

Kinetics and Mechanism of Acetylene Hydrochlorination Catalyzed by Cuprous Complexes in Solution

IV.* Catalyst Solution in Equilibrium with Solid Cuprous Chloride. Determination of the Reaction Order in Acetylene

RAGNAR VESTIN, TORBJÖRN LINDBLOM and
BENGT WAHLUND

*Institute of Inorganic and Physical Chemistry (Catalytical Laboratory), Stockholm University,
Stockholm, Sweden*

We aim at an analysis of the velocity function

$$\frac{dB}{dt} = F_{sc}(HCl_t, A_d)$$

where B stands for formed vinyl chloride (in moles per unit amount of catalyst) and where the hydrogen chloride concentration HCl_t and the total concentration of dissolved acetylene A_d appear as independent variables. In the preceding paper the following two steps were accomplished:

a) For every pair of values in the pressure time curve we compute the quantity

$$\kappa_c = \frac{1}{t} \int_0^t \frac{dB}{A_d}$$

which constitutes the time mean of the quotient $f_c = F_{sc}/A_d$. The quantity κ_c shows a consequent decrease of 4-6 % during the conversion - thus f_c decreases too.

b) A graphic extrapolation method is described for determination of the value κ_c^0 corresponding to the initial value HCl_t^0 .

In this part the analysis is finished by the following steps:

c) κ_c^0 -values from experiments with different HCl_t^0 give an approximate relation between f_c and HCl_t showing that the moderate f_c -changes during a given experiment can be represented by the formula $f_c = f_c^0(1 - \rho B)$.

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d) For every read P/t pair of values f_c^0 is computed according to

$$f_c^0 = \frac{1}{t} \int_0^t \frac{dB}{A_d(1-\rho B)}$$

Within each single experiment these values show a good constancy. No noticeable dependence on the conversion degree can be traced and the dispersion is no greater than corresponds to the primary observation errors.

For the present we accept the conclusion that according to the hypothesis the quantity f_c is independent of A_d within the examined HCl_t - and A_d -intervals. Thus the rate function can be written:

$$\frac{dB}{dt} = A_d \cdot f_c(HCl_t)$$

The velocity dB/dt of the vinyl chloride formation in this system is determined by two primary variables related to HCl and C_2H_2 . The manometric experiments give velocity data of a very high accuracy but they have the inconvenience of not separating the variables sharply. When we follow the consumption of added acetylene and the equimolar formation of vinyl chloride in a closed system the HCl concentration does not remain exactly constant. It is true that HCl_t changes only some few percent but the reaction velocity is strongly dependent on HCl_t , so the effect can readily be noticed.

By using the total concentration of dissolved acetylene A_d as a primary kinetic variable the difficulty will diminish as the reaction velocity is less dependent on HCl_t at constant A_d than at constant P_A .

In the preceding paper we introduced a method of determining the limit value κ_c^0 that gives a rather accurate value of the constant f_c at the initial value HCl_t^0 . Hence, every experiment contributes only one f_c -value but a comparison between some experiments with identical HCl_t^0 but different A_d^0 preliminarily verifies the hypothesis that the f_c quantity is independent of A_d .

For a final treatment of the hypothesis we will investigate whether f_c remains constant within each individual experiment where large A_d -changes occur — from the initial value A_d^0 down to some percent thereof. A correction for the influence of the HCl consumption can be accomplished from the approximate relation between f_c and HCl_t that is obtained from the κ_c^0 -values.

Although we have asked for an "approximate" f_c-HCl_t relation only, a certain claim to accuracy must be upheld. The task is — generally speaking — to "correct" for a trend that amounts to *ca.* 5 % with 0.1 % precision kept.

Originally we planned an iteration procedure for a successive improvement of the approximate f_c-HCl_t -relation. As will be found in the following the κ_c^0 -values are accurate enough and a further step is not necessary.

SYMBOLS

$$\varrho = \frac{d\kappa_c^0}{dHCl_t^0} \cdot \frac{1}{\kappa_c^0} ;$$

$$\varrho' = A_{00} \cdot \varrho$$

$$I_f = \int_0^{\Gamma} \frac{dB}{A_d \cdot \Gamma} ;$$

$$f_c^0 = (I_f - I_f^0)/t$$

$$\Gamma = f_c/f_c^0, \text{ approx. determined as } d \ln \kappa_c^0 / dHCl_t^0$$

See also the symbol definitions in the earlier papers of this series.

AN APPROXIMATE RELATION BETWEEN f_c AND HCl_t

In the preceding paper we have determined by graphic extrapolation the quantities κ_c^0 for the experiments 11 and 14 with $HCl_t^0 = 7.25$ m and 9.1 m,

Table 1. Extrapolated κ_c^0 -values. Computation of the correction factor ϱ' and the constants b_3 and c_3 for (13).

