

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

## II.\* Experimental Orientation

RAGNAR VESTIN and LEONIDA ARRO

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

Submitted in honour of the ninetieth birthday of Professor *Hans von Euler*

In a *homogeneous catalyst solution*, consisting of cuprous chloride in hydrochloric acid, the formation rate of vinyl chloride from acetylene is determined by *three variables* — provided the assumption that vinyl chloride formed is without influence. At an analysis of the function

$$\frac{dB}{dt} = F(\text{CuCl}_t, \text{HCl}_t, P_A)$$

starting from the pressure-time curves of the manometric experiments, we have first computed the quantity:

$$\kappa = \frac{1}{t} \int_0^t \frac{dB}{P_A}$$

for every reading of each single experiment using the  $B-P_A-P$ -relations derived in Part I. For an accurate calculation the integration variable is so chosen that necessary (or convenient) approximations can easily be judged by comparison with the accuracy of the data-readings. The reaction is approximately of the first order in  $P_A$  but a more precise computation shows that the ratio  $f_p = F/P_A$  for which  $\kappa$  is a time mean, is not independent of  $P_A$  but clearly increases when  $P_A$  decreases. This circumstance hampers a complete analysis of the kinetics in this type of experiments. It is possible, however, to compute two  $f_p$ -values from the experiments, they refer to identical  $\text{HCl}_t$  and  $P_A$ , but different  $\text{CuCl}_t$ -values; these  $f_p$ -values are proportional to  $\text{CuCl}_t^2$ .

If the *catalyst solution is in equilibrium with solid cuprous chloride* the rate is determined by *two variables* and a method is described for the analysis of the relation:

$$\frac{dB}{dt} = F_s(\text{HCl}_t, P_A)$$

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In these experiments  $\kappa$  and  $f_p$  are sinking, but the change can entirely be explained by the co-variation in  $\text{HCl}_t$ . The quantity  $f_p$  is thus independent of  $P_A$  and future measurements can be directed towards a study of its  $\text{HCl}_t$ -dependence. According to the preliminary experiments  $f_p$  grows very rapidly with  $\text{HCl}_t$ , roughly proportionally to  $\text{HCl}_t^{2.5}$ .

In an experiment where the catalyst solution is in contact both with solid cuprous chloride and solid addition compound  $\text{C}_2\text{H}_2(\text{CuCl})_2$  the pressure increases at an almost constant rate for a long time. Statistical treatment gives a  $dP/dt$  function of high accuracy, from which the reaction velocity can be computed, but unfortunately it is still doubtful whether the dissolution rate of the addition complex is, or will be, sufficient for a determination of the absolute reaction rate with a similar accuracy. However, the experiment demonstrates convincingly that the reaction rate is independent of pressure and concentration of the vinyl chloride.

### Symbols

$$f_p = \frac{1}{P_A} \cdot \frac{dB}{dt}$$

$$I_i = \int \frac{dB}{P_A} \quad \text{Index } i \text{ denotes method of computation}$$

$$\kappa_i = \frac{I - I^0}{t} \quad \text{» } \text{» } \text{» } \text{» } \text{» } \text{»}$$

$$U = dP/dt$$

Index o in  $P_o$ ,  $\varphi_A^o$ ,  $\text{HCl}^o$ ,  $I_i^o$   $a_i^o$  and  $f_p^o$  marks value at  $t = 0$ .  $P_{\infty}$  is the equilibrium pressure corresponding to the acetylene amount  $A_{\infty}$ . The following normalized kinetical variables are used:

$$Y_p = (P - P_{\infty}) / (P_{\infty} - P_{oo})$$

$$Y = B / A_{\infty}, \text{ conversion degree}$$

$$y = (P_{\infty} - P_A) / P_{\infty}$$

$$Z : \text{ see (22)}$$

Constants:  $\sigma$ : cf. (20);  $\pi$ : cf. (7 b);  $P_3$ : equilibrium pressure for reaction (24);  $\gamma = 0.0759 \text{ atm}^{-1}$  defined in (I-18).

Other symbols according to Part I and definitions in the text.

## EXPERIMENTS

Techniques, apparatus, chemicals etc. agree on the whole with the Type experiment, fully described in Part I, where will also be found details regarding estimation of evaporation losses, uncertainty of primary data and computation of  $\varphi_g$ ,  $P_o$ ,  $P_{oo}$  and  $P_{\infty}$ .

*Experiment 2:* 2.753 m  $\text{CuCl}$ ; 8.92 m  $\text{HCl}$ ;  $P_o = 171.0 \text{ mm}$ ;  $25.0^\circ\text{C}$ .

*Procedure:* The Type experiment (exp. 1) is reproduced as exactly as possible, the difference being that the acetylene amount is approximately halved. Only one portion of acetylene is added corresponding to  $A_{\infty} = 0.1963 \text{ m}$ . Vapour pressure determination and calibrations give results which are in good agreement with expt. 1; the gas phase capacity according to the nitrogen calibration is  $\varphi_g = 2.929 \times 10^{-4} \text{ m/mm}$ . End pressure

according to vinyl chloride calibration  $P_{\infty} = 547.1 \pm 1.0$ . Start pressure  $P_0 = P_{\infty} = 171.0$ . Readings  $t$  (h) —  $P$  (mm Hg uncorr.) during start period: 0.09—193.0; 0.17—174.7; 0.2472—174.4; 0.3444—175.8; 0.4236—176.8; 0.5028—178.1; 0.5889—179.3; 0.6708—180.5; 0.8417—182.8; 1.001—185.2; 1.256—188.7; 1.499—191.9. Main period: 4.092—225.1; 4.807—234.7; 7.882—269.4; 8.913—280.8; 9.743—290.0; 21.354—387.5; 21.754—390.2; 22.004—391.6; 22.504—395.0. The experiment is interrupted at approximately 60% conversion.

Computed values:  $\sigma(P) = \pm 0.2$  mm;  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 2.011$  m.atm<sup>-1</sup>; constants for (8)—(10):  $\pi = 0.0501$ ;  $\Delta = 0.0512$ ;  $a_1 \ln 10 = 2.085$  m.atm<sup>-1</sup>;  $b_1 \ln 10 = 1.487$  m.atm<sup>-1</sup>;  $c_1 = 0.0307$  m.atm<sup>-1</sup>.

*Experiment 3: 2.024 m CuCl; 9.05 m HCl;  $P_0 = 335.4$  mm; 25.0°C.*

*Procedure:* 5.020 g CuCl, 2.0 g Cu and 9.05 m HCl of 25.05 g water content at acetylene addition; correction made for evaporation losses. Vapour pressure 12.8 mm; reading after 19 h, for check of tightness, gives 13.1 mm. Nitrogen calibration gives  $n-P$  (units: millimole and mm Hg uncorr.): 2.085—471.8; 3.544—800.9; 4.474—1009.8; 5.547—1249.6 and with vinyl chloride  $n-P$ : 3.305 ( $\pm 0.004$ )—542.6; 6.292 ( $\pm 0.008$ )—1017.7; check after 13 h 1017.9. Acetylene is added in two portions with 7.67 min interval. First portion 3.0 millimoles, total 6.631 ( $\pm 0.008$ ). Timing is started at the last addition. Readings  $t-P$  during start period: 0.16—350.2; 0.25—342.4; 0.3361—342.9; 0.4222—344.3; 0.5361—346.4; 0.7028—349.8; 0.8889—353.6; 1.0750—357.5; 1.5778—367.4. Main period: 1.925—374.2; 7.439—475.9; 8.628—496.1; 18.392—640.2; 19.944—659.3; 21.88—683.2; 23.98—707.2; 26.41—733.0; 30.80—775.8; 31.42—781.2; 42.57—868.2; 44.30—879.7; 46.58—893.1; 49.70—910.0; 52.62—924.5; 69.74—988.7; 71.75—994.1; 75.80—1004.5; 76.31—1005.6. End period: 94.3—1035.0; 97.7—1039.2; 101.7—1043.5; 102.7—1044.7; 115.4—1054.3; 127.6—1060.2; 145.7—1066.1; 168.2—1069.7; 175.9—1070.6; 192.5—1071.7; 214.9—1071.4; 259.9—1069.4.

