows Henry's law. Hydrogen chloride shows less salting out than the other chlorides.

We have found that the absorption coefficient in hydrochloric acid can be expressed by the empiric formula

$$\alpha = \alpha_0 - 2.62 \cdot 10^{-3} \cdot \text{HCl}_t \cdot (1 + 0.116 \text{HCl}_t)^{-2} \quad (5)$$

where $\alpha_0 = 0.0424$ is the absorption coefficient of pure water. Values computed according to this formula agree with the measurements within $\pm 0.4\%$. The formula that Randall and Failey¹¹ have suggested for salting out effects is also applicable, but the agreement with our measured values will not be quite as good.

The concentration of acetylene bound in copper complexes has been calculated according to

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = [\text{C}_2\text{H}_2]_t - \alpha P_A \quad (6)$$

where $[\text{C}_2\text{H}_2]_t$ is the total concentration of dissolved acetylene, directly determined, and α stands for the absorption coefficient in a corresponding solution without cuprous chloride.

e) *Formation of solid acetylene compounds and measurements in supersaturated systems.* In neutral or weakly acid solutions of cuprous chloride with potassium or ammonium chloride, solid yellow acetylidic compounds of the type $\text{K}_2\text{C}_2(\text{CuCl})_8$ are formed³ even at low acetylene pressures, provided that both the cuprous chloride and the alkali chloride activities are sufficiently high, otherwise the violet complex $\text{C}_2\text{Cu}_2(\text{CuCl})_n$ (which contains less cuprous

Table 1. Solubility of acetylene in water and strong chloride solutions at 25° C.
a = absorption coefficient in mole/1000 g water × atm.

Solvent	P_A	a	Solvent	P_A	a
Water	0.281	0.042	2.00 m HCl	0.1—1.1	0.0392 (mean)
	0.356	0.0421			
	0.616	0.0423	3.00 m HCl	0.1—1.4	0.0383 (mean)
	1.003	0.0424			
4.00 m KCl	0.226	0.024	4.00 m HCl	0.173	0.0380
	0.354	0.0250		0.415	0.0379
	0.608	0.0249		0.667	0.0380
	0.928	0.0252		0.799	0.0380
4.00 m LiCl	0.186	0.023		0.968	0.0378
	0.354	0.0224		1.184	0.0379
	0.680	0.0223		1.533	0.0378
	1.003	0.0223	6.97 m HCl	0.3—1.6	0.0371 (mean)
1.00 m HCl	0.140	0.0403	10.00 m HCl	0.120	0.0373
	0.310	0.0405		0.372	0.0372
	0.592	0.0406		0.743	0.0373
	0.970	0.0405		1.378	0.0374

chloride and no alkali chloride) is the stable solid phase. The simple red copper acetylide C_2Cu_2 exists only at a fairly low cuprous chloride activity. If the dissociating chloride is NaCl or LiCl, as a rule no solid yellow complexes form, only the violet complex and copper acetylide.

Supersaturation can occur in all these cases (which may explain puzzling information in earlier literature on the conditions for precipitation of different solid compounds).

In a strongly acid solution the formation of solid acetylidic compounds is of course repressed. Preliminary results show that they may, however, exist in a fairly acid medium. Thus at 25° and 1 atm acetylene pressure the violet complex is coexistent with solid cuprous chloride at a hydrochloric acid concentration slightly above 1 m.

The stability of solid addition compounds of the type $C_2H_2(CuCl)_n$ is determined solely by the acetylene pressure and the cuprous chloride activity. In manometric experiments such a compound has been observed, coexistent with

solid cuprous chloride at an acetylene pressure of 0.38 atm and 25° C. The relation between acetylene absorbed and original content of cuprous chloride seems to demonstrate that the compound has the composition $C_2H_2(CuCl)_3$. But it should be pointed out that the equilibrium pressure of 0.38 atm is much lower than the value of 0.62 atm which has been reported by Österlöf⁴ for a compound of this composition.

In the formation of this addition compound a characteristic supersaturation phenomenon occurs: the acetylene pressure must often be raised to a value more than three times that of the equilibrium pressure before the crystallization takes place (within reasonable time).

The experiments described here only deal with solutions where no solid acetylene compounds form. Thanks to the tendency towards supersaturation it is, however, not necessary to avoid all systems where solid compounds can form, which would impel rather narrow limitations. It is easy to check that no coloured acetylidic compounds occur. But it is difficult to see whether a colourless addition compound precipitates in a system where solid cuprous chloride is present. However, the phase conversion causes a considerable pressure drop, which is easy to observe, and there seems to be no slow formation of solid addition compound before this drop (see Table 5 and commenting text). Measurements in these supersaturated systems are also fully reproducible.

f) *Catalytic acetylene reactions.* In cuprous chloride solutions we have observed catalytic acetylene reactions even at a temperature as low as 20–25° C.

Aliphatic polymerization to mono- and divinylacetylene occurs in concentrated alkali chloride solutions and the reaction is promoted by high concentration of both cuprous and alkali chlorides, low acidity and high acetylene pressure.

Vinyl chloride forms in solutions with high concentration of both cuprous chloride and hydrochloric acid. In a 10 m hydrochloric acid saturated with cuprous chloride we have found a reaction velocity of about 0.015 mole/1000 g water and hour, approximately proportional to the acetylene pressure. The relative acetylene conversion as a rule is rather slow, since the total concentration of acetylene dissolved under the conditions stated amounts to 0.85 mole/1000 g water \times atm. But in the manometric experiments the effect is clearly noticeable since there is an enrichment of vinyl chloride in the gas phase.

Even if catalytic reactions occur with perceivable velocity it is possible to determine with fair accuracy the concentration of complex-bound acetylene. But each experiment will yield only one point; a stepwise increase of the pressure is not suitable. If necessary the pressure-time curve of the reaction is read (in the case of vinyl chloride formation it is a linear time function) and the equilibrium pressure is computed by extrapolation to

Table 2. Relation between acetylene absorption and partial pressure in hydrochloric acid saturated with cuprous chloride. 25° C.

HCl molality	P_A	$[C_2H_2]_t$	$[C_2H_2]_{Cu}/P_A$
1.00	0.0510	0.00831	0.122
	.0975	.01578	.1214
	.1613	.02604	.1209
	.2360	.03812	.1210
	.3233	.0524	.1216
	.4207	.0682	.1217
	.4793	.0776	.1214
	.5660	.0913	.1208
	.6355	.1030	.1214
	.7338	.1182	.1206
	.7953	.1282	.1207
3.00	0.0649	0.0201	0.271
	.1406	.0437	.2725
	.2507	.0785	.2748
	.3774	.1177	.2737
	.4995	.1556	.2732
	.5940	.1858	.2744
	.6630	.2072	.2742
	.7387	.2309	.2743
	.7960	.2492	.2747
	.8372	.2618	.2744
	.8697	.2726	.2752
	.9123	.2845	.2736
	.9524	.2987	.2754
	.9631	.3024	.2756
10.00 *	0.0836	0.0681	0.778
	.2087	.1694	.774
	.2838	.2320	.779
	.2884	.2327	.769
	.6013	.4925	.782

* Each value from a separate experiment, corrected for vinyl chloride formation.

zero time. Such an extrapolation has been employed where the measurements were carried out with a hydrochloric acid stronger than 6 m, except where the cuprous chloride content is small in comparison with the solubility.