HCl_t m	Note	Expt. No.	κ_c^0 h^{-1}	$-b_3 \ln 10$	$c_3 \ln 10$	ϱ'
5.53	—	9	0.0262	0.274	3.25	0.0579
6.50	—	10	0.0361	0.460	3.65	758
7.25	—	11	0.0437	0.426	3.43	662
7.94	—	7	0.0514	0.723	3.97	679
8.57	—	12	0.0583	0.518	3.41	523
9.05	P_0 170 mm	5	0.0638	1.004	4.24	402
9.06	P_0 305 mm	6	0.0637	1.020	4.40	732
9.05	P_0 461 mm	13	0.0636	1.051	4.59	0.1092
9.10	—	14	0.0645	0.928	4.17	685
10.05	—	15	0.0756	1.076	4.25	634

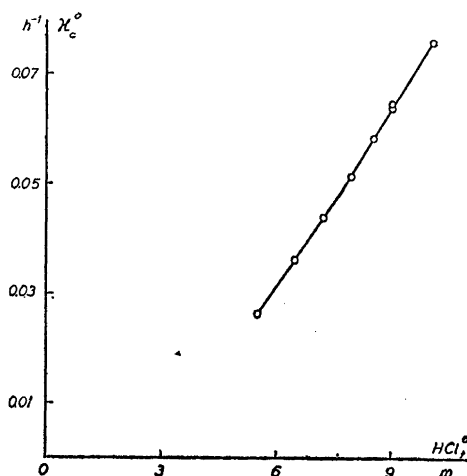


Fig. 1. The quantity κ_c^0 as a function of HCl_t^0 , i.e. the f_c - HCl_t relation required in the first approximation.

respectively. The same method has been applied on data from other experiments within the interval $5.5 < HCl_t < 10.1$ m — see Table 1. Fig. 1 shows κ_c^0 as a function of HCl_t^0 . The relation is far from proportional but rather linear. But a closer examination of the figure in enlarged scale shows a distinct positive curvature presumably highest in the interval $7.3 < HCl_t < 7.9$ m. One gets the impression that the curve consists of two branches, each with a slight or no curvature, with their common point within the interval mentioned.

The approximate relation between f_c and HCl_t obtained in this way can be used for derivation of a simple algebraic function representing the f_c -changes which are caused by the HCl consumption in an individual experiment. It is an advantage that the peculiar functional relation between f_c and HCl_t is so close to a linear one in the actual HCl_t interval. Thus the following expression is sufficiently accurate

$$f_c = f_c^0 + \frac{df_c}{dHCl_t} \cdot \Delta HCl_t \quad (1)$$

The graphically determined quantity $df_c/dHCl_t^0$ can be substituted for the derivative. We introduce the quotient function Γ and put $\Delta HCl_t = -B$ which gives

$$\Gamma(HCl_t^0, B) = f_c/f_c^0 = 1 - \rho B \quad (2)$$

The constant ρ has been obtained by division of the graphically determined derivative by κ_c^0 .

DETERMINATION OF THE KINETIC CONSTANT f_c^0

Starting from the primary rate expression and the f_c definition according to:

$$\begin{cases} \frac{dB}{dt} = F_{sc}(HCl_t, A_d) \\ f_c = \frac{F_{sc}(HCl_t, A_d)}{A_d} \end{cases} \quad (3)$$

and using the formula (2) we get:

$$\frac{dB}{dt} = A_d \cdot f_c(HCl_t^0) \cdot \Gamma(HCl_t^0, B) \quad (4)$$

Here we — according to the main hypothesis — test the assumption that f_c is a pure HCl_t -function. With separated variables and simplified designations the relation can be written

$$\frac{dB}{A_d \cdot \Gamma} = f_c^0 \cdot dt \quad (5)$$

The quantity f_c^0 is now calculated for every read couple of values P/t according to:

$$f_c^0 = \frac{1}{t} \int_0^t \frac{dB}{A_d \cdot \Gamma} \quad (6)$$

Algebraic and numerical treatment. If the conversion degree Y is introduced as a variable in the Γ -function (2) we get the expression:

$$\Gamma = 1 - \rho' Y \quad (7)$$

which describes the Γ -changes during a given experiment. The quantity

$$\rho' = A_{00}\rho \quad (8)$$

is regarded as a constant with numerical values from Table 1.

