

Cuprous Compounds of Acetylene

IV. Solid Addition Compounds with Cuprous Chloride; Composition and Equilibria

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In the first paper of this series¹ Österlöf has reported on his earlier investigations of two solid addition compounds, for which he suggests the formulae $C_2H_2(CuCl)_3$ and $C_2H_2(CuCl)_2$. These substances were prepared by treating cuprous chloride with acetylene in a reaction medium of ethyl alcohol and hydrochloric acid and collecting the solid reaction products. Analyses of these products, comprising acetylene and copper determinations, gave as a mean 3.2 and 2.1 moles cuprous chloride per mole acetylene. The deviations from the theoretical integers were supposed to be caused by a loss of acetylene during the stage between synthesis and analysis, or possibly by an incomplete conversion; experiments using longer reaction times usually gave values closer to the theoretical ones. In spite of the limited accuracy, the experiments showed with certainty — in contrast to earlier investigations in this field² — that there exist two distinct compounds between acetylene and cuprous chloride.

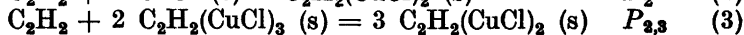
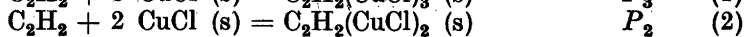
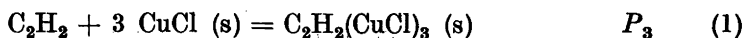
The syntheses were performed at different pressures, which were kept constant during each single experiment. An approximate determination of the dissociation pressures of the compounds was attempted by a stepwise narrowing of the pressure interval within which a change of the composition of the solid occurs. It has later turned out that supersaturation phenomena render such a determination of the dissociation pressures unsatisfactory.

The continued investigations have covered measurements of the dissociation pressures and their temperature coefficients with a manometrical method and accurate determinations of the stoichiometrical composition of the compounds.

It has been confirmed that no reaction occurs within a reasonable time between dry solid cuprous chloride and acetylene, even if the pressure is raised to about 10 atm. Nor do the solid addition compounds decompose in vacuo if the substances are carefully dried, *e.g.* by P_2O_5 -dry acetylene. A liquid medium is therefore necessary for these reactions. After tentative comparisons between different media aqueous solutions containing hydrochloric acid were chosen.

If the acetylene pressure is successively raised over aqueous hydrochloric acid solutions containing solid cuprous chloride in excess, the first crystallization of solid addition compound occurs only at a pressure considerably higher than the equilibrium pressure³. This supersaturation phenomenon is typical and appears both at the conversion of CuCl into $C_2H_2(CuCl)_3$ and at the further conversion into $C_2H_2(CuCl)_2$. In both cases the crystallization can be initiated by seeding.

In several experiments the crystallization of $C_2H_2(CuCl)_3$ failed to appear and, instead, the cuprous chloride turned directly into $C_2H_2(CuCl)_2$. Therefore it was possible to determine the equilibrium pressure of systems where the substances CuCl and $C_2H_2(CuCl)_2$ are coexisting solid phases, although such systems are unstable with respect to $C_2H_2(CuCl)_3$. It has thus been possible to measure, independent of each other, the following three equilibria:



Actually it is easier to study the metastable equilibrium (2) than the stable equilibrium (3) which is approached much more slowly.

There exists a theoretical relation between the three equilibrium pressures P_3 , P_2 , and $P_{2,3}$. If acetylene is regarded as an ideal gas (and the differences between the volumes of the solid substances are disregarded in comparison to the mole volume of acetylene) the following relation holds:

$$P_{2,3} = P_2^3 / P_3^2 \quad (4)$$

The manometric method can be used also for the determination of the composition of the solid complexes formed, without the necessity of isolating the substances for analysis. The first step is a *qualitative* analysis, whose purpose is to prove that only C_2H_2 and CuCl enter into the complexes formed, and none of the other components of the reaction medium, *e.g.* hydrochloric acid or water. This is achieved by comparing different experiments which give identical equilibrium pressures, although the composition of the medium has been so changed that the activities of these other components vary.

The *quantitative* analyses are performed by measuring the amount of acetylene required for complete conversion of a given quantity of cuprous chloride. The amount of liquid is small in comparison to the solid phase and even the ratio between the total amounts of cuprous chloride and acetylene gives a good approximate value for the composition of the compound formed. In most experiments the amount of cuprous chloride and acetylene dissolved in the liquid phase can be corrected for by applying empirical functions from earlier investigations^{3,4}.

APPARATUS AND PROCEDURE

The manometrical apparatus sketched in Fig. 1 has been used for the measurements. The apparatus consists of a gas burette, used both for the addition and removal of gas, an open mercury manometer and a reaction flask,

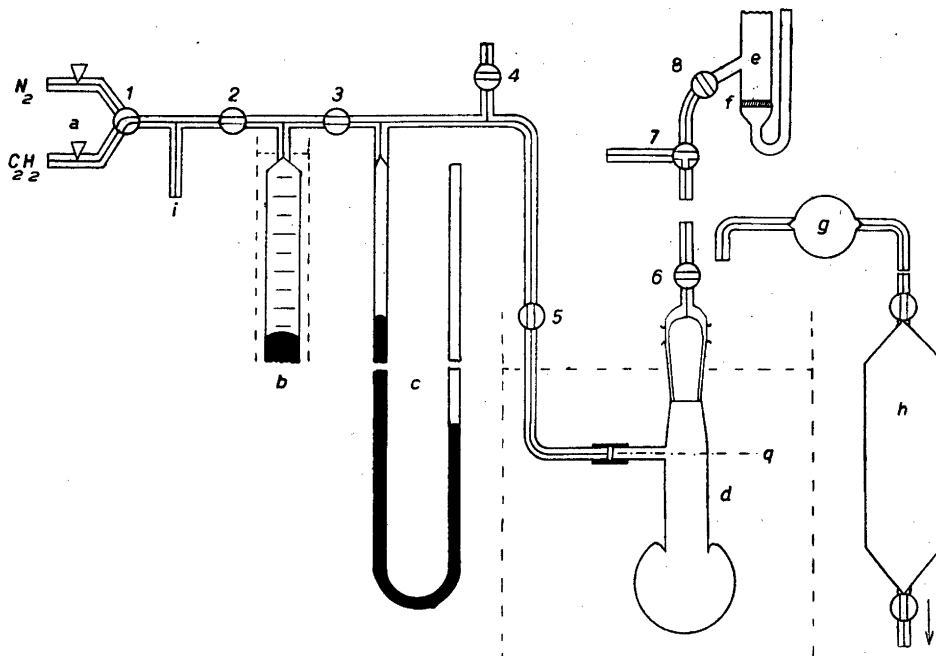


Fig. 1. Manometrical apparatus.

a) Mercury seals. b) Gas burette, water-jacketed. c) Mercury manometer. d) Reaction flask. Sways with line *q* as axis. e) Burette for liquid. f) Fritted disc. g) Splash trap. h) Evacuation vessel. i) To differential manometer for burette pressure.

immersed in a water thermostat and equipped with a mechanical shaking device. At the beginning of the experiment the flask contains known amounts of solid cuprous chloride and liquid. Measured quantities of acetylene are added under vigorous shaking of the vessel. The pressure momentarily rises with each addition and then slowly sinks towards equilibrium. At suitable points during the experiment, a certain amount of acetylene is sucked out and the rising pressure-time curve is followed. The experiments aim at an empirical following-up of both horizontal and vertical branches of a phase diagram, as in Fig. 6.

In the experiments two types of hydrochloric acid solutions have been used:

- a. Hydrochloric acid of concentration from 1 to 4 m.
- b. 4 m mixtures of hydrochloric and perchloric acid with a recipe concentration of hydrochloric acid between 0.2 m and 1.0 m.

Lower concentrations of hydrochloric acid prove inconvenient since solid acetylidic compounds may form, whilst higher concentrations must be avoided because of the catalytic formation of vinyl chloride, which can cause a disturbing pressure increase, even if the quantity is stoichiometrically unimportant.

Determination of the equilibrium pressures

The reaction velocity, at which equilibrium is approached, depends on the composition of the liquid and on the ratio between the amounts of liquid and solids. No systematic investigation of the kinetics has been intended. The reaction velocities are irreproducible; changes in particle size etc. of the solid substances may produce considerable variations during one and the same experiment. The impression is, however, that it is advantageous to use a fairly small amount of liquid, which is desirable also in order to depress the effect of by-reactions, which occur in the liquid phase only. However, the mixture should contain so much liquid that it remains mobile on shaking. A quantity of about 1 ml solution per g solid substance has been used in most experiments.

The free gas volume of the reaction flask should be kept small; a large gas volume increases the "buffer capacity" of the system and delays the attainment of equilibrium. This, however, has the disadvantage that insoluble impurities in the acetylene are enriched in the remaining gas. When acetylene is successively added for the synthesis of a larger quantity of addition compound, the total pressure will therefore rise even if the partial pressure of acetylene remains constant. It is difficult to prepare acetylene, which is so pure that this effect disappears entirely. However, if gas is sucked out, a rapid venting of the gas impurities is achieved and the system fills with pure acetylene formed by a partial splitting of the addition compound. If the free volume of the vessel is small and the equilibrium pressure low it is possible to remove all impurities completely by withdrawing a comparatively small portion of the total acetylene content.