2. Variation of the acetylene pressure

a) *Conditions: Solid cuprous chloride present, constant concentration of hydrochloric acid.* In a solution which is in equilibrium with solid cuprous

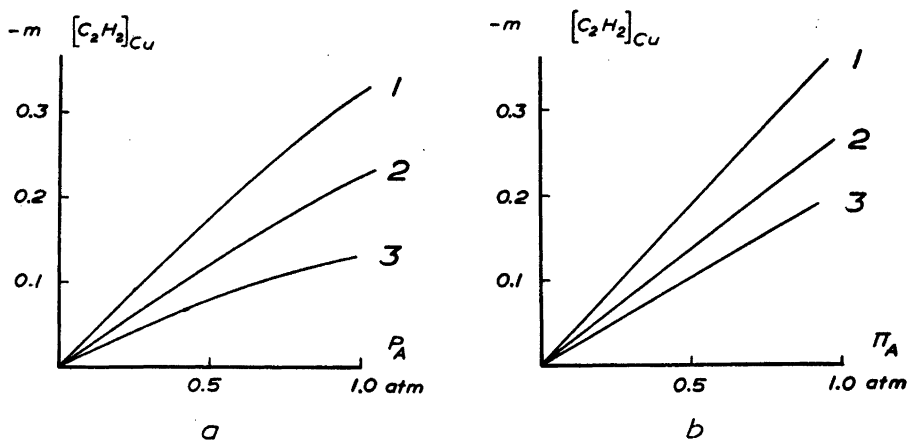


Fig. 2. The acetylene absorption as a function of the pressure: 1: 3.71 *m* CuCl; 6.00 *m* KCl 2: 1.86 *m* CuCl; 9.00 *m* LiCl 3. 0.40 *m* CuCl; 4.00 *m* HCl.

chloride the concentration of Cu^I-bound acetylene increases proportionally with the acetylene pressure.

In the experiments summarized in Table 2 the quotient $[C_2H_2]_{Cu}/P_A$ remains constant within $\pm \frac{1}{2} \%$ at P_A -variations up to 1 atm. The same holds for the experiment of Table 5.

The variations in the quotient values are no larger than the uncertainty in the experimental data. (According to the estimation of the accuracy, in the experimental section, the ratio should have an uncertainty of $\pm 0.25 \%$ at 1 atm, $\pm 0.5 \%$ at 0.1 atm, then rapidly increasing with diminishing pressure.)

Even in systems containing 10 *m* hydrochloric acid, where vinyl chloride formation interferes and where each value is determined in a separate experiment, we obtained ratios of excellent constancy. We conclude:

$$[C_2H_2]_{Cu}/P_A \text{ constant at } \begin{cases} \{CuCl\} = 1 \\ \{HCl\}_t \text{ constant} \end{cases} \quad (7)$$

A corresponding rule seems to hold for systems containing alkali chlorides.

b) *Conditions: Constant total concentration of dissolved cuprous chloride. Constant concentration of hydrochloric acid.* In a homogenous aqueous solution of cuprous chloride and hydrochloric acid the concentration of complex bound acetylene increases as illustrated by Fig. 2 a (from preliminary series). These absorption curves are not linear, the ratio $[C_2H_2]_{Cu}/P_A$ diminishes with rising P_A . A closer investigation of the pressure dependence of the absorption quotient in various systems has yielded the following results:

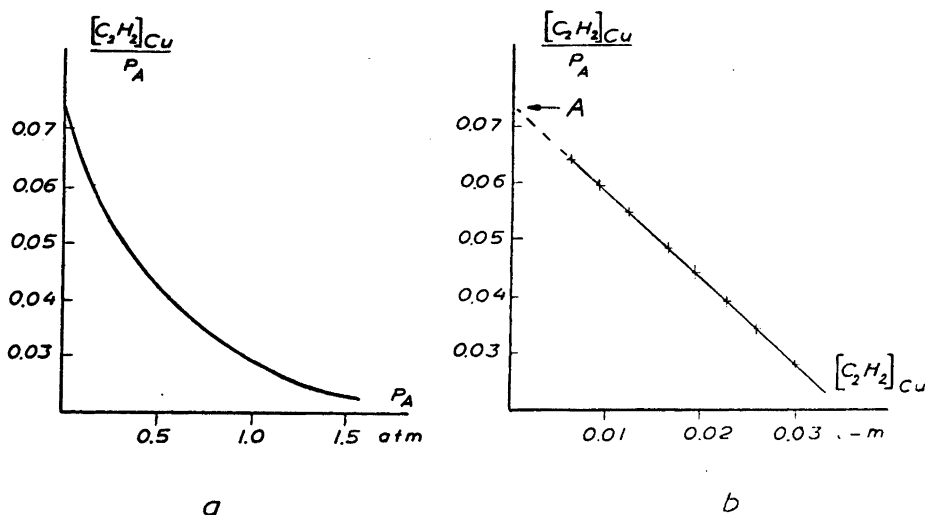


Fig. 3. The quotient $[C_2H_2]_{Cu}/P_A$ as a function of P_A and of $[C_2H_2]_{Cu}$
System: 0.05003 m CuCl; 1.000 m HCl, 25° C.

α) If $[C_2H_2]_{Cu}/P_A$ is plotted against P_A the resulting curve is of the type illustrated in Fig. 3 a.

β) The absorption ratio is a linear function of $[C_2H_2]_{Cu}$ in all cases investigated, cf. Fig. 3 b. In each individual case the correlation can thus be expressed by a formula of the type: $[C_2H_2]_{Cu}/P_A = A - B[C_2H_2]_{Cu}$.

γ) A depends on both $CuCl_t$ and HCl_t , B only on HCl_t . Experiments at different $CuCl_t$ but identical HCl_t thus give a group of parallel lines in a graph plotted as Fig. 3 b.

δ) Generally the ratio A/B has a numeric value which closely agrees with that of $CuCl_t$. In the experiment of Fig. 3, $CuCl_t$ is 0.05003; the diagram gives $A/B = 0.0501$. The function under β) can thus be written: $[C_2H_2]_{Cu}/P_A = A \cdot (1 - [C_2H_2]_{Cu}/CuCl_t)$.

These observations lead to the introduction of the parameter π_A , defined as

$$\pi_A \equiv P_A (1 - [C_2H_2]_{Cu}/CuCl_t) \quad (8)$$

and Tables 3 and 4 show the pressure independence of the quotient $[C_2H_2]_{Cu}/\pi_A$, in various systems. In Table 3 the quotient remains constant within $\pm 1\%$ at acetylene pressures from 0.08 to 1.7 and 1.2 atm. resp. A definite trend can hardly be observed.

Condensed results from these and other experiments are found in Table 4, where are given highest and lowest figures for the quotient, observed within

Table 3. Relation between acetylene absorption and partial pressure in homogenous solutions with constant concentrations of cuprous chloride and hydrochloric acid. 25° C.

$[C_2H_2]_{Cu}$ computed as $[C_2H_2]_t - aP_A$. a -values from Table 1.

P_A	$[C_2H_2]_t$	$\frac{[C_2H_2]_{Cu}}{P_A}$	$\frac{[C_2H_2]_{Cu}}{\pi_A}$
4.00 m HCl _t and 0.5515 m CuCl _t			
0.0801	0.0232	0.252	0.262
.1616	.0456	.245	.263
.2428	.0661	.235	.262
.3269	.0862	.226	.261
.3853	.0997	.221	.262
.4820	.1206	.213	.261
.5710	.1392	.206	.262
.7074	.1650	.196	.261
.8192	.1847	.188	.261
.9531	.2071	.180	.261
1.1034	.2305	.171	.261
1.2908	.2576	.162	.261
1.4635	.2800	.154	.260
1.740	.3157	.144	.264
10.00 m HCl _t and 0.975 m CuCl _t			
0.0410	0.0100	0.207	(0.210)
.0831	.0208	.212	.217
.1038	.0259	.212	.218
.1586	.0393	.211	.219
.2108	.0519	.209	.220
.2619	.0641	.207	.220
.3187	.0771	.205	.220
.3900	.0929	.201	.219
.4302	.1016	.199	.219
.5479	.1200	.195	.219
.6718	.1517	.189	.218
.8007	.1771	.184	.217
.9231	.2008	.180	.218
.9764	.2009	.178	.217
1.0561	.2237	.175	.216
1.1949	.2486	.171	.216

the interval 0.1–1.3 atm. The rather large variations in some series, particularly with 1 m HCl_t – 0.016 m CuCl_t, obviously depend on the circumstance that $[C_2H_2]_{Cu}$ cannot be determined with satisfactory accuracy since the value is smaller than the contribution from physically dissolved acetylene, especially at higher pressures. (According to the estimate in the experimental section

the ratio would in the extreme case quoted have an accuracy of $\pm 1\%$ at 0.1 atm and $\pm 4\%$ at 1 atm; the experiment gives a scattering around the mean of maximum 5%.)