Computed values: Gas phase capacity  $\varphi_g = (1.768 \pm 0.002) \times 10^{-4}$  m.mm<sup>-1</sup>. Theoretical end pressure according to vinyl chloride calibration  $1071 \pm 2$  mm, highest pressure measured in acetylene experiment 1071.7. This latter figure is used for the calculation of  $\kappa_1$ . Start pressure  $P_0 = 335.4$  and equilibrium pressure  $P_{\infty} = 334.3$  mm.  $\sigma(P) = \pm 0.3$  mm.  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 1.3870$  m.atm<sup>-1</sup>.

*Experiment 4: 2.014 m CuCl; 9.96 m HCl;  $P_0 = 328.6$  mm; 25.0°C.*

*Procedure:* 4.960 g CuCl, 2.02 g Cu and hydrochloric acid; at the acetylene addition the water content of the solution is 24.87 g and its HCl concentration 9.96 m. Vapour pressure 13.1 mm; check reading after 16 h gives 13.0 mm. Nitrogen calibration gives  $n-P$ : 1.374—259.6; 2.908—550.4; 3.852—728.0; 5.284—999.1; 6.888—1302.9. Vinyl chloride calibration  $n-P$ : (3.856  $\pm$  0.004)—553.2; (5.530  $\pm$  0.008)—786.3; (7.494  $\pm$  0.008)—1056.6; a check of the last reading after 16 h gives 1055.6. Acetylene is added in two portions at an interval of 0.092 h. The first portion 3.79 millimoles, total 6.700  $\pm$  0.008. Timing is started at the last addition. Readings  $t-P$  during the start period: 0.2181—334.2; 0.3014—334.2; 0.3944—336.1; 0.5042—338.1; 0.6153—340.4; 0.7333—342.2; 0.8972—345.6; 1.0667—348.6; 1.3222—353.4; 1.5750—357.6. Main period: 2.093—366.9; 2.368—371.7; 2.615—376.1; 7.308—453.5; 8.506—471.9; 9.076—480.4; 10.154—496.3; 19.789—615.8; 20.79—626.4; 21.46—633.1; 22.55—644.7; 24.71—664.8; 25.71—674.2; 26.63—681.9; 44.33—800.0; 45.43—805.5; 46.83—812.6; 48.51—819.8; 50.61—828.7; 71.99—890.4; 74.73—895.7. End period: 119.3—935.3; 121.1—936.3; 139.8—940.9; 146.7—942.1; 164.6—943.8; 170.6—944.4; 188.1—944.8; 212.2—945.3; 218.1—945.3.

Computed values: Gas phase capacity  $\varphi_g = (2.126 \pm 0.002) \times 10^{-4}$  m.mm<sup>-1</sup>. Theoretical end pressure according to vinyl chloride calibration 947.5  $\pm$  2.0; highest pressure measured in acetylene experiment 945.3. The value  $P_{\infty} = 945.4$  is used for the calculation of  $\kappa_1$ . Start pressure  $P_0 = 328.6$  and equilibrium pressure  $P_{\infty} = 327.6$  mm.  $\sigma(P) = \pm 0.3$  mm.  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 1.4403$  m.atm<sup>-1</sup>.

*Experiment 5: CuCl(s); 9.05 m HCl;  $P_0 = 169.5$ ; 25.0°C.*

*Procedure:* 16.0 g CuCl, 2.0 g Cu and hydrochloric acid of 16.87 g water content at the acetylene addition. Vapour pressure 12.3 mm; check of tightness after 17 h gives 12.2 mm. Vinyl chloride calibration gives  $n-P$ : (1.075  $\pm$  0.004)—158.4; (3.699  $\pm$  0.004)—537.3; (5.333  $\pm$  0.008)—769.0; (7.064  $\pm$  0.008)—1008.8; check of the last reading

after 19 h 1005.2 (?). Only one portion of acetylene is added:  $3.700 \pm 0.004$  millimoles. Timing is started 0.1450 h after addition. Readings  $t-P$  during start period: 0.1694–173.0; 0.2667–174.4; 0.3556–175.7; 0.4458–177.1; 0.5319–178.7; 0.7125–181.8; 0.8931–185.0; 1.0625–187.7; 1.2278–190.7. Main period: 1.426–193.7; 1.779–199.4; 2.093–204.2; 2.594–212.0; 3.250–221.9; 3.826–230.4; 4.363–238.1; 4.913–245.6; 5.631–255.1; 6.342–264.5; 7.038–273.3; 11.940–327.4; 14.768–353.1; 29.79–444.4; 31.26–450.6; 36.72–469.3; 38.27–473.9; 47.74–495.2; 50.14–499.1; 52.69–503.0. End period: 95.0–530.3; 100.0–531.2; 103.0–531.6; 122.0–534.0; 143.0–534.9; 146.0–534.6; 147.0–534.4; 151.0–534.4; 170.0–534.8; 175.0–534.8; 220.5–534.3; 263.5–533.1.

*Computed values:* Undissolved CuCl approximately 11 g. Theoretical end pressure according to vinyl chloride calibration  $537.8 \pm 1.7$  mm; highest pressure measured in the acetylene experiment 534.9 mm. For the computation of  $\kappa$  the value  $P_{\infty} = 535.0$  has been used. Start pressure  $P_0 = 169.5$  and equilibrium pressure  $P_{\infty} = 166.6$  mm.  $\sigma(P) = \pm 0.3$  mm.  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 2.306$  m·atm<sup>-1</sup>; constants for (16) and (17):  $\psi = 0.0075$ ;  $\gamma A_{\infty} = 0.0166$  m·atm<sup>-1</sup>.

*Experiment 6: CuCl(s); 9.06 m HCl,  $P_0 = 305.0$ ; 25.0°C.*

*Procedure:* 16.0 g CuCl and 2.0 g Cu, hydrochloric acid of 16.81 g water content at the acetylene addition. Vapour pressure 12.9 mm; 12.8 mm is read after 17 h. Vinyl chloride calibration gives  $n-P$ : (2.919  $\pm$  0.004)–427.5; (4.568  $\pm$  0.008)–662.7; (6.768  $\pm$  0.008)–971.5; check after 13 h 970.6 mm. Acetylene is added in two portions at a time interval of 0.129 h. First portion 3.5 millimoles, total 6.666  $\pm$  0.008. Timing is started at last addition. Readings  $t-P$  during start period: 0.1319–311.3; 0.2181–311.9; 0.3069–314.2; 0.3819–316.7; 0.4569–319.2; 0.6236–324.0; 0.7986–329.4; 0.9542–334.3. Main period: 1.074–337.9; 1.233–342.6; 1.474–349.3; 1.715–356.1; 2.232–371.2; 3.736–412.0; 4.243–424.6; 5.157–447.4; 5.988–466.9; 7.015–489.8; 8.910–530.0; 11.513–578.2; 12.735–599.4. End period: 95.5–949.2; 98.0–949.9; 103.0–951.7; 127.0–955.3; 143.5–955.9; 147.5–955.8; 151.5–955.5; 169.0–955.0; 175.5–955.3; 193.5–954.3; 197.0–954.5; 263.5–952.2.