The normal routine for measuring an equilibrium pressure comprises the following steps:

a. Synthesis of a suitable quantity of solid addition compound (corresponding *e. g.* to one fourth of the total cuprous chloride) by introducing a large portion of acetylene.

b. One or two withdrawals of gas for the complete removal of gas impurities. To check the reproducibility of the decomposition pressure even further withdrawals may be performed.

c. Addition of a small portion of acetylene which may be the pure gas from the previous withdrawal.

The pressures read under a. are rejected; the readings under b. give the pressure-time curve after splitting (the first one may be rejected if there is reason to suspect noticeable amounts of impurities) and under c. the curve after synthesis.

Determination of the composition of the solid substances

The total amount of cuprous chloride is known by weighing and the amount of acetylene introduced is volumetrically measured. The compressibility of acetylene is nearly ideal; according to measurements in this laboratory⁵ at 25.0 °C and within the pressure interval dealt with here, we can use the relation $\bar{V}P = RT \cdot (1 + k \cdot P)$ where the coefficient k amounts to $-7 \cdot 10^{-3} (\text{atm})^{-1}$. At the volumetric measuring (conditions 20–25 °C, 1 atm) the mole volume of acetylene thus is 0.7 % smaller than that for an ideal gas.

The impurities in the acetylene (about 0.4 % in most experiments) need not be corrected for since they are essentially removed (and measured) in the withdrawal steps.

The total amount of acetylene added will be distributed over the gaseous, liquid, and solid phases. The amount of gaseous acetylene is calculated from the pressure, temperature and volume; the free volume of the reaction vessel is determined in each experiment by calibration with nitrogen.

For the computation of dissolved acetylene and cuprous chloride the following empirical functions are used, derived from earlier investigations^{3,4} of inorganic complexes of cuprous chloride and of dissolved acetylene compounds.

$$[\text{C}_2\text{H}_2]_t = [\alpha + \{\text{CuCl}\} \cdot (A + B \cdot \text{HCl}_t)]P_A \quad (5a)$$

$$\{\text{CuCl}\} = \{\text{CuCl}\} [S + (A + B \cdot \text{HCl}_t) \cdot P_A] \quad (5b)$$

$\{\text{CuCl}\}$ is the activity of cuprous chloride, with the solid substance as standard state, and P_A the partial pressure of acetylene in atm. If the solvent is hydrochloric acid only

(of concentration HCl_t), the constants below give the desired concentrations in moles/1 000 g H_2O at 25.0° C.

$$a = 0.0424 - 2.62 \cdot 10^{-3} \cdot \text{HCl}_t \cdot (1 + 0.116 \text{HCl}_t)^{-2}$$

$$A = 0.046 \quad B = 0.0759$$

$$S = 0.048 \text{ (1 m HCl)}, 0.225 \text{ (2 m HCl)}, 0.450 \text{ (3 m HCl)}, 0.744 \text{ (4 m HCl)}$$

For 4-molal mixtures of hydrochloric and perchloric acid hold:

$$a = 0.0509 - 3.5 \cdot 10^{-3} \cdot \text{HCl}_t$$

$$A = 0.016 \quad B = 0.086$$

$$S = 0.0435 \cdot \text{HCl}_t + 0.0294 \cdot \text{HCl}_t^2$$

In a system containing solid cuprous chloride, *i. e.* when measuring the pressures P_s and P_n , these expressions — with $\{\text{CuCl}\} = 1$ — are valid, provided the system is in equilibrium.

After complete conversion into solid addition compound, and on measurement of the equilibrium pressure $P_{s,s}$, the cuprous chloride activity sinks below unity. In a system which is in equilibrium with a solid addition compound of the composition $\text{C}_2\text{H}_2(\text{CuCl})_n$, the cuprous chloride activity depends on the acetylene pressure, P_A , according to

$$\{\text{CuCl}\} = (P_n/P_A)^{1/n} \quad (6)$$

where P_n represents the dissociation pressure of the solid addition compound, constant at a given temperature. (Expression (6) presupposes ideal compressibility of acetylene, but no correction is necessary in this case or on the whole when applying any of expressions (5)–(7).) If (6) is inserted into (5a) and (5b) the following expressions result:

$$[\text{C}_2\text{H}_2]_t = P_A [a + (A + B \cdot \text{HCl}_t) \cdot (P_n/P_A)^{1/n}] \quad (7a)$$

$$\text{CuCl}_t = [S + (A + B \cdot \text{HCl}_t) \cdot P_A] \cdot (P_n/P_A)^{1/n} \quad (7b)$$

These expressions have been used in Tables 2–4 for computing the composition of the liquid. For the equilibrium pressures P_n the values given later on have been used.

The quantities of acetylene and cuprous chloride which are dissolved in the liquid are fairly small (maximum 10 %) in comparison with the total amounts. The values computed are only corrections (which partly compensate each other in the computation of the composition of the solid phase). When applying the formulae (7a) and (7b), one may therefore start from an assumption concerning the value of n , *i. e.* the mole ratio cuprous chloride / acetylene in the solid compound, although the aim of the whole calculation is just an empirical determination of this number.

The details of the manometrical experiments are given in the type experiment section; other experiments are only briefly summarized. The type experiment has been chosen so that it comprises measurements of all three equilibria.

For the microscopic examination of the solid addition compounds a technique has been devised which permits sampling into a closed, acetylene-filled microscope chamber. A simple sampling with pipette and standard slide with cover glass, however, normally gives a specimen sufficiently stable for photographing etc.; $\text{C}_2\text{H}_2(\text{CuCl})_2$ can be treated at room temperature, $\text{C}_2\text{H}_2(\text{CuCl})_2$ at + 10° C or less. It is easy to observe when disintegration, caused by evaporation of acetylene, occurs.

Type experiment; reaction medium 0.865 m HCl, 3.135 m HClO_4

The experimental method, observations and data appear in Table 1, in the time-pressure curves of Fig. 2 and in the following account.

The formulae in the first and second columns are those which have been verified by the experiment. V_f denotes the total amount of gas which has been introduced into the reaction vessel d (including the tubing up till stopcock 5). The value is obtained from the sum of the burette readings minus the gas content enclosed between stopcocks 3 and 5; this volume is given by a linear function of the reading of the inner meniscus of the manometer. After withdrawal, the gas in the burette will contain water vapour. The volumes

Table 1. Readings and computed data from type experiment: 0.865 m HCl, 3.135 m HClO₄.

Charge: 100.4 millimoles cuprous chloride

18.89 g acid mixture, with 14.03 g water

Symbols: V_t -total amount of gas in the reaction vessel, in ml at 21.0° C and 1 atm p_t -total pressure in mm Hg, uncorrected = (761.5)⁻¹ atm.

Stage of experiment	Solid phase	No.	V_t	Temp. °C	p_t	Time hours	
Determination of vapour pressure	CuCl	Ev 1	0.0	25.0	19.1	—	
		2	0.0	10.0	7.4	—	
Nitrogen calibration	CuCl	N ₂ 1	14.9	25.0	247.3	—	
		2	30.9		491.9	—	
		3	43.6		686.6	—	
		4	60.6		946.5	—	
Evacuation Acetylene absorption before formation of solid addition compound (and overall check)	CuCl	Ev 3	0.0	25.0	19.1	—	
		a 1	12.6		119.2	½	
	CuCl	2	32.5	275.2	½		
		2	32.5	274.1	24		
		3	60.5	496.5	½		
		4	75.8	617.8	½		
		5	93.7	758.9	½		
		6	103.8	838.0	½		
	Equilibrium (2) metastable	CuCl + C ₂ H ₂ (CuCl) ₂	b 1	267.1	25.0	(484.8)	16
			2	231.9		(455.1)	1
3			198.1	453.0		1	
4			165.3	452.9		1½	
5			195.9	455.2		1½	
Equilibrium (1), first series	CuCl + C ₂ H ₂ (CuCl) ₃	c 1	453.2	25.0	(337.1)	17	
		2	422.2		(309.6)	1½	
		3	390.8		306.1	1	
		4	359.1		305.6	1½	
		5	391.8		306.4	1½	
Equilibrium (1), second series	CuCl + C ₂ H ₂ (CuCl) ₃	d 1	764.5	25.0	(336.8)	16	
		2	734.3		(309.0)	1½	
		3	703.4		304.7	1½	
		4	673.8		306.2	4	
		5	642.2		304.3	4	
		6	673.3		309.4	4	
Absorption after complete conversion to C ₂ H ₂ (CuCl) ₃	C ₂ H ₂ (CuCl) ₃	e 1	881.5	25.0	767.4	90	
		2	846.6		418.7	1	
		3	861.0		556.6	1	
		4	883.0		772.6	1	
	C ₂ H ₂ (CuCl) ₃	f 1	887.2	10.0	682.4	16	
		2	853.2		378.4	1	
		3	877.4		592.1	1	
		4	893.7		738.2	1	
		5	920.2		970.7	1	
	Equilibrium (3), first series	C ₂ H ₂ (CuCl) ₃	g 1	1038.4	10.0	(409.5)	30
2			1001.3	383.4		50	
+ C ₂ H ₂ (CuCl) ₂		3	965.2	378.7		50	
		4	996.5	406.8		50	