The scattering in the ratio values found in Table 3 can thus be regarded as representative; being more pronounced only where the measurements are of inferior accuracy. We thus obtain the rule

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/\pi_{\text{A}} \text{ constant at } \begin{cases} \text{CuCl}_t \text{ constant} \\ \text{HCl}_t \text{ constant} \end{cases} \quad (9)$$

An analogous rule seems to hold in systems where the dissociating chloride mainly consists of an alkali chloride.

c) *Conditions:* CuCl_t altered in such a manner that $\text{CuCl}_t - [\text{C}_2\text{H}_2]_{\text{Cu}}$ is constant; HCl_t constant. Absorption experiments in strict accordance with these conditions can hardly be performed. But the result from such covariation can easily be deduced starting from rule (9), according to which $[\text{C}_2\text{H}_2]_{\text{Cu}}/\pi_{\text{A}}$ can be regarded as a function of CuCl_t and HCl_t , then studying how this quotient depends on CuCl_t at a constant HCl_t . Such experiments are treated in detail in the next section and the results are condensed in equation (14). From this formula, which includes (9) also, it is evident that $[\text{C}_2\text{H}_2]_{\text{Cu}}$ is proportional to the product π_{A} . CuCl_t , which, according to (8) is identical with $P_{\text{A}} \cdot (\text{CuCl}_t - [\text{C}_2\text{H}_2]_{\text{Cu}})$. If the bracketed difference remains constant, the concentration of Cu^{I} -bound acetylene will increase proportionally to the acetylene pressure. Thus holds

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_{\text{A}} \text{ constant at } \begin{cases} \text{CuCl}_t - [\text{C}_2\text{H}_2]_{\text{Cu}} = \text{CuCl}_{t,i} \text{ constant} \\ \text{HCl}_t \text{ constant} \end{cases} \quad (10)$$

where $\text{CuCl}_{t,i}$ denotes the initial concentration of cuprous chloride in the absence of acetylene. Rule (10) has been experimentally verified within the same concentration and pressure intervals as (9) and with approximately the same accuracy.

When $\text{CuCl}_{t,i}$ is equal to S (*i. e.* the solubility of CuCl in absence of acetylene) rule (10) will express the results from the earlier described experiments with *solid* cuprous chloride, though in other variables. For in such systems CuCl_t increases equimolarly with $[\text{C}_2\text{H}_2]_{\text{Cu}}$, as has been confirmed by analyses. Already the derivation of (10) however, demonstrates that the CuCl_t -condition of the rule is the necessary condition for a constant absorption quotient at a given concentration of hydrochloric acid, and the saturated systems do not fall outside the interval investigated.

Of particular interest is the following conclusion: a system whose composition is changed according to the conditions of rule (10) remains in equilibrium

with solid cuprous chloride if $\text{CuCl}_{t,i} = S$. This holds independent of the hydrochloric acid concentration.

Rules (10) and (14) are verified (*cf.* Table 4) even at such low cuprous chloride concentrations that $[\text{C}_2\text{H}_2]_{\text{Cu}}$ amounts to only 1.5 % of HCl_t at 1 atm. It then follows that formula (3) can be applied with the following approximations: $[\text{Cl}^-]$ and activity coefficients constant, polynuclear complexes negligible, and CuCl -activity proportional to the concentration of "free" cuprous chloride. Then it follows that the activity of cuprous chloride must be independent of P_A if the conditions of rule (10) are maintained.

These conditions then fix the activity of cuprous chloride both at a maximum and at a low $\text{CuCl}_{t,i}$, and a different state at intermediate concentrations seems most improbable. (Potentiometric checks are difficult since the prescribed covariation cannot be experimentally arranged and a combination of separate measurements gives too low an accuracy.)

If the generalization

$$\{\text{CuCl}\} \text{ constant at } \begin{cases} \text{CuCl}_t - [\text{C}_2\text{H}_2]_{\text{Cu}} = \text{CuCl}_{t,i} \text{ constant} \\ \text{HCl}_t \text{ constant} \end{cases} \quad (11)$$

is accepted for all $\text{CuCl}_{t,i}$ values the empirical rule (10) can be formulated

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A \text{ constant at } \begin{cases} \{\text{CuCl}\} \text{ constant} \\ \text{HCl}_t \text{ constant} \end{cases} \quad (12)$$

Rule (7) valid for a cuprous chloride activity of unity thus is a special case, but directly experimentally verified.

d) *Conclusion on the composition of the acetylene complexes.* When applying the general equilibrium expression (3) to the results summarized in rule (12) it is necessary to estimate how the remaining variables: the concentration of free chloride ion and the quotients of the activity coefficients, change with the acetylene pressure.

The concentration of acetylene complexes normally is small in comparison with the total concentration of hydrochloric acid. In the experiments of Table 2, where solid cuprous chloride is present, $[\text{C}_2\text{H}_2]_{\text{Cu}}$ will reach values corresponding to 5–10 % of HCl_t . Experiments in a homogenous system as a rule give lower figures (unless the acetylene pressure exceeds 1 atm) and sometimes the maximum complex concentration does not reach 1 % of the hydrochloric acid concentration. The acetylene absorption can thus cause only comparatively small changes in the concentration of free chloride ion. For the same reasons the variations in the quotients of the activity coefficients remain small. The proportionality between $[\text{C}_2\text{H}_2]_{\text{Cu}}$ and P_A according to (12) shows that *the main part of the complex bound acetylene exists in compounds where the coefficient n equals 1, i. e. containing one acetylene molecule only.*

3. Variation of the activity of cuprous chloride

a) *Empirical relation between acetylene absorption and concentration of cuprous chloride at constant concentration of hydrochloric acid.* Table 4 contains results from absorption experiments with 1, 4, and 10 m hydrochloric acid as solvents. Most determinations refer to homogenous systems with a given total concentration of dissolved cuprous chloride; the results of the measurements are rendered by the quotient $[C_2H_2]_{Cu}/\pi_A$ which is independent of P_A under these conditions (9). Further the table includes some experiments on systems with solid cuprous chloride; the result then appears as the quotient $[C_2H_2]_{Cu}/P_A$, being in such cases the pressure-independent quantity (7).

In the series with 1 m and 4 m hydrochloric acid resp., each experiment gives on absorption curve, *i. e.* pairs of $[C_2H_2]_{Cu}$ and P_A values in analogy with Table 2, or $[C_2H_2]_{Cu}$ and π_A pairs as in Table 3. In Table 4 is given the mean of all (10–15) the quotients which correspond to acetylene pressures over 0.1 atm, and also the highest and lowest figures. In the series with 10 m acid the procedure has been the same at the lower copper concentrations but at a higher $CuCl_t$, where vinyl chloride forms with an appreciable velocity, only one, or some few, quotient values were determined in each experiment.

The quantity $([C_2H_2]_{Cu}/P_A)_0$ has been obtained by linear extrapolation to $[C_2H_2]_{Cu} = 0$, using a diagram where the values for $[C_2H_2]_{Cu}/P_A$ are plotted against $[C_2H_2]_{Cu}$. (*Cf.* Fig. 3 b, where the intercept is the extrapolated value.)

The two last columns contain the values of the following quantities:

$$k_c \equiv \frac{[C_2H_2]_{Cu}}{\pi_A} \cdot \frac{1}{CuCl_t} \text{ and } k \equiv \left(\frac{[C_2H_2]_{Cu}}{P_A} \right)_{CuCl(s)} \cdot \frac{1}{S} \quad (13)$$

These experiments give the following results:

α) The quantity k_c is independent of the concentration of cuprous chloride and can thus be regarded as a constant at a given HCl_t . The only variations occurring can be attributed to the uncertainty in the $[C_2H_2]_{Cu}/\pi_A$ quotient, discussed under 2 b above. In the series with 1 m hydrochloric acid, which must be regarded as being at the limit of what can be studied with the technique described, k_c is changed by about 3 % when $CuCl_t$ is increased four times. In the two other series, where $CuCl_t$ is varied by approximately a power of ten, k_c remains constant within ± 1 %. We get:

$$k_c = [C_2H_2]_{Cu}/\pi_A \cdot CuCl_t \text{ constant (condition } HCl_t \text{ constant)} \quad (14)$$

β) At a given HCl_t the quantity k_c has, within the experimental accuracy, the same numerical value as k ; in the following we use the letter k for both quantities. Substitution of (8) in (13) shows that $CuCl_t \cdot [C_2H_2]_{Cu} = S$, if the solution is saturated with cuprous chloride.