*Computed values.* Undissolved CuCl approximately 11 g. Theoretical end pressure according to vinyl chloride calibration  $957.5 \pm 1.7$  mm; highest pressure measured in acetylene experiment 955.9, which has been used for the computation of  $\kappa$ . Start pressure  $P_0 = 305.0$  and equilibrium pressure  $P_{\infty} = 301.0$ .  $\sigma(P) = \pm 0.3$  mm.  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 2.308$  m·atm<sup>-1</sup>; constants for (16) and (17):  $\psi = 0.0137$ ;  $\gamma A_{\infty} = 0.0301$  m·atm<sup>-1</sup>.

*Experiment 7: CuCl(s); 7.94 m HCl;  $P_0 = 261.0$ ; 25.0°C.*

*Procedure:* 11.0 g CuCl and 2.0 g Cu with hydrochloric acid of 19.64 g water content at acetylene addition. Vapour pressure 14.2 mm, after 18 h 14.1 mm. Nitrogen calibration gives  $n-P$ : 2.069–397.7; 2.858–549.9; 3.778–726.2; 4.485–861.4; 6.464–1241.4 and calibration with vinyl chloride  $n-P$ : (1.599  $\pm$  0.004)–251.3; (4.494  $\pm$  0.008)–700.2; (6.253  $\pm$  0.012)–967.5. Two acetylene additions at a time interval of 0.060 h. First portion 3.7 millimoles, total 5.858  $\pm$  0.008 millimoles. Timing is started at last addition. Readings  $t-P$  during start period: 0.1364–264.9; 0.2170–267.0; 0.3003–269.1; 0.3864–271.2; 0.5476–275.3; 0.7184–279.3; 0.9073–284.5; 1.0503–287.8; 1.2170–291.8; 1.4670–298.1; 1.7128–304.1. Main period: 1.965–309.5; 2.214–315.6; 3.464–344.9; 3.714–350.1; 4.214–360.0; 11.842–502.1; 22.06–633.4; 22.71–639.7; 23.21–645.0; 30.29–706.8; 31.46–715.5; 42.11–779.7; 44.14–789.6; 46.13–797.4; 48.13–805.5; 50.08–812.7. End period: 118.5–900.5; 138.5–904.5; 142.5–905.0; 146.5–905.5; 166.5–906.8; 191.5–907.1; 215.0–907.4; 235.0–907.8; 239.0–908.1; 242.5–907.9; 262.0–907.8.

*Computed values:* Undissolved CuCl approximately 6 g. Gas phase capacity  $\varphi_g = (2.651 \pm 0.003) \times 10^{-4}$  m·mm<sup>-1</sup>. Theoretical end pressure according to vinyl chloride calibration  $908.0 \pm 2.1$ ; highest measured pressure in the acetylene experiment 908.1. For the computation of  $\kappa$  the value  $P_{\infty} = 908.0$  has been used. Start pressure  $P_0 = 261.0$  and equilibrium pressure  $P_{\infty} = 260.0$ .  $\sigma(P) = \pm 0.3$  mm.  $(A_{\infty}/P_{\infty}) \cdot \ln 10 = 2.009$  m·atm<sup>-1</sup>; constants for (16) and (17):  $\psi = 0.0104$ ;  $\gamma A_{\infty} = 0.02264$  m·atm<sup>-1</sup>.

*Experiment 8: CuCl(s) and C<sub>2</sub>H<sub>2</sub> (CuCl)<sub>3</sub>(s); 8.51 m HCl; 25.0°C.*

*Procedure:* 15.97 g CuCl, 2.1 g Cu and hydrochloric acid of 16.70 g water content and 8.55 m concentration at acetylene addition. Vapour pressure 13.0 mm; 12.8 mm is read

after 12 1/2 h. Nitrogen calibration gives  $n-P$ : 2.986—527.1; 3.881—685.0; 5.654—996.9; 7.098—1252.4 and calibration with vinyl chloride: 3.412—506.0; 6.985—1023.5. After evacuation to vapour pressure 14.19 millimoles acetylene is added in four portions. When the pressure reaches about 1100 mm a solid addition complex suddenly crystallizes, the solution becomes turbid and the pressure falls abruptly. The acetylene thereafter added is rapidly absorbed. The whole addition operation takes 22 min.

*Pressure-time curve I* has been observed for approximately 20 h. The initial values are found in Fig. 7 and later ones in Table 4. As starting point ( $t = 0$ ) for this curve has been picked a point where the curve gives the impression that the acetylene absorption is completed and that the reaction has reached a stationary state.

Venting is performed by pressure equilibration with an evacuated 140 ml vessel, and *pressure-time curve II* is then observed for 5 h. As starting point for this curve is chosen the time of the venting. The initial phase is illustrated by Fig. 7 II and readings from the stationary phase are found in Table 4.

*Computed values:* From the nitrogen calibration we get the gas phase capacity  $\varphi_g = 3.394 \times 10^{-4} \text{ m}\cdot\text{mm}^{-1}$  and from the vinyl chloride calibration  $\varphi_B = 3.990 \times 10^{-4} \times (1 + 2.40 \times 10^{-5} \cdot P)$  and  $D_B = dB/dP_B = 3.990 \times 10^{-4}(1 + 4.8 \times 10^{-5} \cdot P)$ . At the start of curve I the solid phase can be computed to hold 112 millimoles  $\text{CuCl}$ , whereof 24 millimoles in the form of  $\text{C}_2\text{H}_2(\text{CuCl})_3(\text{s})$ . The pressure in this moment is 93 mm higher than the equilibrium pressure of the acetylene complex. Using the  $\varphi_B$ -value above it is possible to estimate the amount of vinyl chloride formed before  $t = 0$  to 0.038 m. Hydrochloric acid concentration at  $t = 0$  will then be 8.51 m.

#### HOMOGENEOUS CATALYST SOLUTION

We start from the *assumption* that the acetylene hydrochlorination rate in a homogeneous solution of cuprous chloride in hydrochloric acid is determined by *three* variables according to:

$$\frac{dB}{dt} = F(\text{CuCl}_t, \text{HCl}_t, P_A) \quad (1)$$

It should be underlined that the assumption is not self-evident. It means, *i.a.*, that the reaction velocity is regarded as independent of the concentration (and partial pressure) of the vinyl chloride formed. Not until we had observed that vinyl chloride does not form observable amounts of dissolved  $\text{Cu}_I$ -complexes, competing with acetylene for available cuprous copper, could such an assumption at all be regarded as probable.

Another necessary condition has been discussed already in Part I, *i.e.* that the equilibration of acetylene and vinyl chloride between gas and liquid phases *must* be sufficiently rapid.