Stage of experiment	Solid phase	No.	V_f	Temp. °C	p_t	Time hours
Equilibrium (3), second series	$C_2H_2(CuCl)_2$ +	h 1	1181.9	10.0	(445.3)	40
		2	1149.5		380.0	50
		3	1120.1		373.8	40
		4	1085.9		367.5	50
		5	1115.7		396.9	50
Absorption after complete conversion to $C_2H_2(CuCl)_2$	$C_2H_2(CuCl)_2$	i 1	1286.8	10.0	834.2	75
		2	1252.0		498.1	1
		3	1263.5		603.4	1
		4	1277.2		731.5	1
		5	1295.0		896.3	1
	$C_2H_2(CuCl)_2$	k 1	1290.9	25.0	967.4	16
		2	1282.2		875.2	1
		3	1270.8		757.7	1
	$C_2H_2(CuCl)_2$	m 1	1298.2	10.0	886.2	14
		2	1284.4		752.9	1

read are then reduced to dry gas, the mixture being regarded as ideal. The partial pressure of the water vapour is computed from the vapour pressure of the solution, taking into consideration the compression which takes place before the reading of the burette. The total pressure p_t is obtained from the barometer pressure and the manometer readings. In the last column of the table, the time which has passed between the alteration in V_f (addition or removal) and the reading of the p_t -value in the preceding column is given; the times are approximate.

Charge: Chemicals, cf. paper II of this series³, p. 428. The reaction flask is charged with coarse crystalline cuprous chloride and is evacuated to about 0.01 mm with shaking. Oxygen-free nitrogen is then introduced to a pressure of approximately 50 mm. A mixture of acids of the composition stated is made from 4 molal stock solutions; dissolved oxygen is removed by stripping with nitrogen in a burette device *e*, provided with a fritted disc *f* for gas distribution and a liquid seal at the top. The stopcock of this burette is connected to the stopcock *6*. The desired amount is measured volumetrically; the density of the solution is determined separately.

Determination of the vapour pressure: The system is evacuated through stopcock *6*. To avoid unnecessary evaporation a closed vessel *h* is employed — volume about 5 times that of the reaction flask — and is alternatively connected to the flask and the vacuum pump. After five evacuations the pressure becomes constant. The splash trap *g* is then flushed with water; titration with NaOH shows that splash losses of acid are negligible. Nitrogen remaining in the manometer duct is removed by repeated evacuations of the tubing between *3* and *5*, through *4*. The temperature of the glass tubes is high enough to prevent condensation.

The acetylene absorption before the formation of a solid addition compound is measured by adding acetylene with brisk shaking of the reaction flask. Equilibrium is rapidly attained and a constant pressure reached after about 5 min. As an example, the pressure-time curve of mom. *a 5* is reproduced in Fig. 2: I.

Overall check of the pressure constancy of the system is inserted in mom. *a 2*. After 15 min, p_t equals 276.2 and 24 hours later 275.1 mm. This small change may depend on a slow irreversible acetylene reaction and / or deficiencies in the apparatus. The pressure constancy can be regarded as better than 0.05 mm / h.

Equilibrium (2), metastable. After *a 6*, one more portion of acetylene is added and the pressure rises to 970 mm. This pressure remains constant for about 15 min and then suddenly drops when crystallization of addition compound begins. Simultaneously the solution becomes turbid. After 10 min the pressure has sunk to 500 mm,

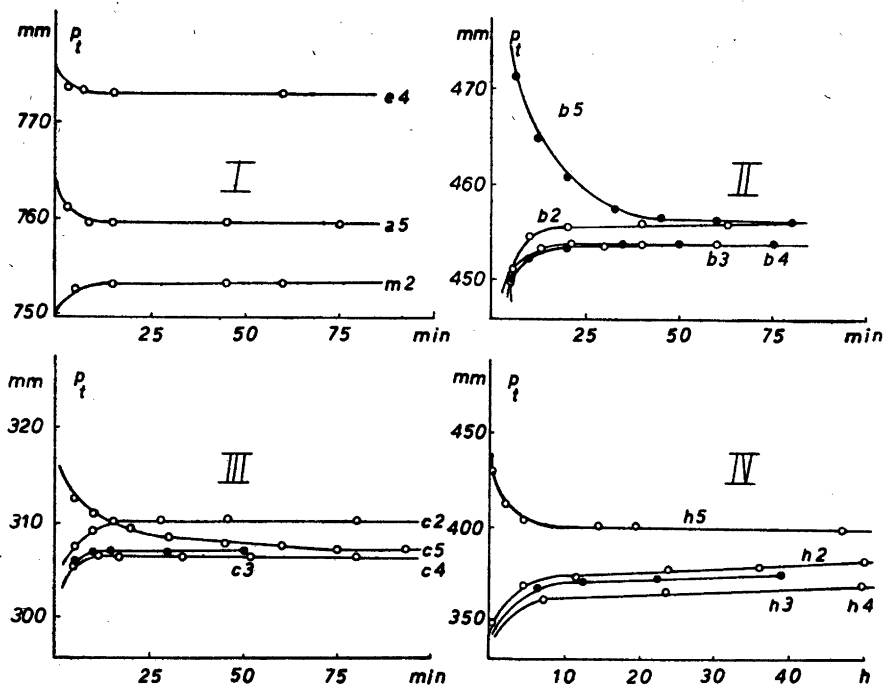


Fig. 2. Pressure-time curves from the type experiment.

- I. One single solid phase
 a 5: CuCl 25.0° C
 e 4: $C_2H_2(CuCl)_3$ 25.0° C
 m 2: $C_2H_2(CuCl)_3$ 10.0° C
- II. Solid phases: CuCl and $C_2H_2(CuCl)_3$ — metastable equilibrium — 25.0° C
 b 2–4 after successive removals of acetylene
 b 5 after addition of acetylene
- III. Solid phases: CuCl and $C_2H_2(CuCl)_3$; 25.0° C
 c 2–4 after successive removals
 c 5 after addition
- IV. Solid phases: $C_2H_2(CuCl)_3$ and $C_2H_2(CuCl)_3$; 10.0° C
 h 2–4 after successive removals
 h 5 after addition

and after 20 min to 490. The pressure decrease then slows down and after another half hour the pressure still exceeds 480 mm. This shows — according to earlier experiments — that the compound formed is $C_2H_2(CuCl)_3$ and that the system is still supersaturated with respect to $C_2H_2(CuCl)_3$. More acetylene is added before recording the time curve b 1; during this operation the pressure is not allowed to rise above 550 mm. — Then follows three withdrawals, b 2, 3 and 4. In each step the main portion is sucked out during a period of about 20 min at 425 mm, a pressure which will then be the initial one for these three time curves. Finally there is a small addition in mom. b 5. The main part is added during 10 minutes at 500 mm, which is the starting point for the time-curve. For this addition, the same gas as has been sucked out in b 4 is used. The time curves of Fig. 2 : II show that equilibrium is reached within about 30 minutes after decomposition, after synthesis this requires about 60 min. In the time curve b 5, there is one more reading after 4 hours and the pressure still remains unchanged.

After *b 5*, a further portion of acetylene is added at about 550 mm. The pressure then suddenly plunges, indicating that $C_2H_2(CuCl)_3$ begins to crystallize and that the previously formed $C_2H_2(CuCl)_2$ disappears.

Equilibrium (1), first series comprises one larger addition *c 1*, three evacuations *c 2, 3, 4* which are performed at 275 mm (10–15 min), and finally an addition, *c 5*, at 350 (10 min) of gas which was sucked out in mom. *c 4*. The time curves starting from these two pressures are given in Fig. 2: III and show that equilibrium is reached after about 20 min (decomposition) and 60 min (synthesis) respectively.

Equilibrium (1), second series is performed in the same manner, but includes one more withdrawal. The time curves are of the same type as in the *c*-series.

Absorption after complete conversion to $C_2H_2(CuCl)_2$. To ensure complete conversion of the cuprous chloride, the pressure is kept at 760 mm during 90 hours of shaking. The acetylene absorption, however, comes to a standstill at an earlier stage, and for the last 24 hours of *e 1* no acetylene absorption of importance is observed. To remove gas impurities an evacuation *e 2* is inserted, when the pressure is lowered to just above the dissociation point. Then follows four small additions, *e 3, 4, 5, 6*. The time curves *e 2–6* reach equilibrium rapidly — see Fig. 2: I where values from *e 4* are used as examples. An analogous series *f 1–5* is performed at 10.0° C, as a basis for the measurements at this temperature.

Equilibrium (3), first series. Towards the end of period *f 5*, after 1 h shaking at 970 mm, crystallization of $C_2H_2(CuCl)_2$ begins, causing a rapid pressure drop and a turbidity in the solution. The series comprises one larger addition *g 1*, two removals *g 2* and *3* at 300 mm, and a small addition *g 4* at 400 mm. Initially the equilibrium seems to be approached rapidly, but the reaction then proceeds very slowly and when the readings are interrupted after 50 hours, equilibrium has not yet been reached. The reaction velocity, however, decreases so much that a prolongation of the experiment becomes impracticable.