Table 4. Relation between acetylene absorption and concentration of cuprous chloride at constant concentration of hydrochloric acid. 25° C.

CuCl _t	$\left(\frac{[C_2H_2]_{Cu}}{P_A}\right)_0$	$[C_2H_2]_{Cu}/\pi_A$			$\frac{[C_2H_2]_{Cu}}{P_A}$	k_c	k
		Mean	Lowest value	Highest value			
a) 1.000 m hydrochloric acid							
0.01628	0.0240	0.0238	0.0226	0.0246	—	1.46	—
0.03531	0.0502	0.0498	0.0490	0.0508	—	1.41	—
0.05003	0.0708	0.0707	0.0704	0.0709	—	1.41	—
CuCl (s)	0.1210	—	—	—	0.1211	—	1.43
$S = 0.0848$							
b) 4.00 m hydrochloric acid							
0.0500	0.0240	0.0240	0.0237	0.0247	—	0.480	—
0.1503	0.0730	0.0727	0.0724	0.0730	—	0.484	—
0.2499	0.1210	0.1210	0.1206	0.1216	—	0.484	—
0.4490	0.215	0.215	0.214	0.216	—	0.479	—
0.5515	0.262	0.262	0.260	0.264	—	0.475	—
0.6500	0.308	0.308	0.307	0.310	—	0.474	—
0.750	0.358	0.357	0.354	0.360	—	0.476	—
CuCl (s)	0.354	—	—	—	0.354	—	0.476
$S = 0.744$							
c) 10.00 m hydrochloric acid							
0.506	0.115	0.116	0.114	0.117	—	0.229	—
0.975	0.218	0.218	0.216	0.220	—	0.224	—
1.497	0.337	0.336	0.334	0.338	—	0.225	—
1.998	—	0.455	—	—	—	0.228	—
2.308	—	0.531	—	—	—	0.230	—
2.501	—	0.574	—	—	—	0.228	—
2.978	—	0.678	—	—	—	0.228	—
3.112	—	0.710	—	—	—	0.228	—
3.271	—	0.747	—	—	—	0.228	—
3.512	—	0.806	—	—	—	0.229	—
CuCl (s)	0.776	—	—	—	0.780	—	0.229
$S = 3.410$							

γ) The extrapolated quotient $([C_2H_2]_{Cu}/P_A)_0$ agrees closely with the corresponding mean for $[C_2H_2]_{Cu}P_A$ (condition solid CuCl) and $[C_2H_2]_{Cu}/\pi_A$ (condition CuCl_t constant) respectively, which can be foreseen from earlier results (formulas 7—9).

For several reasons it is valuable to know the limit value, which the quotient $[C_2H_2]_{Cu}/P_A$ approaches when $[C_2H_2]_{Cu}$ or P_A tends to zero under given

conditions. The value for $([C_2H_2]_{Cu}/P_A)_0$, obtained as described above, is accepted as limit, since in the diagram no such deviation is found as could indicate that the curve might bend at very low $[C_2H_2]_{Cu}$ -values.

The limit value increases proportionally with the concentration of cuprous chloride, at a given concentration of HCl_t :

$$([C_2H_2]_{Cu}/P_A)_0 = k \cdot CuCl_t \quad (15)$$

The results so far can be summed up in the following formula, derived from (8) and (14)

$$[C_2H_2]_{Cu} = k \cdot P_A \cdot (CuCl_t - [C_2H_2]_{Cu}) \text{ or } [C_2H_2]_{Cu} = k \cdot P_A \cdot CuCl_t / (1 + k \cdot P_A) \quad (16)$$

where k is an empirical constant valid for each concentration of hydrochloric acid.

At a given hydrochloric acid concentration the absorption quotient $[C_2H_2]_{Cu}/P_A$ thus is proportional to the difference $CuCl_t - [C_2H_2]_{Cu}$ whichever of these terms is varied. Analogous results have been achieved by Gilliland and coworkers¹¹ from investigations of the absorption of ethylene and other olefinic hydrocarbons in cuprous chloride solutions. This difference has often been regarded as a measure of the concentration of "free" cuprous chloride; it is then assumed that each molecule of the hydrocarbon binds one molecule of cuprous chloride. Probably this is essentially correct, and anyway it enables a simple description of the functional relation. But it should be pointed out that the empirical relation can be determined without any assumptions as to the composition of the complexes.

From the explicit formulation of (16) it is evident that the concentration of complex-bound acetylene (and thus the total concentration of dissolved acetylene), as measured at a given acetylene pressure, is proportional to the concentration of cuprous chloride, the coefficient of proportionality depending on the pressure. *Cf.* Fig. 4.

Analogous relations seem to hold for cuprous chloride solutions containing alkali chlorides. *Cf.* Fig. 4 showing results from preliminary experiments, somewhat less accurate.

b) *Relation between activity and concentration of cuprous chloride at constant concentration of hydrochloric acid; acetylene absent.* It seems to be characteristic for systems consisting of cuprous chloride, a dissociating 1 : 1 chloride, and water, that the activity of the cuprous chloride is closely proportional to its concentration if the total concentration of dissociating chloride is kept constant. Earlier investigations by Szabo *et al.*¹² point in this direction. Their measurements show that the activity of Cu^+ (determined potentiometrically

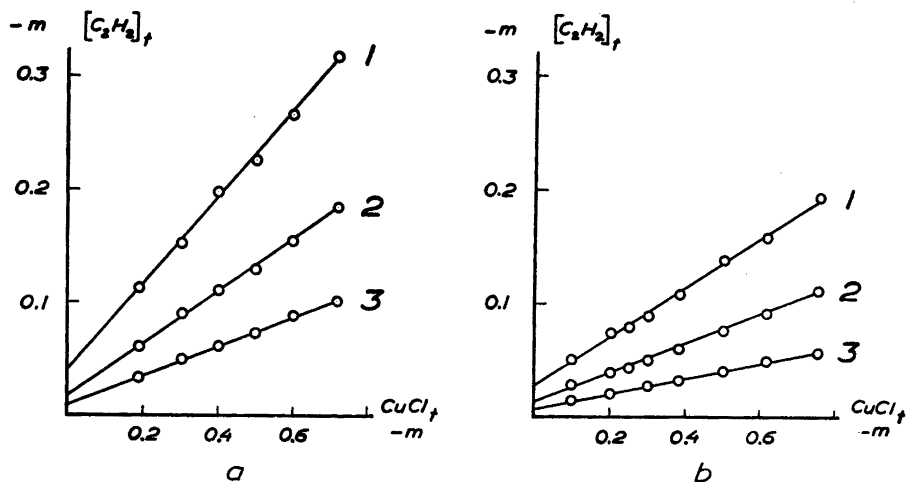


Fig. 4. Total acetylene absorption as a function of the cuprous chloride concentration at constant concentration of dissociating chloride, and constant pressure. 20°:

- | | |
|---------------|---------------------------|
| a. 4.00 m HCl | b. 3.80 m KCl; 0.20 m HCl |
| 1. 1.00 atm | 2. 0.50 atm |
| | 3. 0.25 atm |

in a cell with liquid junction) is approximately proportional to the concentration of cuprous chloride in solutions with approximately constant concentration of dissociating chloride.

Our own measurements¹³ are also potentiometrical but so performed that the activity of the uncharged CuCl molecule is determined directly, utilizing Ag/AgCl and amalgamated copper as electrodes in a cell without liquid junction. The experiments were performed as dilution series starting from a solution saturated with cuprous chloride; as a rule the hydrochloric acid concentration was maintained constant. The standard potential of the electrode couple was determined in each series by measuring in the presence of solid cuprous chloride. See further "Apparatus and Procedure".