If we introduce the differential $dB = A_{00} \cdot dY$ in the f_c -definition (6) the task is now to compute

$$f_c^0 = \frac{1}{t_0} \int \frac{A_{00} \cdot dY}{A_d \cdot \Gamma} \quad (9)$$

The quotient $A_{00}/A_d \cdot \Gamma$ that occurs here can be expressed as a Y -function of the form

$$\frac{A_{00}}{A_d \Gamma} = a_1(1-Y)^{-1}(1-\rho' Y)^{-1} - b_1(1-\gamma' Y)^{-1}(1-\rho' Y)^{-1} \quad (10)$$

where $a_1 = \frac{A_{00}}{A_{00} - \rho_g P_{00}} \left(1 + \frac{\rho_g P_{00}}{A_{00}} \cdot \frac{\gamma'}{1-\gamma'} \right)$

$$b_1 = \frac{\rho_g P_{00}}{A_{00} - \rho_g P_{00}} \cdot \frac{\gamma'}{1-\gamma'}$$

$$\gamma' = \frac{\rho A_{00}}{A_{00}/P_{00} - \rho_g}$$

After a subdivision in partial fractions and term "splitting" according to the same principles as in (III-15) we obtain

$$\frac{A_{00}}{A_d \Gamma} = a_2(1-Y)^{-1} + b_3 \gamma' [(1-Y)^{-1} - (1-\gamma' Y)^{-1}] + c_3 \rho' [(1-Y)^{-1} - (1-\rho' Y)^{-1}]$$

where $a_2 = A_{00}/(A_{00} - \rho_g P_{00}) = n_t/(n_t - \Phi_g P_{00})$ (11)

$$b_3 = \frac{\rho_g P_{00}}{A_{00} - \rho_g P_{00}} \cdot \frac{\gamma'}{\gamma' - \rho'} \cdot \frac{1}{1-\gamma'}$$

$$c_3 = \frac{1}{1-\rho'} \left\{ 1 + \frac{\rho_g P_{00}}{A_{00} - \rho_g P_{00}} \cdot \frac{\rho'}{\rho' - \gamma'} \right\}$$

or $c_3 = \frac{a_2 - b_3(1-\gamma')}{1-\rho'}$

Here, as in (III-14), the quantities A_{00} and ρ_g occur in the constants b_3 and c_3 in such a way that they can be simultaneously replaced by the corresponding absolute quantities n_t and Φ_g .

The integral

$$I_t = \int_0^1 \frac{dB}{A_d \Gamma} = \int_0^1 \frac{A_{00} \cdot dY}{A_d \Gamma} \quad (12)$$

which is obtained directly from (11) gets the form

$$\left\{ \begin{array}{l} I_f = -a_2 \ln(1-Y) + b_3 R(\gamma', Y) + c_3 R(\varrho', Y) \\ \text{with the "correction functions"} \\ R(\gamma', Y) \equiv \ln(1-\gamma'Y) - \gamma' \ln(1-Y) \\ R(\varrho', Y) \equiv \ln(1-\varrho'Y) - \varrho' \ln(1-Y) \end{array} \right. \quad (13)$$

The constants a_2 , b_2 , and c_3 are the same as in (11). The conversion degree Y is computed from the read P -value (and constants) according to (III-10).

Finally f_c^0 is obtained from

$$f_c^0 = \frac{I_f - I_f^0}{t} \quad (14)$$

where I_f^0 stands for the I_f -value at $t = 0$.

The result of such a calculation appears from Table 2 with data from experiment No. 11. It is evident from the table that f_c^0 shows a good constancy within the experiment; the differences between the f_c^0 values are regularly small also compared with the dispersion — stated in the last column of the table — which can be predicted from the observation errors in P .

Table 2. Computation of I_f and f_c^0 . Experiment 11.

Y %	$-a_2 \ln(1-Y)$	$-b_3 R(\gamma'Y)$	$c_3 R(\varrho'Y)$	I_f	$10^2 f_c^0$ h^{-1}
0.23	0.0028	0.0000	0.0000	0.0028	—
5.85	729	0	0	729	4.38 ± 0.04
8.64	1093	0	3	1096	4.40 ± 3
16.16	2133	1	14	2146	4.335 ± 15
17.43	2317	1	17	2333	4.369 ± 14
18.69	2504	1	17	2520	4.354 ± 13
20.08	2712	1	21	2732	4.361 ± 13
28.55	4068	3	48	4113	4.359 ± 9
30.29	4366	3	55	4418	4.365 ± 9
48.87	8116	10	172	8278	4.360 ± 6
51.61	8783	12	199	8970	4.369 ± 6
53.54	9275	13	220	0.9482	4.371 ± 6
55.47	0.9789	14	244	1.0019	4.372 ± 6
57.38	1.0319	15	264	1.0568	4.369 ± 6
59.17	1.0838	17	288	1.1109	4.369 ± 6
61.26	1.1474	19	319	1.1774	4.370 ± 6
67.33	1.3536	25	425	1.3936	4.362 ± 6
77.57	1.8087	40	689	1.8736	4.354 ± 7
79.20	1.9000	43	744	1.9701	4.362 ± 7
80.81	1.9974	47	809	2.0736	4.356 ± 7
81.90	2.0682	49	854	2.1487	4.356 ± 7
82.73	2.1250	52	892	2.2090	4.357 ± 7
90.50	2.8482	81	1403	2.9804	4.348 ± 10
91.59	2.9956	87	1513	3.1382	4.353 ± 10
96.14	3.9379	129	2233	4.1483	4.341 ± 17
96.19	3.9537	130	2240	4.1647	4.337 ± 17