Equilibrium (3), second series. Identical with the first series but with one more withdrawal; time curves in Fig. 2: IV.

Absorption after complete conversion to $C_2H_2(CuCl)_2$. Complete conversion is effected by 75 hours shaking at about 850 mm; after 20 hours there is no absorption of importance. Then follows removal *i 2* and three small additions *i 3, 4* and *5*. Some measurements — *k 1, 2* and *3* — of the acetylene absorption at 25° in this system are inserted; in *k 3*, at a pressure of 750 mm, a minor pressure increase is observed after 1 ½ h, indicating a commencing of the re-formation of $C_2H_2(CuCl)_3$. The experiment is concluded by some further readings at 10°, *m 1* and *m 2*. In *m 1*, the re-formed amount of $C_2H_2(CuCl)_3$ is again dissolved by 45 h shaking at about 950 mm.

All time curves in the series *i, k* and *m* (except *i 1* and *m 1*) reach equilibrium rapidly. Cf. Fig. 2: I where curve *m 2* is given as an example.

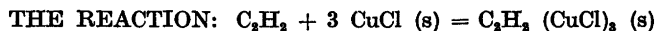
The total duration of the experiment was 41 days.

Calculations: The partial pressure of acetylene — and nitrogen — is calculated as the difference between the measured total pressure, p_t , and the vapour pressure of the liquid at the prevailing temperature, as determined in stages *Ev 1* and *2*.

The acetylene content of the free gas volume is calculated according to $V_g = p \cdot \emptyset$ where p is the partial pressure (in mm) and the constant \emptyset is determined by nitrogen calibration in stage $N_2 1–4$, where $V_f = V_g$. The four measurements give $\emptyset = (0.065), 0.0654, 0.0653, 0.0653$, mean 0.0653 at 25°. At 10° the computed value $\emptyset = 0.0688$ has been used. The same \emptyset -values can be used for acetylene — no correction for the compressibility is required.

From the difference $V_f - V_g$, the total numbers of acetylene millimoles in the liquid and solid phases are calculated, considering the non-ideal mole volume of acetylene at 21° and 1 atm, cf. p. 536.

The results calculated are found in Tables 2 A, 3 A and 4 A.



The measurements which have bearing upon this reaction are experimentally very satisfactory. The equilibrium is reached quickly and the agreement between the values for synthesis and decomposition is good. Also,

Table 2 A. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_3(s)$; reaction medium 0.865 m HCl, 3.135 m HClO_4 ; 25.0° C.

System: 100.4 millimoles CuCl
18.89 g acid mixture with 14.03 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase		
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_6$	Substance	
c	1	18.04	(0.4176)	0.81	1.37	1.04	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	16.83	(0.3815)	0.74	1.32	0.97	
	3	15.53	0.3769	0.73	1.32	0.90	
	4	14.20	0.3762	0.73	1.32	0.82	
	5	15.57	0.3773	0.73	1.32	0.90	
d	1	31.04	(0.4172)	0.81	1.37	1.83	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	29.85	(0.3807)	0.74	1.32	1.76	
	3	28.58	0.3750	0.73	1.32	1.69	
	4	27.34	0.3770	0.73	1.32	1.61	
	5	26.02	0.3745	0.72	1.31	1.53	
	6	27.30	0.3812	0.74	1.32	1.61	
e	1	34.74	0.9827	1.56	1.51	2.013	$\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	34.24	0.5248	0.94	1.34	2.016 ^t	
	3	34.46	0.7058	1.25	1.45	2.015	
	4	34.79	0.9895	1.71	1.65	2.011	

Experimental data see Table 1

it is easy to achieve complete conversion of all solid cuprous chloride for the determination of the composition of the addition compound.

Table 2 A contains the results of the type experiment. Under the heading, C_2H_2 , in the second column, the total quantity of acetylene in the liquid and solid phases is given and, in the third column, the equilibrium pressure P_A is given in atm. Pressure values which must be rejected because of the presence of gas impurities are bracketed. The third and fourth columns contain the calculated values for the amounts of acetylene and cuprous chloride in the liquid phase. (It should be observed that all quantities are totals — in millimoles — not concentrations.) In the last column is found the calculated composition of the precipitate, expressed by the quotient $\text{C}_2\text{H}_2/(\text{CuCl})_6$, which should approach 2, when the reaction goes towards complete conversion into $\text{C}_2\text{H}_2(\text{CuCl})_3$.

Other experiments on this reaction at 25.0° are similarly accounted for in Tables 2 B—E; in Table 2 F are summed up the results from an earlier series at 20.0° C. — The synthesis values *e* 5 and *f* 5 in Table 2 B had to be rejected, as marked by the parentheses, since the time of reaction was too short; the pressures were still decreasing. — In Table 2 C no information is given concerning the composition of the liquid phase because the constants of formulae (5)—(7) have not been determined. The value stated in the table for the quotient $\text{C}_2\text{H}_2/(\text{CuCl})_6$ refers to the entire system, including both liquid and solid phases. — In the experiment of Table 2 F (20.0° C) there is only one acetylene withdrawal in each series. The amount sucked out is however fairly large and the venting of foreign gas components is as good as in other experiments.

Table 2 B. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_3(s)$, reaction medium 0.2 *m* HCl, 3.8 *m* HClO_4 ; 25.0° C.

System: 101.0 millimoles CuCl
11.98 g acid mixture with 8.62 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase		
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_3$	Substance	
a	1	0.11	0.1891	0.14	—	0.000	CuCl
	2	0.28	.4036	.29	—	.000	
	3	0.49	.7033	.50	—	.000	
b	1	8.73	(0.4053)	0.29	0.20	0.50	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	7.51	(.3807)	.27	.19	.43	
	3	6.47	.3776	.27	.19	.37	
	4	7.80	.3796	.27	.19	.44	
c	1	15.58	(0.4075)	0.29	0.20	0.91	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	14.42	(.3808)	.27	.19	.84	
	3	13.88	.3779	.27	.19	.81	
	4	12.57	.3761	.27	.19	.73	
	5	11.27	.3766	.27	.19	.66	
	6	12.30	.3789	.27	.19	.72	
d	1	20.20	(0.3979)	0.29	0.20	1.18	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	19.01	(.3792)	.27	.19	1.11	
	3	17.73	.3764	.27	.19	1.04	
	4	16.44	.3758	.27	.19	0.96	
	5	17.52	.3808	.27	.19	1.03	
e	1	25.41	(0.4026)	0.29	0.20	1.50	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	24.16	(.3802)	.27	.19	1.42	
	3	22.88	.3786	.27	.19	1.35	
	4	21.55	.3787	.27	.19	1.27	
	5	22.46	(.3863)	.28	.19	1.32	
f	1	31.87	(0.4160)	0.30	0.20	1.89	$\text{CuCl} +$ $\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	30.78	(.3853)	.28	.19	1.81	
	3	29.50	.3807	.27	.19	1.74	
	4	28.24	.3794	.27	.19	1.66	
	5	29.49	(.3857)	.28	.19	1.74	
g	1	33.74	0.9080	0.59	0.26	1.976	$\text{C}_2\text{H}_2(\text{CuCl})_3$
	2	33.53	.4524	.32	.20	1.977	
	3	33.73	.8602	.56	.25	1.977	

In Tables 2 B, D and E the acetylene absorption before the crystallization of the addition compound has been accounted for and the results are found in the *a*-series of the tables. During this stage all acetylene absorbed should remain in the liquid phase. The good agreement between the values in the second and fourth columns confirms equation (5) and its constants.

The equilibrium pressure at 25.0° is independent of the ratio between the solid phases and independent of the composition of the reaction medium, as is shown by an inspection of Tables 2. In the dispersion diagram of Fig. 3 *a*, all accepted measurements are given. There is a significant difference between the means for decomposition, 0.3769 ± 0.0003 atm, and synthesis, 0.3785 ± 0.0005 atm. During the synthesis experiments there is a risk

Table 2 C. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_2(s)$; reaction medium 0.30 *m* HCl, 5.70 *m* HClO_4 ; 25.0° C.

System: 93.60 millimoles CuCl
12.26 g acid mixture

No.	C_2H_2 total	P_A atm	$\text{C}_2\text{H}_2/(\text{CuCl})_2$ total	Substance
b	1	9.66	(0.4205)	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	8.74	(0.3812)	
	3	7.52	0.3775	
	4	6.60	0.3775	
	5	7.76	0.3786	
c	1	19.12	(0.3856)	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	18.16	(0.3782)	
	3	17.10	0.3774	
	4	15.97	0.3762	
	5	17.52	0.3783	
d	1	17.48	(0.4187)	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	26.55	(0.3853)	
	3	25.30	0.3773	
	4	24.12	0.3779	
	5	25.01	0.3790	

for small amounts of gas impurities in some of the experiments and the decomposition values should thus be given preference. But, mainly, the difference seems to be real, the dissimilar shapes of the pressure-time curves of Fig. 2 : III

Table 2 D. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_2(s)$; reaction medium 2 *m* HCl; 25.0° C.