At hydrochloric acid concentrations below 6 m the reproducibility is satisfactory even though the accuracy is hardly better than ± 1 mV corresponding to $\pm 4\%$ in $\{\text{CuCl}\}$. At higher acid concentrations the results become less satisfactory, particularly if the concentration of cuprous chloride is high also. (The disturbances seem to arise from the solubility of the silver chloride of the electrode.)

Fig. 5 a shows the relation between activity and concentration of cuprous chloride (concentration expressed by CuCl_t/S) in 4 m hydrochloric acid, according to three separate series. The deviations from the straight line are hardly

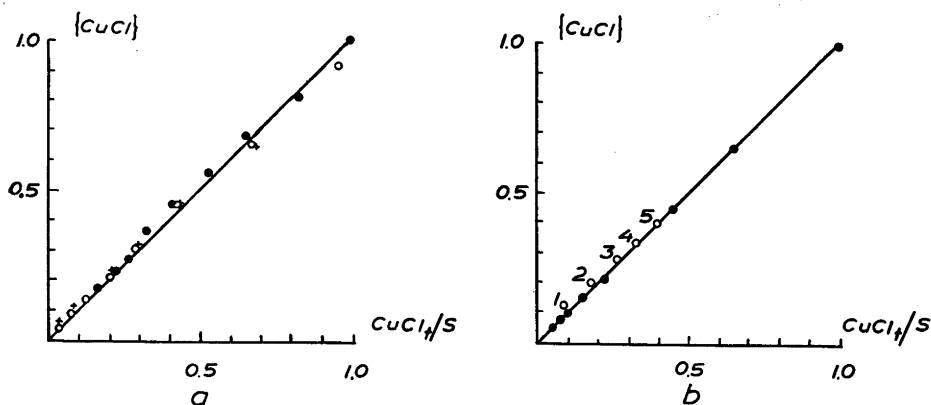


Fig. 5. The activity of cuprous chloride as a function of the saturation degree in hydrochloric acid solution (acetylene absent). Potentiometric measurement at 25°.

a: 4 m HCl, 3 series

b. ●—● 1 m HCl
 ○—○ $\text{CuCl}_t/\text{HCl}_t$ constant = 0.0306
 HCl_t: 10.0 m (point 1);
 3.42 (2); 2.07 (3);
 1.24 (4); 0.715 (5).

larger than corresponding to an uncertainty in the potential of ± 1 mV. (The linear scale at higher activities demands rather accurate measurements; the difference in $\{\text{CuCl}\}$ between the two uppermost points corresponds to about 2 mV.)

Results from analogous experiments in 1 m HCl are found in Fig. 5 b, where also are included measurements on a solution which has been stepwise diluted with water, the ratio $\text{CuCl}_t/\text{HCl}_t$ remaining constant. (The standard potential was determined at $\text{HCl}_t = 0.5$ after addition of solid cuprous chloride.)

The potentiometric measurements hitherto performed within the HCl_t -interval 1–10 m show no systematic deviation from a proportionality between activity and saturation when the hydrochloric acid concentration is below 6 m.

Thus in this range

$$\{\text{CuCl}\} = \text{CuCl}_t/S \quad (17)$$

At higher concentrations of hydrochloric acid $d\{\text{CuCl}\}/d(\text{CuCl}_t)$ is constant over the main part of the CuCl_t interval but probably diminishes in the vicinity of saturation. But these determinations are too uncertain to admit any safe conclusions.

It is to be expected that the quotient $\{\text{CuCl}\}/\text{CuCl}_t$ will keep constant when CuCl_t is small; the only condition being that mononuclear complexes of cuprous

chloride exist. But it is astonishing, that in almost all systems measured the quotient has the same value, even where the concentration of dissolved cuprous chloride is appreciable. This question will be discussed later.

c) *Relation between acetylene absorption and activity of cuprous chloride at constant concentration of hydrochloric acid.* In a system where CuCl_t and HCl_t are given, the absorption quotient will approach its limit value $([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0$ when $[\text{C}_2\text{H}_2]_{\text{Cu}}$ tends to zero. Simultaneously the cuprous chloride activity will approach the value $\{\text{CuCl}\}_0$ which holds in the absence of acetylene. According to (15) and (17) resp. both these limit values are proportional to CuCl_t at a given HCl_t . Thus holds:

$$([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0 = k_a \{\text{CuCl}\}_0 \quad (18)$$

where k_a is an empirical constant, depending on HCl_t only. The expression is valid with an accuracy depending mainly on (17), *i. e.* on the potentiometric measurements.

Referring to the generalization (12), according to which the absorption quotient remains independent of $[\text{C}_2\text{H}_2]_{\text{Cu}}$ (and of P_A) when $\{\text{CuCl}\}$ and HCl_t are kept constant, this same expression can be applied to the absorption quotient when measured at a finite pressure:

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A = k_a \{\text{CuCl}\} \quad (19)$$

d) *Conclusions on the composition of the acetylene complexes.* Attempts to interpret these results using the general equilibrium expression (3) yields rather uninformative results. If the sum is expressed as a polynomial in $\{\text{CuCl}\}$ we get

$$\begin{aligned} \left(\frac{[\text{C}_2\text{H}_2]_{\text{Cu}}}{P_A}\right)_0 &= \{\text{CuCl}\} \sum_q K_{11q} [\text{Cl}^-]^q \gamma_{\text{Cl}}^q / \gamma_{11q} + \{\text{CuCl}\}^2 \sum_q K_{12q} [\text{Cl}^-]^q \gamma_{\text{Cl}}^q / \gamma_{12q} + \dots \\ &= k_a \{\text{CuCl}\} \end{aligned} \quad (20)$$

where the first term corresponds to mononuclear complexes, the second term to dinuclear complexes *etc.* We have simplified the formula, presuming that only complexes with $n = 1$ appear. Such a generalization of the conclusion in section 2. is evidently justified since the limit value holds when the pressure tends to zero. The use of the limit value also permits the disregard of the influence of the acetylene complexes on the composition of the solution.

The measurements apply to systems with constant HCl_t . When the activity of cuprous chloride is increased from zero to unity, the concentration of free chloride ion must decrease — if the solubility at all is due to the formation of complex compounds containing chloride ion. The decrease would be quite noticeable, particularly at higher acid concentrations. If we accept the assump-

tion, commonly held ¹², that the main part of the cuprous chloride is solubilized as CuCl_3^{2-} , then in the series with 4 m HCl $[\text{Cl}^-]$ should fall from 4.0 to 2.5, and in the series with 1 m HCl from 1.0 to 0.83.

If we assume that only mononuclear complexes exist, the first Σ -function in expression (20) must remain constant, *i. e.* the activity coefficients must vary in such a way that the changes in $[\text{Cl}^-]$ are compensated for. But we might as well assume a not insignificant contribution from di- or polynuclear complexes. Whichever the case may be the linear relation must be explained as a result of accidental compensation.

As previously alluded to, a similar phenomenon occurs in the equilibria of the inorganic system $\text{CuCl}-\text{Cl}^-$. If the inorganic cuprous chloride complexes are denoted $(\text{CuCl})_a(\text{Cl}^-)_b$, their equilibrium constants β_{ab} , and their activity coefficients γ_{ab} we get the following equation, comprising the empiric function (17):

$$\begin{aligned} \text{CuCl}_t &= \{\text{CuCl}\} \sum_b \beta_{1b} [\text{Cl}^-]^b \gamma_{\text{Cl}}^b / \gamma_{1b} + \{\text{CuCl}\}^2 \sum_b 2\beta_{2b} [\text{Cl}^-]^b \gamma_{\text{Cl}}^b / \gamma_{2b} + \dots \\ &= S \cdot \{\text{CuCl}\} \end{aligned} \quad (21)$$

This formula is analogous with (20). Here also the assumption of the sole existence of mononuclear complexes would involve that the activity coefficients of the first term compensate for the changes in $[\text{Cl}^-]$. To illustrate how large this benevolent compensation would have to be, we assume that CuCl_3^{2-} is the predominating complex, and that the activity coefficients remain constant. We then find that in 4 m HCl the quotient $\text{CuCl}_t / \{\text{CuCl}\}$ should increase from its saturation value 0.75, to a value of 1.74 in a 1/10-saturated solution. But the measurements have given 0.75 and 0.73 respectively, the difference not being significant.