GRAPHIC AND NUMERICAL EVALUATION OF THE f_c^0 -DETERMINATIONS

Graphic evaluation is made by diagrams of the type that occurs in Fig. 2 with data from experiments 11 and 14 — cf. the corresponding κ_c diagram in Fig. 3 of Part III.

When choosing the best f_c^0 -value from the series of values of an individual experiment we have to consider that the values are not of equal accuracy. The same thing holds when we try to evaluate the degree of constancy within the series. The effect of errors in P , P_0 , and P_∞ can be computed by the grossly approximate formula

$$f_c^0 = \frac{1}{t} \cdot \frac{n_t}{n_t - \Phi_g P_{00}} \cdot \ln \frac{P_\infty - P_0}{P_\infty - P} \quad (15)$$

(Here we disregard the two "correction functions" in (33) and the difference between Y and Y_p in III-10).

At a comparison of the f_c^0 -values within the same experiment one can disregard the common and constant errors in n_t , ϕ_g , and P_{00} . The quantities P_0 and P_∞ are singular too but the errors they cause in f_c^0 are not constant. They therefore have to be considered as, of course, the randomly distributed errors in the individual P -values while the other variable, t , can be regarded as errorless. If (35) is differentiated with respect to P_0 , P_∞ and P we get the expression

$$d \ln f_c^0 = \frac{1}{\ln(1-Y)} \cdot \left(\frac{dP_0}{P_\infty - P_0} - \frac{1}{1-Y} \cdot \frac{dP}{P_\infty - P_0} + \frac{Y}{1-Y} \cdot \frac{dP_\infty}{P_\infty - P_0} \right) \quad (16)$$

The same expression holds for κ_c and κ_p as appears from Part II, formula (II-42) — see also discussion and table values on the same page.

In the application of this formula we start with an estimate of $\sigma(P)$ founded on a direct determination of the reproducibility of the P -readings during the end period of the experiment when the pressure is constant or nearly constant. But for the dispersions $\sigma(P_0)$ and $\sigma(P_\infty)$ we have no estimate.

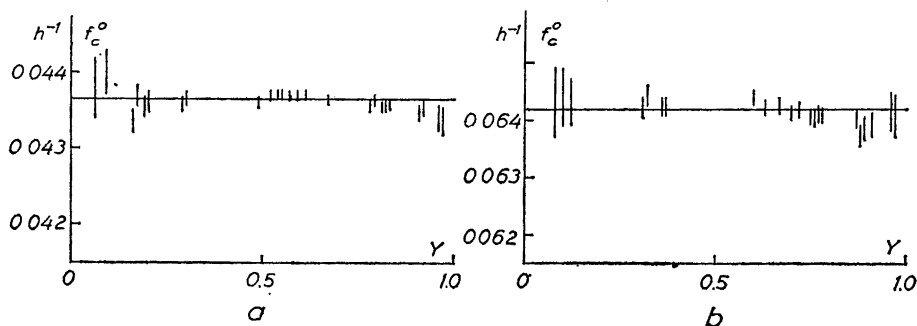


Fig. 2. The quantity f_c^0 , computed for all readings within the individual experiment; plotted against the conversion degree Y . a: Experiment 11; 7.25 m HCl; CuCl(s). b: Experiment 14; 9.10 m HCl; CuCl(s).

Therefore until further we only consider the errors derived from P . In Fig. 2 the vertical bars show the dispersion $\pm \sigma$, computed according to

$$\sigma = \frac{f_c^0}{\ln(1-Y)} \cdot \frac{1}{1-Y} \cdot \frac{\sigma(P)}{P_\infty - P_0} \quad (17)$$

The horizontal lines state the graphically accepted mean values 0.04365 h⁻¹, resp. 0.0642 h⁻¹. Of the 25 measured points in Fig. 2a 17 fall at a distance less than $\pm \sigma$. The remaining 8 points lie within $\pm 2\sigma$. A trend occurs towards a systematic deviation at high Y -values probably due to a P_∞ -error. But the deviation is so small that there is no need to refer to such an explanation to be allowed to draw the following conclusion: within the whole interval 0–97 % conversion the constancy of the f_c^0 -value is proved as exactly as the experimental technique allows. (The lowest interval that has been brought into the figure and into Table 4 corresponds to 0–5.85 % conversion. Earlier measurements have been reserved for the P_0 -determination and consequently not used here. But they create no suspicion of a systematic deviation at low conversion degrees.) In some experiments a more evident deviation can be seen from the best horizontal line either in the beginning or at the end of the diagram — or both. But the deviations can in all cases be explained by constant errors in P_0 or P_∞ of a reasonable size.