The reaction velocity is — but only in the first approximation — proportional to  $P_A$  and therefore it is adequate to direct the investigations towards a study of the function  $f_p$ , defined according to:

$$f_p \equiv \frac{1}{P_A} \cdot \frac{dB}{dt} = \frac{F(\text{HCl}_t, \text{CuCl}_t, P_A)}{P_A} \quad (2)$$

At the *experiments* a pressure-time curve is observed and by means of formulae given in Part I it is possible to compute the amount of vinyl chloride formed  $B$ , the acetylene partial pressure  $P_A$ , and other quantities of interest for a kinetic calculation. Thus it will be possible to calculate, more or less approximately, the value of the quantity

$$I \equiv \int \frac{dB}{P_A} = \int f_p \cdot dt \quad (3)$$

for each  $P$ -value in a single experiment. Primarily has been studied how  $I$  varies with the time — a linear relation indicates a constant  $f_p$ , independent of  $P_A$ , which during the experiment decreases from  $P_0$  to zero. An interpretation of the result, however, will have to take into account that there is a certain HCl-consumption during the experiment — about 4 % in the Type experiment.

At an *approximate computation* of the integral — result being denoted  $I_1$  — not only  $\varphi_B$ , *i.e.* the vinyl chloride capacity, but also  $\varphi_A$ , the acetylene capacity of the system, are regarded as constant quantities. It is found, according to (I-2) and (I-3), that both  $B$  and  $P_A$  can be expressed as linear  $P$ -functions and the result will be (I-4):

$$I_1 = - \frac{A_{\infty}}{P_{\infty}} \ln (P_{\infty} - P) + \text{const.} \quad (4)$$

The pressure-time curve from a homogeneous experiment at first gives an impression of a first-order process, *i.e.* with a linear relation between  $I_1$  and  $t$ . In Fig. 1  $\log(P_{\infty} - P)$ -values from the Type experiment have been plotted against  $t$ ; the diagram covers the whole experiment up to 95 % conversion. For the sake of clearness, however, 19 of the 31 readings have been excluded, *i.a.* those 9 readings which belong to the start period of the experiment, up to approximately 4 % conversion. These points are rendered in a magnified scale in Fig. 7 b, Part I, and in Fig. 1 they are represented by the starting point on the ordinate. The curve, which exactly covers (*i.e.* within  $\pm 0.1$  mm in this scale) all measurements, even excluded ones, has a downward bend, but the deviation from a straight line seems small.

A diagram of this type, however, is very unsatisfactory for checking whether a process is *exactly* of the first order. If we apply the formula  $\ln(P_{\infty} - P) = -k \cdot dt$ , but with  $k$  as a variable, in order to gauge the deviation we find that the curve of Fig. 1 is consistent with a change in  $k$  (proportional to the conversion) which amounts to no less than 27 %. It does occur, at least in older literature, that kinetical diagrams of this type, in spite of even less consistency with a straight line and an even smaller extent of reaction, are regarded as proofs of an exactly first order relation. Although it is a sheer triviality we should like to underline that a diagram of this kind can be used for a preliminary examination only, and only will point at a relative prevalence of a first-order process.

If instead an "apparent kinetical constant" is computed, defined as

$$\kappa_1 = \frac{I_1 - I_1^{\circ}}{t} \quad (5)$$

a considerable trend will be found. In Fig. 2 a the  $\kappa_1$ -values are plotted against the quantity  $Y_p = (P - P_{\infty}) / (P_{\infty} - P_{\infty})$ , an approximate measure of the conversion degree. In the diagram the vertical stretches denote only such errors in  $\kappa_1$  which are derived from the uncertainty in  $P$ ; *cf.* also Table 1 where the last column gives the corresponding uncertainty in  $I_1$ .

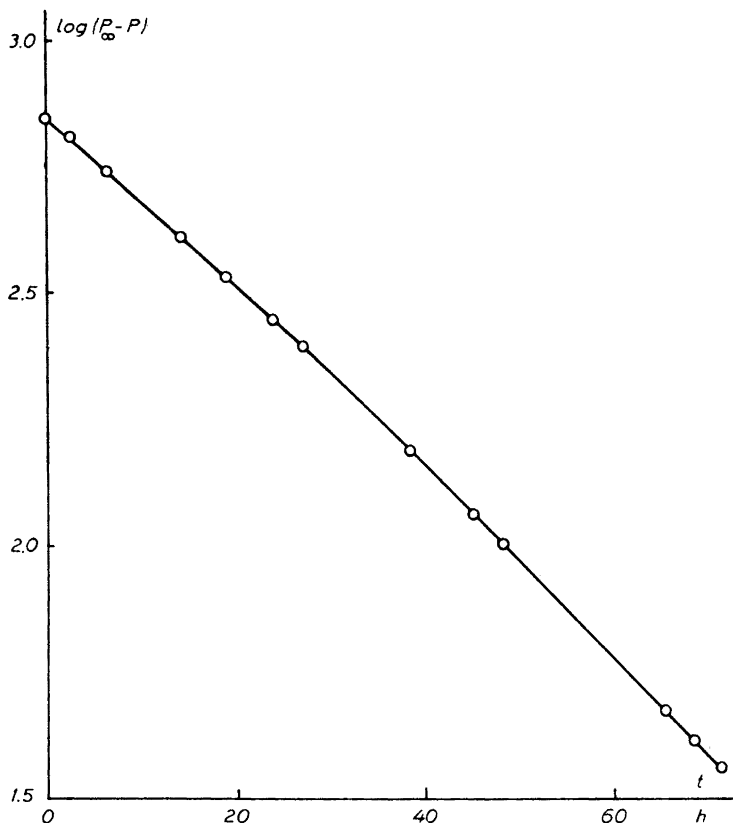


Fig. 1.  $\log(P_\infty - P)$  as function of  $t$ , experiment 1; 0–95 % conversion.

The quantity  $\kappa_1$  is so defined that the same couple of values, *i.e.*  $I = I_1^0$  at  $t = 0$ , is utilized throughout. Statistically this is of course a disadvantage, but for other reasons it is advantageous to study  $I$ - and  $t$ -intervals which have a common end point in or at the start of the experiment. In order to have a start value of better reliability than can be expected from one single reading, the whole start period (corresponding to Fig. 7 b in Part I) is utilized for this purpose. The earliest values are of course discarded, since the acetylene absorption has not yet reached equilibrium. Between remaining points a straight line is fitted. Any point on this line may be picked as a reference for the computation of  $\kappa_1$ . An interpolated point at  $t = 0.5$ – $0.6$  h will probably give the highest accuracy, but the simplest way is to choose the extrapolated intersection with the ordinate, *i.e.* the  $P_0$ -value; the loss in accuracy will be small. (*Cf.* also Part I for an exhaustive discussion of the determination of  $P_0$  and  $P_\infty$  for computation of the acetylene capacity.)