It is possible that the two systems have analogous distributions between mono- and polynuclear complexes. But it seems more natural to try and trace the linear correlation to one and the same phenomenon, assuming that the chloride ion activity, *i. e.* the product $[\text{Cl}^-] \cdot \gamma_{\text{Cl}}$, is independent of $\{\text{CuCl}\}$ at a given HCl. This would mean that in both systems mononuclear complexes predominate, provided that their activity coefficients are constant at given HCl. But as long as the inorganic system is not fully understood it seems fruitless to attempt a complete analysis of the composition of the acetylene system.

We are however entitled to conclude that mononuclear complexes *exist*. The linear relations (15) and (17), thus (18) also, are experimentally verified at low cuprous chloride activities where the concentration of dissolved cuprous chloride is small in comparison with the concentration of hydrochloric acid, and where the concentration of free chloride ion and the activity coefficients

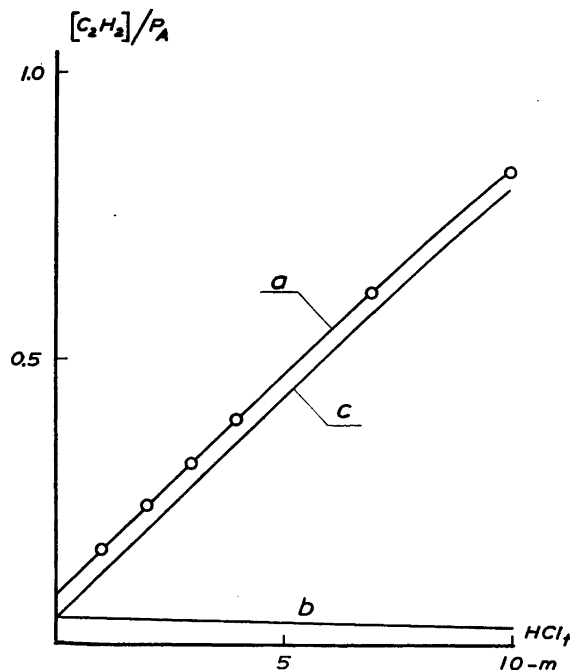


Fig. 6. Acetylene absorption as a function of the concentration of hydrochloric acid in the presence of solid cuprous chloride. 25° C.

- a: with cuprous chloride
 b: cuprous chloride absent — “physical” solubility
 c: difference $a-b$, i.e. $[C_2H_2]_{Cu}/P_A$

consequently should remain approximately constant. As shown by Table 4 acceptable measurements of the acetylene absorption can be performed even in solutions where $CuCl_t$ only amounts to a few percent of HCl_t . But to what extent complexes of other composition appear at higher activities of cuprous chloride cannot be definitely established.

4. Variation of the hydrochloric acid concentration

a) *Condition: solid cuprous chloride present.* Fig. 6 shows how the quotients $[C_2H_2]_t/P_A$ and $[C_2H_2]_{Cu}/P_A$ depend on the concentration of hydrochloric acid in systems containing solid cuprous chloride, where these two quotients are independent of P_A . The points of curve *a* are means from experiments with P_A -variations between 0.1 and 1.0 atm; treated as in Table 2.

The relation between $[C_2H_2]_{Cu}/P_A$ and HCl_t thus is linear; possibly a small deflection, concave towards the HCl -axis, can be observed in the uppermost part of the c -curve. If only the interval 1–7 m hydrochloric acid is taken into account the result can best be expressed by the empirical formula

$$[C_2H_2]_{Cu}/P_A = A + B \cdot HCl_t \quad (\text{Condition } \{CuCl\} = 1) \quad (22)$$

$$A = 0.046 \text{ m/atm} \quad B = 0.0759 \text{ atm}^{-1}$$

Computed and measured values agree within $\pm 1\%$. If the same expression is applied to 10 m hydrochloric acid the computed value is 3% higher than the measured one. The deviation appears in the interval where the formation of vinyl chloride is noticeable, and where the measurements have been performed slightly differently. Therefore it is difficult to judge whether the difference is real. Anyway the deviation is so small that we can regard (22) as approximately valid for the whole interval 1–10 M hydrochloric acid.

The same expression applies also for the limit $([C_2H_2]_{Cu}/P_A)_0$.

b) *General function of the variables P_A , $\{CuCl\}$ and HCl_t .* The combination of (18) and (22) yields

$$([C_2H_2]_{Cu}/P_A)_0 = \{CuCl\} \cdot (A + B \cdot HCl_t) \quad (23)$$

The expression has been experimentally verified only within that limited interval for HCl_t , and with that limited accuracy, under which (17) and (18) are valid. Only at the extreme: $\{CuCl\} = 1$ does the expression directly follow from (22).

If the generalization formulated in (12) is applied here, the same expression will hold also for the absorption quotient at a finite pressure:

$$[C_2H_2]_{Cu} = P_A \cdot \{CuCl\} \cdot (A + B \cdot HCl_t) \quad (24)$$

At a constant cuprous chloride activity the absorption quotient thus is a linear function of the hydrochloric acid concentration, with a constant term corresponding to the ordinate intercept of the extrapolated c -curve in Fig. 6.

c) *Conclusions on the composition of the acetylene complexes.* From the linear HCl_t function one gets the immediate impression that two complexes predominate, one with $q = 1$, *i. e.* the anion $C_2H_2 \cdot CuCl_2^-$ whose concentration rises proportionally with HCl_t , and the other with $q = 0$, *i. e.* the uncharged compound $C_2H_2 \cdot CuCl$ whose concentration is independent of HCl_t . It seems most likely that this interpretation is correct, but the evidence is only circumstantial. But if the discussion is limited to those cases where $\{CuCl\}$ is so low that the concentration of inorganic copper complexes and of acetylene complexes can be neglected in comparison with HCl_t , and where complexes with

$p = 1$ can be expected to predominate, we get from (3) and (24) the following equation

$$\frac{[\text{C}_2\text{H}_2]_{\text{Cu}}}{P_A} \cdot \frac{1}{\{\text{CuCl}\}} = \sum K_{11q} \cdot \text{HCl}_t^q \cdot \gamma_{\text{Cl}}^q / \gamma_{11q} = A + B \cdot \text{HCl}_t$$

(Condition: $\{\text{CuCl}\} \ll 1$)

(25)

Thus a possible explanation is that only the complexes mentioned, with $q = 0$ and $+1$ resp., do exist, and that the following expressions hold

$$\begin{cases} \text{For } \text{C}_2\text{H}_2 \cdot \text{CuCl}: & K_{110} / \gamma_{110} = A = 0.046 \text{ m/atm} \\ \text{For } \text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-: & K_{111} \cdot \gamma_{\text{Cl}} / \gamma_{111} = B = 0.0759 \text{ atm}^{-1} \end{cases} \quad (26)$$

This would mean that the uncharged complex has an activity coefficient which is independent of the hydrochloric acid concentration, and that the activity coefficient of the anion complex remains proportional to that of the chloride ion when HCl_t is varied. These two assumptions might both be plausible. But in this system the variations of the activity coefficients of the ions present are quite large. (The mean activity coefficient of HCl ¹⁴ is 0.81 in 1 m and 10.5 in 10 m solution.) Other interpretations are thus feasible, even though they seem less probable.

To attain reliable conclusions on the chloride content of the complexes it is desirable to study systems where the chloride ion concentration can be altered without major displacements of the activity coefficients. We have achieved good results with mixtures of hydrochloric and perchloric acid. These experiments, which will be described in a forthcoming paper, give good evidence that the complexes mentioned, $\text{C}_2\text{H}_2 \cdot \text{CuCl}$ and $\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-$, predominate. It is therefore likely that this holds also for the system with hydrochloric acid only.