System: 95.5 millimoles CuCl
12.55 g acid with 11.70 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase	
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_2$	Substance
a	1	0.33	0.33	—	0.00	CuCl
	2	0.94	0.92	—	.00	
	3	1.79	1.78	—	.00	
	4	2.54	2.52	—	.00	
	5	2.95	2.93	—	.00	
b	1	18.54	1.06	3.52	1.14	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	17.44	1.04	3.50	1.07	
	3	18.31	1.05	3.51	1.13	
c	1	28.25	1.07	3.52	1.77	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	27.14	1.05	3.51	1.70	
	3	26.03	1.05	3.51	1.63	
	4	27.01	1.05	3.51	1.69	
d	1	32.46	1.83	3.06	1.981	$\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	31.75	1.28	3.27	1.982	
	3	32.07	1.54	3.13	1.982	
	4	32.27	1.71	3.09	1.984	
	5	32.44	1.83	3.06	1.988	

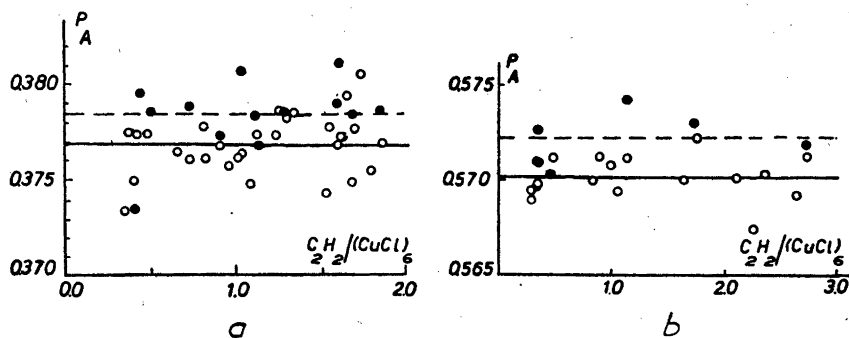


Fig. 3. Dispersion diagrams for the measurements of the equilibrium pressures P_A and P_3 at 25.0° C.

- After synthesis of addition compound
- After decomposition
- a) $C_2H_2 + 3 CuCl (s) = C_2H_2(CuCl)_3 (s)$ P_A
- b) $C_2H_2 + 2 CuCl (s) = C_2H_2(CuCl)_2 (s)$ P_3

also favours this assumption. Probably there are minor variations in the activity of the solid substance. The accepted value for the equilibrium pressure is:

$$P_3 = 0.377 \pm 0.001 \text{ atm.} \quad (\text{at } 25.0^\circ \text{ C})$$

Table 2 E. $CuCl (s) + C_2H_2(CuCl)_2 (s)$; reaction medium 4 m HCl; 25° C.

System: 109.62 millimoles CuCl
14.38 g acid with 12.55 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase		
			C_2H_2	CuCl	$C_2H_2/(CuCl)_2$	Substance	
a	1	0.1255	0.61	—	0.00	CuCl	
	2	0.2762	1.34	—	.00		
	3	0.7534	3.67	—	.00		
	4	1.1064	5.19	—	.00		
b	1	(0.3942)	1.92	11.10	0.46	CuCl +	
	2	0.3750	1.82	10.97	0.40	$C_2H_2(CuCl)_2$	
	3	0.3735	1.82	10.97	0.34		
	4	0.3736	1.82	10.97	0.41		
c	1	(0.4082)	1.99	11.12	1.38		CuCl +
	2	0.3782	1.84	10.99	1.30	$C_2H_2(CuCl)_2$	
	3	0.3774	1.84	10.98	1.24		
	4	0.3786	1.85	10.99	1.29		
d	1	(0.4174)	2.03	11.16	1.93		CuCl + $C_2H_2(CuCl)_2$
	2	0.3770	1.83	10.98	1.87		
	3	0.3756	1.83	10.98	1.80		
	4	0.3787	1.85	10.99	1.86		
e	1	1.1057	3.82	9.92	2.003	$C_2H_2(CuCl)_2$	
	2	0.4654	2.14	10.62	2.010		
	3	0.6469	2.70	10.18	1.998		
	4	36.73	0.9391	3.41	9.94		2.006
	5	37.18	1.1099	3.92	9.92		2.001

Table 2 F. $\text{CuCl} (s) + \text{C}_2\text{H}_2(\text{CuCl})_2 (s)$; reaction medium 2 *m* HCl; 20.0° C.

System: 131.6 millimoles CuCl

a-c 6.895 g acid with 6.43 g water

d-f 12.05 g acid with 11.23 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase	
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_2$	Substance
b 1	11.78	(0.2864)	0.54	1.76	0.52	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2 10.05	0.2653	0.47	1.73	0.44	
	3 11.36	0.2676	0.48	1.73	0.50	
c 1	18.44	(0.2842)	0.51	1.76	0.83	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2 16.75	0.2650	0.47	1.73	0.75	
	3 17.83	0.2677	0.48	1.73	0.80	
d 1	25.28	(0.2842)	0.51	1.76	1.14	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2 20.67	0.2637	0.47	1.73	0.93	
e 1	33.96	(0.2893)	0.90	3.09	1.54	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2 32.08	0.2671	0.83	3.03	1.46	
	3 32.97	0.2718	0.85	3.05	1.50	
f 1	44.76	0.6764	1.64	3.01	2.012	$\text{C}_2\text{H}_2(\text{CuCl})_2$
	2 43.37	0.3035	0.92	3.00	1.981	
	3 43.85	0.4129	1.14	2.95	1.993	
	4 44.27	0.5538	1.42	2.97	2.000	
	5 44.35	0.6848	1.65	3.02	1.993	
	6 44.48	0.8196	1.89	3.09	1.988	
	7 44.61	0.9528	2.11	3.17	1.986	
	8 44.86	1.0803	2.31	3.25	1.990	
	9 45.02	1.1608	2.44	3.30	1.992	
	10 45.13	1.2419	2.56	3.35	1.992	

The composition of the liquid phase has been calculated according to (5) - (7), using the constants $a = 0.0429$; $(A + B \cdot \text{HCl}_l) = 0.235$; $S = 0.207$

In the synthesis experiments of Österlöf¹, a pressure of 0.62 atm was required to effect a conversion of CuCl into $\text{C}_2\text{H}_2(\text{CuCl})_2$ within 24 h at 25° C, which can easily be explained by supersaturation. Decomposition is said to take place at 0.48 atm, and this value is derived from two experiments where the complex $\text{C}_2\text{H}_2(\text{CuCl})_2$ is decomposed at 0.92 and 0.48 atm, $\text{C}_2\text{H}_2(\text{CuCl})_2$ and CuCl respectively resulting. In the CuCl-case a stepwise decomposition was assumed. But even 0.48 atm is considerably higher than the equilibrium pressure. A reasonable explanation seems to be that a direct decomposition has occurred, according to reaction (2) whose equilibrium pressure is 0.57 atm.

The temperature dependence of the equilibrium pressure has been determined in an experiment illustrated by Fig. 4. (The measurements are part of the experiment from which the data of Table 2 F have been taken.) The experiment was performed by varying the temperature without any change in the composition of the system, and has been supplemented by determinations of the vapour pressure of the solvent at different temperatures. The points in the diagram have been numbered according to the experiment; the agreement between the rising and falling series is good. The linear relation can be given by the formula:

$$\log P_3 = \log 0.377 - 2.68 \cdot 10^3 \cdot \left(\frac{1}{T} - \frac{1}{298.2} \right) \quad (8)$$

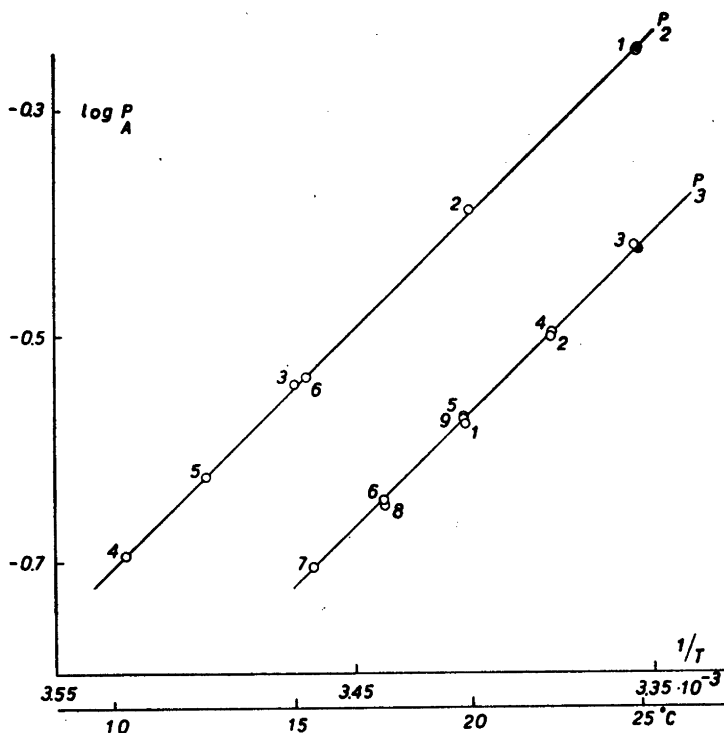


Fig. 4. Temperature dependence of the equilibrium pressures.

P_2 : Reaction $C_2H_2 + 3 CuCl (s) = C_2H_2(CuCl)_3 (s)$; reaction mixture as in Table 2 F; $C_2H_2/(CuCl)_6$ for solid phases about 0.8.