These circumstances make it difficult, however, to express in objective terms the degree of certainty with which the constancy of the f_c^0 -value has been demonstrated by experiments of this type.

In Table 3 the result of the graphical evaluation of all experiments is summarized.

Check of the used Γ -function. A comparison between Tables 1 and 3 shows that the difference between κ_c and f_c^0 is very small. (But the second quantity has of course a higher and better defined accuracy.) In the tables the difference is nowhere greater than 0.5 % and hardly significant. In a diagram with a scale as in Fig. 1 the differences are scarcely visible — in some cases 0.1 mm

Table 3. Graphically determined f_c^0 -means and the dispersion within the individual experiment.

HCl_t m	Expt. No.	$10^2 f_c^0$ h ⁻¹	Number of values			Highest conversion %
			Totally	Within $\pm \sigma$	Within $\pm 2\sigma$	
5.53	9	2.615	24	17	22	97.2
6.50	10	3.60	18	13	16	92.7
7.25	11	4.365	25	17	25	96.2
7.94	7	5.145	16	9	16	84.9
8.57	12	5.82	32	24	31	96.7
9.05	5	6.370	20	18	20	91.1
9.06	6	6.37	13	10	13	45
9.05	13	6.370	14	10	13	66
9.10	14	6.42	23	17	22	96.3
10.05	15	7.55	23	17	22	92.8

deviation, in one case 0.3 mm. Hence we can no doubt accept the used approximate Γ -function with ρ' constants according to Table 1. A further iteration step is not necessary.

In a *numerical evaluation* we also have to consider the non-equivalence of the individual f_c^0 -values. As a weight factor we use their inverse *a priori* dispersion σ^{-1} computed according to (17). Of course one can use the quantity $(\partial f_c^0/\partial P)^{-1}$ or the proportional Y -function $(1-Y) \ln(1-Y)$. However, the following formulae will be more simple if based on the numerical σ -value computed according to (17).

It should be pointed out that a weighting of this kind actually means that we define a f_c^0 -value which gives the least square sum of the differences between measured and calculated P -values. The following formulae have been used:

$$\begin{aligned} \text{Mean } \bar{f}_c^0 &= \frac{\sum f_c^0 \sigma^{-2}}{\sum \sigma^{-2}} \\ \text{Variance } a \text{ priori } \sigma^2(f_c^0) &= 1/\sum \sigma^{-2} \\ \text{Variance } a \text{ posteriori } \sigma^2(f_c^0) &= \frac{\sum (f_c^0 - \bar{f}_c^0)^2 \sigma^{-2}}{(n-1)\sum \sigma^{-2}} \end{aligned} \quad (18)$$

Here σ (without argument or index) stands for the *a priori* dispersion of the individual f_c^0 -value according to (17).

For the numerical treatment we have chosen experiment 11 (Fig. 2a) as an example with the following result. The numerically calculated mean is 0.04363 h^{-1} that corresponds well to the graphically accepted 0.04365 h^{-1} . The anticipated dispersion of the mean is ± 0.000016 — calculated from the estimated $\sigma(P)$. The dispersion computed from the difference $(f_c^0 - \bar{f}_c^0)$ is ± 0.000017 . The agreement between these estimates is thus more than satisfactory. The level of precision as such is also quite impressive; in relative measure the standard deviation of the determined kinetical constant is less than $\pm 0.04 \%$.

DISCUSSION

A *more complete statistical treatment* is to be preferred, however, to the simple numerical evaluation tested in the previous paragraph. The aim of such a treatment is a determination not only of the best f_c^0 -value but also of the other constants, P_0 and P_∞ . Of special importance is the possibility of making an independent determination of the end value P_∞ as this quantity depends on a correction whose basis and numerical accuracy are difficult to judge.

The statistical treatment becomes quite extensive, however, and is therefore postponed to a later part of this series.

The hypothesis is thus well confirmed that the vinyl chloride formation is of first order in A_d — at constant HCl_t and in the presence of solid $CuCl$. The total concentration of dissolved acetylene, A_d , decreases in these experiments approximately proportionally to $(1-Y)$. The quantity f_c^0 thus also is independent of A_d which in most experiments decreases from its start value,

100 %, to an end value of 3–4 %. Within a series of experiments including Nos. 5, 6, and 13 — all at $HCl_t^0 = 9$ m — an A_d -variation occurs that extends almost over two powers of ten; no significant trend can be seen in the f_c^0 -values. The velocity function thus can be written:

$$\frac{dB}{dt} = A_d f_c(HCl_t) \quad \text{Condition: CuCl}(s) \quad (19)$$

But a statistical treatment of the experiments is required to get a more exact evaluation of the degree of certainty by which it is proven that f_c is independent of A_d .