The conclusion is: the measurements are compatible with the assumption that the complexes $\text{C}_2\text{H}_2 \cdot \text{CuCl}$ and $\text{C}_2\text{H}_2 \cdot \text{CuCl}_2^-$ predominate at a low cuprous chloride activity. Measurements at higher activities allow no definite conclusions, although the same empirical relations hold.

5. Comprehensive discussion of the equilibrium experiments

The absorption of acetylene in an aqueous solution of cuprous chloride and a dissociating 1 : 1 chloride depends on the composition of the solution as can be described by simple empirical functions. In systems where hydrochloric acid is the dissociating chloride the concentration of Cu^{I} -bound acetylene can

be expressed as a function, derived from (22), (16) and (13), of the variables P_A , CuCl_t and HCl_t .

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = P_A \cdot \frac{\text{CuCl}_t - [\text{C}_2\text{H}_2]_{\text{Cu}}}{S} \cdot (A + B \cdot \text{HCl}_t) \quad (27)$$

where the constants (25° C) are $A = 0.046 \text{ m/atm}$, $B = 0.0759 \text{ atm}^{-1}$ (28)

The corresponding explicit expression is

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = \frac{P_A \cdot \text{CuCl}_t \cdot (A + B \cdot \text{HCl}_t)}{S + P_A \cdot (A + B \cdot \text{HCl}_t)} \quad (28)$$

S denotes the solubility of cuprous chloride in hydrochloric acid in the absence of acetylene, and is regarded as an empirical function of HCl_t . The expressions are derived from measurements, where the hydrochloric acid concentration has been varied within the interval 1–10 m, and each of the other variables over the largest interval practicable (about one power of ten). Only at the upper boundary of the HCl_t -interval the results might indicate a systematic deviation from these expressions, amounting however to some few percent only. Otherwise the expressions are valid with an accuracy of $\pm 1\%$, which approximately corresponds to the experimental error.

Using the activity of cuprous chloride as a variable we get a simpler expression:

$$[\text{C}_2\text{H}_2]_{\text{Cu}}/P_A = \{\text{CuCl}\} \cdot (A + B \cdot \text{HCl}_t) \quad (24)$$

This also is an empirical function, at least when applied to the limit value $([\text{C}_2\text{H}_2]_{\text{Cu}}/P_A)_0$, otherwise a generalization according to (11) and (12) must be introduced. This formula, founded on potentiometric measurements also, has a lesser accuracy and a smaller interval of validity. But it is supported by measurements on systems with solid cuprous chloride, which result in:

$$[\text{C}_2\text{H}_2]_{\text{Cu}} = P_A \cdot (A + B \cdot \text{HCl}_t) \quad (\text{Condition } \{\text{CuCl}\} = 1) \quad (22)$$

where the empirical constants are the same as above.

In order to determine the composition of the acetylene complexes $(\text{C}_2\text{H}_2)_n(\text{CuCl})_p(\text{Cl}^-)_q$ we have to compare (24) and the thermodynamic expression (3):

$$P_A \cdot \{\text{CuCl}\} \cdot (A + B \cdot \text{HCl}_t) = \sum n \cdot K_{n,p,q} \cdot P_A^n \cdot \{\text{CuCl}\}^p \cdot \text{HCl}_t^q \cdot F_{n,p,q} \quad (29)$$

where $F_{n,p,q}$, which we regard as functions of P_A , $\{\text{CuCl}\}$, and HCl_t are defined according to

$$F_{n,p,q} \equiv \frac{[\text{Cl}^-]^q \cdot \gamma_{\text{Cl}^-}^q}{\text{HCl}_t^q \cdot \gamma_{n,p,q}} \quad (30)$$

We do not know how the $F_{n,p,q}$ functions depend on the three variables. But under certain conditions we have reason to assume approximately constant $F_{n,p,q}$ values, when altering one of the variables. Therefore we have drawn definite conclusions on the composition of the complexes only for such conditions. The result is that the acetylene content (n) of the complexes can be determined with fair certainty, the copper content (p) less accurately, and regards the chloride content (q), the premises for definite conclusions are not very substantial.

Since the simple empirical functions are valid over the whole range, we are forced to consider the assumption that the $F_{n,p,q}$ values for the existing complexes are *entirely independent* of the three variables, and that the complexes $C_2H_2 \cdot CuCl$ and $C_2H_2 \cdot CuCl_2^-$ predominate. The assumption would imply

$$\left\{ \begin{array}{l} \text{For } C_2H_2 \cdot CuCl: F_{1,1,0} = \gamma_{1,1,0} \text{ constant} \\ \text{For } C_2H_2 \cdot CuCl_2^-: F_{1,1,1} = [Cl^-] \cdot \gamma_{Cl} / HCl_t \cdot \gamma_{1,1,1} \text{ constant} \end{array} \right. \quad \begin{array}{l} (31 \text{ a}) \\ (31 \text{ b}) \end{array}$$

It is reasonable to assume a constant activity coefficient for the uncharged complex, also $F_{1,1,1}$ being independent of HCl_t , which would imply a proportionality between the activity coefficients of the complex anion and of the chloride ion at variations of HCl_t . But it is more difficult to understand how $F_{1,1,1}$ could possibly remain constant when the cuprous chloride activity is varied. *Cf.* the previous discussion of this question where it is pointed out that an assumption of a constant product $[Cl^-] \cdot \gamma_{Cl}$, *i.e.* a hydrochloric acid activity independent of $\{CuCl\}$ and P_A , might be feasible.

To judge the possibility of these hypotheses further investigations are necessary, particularly concerning the inorganic $CuCl-Cl^-$ system. But it should be stressed that the simple empirical relations indicate a system of simple complexes, and that the activity coefficients, in spite of (or perhaps due to) the high electrolyte concentration, depend on the composition of the system in a simple manner.

Continued investigations aim at an analysis of the composition of the acetylene complexes in other systems and at an explanation of the empirical relations in the equilibrium experiments described here.

APPARATUS AND PROCEDURE

For the *absorption experiments* has been used the simple apparatus of Fig. 7. The vessel *a* is exchangeable, its size is so chosen that the amount of liquid suits the absorption capacity of the solution. The relation between liquid and total volume of the vessel is so adjusted that 20–40 % of the acetylene introduced remains in the gas-phase.

The distribution between liquid and gas remains practically unaltered at the successive additions of acetylene, since the absorption in these experiments is almost propor-

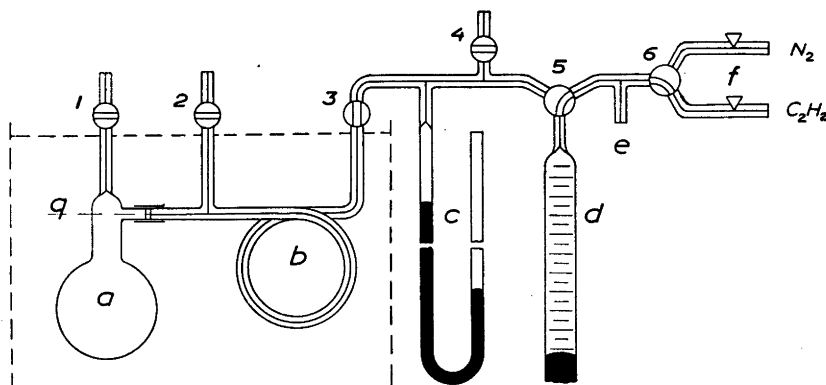


Fig. 7. Apparatus for absorption measurements.

- a) Reaction flask. Sways with line *q* as axis.
- b) Diffusion capillary, length 600 mm, int. diam. 1 mm
- c) Mercury manometer
- d) Burette, water-jacketed
- e) To differential manometer for burette pressure
- f) Mercury seal

tional to the acetylene pressure. Impurities in the acetylene (about 0.4 vol. per cent) thus cause a constant relative error in P_A . If 40 % of the acetylene remains in the gaseous phase and the impurities be insoluble in the liquid, an enrichment occurs which gives a P_A -error of 1 %. If the impurities are partly soluble the relative error is smaller, but still remains approximately constant.

The flask is connected by rubber tubing whose impermeability for the gases used has been checked. The capillary *b* facilitates measurements at higher temperatures; no condensation will occur in the manometer or other cold parts, if the experiment is so performed that the gas is flowing towards the flask only.