P_3 : Reaction $C_2H_2 + 2 CuCl (s) = C_2H_2(CuCl)_2 (s)$ reaction mixture as in Table 3 C; $C_2H_2/(CuCl)_6$ for solid phases about 0.8.

The dots ● correspond to mean values for other measurements at 25.0° C.

The first term in this expression corresponds to the mean stated above for all measurements at 25.0° while the temperature coefficient has been obtained graphically from the diagram.

The composition of the complex formed is given by the quotient, $C_2H_2/(CuCl)_6$, which after complete conversion reaches values very close to the theoretical one, i.e. 2.000. The composition of the addition compound is established with an accuracy better than 1%.

The coinciding equilibrium pressures of experiments 2 A and 2 B show that hydrochloric acid does not enter into the compound. The reaction medium consists of 4 m mixtures of hydrochloric and perchloric acid, with a hydrochloric acid concentration of 0.20 m (2 B) and 0.87 m (2 A). A comparison between experiments 2 D and E, where the medium consists of hydrochloric acid of different concentrations, gives the same result. Water, also, can be excluded, as appears very clearly from a comparison between Tables 2 C and 2 D where the media are 0.3 m HCl—5.7 m $HClO_4$, and 2 m HCl solely. The

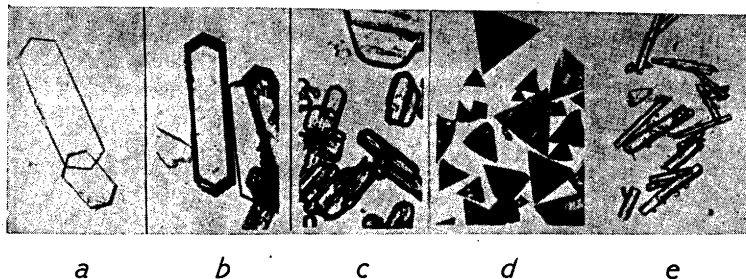


Fig. 5. Crystals of $C_2H_2(CuCl)_3$, $CuCl$ and $C_2C_2(CuCl)_2$.

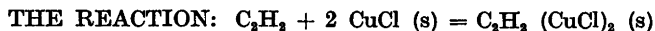
- a) $C_2H_2(CuCl)_3$, freshly formed, 185 ×
 b) —»— after 24 h undisturbed, growth, 90 ×
 c) —»— after equilibrium experiment with prolonged brisk shaking, 45 ×
 d) $CuCl$, formed by decomposition of $C_2H_2(CuCl)_3$, 50 ×
 e) $C_2H_2(CuCl)_3$, freshly formed, 60 ×

activity of H_2O is approximately 20 % less in the firstmentioned system, but the equilibrium pressures agree within 0.5 %; consequently the compound formed does not contain water, anyway not in an appreciable molar amount.

A microscopical examination shows that the addition compound $C_2H_2(CuCl)_3$ is well crystallized, but after an equilibrium experiment the crystals have been rather abraded by the shaking — cf. Fig. 5 c. In experiments without or with only slight shaking, the freshly formed crystals are as a rule thin six-sided plates with edge angles of nearly 60° — cf. Fig. 5 a. They show, however, a double refraction (with extinction parallel to the long edge) even under perpendicular light and thus are only pseudo-hexagonal. After about 25 h the plates grow thicker and assume a shape — cf. Fig. 5 b — which makes an orthorhombical symmetry seem most likely.

Earlier powder X-ray photographs¹, indicating a preservation of the $CuCl$ -structure in $C_2H_2(CuCl)_3$ must be misleading, since optical double refraction is incompatible with cubic symmetry. Probably a surface layer of cuprous chloride has formed during the exposure. Later x-ray investigations by another technique have shown interferences different from those of $CuCl$.

More complete information on crystallographic data will be given in a separate paper.



The direct conversion of cuprous chloride into the complex $C_2H_2(CuCl)_2$ has occurred spontaneously in most of the experiments. Only in the experiment corresponding to Table 3 C was the reaction initiated by seeding which was effected by adding a small amount of acid mixture containing a suspension of $C_2H_2(CuCl)_2$, prepared in a stepwise synthesis according to reactions (1) and (3). The addition causes a rapid pressure drop from the original 0.80 atm to the pressure of b 1 0.57 atm.

Generally the measurements pertaining to this reaction are interrupted by crystallization of the stable complex, $C_2H_2(CuCl)_3$. Often the supersaturation

Table 3 A. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_2(s)$, reaction medium 0.865 m HCl, 3.135 m HClO_4 ; 25.0° C.

System: 100.4 millimoles CuCl
18.89 g acid mixture with 14.03 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase		
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_6$	Substance	
a	1	0.25	0.1315	0.25	—	0.00	CuCl
	2	0.66	0.3363	0.65	—	.00	
	3	1.22	0.6269	1.21	—	.00	
	4	1.53	0.7862	1.52	—	.00	
	5	1.89	0.9715	1.88	—	.00	
	6	2.10	1.0754	2.08	—	.00	
b	1	9.88	(0.6116)	1.18	1.61	0.53	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	8.49	(0.5726)	1.11	1.56	0.45	
	3	7.09	0.5698	1.10	1.56	0.36	
	4	5.72	0.5697	1.10	1.56	0.28	
	5	6.99	0.5727	1.11	1.56	0.36	

Experimental data see Table 1.

ceased before it was possible to take any readings. One then only observes that the falling pressure-time curve pauses for a longer or shorter period at 0.57—0.60 atm (25.0° C) and then drops to the vicinity of 0.377 atm, *i.e.* the equilibrium pressure for reaction (1). The crystallization of $\text{C}_2\text{H}_2(\text{CuCl})_3$ is usually initiated by the momentary pressure increase upon the addition of acetylene, but it has occurred also that the supersaturation has ceased on de-

Table 3 B. $\text{CuCl}(s) - \text{C}_2\text{H}_2(\text{CuCl})_2(s)$, reaction medium 0.2 m HCl, 3.8 m HClO_4 ; 25.0° C.

System: 73.18 millimoles CuCl
10.62 g acid mixture with 7.65 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase		
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_6$	Substance	
a	1	0.11	0.1766	0.11	—	0.00	CuCl
	2	0.23	0.3551	0.23	—	.00	
	3	0.43	0.6954	0.44	—	.00	
	4	0.75	1.1782	0.75	—	.00	
b	7.43	(0.6140)	0.39	0.91	0.58	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$	
c	1	27.20	(0.6321)	0.40	0.92		2.23
	2	25.95	0.5702	0.36	0.90	2.12	
d	1	34.83	(0.6123)	0.39	0.91	2.86	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	33.41	0.5712	0.36	0.90	2.74	
	3	32.22	0.5692	0.36	0.90	2.64	
	4	33.05	0.5718	0.36	0.90	2.71	
e	1	36.67	1.1869	0.67	0.73	2.980	$\text{C}_2\text{H}_2(\text{CuCl})_2$
	2	36.35	0.6437	0.40	0.86	2.983	
	3	36.41	0.7395	0.44	0.82	2.983	
	4	36.55	0.9928	0.57	0.76	2.981	

Table 3 C. $\text{CuCl} (s) - \text{C}_2\text{H}_2(\text{CuCl})_2 (s)$, reaction medium 0.30 m HCl, 5.70 m HClO_4 ; 25.0° C.

System: 90.23 millimoles CuCl
10.77 g acid mixture

No.	C_2H_2 total	P_A atm	$\text{C}_2\text{H}_2/(\text{CuCl})_2$ total	Substance
b 1	6.36	(0.5733)	0.42	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	5.22	0.5708	0.35	
3	4.15	0.5690	0.28	
4	5.41	0.5710	0.36	
c 1	14.65	(0.6203)	0.97	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	13.52	0.5712	0.90	
3	12.38	0.5700	0.82	

Table 3 D. $\text{CuCl} (s) - \text{C}_2\text{H}_2(\text{CuCl})_2 (s)$, reaction medium 2 m HCl; 25.0° C.

System: 53.18 millimoles CuCl
8.69 g acid with 8.10 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase	
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_2$	Substance
b 1	6.30	(0.6008)	1.15	2.78	0.61	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	5.14	0.5712	1.09	2.74	0.48	
3	3.93	0.5697	1.09	2.73	0.34	
4	4.99	0.5704	1.09	2.74	0.46	
c 1	11.07	(0.6112)	1.17	2.80	1.18	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	9.51	0.5709	1.09	2.74	1.00	
d 1	14.83	(0.6103)	1.17	2.80	1.63	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
e 1	17.16	(0.6290)	1.20	2.83	1.90	
2	15.93	0.5723	1.10	2.74	1.76	
3	14.69	0.5701	1.09	2.73	1.62	
4	15.63	0.5731	1.09	2.74	1.73	
f 1	27.15	1.1139	1.63	2.58	3.027	$\text{C}_2\text{H}_2(\text{CuCl})_2$
2	26.62	0.6532	1.18	2.68	3.021	
3	26.86	0.8068	1.35	2.62	3.026	
4	27.02	0.9431	1.48	2.59	3.030	
5	27.21	1.2491	1.74	2.58	3.021	

Table 3 E. $\text{CuCl} (s) - \text{C}_2\text{H}_2(\text{CuCl})_2 (s)$, reaction medium 3 m HCl; 25.0° C.