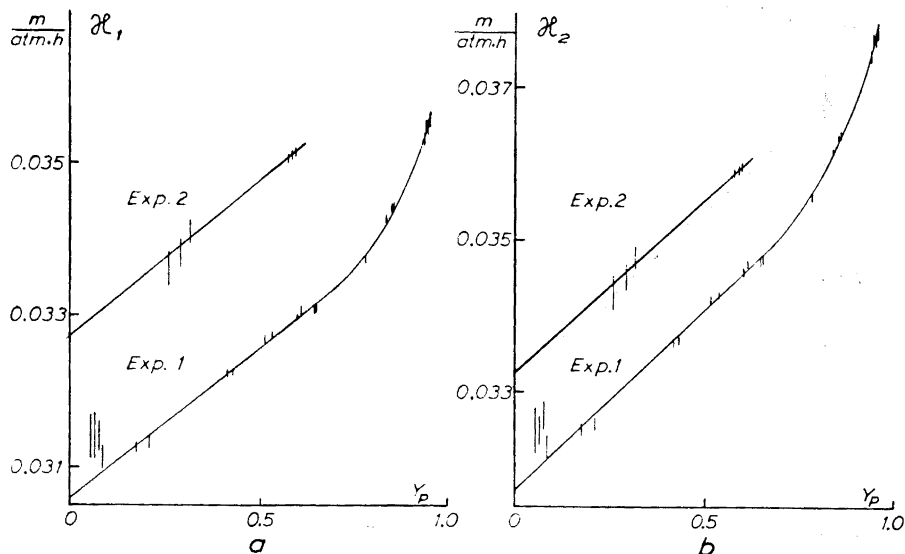


Fig. 2. Increase of  $\kappa$  with conversion degree in experiment with homogeneous catalyst: 2.75 m CuCl and 8.92 m HCl. Experiment 1 with  $P_o = 342.7$ , experiment 2 with  $P_o = 171.0$ . a:  $\kappa_1$  according to approximate formulae (4) and (5), b:  $\kappa_2$  according to more exact formulae (8)–(10).

Although the  $P$ -value, and the corresponding  $I_1^\circ$ -value, is determined with special care it will inevitably cause a systematic error in the  $\kappa_1$ -diagram. The first group of points in Fig. 2 seems a bit high up in comparison with the rest of the diagram; a somewhat too high  $P_o$ -value (about 0.5 mm) may be the source of such an error. But otherwise a possible error in the  $P_o$ -value is insignificant for the general shape of the diagram. (What has been said about the  $I_1^\circ$ -value will hold also for  $I_2^\circ$  and  $I_3^\circ$  below.)

The main result thus is that the "apparent kinetic constant"  $\kappa_1$ , rises very markedly, at least by 16 % during the experiment. It is also to be observed that  $\kappa_1$  shows an approximately linear increase with the conversion  $Y_p$  during the main part of the experiment. This might be more or less accidental. Also, the aim of the diagram is not primarily to elucidate the functional relation between  $\kappa_1$  and  $Y_p$ , but only to illustrate the monotonous increase of the  $\kappa_1$ -values in the course of the experiment; for a graphical rendering it is feasible to plot the values against the conversion.

The computation of  $\kappa_1$  thus proves that the pressure-time curve as such does not have a first order shape. Still it is not justified immediately to draw the conclusion that the  $f_p$ -function depends on  $P_A$ , as the quantity  $\kappa_1$  is only an approximate measure of the time mean of the  $f_p$ -function. The following two approximations have to be discussed: The concentration of hydrochloric acid is assumed constant although the reaction causes a consumption of HCl (about 4 % in the Type experiment) which may influence both the capa-



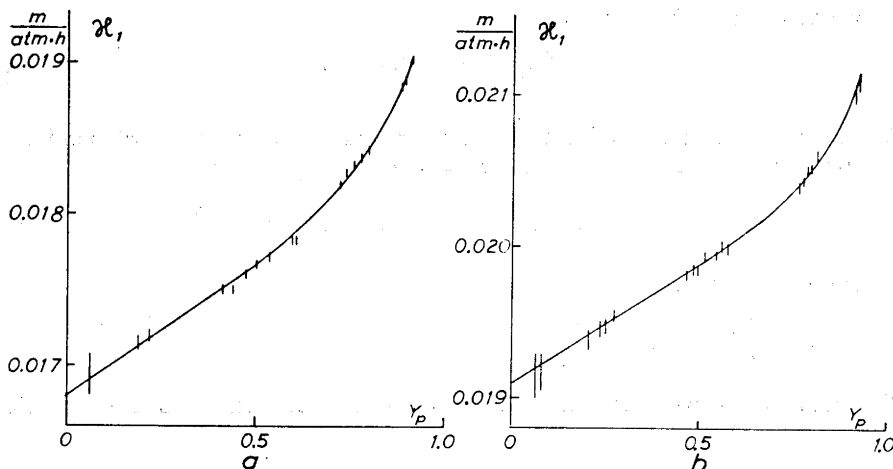


Fig. 3.  $\alpha$  as function of the conversion degree. Effect of  $\text{HCl}_t$ -change. a: 9.05 m  $\text{HCl}$ , 2.02 m  $\text{CuCl}$ ,  $P_o = 335.4$ , experiment 3. b: 9.96 m  $\text{HCl}$ , 2.01 m  $\text{CuCl}$ ,  $P_o = 328.6$ , experiment 4.

city values and the reaction rate. A comparison between experiments with different  $\text{HCl}_t$  but identical  $\text{CuCl}_t$  and almost identical  $P_o$  (cf. Fig. 3), however, indicates that the effect of  $\text{HCl}_t$ -variations (in this system of variables) is not so large that the small change in  $\text{HCl}_t$  occurring during the single experiment will be of any noticeable importance. More serious is the approximation immanent in the assumption of a constant acetylene capacity  $\varphi_A$ .

A more exact computation — results denoted  $I_2$  and  $\alpha_2$  — can be carried through if we start from the expression (I-31) which gives  $\varphi_A$  as a function of  $P_A$  under the premises "CuCl<sub>t</sub> and HCl<sub>t</sub> constant". The expressions (I-32) and (I-27) form an equation system with the variables  $\varphi_A$ ,  $B$  (or  $Y$ ),  $P$  and  $P_A$  (or  $y$ ) and the task is to calculate  $dI_2 = dB/P_A$  and the  $I_2$ -integrals from the primary  $P$ -readings.

Of course it is not necessary to choose either  $P$  or  $B$  as integration variable; we have preferred to use  $y$ , i.e. the normalized  $P_A$ -variable, defined according to:

$$y \equiv \frac{P_{\infty} - P_A}{P_{\infty}} \quad (6)$$

which is a dimensionless quantity (growing from 0 to 1) related to the conversion degree.

From the formulas mentioned it is easy to find, without any further assumptions or approximations, the following expression for  $dI_2$ :

$$dI_2 = \frac{A_{\infty} - \text{CuCl}_t \pi}{P_{\infty}} \cdot \frac{dy}{1-y} + \frac{\text{CuCl}_t \pi (1-\pi)}{P_{\infty}} \cdot \frac{dy}{(1-\pi y)^2 (1-y)} \quad (7a)$$

where we have used the abbreviation:

$$\pi = \frac{A_{\infty} - (\varphi_g + \alpha_w) \cdot P_{\infty}}{\text{CuCl}_t} \quad (7b)$$

A subdivision in partial fractions and integration with the start condition  $I_2 = 0$  when  $y = 0$  (arbitrarily chosen) gives the expression:

$$I_2 = -a_1 \ln(1-y) + b_1 \ln(1-\pi y) - c_1 \frac{y}{1-\pi y} \quad (8a)$$

where the constants are

$$a_1 = \frac{A_{\infty}}{P_{\infty}} + \frac{\text{CuCl}_t \cdot \pi^2}{P_{\infty}(1-\pi)} ; b_1 = \frac{\text{CuCl}_t \cdot \pi}{P_{\infty}(1-\pi)} ; c_1 = \frac{\text{CuCl}_t \cdot \pi^2}{P_{\infty}} \quad (8b)$$