The volume of the gas phase is determined in each experiment by calibration with nitrogen. The deflections of the manometer will cause minor changes in the volume of the system; the quotient between nitrogen introduced (V_N) and the partial pressure (P_N) increasing linearly with P_N , which may be used for a graphical check.

Type Experiment

Determination of acetylene absorption in 4 M HCl; CuCl (s); 25.0°. In a 100 ml flask is introduced 6.0 g of fine-crystalline cuprous chloride. The side tube is sealed and the flask is evacuated (c. 0.01 mm Hg) for half an hour with intermittent shaking. 4.00 m hydrochloric acid, prepared from constant-boiling acid, is freed from dissolved oxygen by bubbling with nitrogen in a burette-like device with a fritted disk in the bottom and a liquid seal at the top. The burette valve is connected via a three-way stopcock to the closed evacuated flask. When this passage has been evacuated a suitable quantity of

acid is sucked into the flask; in this case 21.28 g of 4.00 *M* hydrochloric acid, containing 18.57 g water.

The flask, filled with nitrogen through 1, is then connected to the nitrogen-filled apparatus; during this operation a rapid stream of nitrogen is flowing out through the side tube, after connection venting through 2.

The whole system is evacuated to determine the vapour pressure of the solvent. Unnecessary evaporation is avoided by using a closed vessel (volume about 200 ml) which is alternatively evacuated and connected to 1 until a constant pressure is achieved, in this experiment 19.6 mm.

After complete evacuation above 3, the apparatus is calibrated by introducing portions of nitrogen, the flask remaining immobile. The operation gives the following values for V_N/P_N and P_N (units: ml at 16.3°, 759.8 mm Hg uncorrected): 0.1112–193.4; 0.1150–395.6; 0.1226–783.2; 0.1310–1239.2.

After a second evacuation to vapour pressure (complete above 3) portions of acetylene are introduced under brisk shaking of the flask.

As shown in Table 5 constant pressure readings are obtained after 1–3 minutes. But when the pressure has reached about 1 atm the solid addition compound begins to crystallize from the supersaturated solution, and the pressure suddenly drops. From this particular experiment we have utilized even the introductory readings from the last acetylene addition ($V_t = 244.6$) since the pressure remained constant for about 5 min. before it dropped.

The accuracy of the experimental data can be estimated in the following way:

The partial pressure value is a difference between 2 readings (4 meniscuses) and the accuracy in P_A can be estimated to $\pm 3 \times 10^{-4}$ atm. The gas volumes are read in a 100 ml burette, graduated in 0.1 ml. The absolute error would be ± 0.15 ml when V_t is less than 100 ml, and for volumes over 100 ml (more than one burette) we assume a relative error of ± 0.15 %. V_g is known with the numerical accuracy of the tabulated values. The relative error in $[C_2H_2]_t$ is computed from the relative error in V_t , using the factor $V_t/(V_t - V_g)$, in this experiment approximately equal to 1.5. The first four values of $[C_2H_2]_t$ thus have an uncertainty of ± 3 units in the fourth place, other values about ± 0.2 %.

Potentiometric measurements. Amalgamated copper wire, and silver wire with electrolytically deposited silver chloride have been used as electrodes. To eliminate disturbances arising from the dissolution of the silver chloride a fresh covering is obtained by electrolyzing in the test solution (silver electrode as anode) using a low current density (1 mA/cm²) for 2 minutes. The polarization potential quickly disappears and the potential then remains constant for a satisfactory period, 15–30 min. This electrolysis does not influence the composition of the solution. At the first measurement the vessel contains 4 m hydrochloric acid, saturated with cuprous chloride; this measurement thus yielding the standard potential, E_0 , of the electrode couple. The solution is then diluted with acid, and the resulting molality of cuprous chloride is calculated, and checked by analysis. The experiment is concluded by the addition of cuprous chloride in excess to check the constancy of the standard potential.

The vessel, immersed in an oil-thermostat at 25.0°, is closed and has a slight overpressure of nitrogen, and is connected with a burette permitting the addition of oxygen-free solvent. The potentiometer is a PHM 3i (Radiometer, Copenhagen) so adjusted that the values of $f(E) = E \cdot F/RT \cdot 2.303$ at 25.00° is read directly. The difference $f(E_0) - f(E)$ gives $\log [CuCl]$.

Table 5. Readings and computed data from an absorption experiment: 4 m hydrochloric acid, containing solid cuprous chloride. 25° C.

V_t	Minutes	P_A in mm	V_g	$[C_2H_2]_t$	$[C_2H_2]_{Cu}/P_A$ (atm.)
18.4	1	55.2			
	2	55.2	6.0	0.02825	0.351
43.9	1	130.9			
	2	130.7			
	3	130.7	14.0	0.06720	0.3545
76.0	2	225.2			
	4	225.0	25.2	0.1157	0.3537
95.9	1	283.6			
	2	283.4			
	4	283.4	32.0	0.1456	0.3529
123.0	3	361.9			
	4	361.9			
	5	361.9	41.4	0.1859	0.3533
155.0	1	453.2			
	2	453.3	52.6	0.2333	0.3541
188.4	2	548.2			
	3	547.9			
	4	547.9	64.7	0.2818	0.3540
203.6	3	591.0			
	3	591.0	70.2	0.3039	0.3538
218.3	1	633.2			
	3	633.1	75.7	0.3248	0.3527
228.8	2	662.4			
	3	662.4			
	7	662.3	79.5	0.3401	0.3534
244.6	2	706.3			
	4	706.1	85.4	0.3627	0.3524
	6	695.2			
	10	602.1			
	20	465			
	30	375.4			
	40	330.2			
	50	310.6			
	60	305.3			

V_t Amount of acetylene introduced, in ml (16.3°, 759.8 mm Hg).

V_g Amount of acetylene in gas phase, in ml (conditions as above). Computed from calibration described in text.

$[C_2H_2]_t$ Concentration (molality) of acetylene absorbed, computed from $V_t - V_g$ and quantity of water (18.57 g).

$[C_2H_2]_{Cu}$ Computed from $[C_2H_2]_t - \alpha P_A$ with α -value from table 1.

$[C_2H_2]_{Cu}/P_A$ Absorption quotient in molality/atm.

Chemicals

Cuprous chloride of high purity, entirely free from cupric and metallic copper¹⁵.

Acetylene of good purity in tubes with normal filling but without acetone.

Oxygen-free nitrogen has been prepared according to v. Wartenberg¹⁶. Analyses show the oxygen content to be below 0.001 % by volume.

Other chemicals of reagent grade.

SUMMARY

1. In an aqueous chloride solution of monovalent copper two types of dissolved acetylene compounds appear: yellow acetylidic compounds, where copper is substituted for the hydrogen atoms, and colourless addition compounds, where the hydrocarbon retains its hydrogen. As a rule the main part of the acetylene absorbed is present in addition complexes.

2. For systems consisting of cuprous chloride and hydrochloric acid empirical relations have been determined, connecting the total concentration of acetylene in addition complexes and the three variables: acetylene pressure, total concentration of dissolved cuprous chloride, and total concentration of hydrochloric acid. If the solubility of cuprous chloride is introduced as a parameter a simple algebraic function results (27, 28). Preliminary experiments in systems containing alkali chlorides instead of hydrochloric acid suggest analogous relations.

3. With cuprous chloride activity, acetylene pressure, and total hydrochloric acid concentration as variables a function (24) is obtained, according to which the total concentration of addition complexes is proportional to the two first variables and a linear function (with a constant term) of the third one.

4. From equilibrium experiments only the following conclusions can be drawn with certainty on the composition of the addition complexes:

- a) complexes with *one* acetylene molecule predominate
- b) complexes with *one* atom of copper exist
- c) complexes with *one* and *two* atoms of chlorine can be assumed.

But the simple relations provoke some radical assumptions concerning activity coefficients *etc.* If these be accepted the experiments show that the complexes $C_2H_2 \cdot CuCl$ and $C_2H_2 \cdot CuCl_2^-$ predominate in 1–10 m hydrochloric acid.

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