EXPERIMENTS

Techniques and apparatus are described in earlier parts of this series, especially in Part I.

Experiment 5: CuCl(s); 9.05 m HCl; $P_0 = 169.5$; $25.0^\circ C$

Data in Part III.

Experiment 6: CuCl(s); 9.06 m HCl; $P_0 = 305.0$; $25.0^\circ C$

Data in Part III.

Experiment 7: CuCl(s); 7.94 m HCl; $P_0 = 261.0$; $25.0^\circ C$

Procedure and experimental data in Part II.

The pressure fall due to the vinyl chloride loss does not amount to more than 0.010 mm·h⁻¹ at 910 mm. This gives the correction factor $\xi = 1.53 \times 10^{-6}$ h⁻¹. The corrections computed according to (III-8) are + 0.1 mm for pressure values between 22 and 40 h, + 0.2 mm between 40 and 47 h and + 0.3 mm for the two last values during the main period. The corrected values $t-P$ of the end period are: 118.5–901.4; 138.5–905.6; 142.5–906.1; 146.5–906.7; 166.5–908.2; 191.5–908.7; 215.0–909.3; 235.0–909.9; 239.0–910.2; 242.5–910.0; 262.0–910.1.

Computed values: Gas phase capacity $\Phi_g = (5.227 \pm 0.006) \times 10^{-6}$ mole·mm⁻¹. Theoretical end pressure according to the vinyl chloride calibration 908.0 ± 2.1 , highest value measured in the acetylene experiments 908.1; the corrected pressure time curve ends at 910.0 ± 0.3 , a value that is accepted as P_∞ in the calculations. Start pressure $P_0 = 261.0$ and equilibrium pressure $P_{00} = 260.0$. $\sigma(P) = \pm 0.3$ mm. Constants for (III-10) and (III-15): $\psi = 0.0104$; $\gamma' = 0.0339$; $a_2 \cdot \ln 10 = 3.0026$; $b_2 \cdot \ln 10 = 0.725$.

Experiment 9: CuCl(s); 5.53 m HCl; $P_0 = 168.3$; $25.0^\circ C$

Procedure: 10.9 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition can be calculated to 29.77 g after correction for evaporation losses. Vapour pressure 17.7 mm, reading after 17 h, for check of tightness, gives 17.9 mm. After calibration with nitrogen and calibration and tightness check (from 826.4 to 826.2 mm during 17 h) with vinyl chloride, 3.863 ± 0.004 mmoles acetylene are added in one portion, at which timing is started. Readings $t(h) - P(\text{mm Hg})$ during the start period: 0.1294–170.6; 0.2239–171.2; 0.2961–172.0; 0.3781–172.5; 0.4600–173.4; 0.6267–174.9; 0.7906–176.6; 0.9753–178.0; 1.2058–180.1; 1.4628–182.7. Main period: 1.977–187.3; 5.443–218.5; 7.960–239.4; 18.127–314.4; 18.477–316.3; 23.360–346.2; 28.810–376.7; 35.177–407.2; 54.243–477.3; 55.043–479.5; 66.110–508.6; 69.460–515.9; 73.827–524.9; 90.127–552.7; 93.627–557.3; 98.110–562.8; 114.043–579.4; 117.777–582.8; 121.660–585.9; 138.410–596.6; 141.793–598.5; 145.693–600.7; 163.060–607.1; 170.260–609.5. End period: 163.6–607.4; 170.8–609.5; 191.9–613.9; 196.8–615.2; 219.9–617.9; 234.7–618.2; 241.5–618.6; 260.1–619.7; 286.5–621.2; 290.5–621.3; 308.4–620.9; 310.7–621.0; 313.7–621.0; 337.3–621.3; 357.6–621.8; 389.2–622.1; 433.2–622.0.

Correction for vinyl chloride loss is not necessary.

Computed values. Undissolved amount of CuCl ca. 7.0 g. Gas phase capacity $\Phi_g = (4.049 \pm 0.006) \times 10^{-6}$ mole·mm⁻¹. Theoretical end pressure according to the vinyl chloride calibration 670.8 ± 1.3 , highest pressure measured in the acetylene experiment

622.1 that is accepted as $P_{\infty m}$ in the calculation. Start pressure $P_0 = 168.3$, equilibrium pressure P_{00} the same. $\sigma(P) = 0.4$ mm. Constants for (III-10) and (III-15): $\psi = 0.0062$, $\gamma' = 0.0204$; $a_2 \ln 10 = 2.7954$; $b_2 \ln 10 = 0.503$.