The relation between the integration variable  $y$  and the measured  $P$ -value is:

$$y = Y_p \left( 1 - \Delta \frac{1-y}{1-\pi y} \right)^{-1} \quad (9a)$$

which includes the abbreviations:

$$Y_p = \frac{P - P_{\infty}}{P_{\infty} - P_{\infty}} \quad \text{and} \quad \Delta = \frac{\text{CuCl}_t}{A_{\infty}} \cdot \frac{P_{\infty}}{P_{\infty} - P_{\infty}} \cdot \pi^2 \quad (9b)$$

This expression is of the second order in  $y$  and consequently no approximation is required. From (9)  $y$  can be solved and the accepted root inserted into (8) which gives  $I_2$  as a  $P$ -function. In order to facilitate the numerical computations, however, we have used:

$$y \approx \frac{Y_p}{1 - \Delta(1 - Y_p)} \quad (10)$$

which has proven to be a very favourable approximation. Utilizing data from the Type experiment the expression will give an error which does not exceed 0.02 % in  $y$  (or  $Y_p$ ), corresponding to less than 0.1 mm in  $P$ .

Here we have applied a rule, which has proven valuable in other similar cases, especially where no exact solution exists, and which means that — if possible — an integration variable  $x$  is chosen, whose characteristics are: the derivate  $dI/dx$  should be possible to express as an explicit  $x$ -function, which can be exactly integrated. It is of course not imperative that  $x$  can be written as an explicit  $P$ -function, but there should be an approximate expression for the computation of  $x$ -values from the primary  $P$ -values and a possibility to check the approximation, *e.g.* by numerical iteration, in such a way that the error in the approximation can be compared with the observation error. Approximations in connection with the integration, which are difficult to gauge, are thus avoided. In the actual case the variable  $y$  fulfills these demands, the integration (8) is exact and it is possible to check that the approximation implied in the application of (10) will give an error less important than the reading error in  $P$ .

Table 1. Computation of  $I_1$  and  $I_2$ ; experiment 1. Constants:  $(A_{00}/P_{00}) \cdot \ln 10 = 1.9679$  m-atm $^{-1}$ ;  $\pi = 0.09691$ ;  $A = 0.09998$ ;  $a_1 \cdot \ln 10 = 2.1147$  m-atm $^{-1}$ ;  $b_1 \cdot \ln 10 = 1.515$  m-atm $^{-1}$ ;  $c_1 = 0.0576$  m-atm $^{-1}$ ;  $P_{00}$ ,  $P_0$  etc. and  $P-t$ -values according to "Type experiment" in Part I.

Time h	$Y_p$ %	$I_1$ m-atm $^{-1}$	$y$ %	$a_1 \ln(1-y)^{-1}$ m-atm $^{-1}$	$b_1 \ln(1-\pi y)^{-1}$ m-atm $^{-1}$	$c_1 y/(1-\pi y)$ m-atm $^{-1}$	$I_2$ m-atm $^{-1}$	$\sigma_p(I)$ m-atm $^{-1}$
0	0.16	0.0014	0.18	0.0016	0.0002	0.0001	0.0013	—
1.581	5.78	0.0510	6.38	605	41	37	527	$\pm 0.0004$
1.839	6.67	591	7.36	702	47	43	612	4
2.093	7.55	672	8.32	798	53	48	697	4
2.525	8.93	800	9.82	949	62	57	830	4
5.210	17.49	1644	19.06	1942	123	112	1707	4
6.526	21.40	2059	23.23	2428	150	136	2142	5
14.347	41.87	4638	44.45	5399	289	268	4842	6
14.861	43.01	4806	45.61	5593	297	275	5021	6
18.953	51.64	6209	54.26	7184	356	330	6498	8
19.888	53.39	6526	56.00	7540	367	341	6832	8
23.908	60.31	7898	62.80	9082	414	385	8283	9
24.44	61.22	8096	63.69	9304	420	391	8493	10
26.61	64.62	8880	66.99	1.0179	441	413	9325	10
26.98	64.86	0.8939	67.22	1.0243	442	414	9387	10
38.48	78.15	1.3000	79.90	1.4735	530	499	1.3706	17
45.13	83.65	1.5477	85.04	1.7448	565	534	1.6349	23
47.68	85.35	1.6415	86.62	1.8473	577	545	1.7351	25
48.10	85.62	1.6574	86.87	1.8646	579	546	1.7521	26
65.53	93.34	2.3154	93.97	2.5793	629	596	2.4568	55
67.94	94.05	2.4116	94.61	2.6823	633	600	2.5590	62
68.51	94.19	2.4321	94.74	2.7047	633	601	2.5813	63
71.26	94.86	2.5362	95.35	2.8178	638	605	2.6935	72

$I_2$  thus is computed stepwise as follows: (a) Calculation of  $y$  according to (10); (b) Calculation of  $I_2$  according to (8); (c) finally  $\kappa_2$  is calculated according to:

$$\kappa_2 = \frac{I_2 - I_2^0}{t} \quad (11)$$

The result from such a treatment of the Type experiment data can be seen in Table 1 and Fig. 2 b, where the  $\kappa_2$ -values have been plotted against  $Y_p$ . A comparison with the  $\kappa_1$ -diagram shows that  $\kappa_2$  has an even greater trend — from 0.032 at the start to 0.038 at 95 % conversion, *i.e.* an increase by almost 20 %.

A still more exact computation starts from the expression (I-33) which gives  $\varphi_A$  as a function of  $P_A$  at the premises "CuCl<sub>t</sub> constant and HCl<sub>t</sub> = HCl<sup>0</sup> - B". However, such a computation would result in a  $\kappa$ -quantity of an even more rapidly rising trend, and so we have refrained.

The conclusion is that the quantity  $f_p$  — for which  $\kappa_2$  is a time mean — is not independent of  $P_A$ , but definitely rises with decreasing  $P_A$ . This is confirmed by a comparison between experiments 2 and 1 which are identical except that the amount of acetylene, and thus the start pressure  $P_0$ , is smaller in experiment 2. Fig. 2 illustrates that at a given conversion  $\kappa_2$  is higher in experiment 2.

In the velocity function  $F(\text{CuCl}_t, \text{HCl}_t, P_A)$  the variable  $P_A$  can thus not be "detached", nor is it easy to find any other way to split up the function into simpler factors, thus separating the variables. A further study of the function *e.g.* by experiments where  $P_A$  and one of the other variables are kept constant, while the remaining one is changed, will not be easy in charge experiments of this type. For an orientation it is possible to utilize those  $\kappa^\circ$ -values which can be found by a linear extrapolation to  $Y = 0$  in diagrams of the same type as in Figs. 2 and 3. If we presume that the extrapolation will give the desired limes value, the following expression holds:

$$\kappa^\circ \equiv \lim_{Y \rightarrow 0} \kappa = f_p^\circ \quad (12)$$

The function value  $f_p^\circ$  is referred to the variable values  $P_A = P_\infty$ ,  $\text{HCl}_t = \text{HCl}_t^\circ$  and  $\text{CuCl}_t$  according to the recipe. (The quantity  $f_p^\circ$  can also be estimated, but with a lower accuracy, from the initial sloped  $\ln(P_\infty - P)/dt$  graphically evaluated in diagrams according to Fig. 7 in Part I.)