System: 94.13 millimoles CuCl
10.76 g acid with 9.70 g water

No.	C_2H_2 total	P_A atm	Liquid phase		Solid phase	
			C_2H_2	CuCl	$\text{C}_2\text{H}_2/(\text{CuCl})_2$	Substance
b 1	19.97	(0.6183)	1.86	6.00	1.23	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	18.70	0.5711	1.72	5.87	1.15	
3	17.28	0.5694	1.72	5.87	1.06	
4	18.50	0.5742	1.74	5.91	1.14	
c 1	37.63	(0.6210)	1.87	6.00	2.43	CuCl + $\text{C}_2\text{H}_2(\text{CuCl})_2$
2	36.07	0.5704	1.72	5.87	2.34	
3	34.80	0.5673	1.71	5.85	2.25	

creasing the pressure or after a period when the pressure has been constant for some time. Normally the crystallization of $C_2H_2(CuCl)_3$ causes a pressure drop, but in experiment 3 E we observed the somewhat paradoxical phenomenon that the system shifted to a more stable state with a spontaneous pressure increase. The explanation is that the total amount of acetylene present is so large — $C_2H_2/(CuCl)_3 > 2$; cf. Fig 6 — that the formation of $C_2H_2(CuCl)_3$ consumes all $CuCl$ while $C_2H_2(CuCl)_2$ is still present. Thus both complexes will be present as solid phases and the pressure therefore rises towards that value which characterizes equilibrium (3) at 25.0° C.

If one disregards the practical inconveniences arising from the instability of the equilibrium, the measurements on this reaction are experimentally very satisfactory. The equilibria are reached somewhat slower than in reaction (1), but rapidly enough to render disturbances from by-reactions etc. negligible.

In Table 3 A are given the results corresponding to the two first stages of the type experiment. The *a*-series contains values for the acetylene absorption before the formation of addition compound; the agreement between the measured absorption (second column) and the absorption calculated according to (5 a) (fourth column) is quite satisfactory also in this case. Series *b* comprises the equilibrium measurements which correspond to the pressure-time curves of Fig. 2 : II. The other experiments, referring to this reaction at 25.0° C, are likewise summarized in Tables 3 B—E; in Table 3 C, however, information is lacking concerning the composition of the liquid phase.

The equilibrium pressure at 25.0° C is independent of the ratio between the solid phases and independent of the reaction medium. In Fig. 3 b the accepted measurements are summarized. The means for the decomposition pressures are 0.5702 ± 0.0003 and for the synthesis pressures 0.5722 ± 0.0006 . The accepted value for the equilibrium pressure is:

$$P_2 = 0.571 \pm 0.001 \text{ atm} \quad (\text{at } 25.0^\circ \text{ C})$$

The temperature dependence of the equilibrium pressure has been determined in the experiment illustrated by Fig. 4. The procedure has been the same as described for the corresponding experiment in the preceding section. It is evident that the agreement between the rising and the falling series is satisfactory. After the sixth measurement the experiment is interrupted by crystallization of $C_2H_2(CuCl)_3$. The temperature dependence is expressed by

$$\log P_2 = \log 0.571 - 2.60 \cdot 10^3 \cdot \left(\frac{1}{T} - \frac{1}{298.2} \right) \quad (9)$$

The composition of the complex can be determined after complete conversion, but the synthesis procedure must give evidence that no crystallization of $C_2H_2(CuCl)_3$ has occurred. To achieve this, one should follow the dotted horizontal line of Fig. 6 as far as possible before going over to measurements on the vertical branch. Only in two experiments, Tables 3 B and D, it has been possible to carry the experiment to complete conversion in this way. To diminish the risk of crystallization of $C_2H_2(CuCl)_3$ the duration of the experiment has been kept as short as possible. In order to save time, some series of

readings, *e.g.* *b* and *c* in Table 3 B are incomplete and aim only at checking that supersaturation still exists.

The empirical composition, resulting from these measurements, agrees within 1 % with the theoretical. The fact that the equilibrium pressure is independent of the reaction medium shows that no other components except C_2H_2 and $CuCl$ enter into the compound.

Under the microscope is observed that samples of $C_2H_2(CuCl)_2$ which have not been subjected to violent shaking consist of needle-shaped crystals, double-refracting with parallel extinction — *cf.* Fig. 5 e. They can easily be distinguished from crystals of $C_2H_2(CuCl)_3$, *cf.* Fig. 5 a and b, and from the characteristic single-refracting tetrahedrons of cuprous chloride, *cf.* Fig. 5 d.



When calculating the equilibrium pressure $P_{2,3}$ for this reaction from the values for P_2 and P_3 by inserting (8) and (9) in (4), the following expression results:

$$\log P_{2,3} = \log 1.31 - 2.44 \cdot 10^3 \left(\frac{1}{T} - \frac{1}{298.2} \right) \quad (10)$$

Applying the earlier stated errors in the P_2 - and P_3 -values at 25° C, the $P_{2,3}$ value for this temperature will have an accuracy corresponding to 1.31 ± 0.01 atm. Expression (4) presupposes an ideal gas. The deviation of acetylene from ideal compressibility — *cf.* p. 536 — can be accounted for by including in the expression the approximate correction factor $1 + k \cdot (3 P_2 - 2 P_3 - P_2^3/P_3^2)$. At 25.0° C the correction amounts to + 0.003 atm and may be neglected.

The direct measurement of $P_{2,3}$ does not give quite satisfactory results. The equilibria are approached substantially slower than in the other two reactions. The time curves of Fig. 2 : IV are typical. (Note that the scales differ from the other diagrams of Fig. 2.) Initially the reaction proceeds quite rapidly, but after 5—10 h a stage enters in which the pressure change takes place with a low but almost constant speed. After successive withdrawals of acetylene time curves are obtained which do not coincide but seem to be parallelly displaced towards lower pressures. (A similar displacement occurs in the other equilibrium measurements as a result of successive removals of gas impurities. In the present case the effect is, however, more pronounced and cannot be attributed to gas impurities.) The parallel displacement need however not indicate that the unattained final values of the curves are different.

One has the impression that the reaction velocity during the later, slow stage of the conversion is particularly low if the duration of the experiment has been very long. (In some prolonged experiments, not described here, the reaction velocities are still lower; also the parallel displacement of the decomposition curves is more marked.) Therefore the duration of the experiments has been limited and the reading of the time curves was in some cases interrupted before the velocity of the pressure change had dropped so much that interferences from by-reactions etc. could be feared.

Table 4 A. $C_2H_2(CuCl)_3(s) - C_2H_2(CuCl)_2(s)$, reaction medium 0.865 *m* HCl, 3.135 *m* HClO₄

System: 100.4 millimoles CuCl
18.89 g acid mixture with 14.03 g water

No.	Temp.	C ₂ H ₂ total	P _A atm	C ₂ H ₂ /(CuCl) ₆ total	Liquid phase		Solid phase	
					C ₂ H ₂	CuCl	C ₂ H ₂ /(CuCl) ₆	Substance
f 1	10.0	35.09	0.8864	2.10	—	—	—	C ₂ H ₂ (CuCl) ₃
2		34.54	0.4969	2.06	—	—	—	
3		34.94	0.7678	2.08	—	—	—	
4		35.20	0.9597	2.10	—	—	—	
5		35.64	1.2650	2.13	—	—	—	
g 1	10.0	42.18	(0.528)	2.52	—	—	—	C ₂ H ₂ (CuCl) ₃ + C ₂ H ₂ (CuCl) ₂
2		40.71	0.494	2.43	—	—	—	
3		39.21	0.488	2.34	—	—	—	
4		40.44	0.525	2.41	—	—	—	
h 1	10.0	48.06	(0.575)	2.87	—	—	—	C ₂ H ₂ (CuCl) ₃ + C ₂ H ₂ (CuCl) ₂
2		46.90	0.489	2.80	—	—	—	
3		45.69	0.481	2.73	—	—	—	
4		44.28	0.473	2.64	—	—	—	
5		45.44	0.512	2.71	—	—	—	
i 1	10.0	51.32	1.0858	3.06	—	—	—	C ₂ H ₂ (CuCl) ₂
2		50.84	0.6444	3.04	—	—	—	
3		51.01	0.7827	3.05	—	—	—	
4		51.22	0.9509	3.06	—	—	—	
5		51.49	1.1673	3.08	—	—	—	
k 1	25.0	51.29	1.2453	3.06	1.90	1.63	2.999	C ₂ H ₂ (CuCl) ₂
2		51.17	1.1242	3.06	1.77	1.61	2.999	
3		51.02	0.9699	3.05	1.59	1.58	3.001	
m 1	10.0	51.65	1.1540	3.04	—	—	—	C ₂ H ₂ (CuCl) ₂
2		51.46	0.9790	3.08	—	—	—	

Experimental data see Table 1.