Experiment 10: CuCl(s); 6.50 m HCl; $P_0 = 249.9$; 25.0°C

Procedure: 11.0 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition is calculated as 24.71 g. Vapour pressure 15.3 mm, reading after 18 h for check gives 15.4 mm. After calibration with nitrogen and calibration and tightness check (893.7 to 893.5 during 16 h) with vinyl chloride, acetylene is added in two portions with a time difference of 0.0830 h. The first portion contains 3.11 millimoles; totally 5.810 ± 0.008 millimoles are added. Timing is started at the last addition. Readings $t-P$ during the start period: 0.1144–251.9; 0.1950–253.4; 0.2797–255.0; 0.3644–256.0; 0.4422–257.5; 0.5242–259.1; 0.6964–262.2; 0.8714–265.1; 1.0353–267.9; 1.1950–270.8; 1.4450–274.7. Main period: 1.695–279.6; 4.645–327.8; 8.423–384.9; 8.995–392.3; 20.278–523.6; 20.785–528.3; 30.660–612.4; 30.962–614.3; 42.645–686.0; 45.378–699.8; 49.628–718.5; 51.495–726.4; 65.712–774.9; 69.995–785.5; 73.662–795.1; 89.712–825.1; 93.828–830.9; 97.478–835.5. End period: 114.1–851.9; 119.0–855.5; 121.7–856.1; 139.6–865.9; 146.0–868.8; 162.4–873.1; 167.1–874.1; 215.4–879.0; 262.5–880.4; 310.8–881.1; 359.3–881.0.

Correction for vinyl chloride loss is not necessary.

Computed values. Undissolved amount of CuCl *ca.* 6.6 g. Gas phase capacity $\Phi_g = (4.970 \pm 0.006) \times 10^{-6}$ mole \cdot mm $^{-1}$. Theoretical end pressure according to the vinyl chloride calibration 897.1 ± 1.7 . Highest measured pressure in the acetylene experiment 881.1. For the calculation $P_{\infty m} = 881.1$ is accepted. Start pressure $P_0 = 249.9$ and equilibrium $P_{00} = 249.1$. Constants for (III-10) and (III-15): $\psi = 0.0098$; $\gamma' = 0.0316$; $a_2 \ln 10 = 2.9266$; $b_2 \ln 10 = 0.644$.

Experiment 11: CuCl(s); 7.25 m HCl; $P_0 = 254.7$; 25.0°C

Data in Part III.

Experiment 12: CuCl(s); 8.57 m HCl; $P_0 = 244.5$; 25.0°C

Procedure: 16.1 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition is calculated as 25.75 g. Vapour pressure 13.4 mm; reading after 16 h for tightness check gives 13.5 mm. After calibration with nitrogen and with vinyl chloride acetylene is added in two portions with a time difference of 0.0850 h. The first addition contains 3.77 mmoles; totally 6.75 ± 0.008 mmoles are added. Timing is started at the last addition. Readings $t-P$ during the start period: 0.3181–257.3; 0.3931–260.9; 0.7292–275.2; 0.9250–283.3; 1.0611–288.7. Main period: 1.3181–299.4; 1.5167–307.4; 1.8042–318.9; 2.624–350.5; 4.981–433.2; 5.036–434.6; 5.339–444.7; 5.372–445.6; 5.856–461.2; 5.885–462.0; 6.351–476.6; 6.382–477.6; 6.878–492.6; 6.906–493.3; 7.281–504.6; 7.311–505.3; 7.797–519.5; 7.825–520.3; 8.279–533.3; 8.311–534.1; 8.771–546.9(547.0); 8.790–547.4(547.5); 18.946–764.0(764.3); 42.824–997.5(998.5); 42.882–997.8(998.8); 46.774–1015.9(1017.1); 50.685–1032.2(1033.5); 50.760–1032.2(1033.5); 70.206–1077.9(1080.0); 70.401–1078.0(1080.1); 71.554–1080.0(1082.1); 71.607–1080.1(1082.2). End period: 97.0–1098.6(1101.8); 123.0–1103.7(1108.0); 143.0–1105.0(1110.1); 164.0–1104.3(1110.3); 170.5–1104.2(1110.5); 188.0–1103.6(1110.6); 194.0–1103.4(1110.6); 212.0–1102.9(1110.9); 219.0–1102.5(1110.8); 238.5–1101.9(1111.0); 284.0–1100.2(1111.2).

The pressure fall due to vinyl chloride loss during the end period approaches the constant value 0.042 mm \cdot h $^{-1}$. This gives the correction factor $\xi = 4.85 \times 10^{-5}$ h $^{-1}$. Pressure values corrected according to (III-8) are given within parenthesis in the table above.