The experiments here treated have been so chosen that they — compared in pairs — give information on the effect of a change in one of the three variables. Of course it is difficult to get the same  $P_o$  in two different experiments with different catalyst batches, but a fair coincidence will be sufficient, since  $f_p$  varies but little with  $P_A$ .

The most interesting comparison is furnished by experiments 1 and 3, both with 9 m HCl and almost identical start pressures ( $P_o = 343$  and  $335$ ) but with  $\text{CuCl}_t$  2.753 and 2.024 m, respectively. The ratio between the extrapolated  $\kappa^\circ$ -values is 1.84, whether  $\kappa_1$  or  $\kappa_2$  is used, and agrees well with the square (1.85) of the ratio between the  $\text{CuCl}_t$ -values.

A complete analysis of the kinetical relation in experiments of this type, however, leads to such difficulties that we have been forced to try other methods, firstly experiments of the type treated below.

#### CATALYST SOLUTION IN EQUILIBRIUM WITH SOLID CUPROUS CHLORIDE

One degree of freedom disappears if the cuprous chloride activity is kept constant and *two* variables, *e.g.*  $\text{HCl}_t$  and  $P_A$ , should be sufficient to define all intensive properties of the system, including the reaction velocity at the hydrochlorination of acetylene:

$$\frac{dB}{dt} = F_s(\text{HCl}_t, P_A) \quad \text{Condition: CuCl(s) present} \quad (13)$$

In this case also we thus assume that the vinyl chloride formed has no importance for the reaction velocity. Further a thermodynamic equilibrium is presumed between the phase as regards both acetylene, vinyl chloride and cuprous chloride — prerequisites and check possibilities have been discussed in Part I. Finally is presumed that the solid phase does not cause any observable reaction or gas adsorption — which has been confirmed in control experiments (with varying amounts of solid) — omitted here.

The function

$$f_p \equiv \frac{1}{P_A} \cdot \frac{dB}{dt} = \frac{F_s(\text{HCl}_t, P_A)}{P_A} \quad (14)$$

will in this case also be studied by computation of the integral  $I$  and the "apparent constant"  $\kappa$ , defined as

$$I = \int \frac{dB}{P_A}; \kappa = \frac{I - I^0}{t} \quad (15)$$

where  $I^0$  is the starting point, corresponding to  $t = 0$ . With reservation for approximations at the computation the quantity  $\kappa$  is identical with the time mean of the  $f_p$ -function. If  $\kappa$  remains constant during the experiment,  $f_p$  will also remain constant, *i.e.* independent of  $P_A$ . A covariation in  $\text{HCl}_t$  must be taken into consideration.

At an *approximate calculation* (symbolized by the index 1) of  $I_1$  and  $\kappa_1$  the acetylene capacity  $\varphi_A$  is regarded as constant ( $= A_{\infty}/P_{\infty}$ ). This is a better approximation than the corresponding one for the homogeneous catalyst: the  $\varphi_A$ -changes in the experiments (5—6—7) can be estimated at 1.7—3.0—2.6 % at the highest.  $I_1$  and  $\kappa_1$  are computed by expressions (4) and (5) above.

The  $\kappa_1$ -values have a decreasing trend. As a function of  $Y_p$  (or  $Y$ ) the course is rather linear at the beginning of the experiment and up to  $Y$  *ca.* 0.6. These functions are symbolized by the dotted lines in Fig. 4.

For a *more exact calculation* (symbolized by the index 3) we start from expression (I—29) which describes how  $\varphi_A$  varies with  $B$  at the experimental condition: " $\{\text{CuCl}\}$  constant and  $\text{HCl}_t = \text{HCl}_t^0 - B$ ".

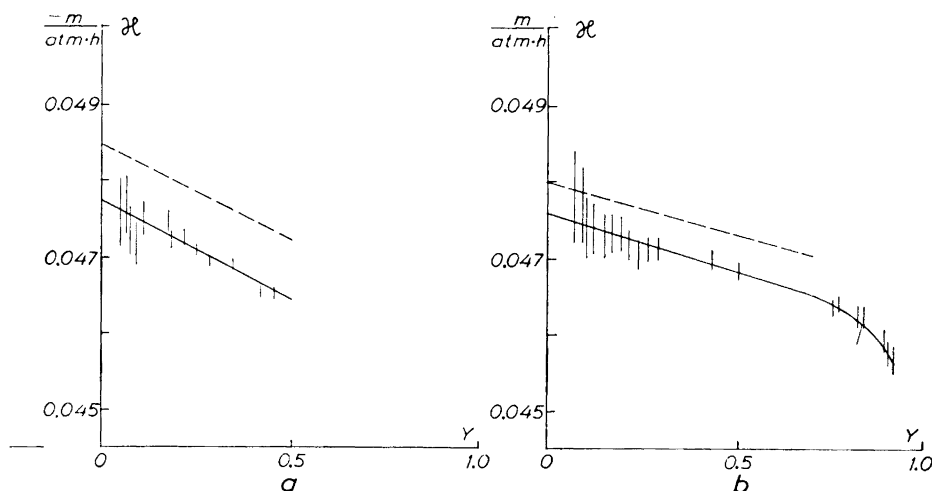


Fig. 4. Decrease of  $\kappa$  with increasing conversion degree in experiments where 9 m HCl is saturated with CuCl. Dotted line shows  $\kappa_1$  computed by approximate formulae. Points and solid line show  $\kappa_3$  computed by more exact formulae (15)—(17). *a*:  $P_0 = 169.5$ , experiment 5. *b*:  $P_0 = 304.8$ , experiment 6.

Table 2. Computation of  $I_1$  and  $I_3$ ; experiment 5. Constants and  $P-t$  values from "Experiment".

Time h	$Y_p$ %	$I_1$ m·atm <sup>-1</sup>	$Y$ %	$-\frac{A_{\infty}}{P_{\infty}} \cdot \ln(1-Y)$	$I_3$ m·atm <sup>-1</sup>	$\sigma_p(I_3)$ m·atm <sup>-1</sup>
0	0.61	0.0061	0.60	0.0060	0.0060	—
1.074	5.63	581	5.56	573	572	± 0.0005
1.233	6.35	658	6.27	649	648	5
1.474	7.38	769	7.29	759	758	5
1.715	8.41	881	8.31	870	869	5
2.232	10.72	0.1137	10.59	0.1122	0.1120	5
3.736	16.95	.1862	16.76	.1838	.1833	6
4.243	18.87	.2096	18.66	.2070	.2064	6
5.157	22.35	.2536	22.12	.2505	.2496	6
5.988	25.33	.2928	25.07	.2892	.2880	6
7.015	28.83	.3409	28.55	.3369	.3353	7
8.910	34.97	.4313	34.66	.4265	.4240	7
11.513	42.33	.5517	42.00	.5459	.5420	8
12.735	45.56	.6095	45.22	.6032	.5985	9

This expression and formula (I-27) give, if the conversion  $Y$  is chosen as the integration variable:

$$I_3 = -\frac{A_{\infty}}{P_{\infty}} \ln(1-Y) + \gamma A_{\infty}[Y + \ln(1-Y)] \quad (16)$$

The integration constant has been arbitrarily fixed so that  $I_3 = 0$  when  $Y = 0$ .