In Table 4 A are given the results from the type experiment. The composition of the system before the lowering of the temperature from 25.0° to 10.0° is evident from Table 2 A, *e* 1—4, which shows that C₂H₂(CuCl)₃ is the sole solid phase. A lower temperature is necessary if the crystallization of C₂H₂(CuCl)₂ is to be initiated by a moderate acetylene pressure. Data for the calculation of the composition of the liquid phase at 10° are missing; in the fourth column the quotient, C₂H₂/(CuCl)₆, is given for the whole system, including both liquid and solid phases. In the equilibrium measurements, moments *g* 2—4 and *h* 2—5, the five decomposition pressures vary from 0.473 atm to 0.494 and the two synthesis pressures are 0.512 and 0.525 atm. The pressure which can be calculated from (10) is 0.482 atm.

There is no difference of importance between the *g*- and *h*-series and the experiment thus indicates that the pressure is independent of the molar ratio of the solid phases.

Table 4 B. $C_2H_2(CuCl)_3(s) - C_2H_2(CuCl)_2(s)$, reaction medium 2 m HCl; 20.0° C.

System: 131.6 millimoles CuCl
12.05 g acid with 11.23 g water

No.	C_2H_2 total	P_A atm	$C_2H_2/(CuCl)_2$ total	Liquid phase		Solid phase	
				C_2H_2	CuCl	$C_2H_2/(CuCl)_2$	Substance
g 1	51.5	(1.022)	2.35	—	—	—	$C_2H_2(CuCl)_3$ +
	49.3	0.977	2.25	—	—	—	
	50.1	1.007	2.29	—	—	—	
h 1	55.2	(1.011)	2.52	—	—	—	$C_2H_2(CuCl)_3$ +
	53.1	0.944	2.42	—	—	—	
	54.4	0.974	2.48	—	—	—	
i 1	56.3	(1.048)	2.57	—	—	—	$C_2H_2(CuCl)_3$ +
	53.5	0.960	2.44	—	—	—	
	52.6	0.964	2.40	—	—	—	
	53.7	1.002	2.45	—	—	—	
k 1	60.5	(1.051)	2.76	—	—	—	$C_2H_2(CuCl)_3$ +
	57.9	0.946	2.64	—	—	—	
	55.9	0.923	2.55	—	—	—	
	57.2	0.967	2.61	—	—	—	
m 1	63.1	(1.035)	2.88	—	—	—	$C_2H_2(CuCl)_3$ $C_2H_2(CuCl)_2$
	61.5	0.930	2.81	—	—	—	
	60.4	0.924	2.76	—	—	—	
	60.9	0.972	2.78	—	—	—	
n 1	67.6	1.532	3.09	2.81	3.27	3.03	$C_2H_2(CuCl)_2$
	67.0	0.980	3.06	2.12	3.15	3.03	
	67.4	1.364	3.08	2.61	3.22	3.03	

In Table 4 B are found the results from equilibrium measurements at 20.0° with a medium of 2 m hydrochloric acid. The experiment is a continuation of the one included in Table 2 F. Here too the crystallization has been initiated by a pressure rise at a lower temperature, which was then again raised to 20.0° before the measurements. The mean of the decomposition pressures is 0.946 ± 0.008 and the mean of the synthesis pressures 0.984 ± 0.009 . It seems permissible to draw the conclusion that the correct equilibrium pressure must lie within the interval 0.96 ± 0.02 , which is in good agreement with the value of 0.95 ± 0.01 calculated according to (10).

The composition of the complex formed can be stated without difficulties in this case also. If the pressure is sufficiently increased beyond the equilibrium pressure there is a complete conversion. And in systems with one single solid phase the equilibrium is attained rather quickly after addition and removal of acetylene. In Table 4 A, mom. *i* 1—5, the measurements of the acetylene absorption after complete conversion at 10.0° are given. The temperature is then raised to 25.0° and, from the measurements *k* 1—3, the composition of the solid phase can be computed exactly. The pressure prevailing in the *k*-series is lower than $P_{2,3}$ at 25° and the system thus is supersaturated with regard to $C_2H_2(CuCl)_3$. The circumstance that no crystallization of this substance occurs until the end of moment *k* 3 — see end of account of type experiment — further emphasizes that the earlier conversion was complete.

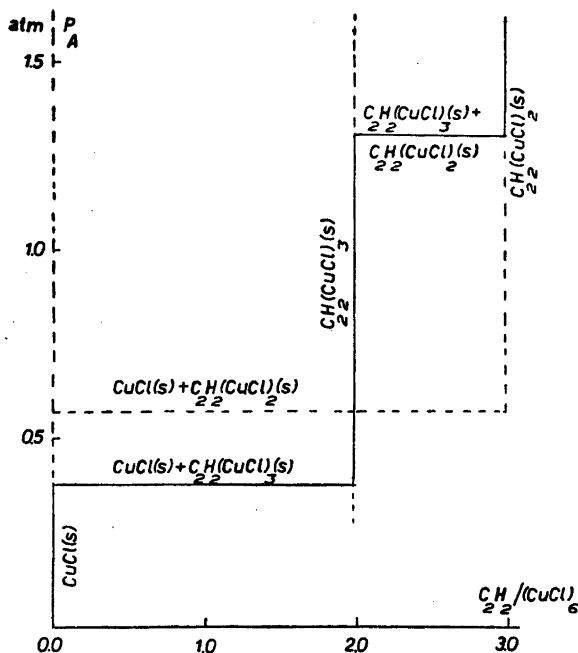


Fig. 6. Phase diagram for the system $C_2H_2 + CuCl$ at $25.0^\circ C$.
Dotted lines indicate measurable metastable states.

The results from this experiment and the corresponding series, n 1—3, of Table 4 B show that the composition of the compound formed agrees with $C_2H_2(CuCl)_2$ within 1 %.

THERMODYNAMIC DATA

The formulae (9), (10) and (11) give the following thermodynamic data for the three reactions at $25.0^\circ C$.

Acetylene at atmospheric pressure is chosen as the standard state for acetylene.

Reaction	ΔG° cal	ΔH° kcal	ΔS° cal/degree
$C_2H_2 + 3 CuCl(s) = C_2H_2(CuCl)_3(s)$	-575 ± 2	-12.23	-39.1
$C_2H_2 + 2 CuCl(s) = C_2H_2(CuCl)_2(s)$	-330 ± 1	-11.85	-38.6
$C_2H_2 + 2 C_2H_2(CuCl)_3(s) = 3 C_2H_2(CuCl)_2(s)$	$+160 \pm 4$	-11.1	-37.7

For the determination of these data, the non-ideal compressibility of acetylene has been corrected for by computation of ΔG_n° and ΔH_n° for the first two reactions according to the approximate formulae $\Delta G_n^\circ/RT = \ln P_n + k(P_n - 1)$ and $\Delta H_n^\circ/R = (1 + k \cdot P_n) \cdot d \ln P_n/d(1/T)$ where k , according to p. 536, equals $-7 \cdot 10^{-3} (\text{atm})^{-1}$. However, the corrections amount only to +3 cal for ΔG_1° , +2 cal for ΔG_2° , and -0.03 and -0.05 kcal for the corresponding ΔH° -values and are thus of the same magnitude as the errors in these values. The remaining data are derived from the thus corrected values.

The connection between the three reactions is illustrated by the phase diagram of Fig. 6 which shows the equilibrium pressures at 25.0° C as functions of the composition of the mixture of the solid phases, as expressed by the quotient $C_2H_2/(CuCl)_6$.

The mole entropy S_{25}° for solid cuprous chloride is stated by Watanabe ⁶ to be 20.66 cal/degree; the best value for acetylene is 48.029, given by Gordon ⁷. Using the ΔS° values given above the results are

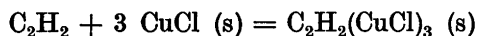
$$\begin{aligned} \text{for } C_2H_2(CuCl)_3 (s) : S_{25}^\circ &= 70.9 \text{ cal/degree} \\ \text{for } C_2H_2(CuCl)_2 (s) : S_{25}^\circ &= 50.7 \text{ cal/degree} \end{aligned}$$

SUMMARY

1. The stoichiometrical composition of two solid compounds between acetylene and cuprous chloride has been determined by manometrical experiments, measuring the quantity of acetylene required for a complete conversion of a given amount of cuprous chloride.

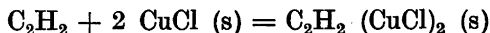
The composition agrees within 1 % with the formulae $C_2H_2(CuCl)_3$ and $C_2H_2(CuCl)_2$ respectively, which were suggested by Österlöf in the first paper ¹ of this series.

2. The equilibrium pressure for the reaction



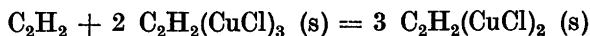
has been determined between 15.0° and 25.0° C and is given by formula (8). Its value at 25.0° is 0.377 ± 0.001 atm.

3. The metastable equilibrium



can be measured with good accuracy, although the system is supersaturated with regard to $C_2H_2(CuCl)_3 (s)$. The results at 10.0°—25.0° are given by (9). At 25.0° C the equilibrium pressure is 0.571 ± 0.001 atm.

4. The equilibrium



can be calculated from these data; direct measurements agree with the computed values.

5. Thermodynamic data for the reactions and mole entropies for the solid compounds have been calculated.

6. Both compounds are colourless and crystalline. In contrast with cuprous chloride they show optical double refraction and their structure thus is non-isometric.

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