Computed values. Undissolved amount of CuCl *ca.* 9.1 g. Gas phase capacity $\Phi_g = (4.372 \pm 0.015) \times 10^{-6}$ mole \cdot mm $^{-1}$. Theoretical end pressure according to the vinyl chloride calibration 1113.2 ± 2.1 ; highest pressure measured in the acetylene experiment 1105.0. The corrected pressure time curve ends at 1111.1 mm, a value that is accepted as $P_{\infty m}$ in the calculation. The start pressure determined by "logarithmic" extrapolation is $P_0 = 244.5$ and the equilibrium pressure $P_{00} = 240.3$. $\sigma(P) = \pm 0.3$ mm. Constants for (III-10) and (III-15): $\psi = 0.0066$; $\gamma' = 0.0284$; $a_2 \ln 10 = 2.7263$; $b_2 \ln 10 = 0.436$.

Experiment 13: CuCl(s); 9.05 m HCl; $P_0 = 461.0$; 25.0°C

Data in Part III.

Experiment 14: CuCl(s); 9.10 m HCl; $P_0 = 299.6$; 25.0°C

Data in Part III.

Experiment 15: CuCl(s); 10.05 m HCl; $P_0 = 309.4$; 25.0°C

Procedure: 13.1 g CuCl and 2.0 g Cu are mixed with hydrochloric acid whose water content at the acetylene addition is 16.55 g. Vapour pressure 13.5 mm, reading after 17 h for tightness check gives unchanged value. After calibration with nitrogen and calibration and test of tightness (1083.0 \rightarrow 1082.0 during 17 h) with vinyl chloride, acetylene is added in two portions with a time difference of 0.1700 h. The first addition contains 3.78 mmoles; totally 6.843 ± 0.008 mmoles are added. Timing is started at the last addition. Readings $t-P$ during the start period: 0.5611-335.0; 0.7361-343.2; 0.9069-351.3; 1.2556-366.6; 1.6097-380.4; 1.9153-393.6; 2.183-404.6; 2.310-409.6. Main period: 4.836-505.1; 6.917-572.8; 7.485-590.4; 7.906-602.5; 8.465-618.5; 8.869-629.3; 18.606-828.9(829.3); 19.735-844.7 (845.1); 20.643-858.3(858.7); 21.253-866.2(866.6); 22.710-884.6(885.1); 23.906-898.2(898.7); 25.138-911.3(911.9); 26.482-924.5(925.1); 29.925-954.4(955.1); 30.449-958.6(959.4); 30.899-962.1(962.9); 31.507-966.5(967.3); 31.786-968.2(969.0); 42.660-1026.4(1027.6); 42.719-1026.7(1027.9); 45.364-1035.2 (1036.6); 46.860-1040.4(1041.8). End period: 93.0-1090.4(1093.9); 118.5-1092.4 (1097.1); 122.0-1092.9(1097.7); 139.5-1093.5(1099.1); 146.5-1093.4(1099.3); 164.0-1091.9(1098.6); 167.5-1092.2(1099.1); 187.5-1090.9(1098.7); 194.5-1090.7(1098.8); 212.5-1090.1(1099.1); 216.5-1089.9(1099.1); 284.0-1086.3(1098.6); 288.0-1086.1 (1098.5).

The pressure fall during the end period approaches the constant velocity $0.053 \text{ mm}\cdot\text{h}^{-1}$ (at 1090 mm) giving the correction factor $\xi = 6.8 \times 10^{-5} \text{ h}^{-1}$. Pressure values corrected according to (III-8) are given within parenthesis in the table above.

Computed values. Undissolved amount of CuCl ca. 7.4 g. Gas phase capacity $\Phi_g = (4.927 \pm 0.008) \times 10^{-6} \text{ mole}\cdot\text{mm}^{-1}$. Theoretical end pressure according to the vinyl chloride calibration 1097.1 ± 2.5 ; highest pressure measured in the acetylene experiment is 1093.5. The corrected pressure time curve ends at 1098.8 ± 0.4 , a value that is accepted as P_{∞} in the calculation. The determination of the start pressure $P_0 = 309.4$ is made by logarithmic extrapolation - which, due to the rapid change of the pressure, has been executed by plotting $\log(P_{\infty} - P) + t/50$ against t . The equilibrium pressure $P_{00} = 304.9$. The dispersion $\sigma(P)$ is estimated to be ± 0.4 during the main and the end periods; during the start period somewhat larger fluctuations occur. Constants for (III-10) and (III-15): $\psi = 0.0117$; $\gamma' = 0.0390$; $a_1 \cdot \ln 10 = 2.9496$; $b_1 \times \ln 10 = 0.673$.

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