For computation of the conversion degree  $Y$  from the read  $P$ -value (and constants) we have used the approximate expression:

$$\left\{ \begin{array}{l} Y = \frac{Y_p}{1 + \psi(1-Y_p)} \\ \text{where } Y_p = (P - P_{\infty}) / (P_{\infty} - P_{\infty}) \\ \text{and } \psi = \gamma P_{\infty}^2 / (P_{\infty} - P_{\infty}) \end{array} \right. \quad (17)$$

The approximation can be checked by the exact formula (I-30). In the experiments here treated the approximation error in  $Y$  is considerably smaller than that caused by the reading error in  $P$ .

The results from these computations of  $I_3$  and  $\kappa_3$  are found in Table 2 and in Figs. 4 and 5. The  $\kappa_3$ -values are somewhat lower than the corresponding  $\kappa_1$ -values. The difference remains practically constant in each single experiment, which causes the  $\kappa_1 - Y$  and  $\kappa_3 - Y$ -curves to run almost parallel. The last column in Table 2 gives that uncertainty in  $I_3$ , which is derived from the reading error in  $P$ . The corresponding uncertainty in  $\kappa_3$  is represented in the figures by the vertical stretches.

The quantity  $\kappa_3$  falls with increasing  $Y$ . At  $Y = 0.5$ , i.e. 50% conversion,  $\kappa_3$  in the three experiments is about 2-3% lower than at the beginning of

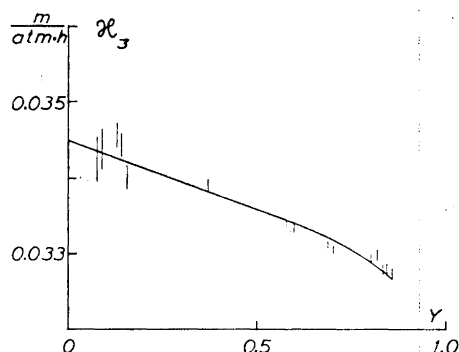


Fig. 5.  $\kappa_3$  as function of the conversion degree in experiment where 8 m HCl is saturated with CuCl. Experiment 7.

the reaction. The relation between  $\kappa_3$  and  $Y$  seems approximately linear, at least in the earlier phase of the reaction, up to  $Y = 0.5-0.7$ ; at a higher  $Y$  a deviation occurs. The two diagrams in Fig. 4 correspond to experiments 5 and 6, which differ only in the quantity of acetylene added, while hydrochloric acid concentration, batch and other experimental conditions have been kept as similar as possible. In the experiment where the acetylene amount is larger (subfigure *a*)  $\kappa_3$  falls more rapidly with  $Y$ . But it seems that, within the experimental accuracy, the extrapolated values

$$\kappa_3^\circ \equiv \lim_{Y \rightarrow 0} \kappa_3 = f_p^\circ \quad (18)$$

were identical in both experiments.

Those approximations which remain even in the  $\kappa_3$ -computation, essentially pertaining to gas compressibility etc., could not have effects of importance in comparison to these  $\kappa_3$ -variations. It is therefore obvious that the decrease must be traced back to a real change in  $f_p$ . In accordance with the relation

$$\kappa_3 = \frac{1}{t} \int_0^t f_p dt \quad (19)$$

the  $f_p$ -change has the same direction and is larger.

The consumption of HCl during the reaction causes a decrease in  $f_p$ . A comparison between experiments of different start concentrations  $\text{HCl}_t^\circ$  actually shows that the  $f_p$ -function increases so rapidly with  $\text{HCl}_t$  that the effect may be noticed already in an isolated experiment. As is evident from Table 3 an increase in the HCl-concentration by 14 % can cause an increase by 39 % in  $\kappa_3^\circ$ .

This justifies the hypothesis that  $f_p$  is independent of  $P_A$  and that the decrease in  $f_p$  and  $\kappa_3$  in a single experiment can be entirely explained by the HCl-consumption. The agreement between the extrapolated  $\kappa_3^\circ$ -values of the two experiments (in Fig. 4) with identical  $\text{HCl}_t^\circ$  but different  $P_0$  can be taken as a support for the hypothesis. (Note the corresponding comparison for homogeneous catalysts: the extrapolated  $\kappa^\circ$ -values of Expts. 1 and 2 in Fig. 2 b differ significantly.)

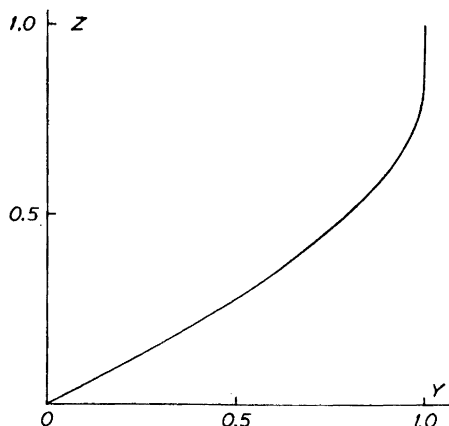


Fig. 6. The quantity  $Z$ , defined by (22), as function of  $Y$ .

One may assume that the HCl-dependence of the  $f_p$ -function can be satisfactorily rendered by:

$$f_p = f_p^\circ + \sigma \cdot \Delta \text{HCl}_t \quad (20)$$

with a constant  $\sigma$  at such small HCl-changes as will occur during a run. If this expression is inserted into (19) with  $\Delta \text{HCl}_t = -A_{oo} \cdot Y$  and  $f_p^\circ = \kappa_3^\circ$  we get:

$$\kappa_3 = \kappa_3^\circ - \sigma A_{oo} \frac{1}{t_0} \int Y \, dt \quad (21)$$

For the computation of  $Y$ 's time mean, which enters into the second term, it is possible to use the approximate first order relation:  $\text{dln}(1-Y) = -k \, dt$ . One will then get:

$$\begin{cases} \kappa_3 = \kappa_3^\circ - \sigma A_{oo} Z \\ Z \equiv 1 + \frac{Y}{\ln(1-Y)} \end{cases} \quad (22)$$

where we introduce the variable  $Z$ , which like the conversion degree  $Y$  goes from 0 to 1, following a course illustrated by Fig. 6.

The experiments here treated also give a linear relation if the  $\kappa_3$ -values are plotted against  $Z$  instead of  $Y$ . The deviation from a straight line which occurs at higher  $Y$ -values in Figs. 4 and 5 disappears. To save space these diagrams have been omitted.

The  $\kappa$ - $Y$  relation also shows a linear trend at low  $Y$ -values. It is easy to show that the limit value of the quotient  $Z/Y$  (when both tend to zero) is  $1/2$  and Fig. 6 shows that the approximation  $Z \approx Y/2$  is roughly acceptable in this connection — but only at low  $Y$ -values. There should thus exist an approximately linear trend with a slope of  $(-\sigma A_{oo}/2)$  at the beginning of a  $\kappa$ - $Y$  diagram and for the initial value of the derivative holds:

$$\left( \frac{d\kappa_3}{dY} \right)_0 = -\frac{\sigma A_{oo}}{2} \quad (23)$$

with the same validity as (22).



Table 3. Comparison between computed and measured slope ( $d\kappa_3/dY$ )<sub>o</sub>.

Expt. No	Conditions		Acc. to $\kappa - Y$ -diagram		Computed $-d\kappa_3/dY$ m·atm <sup>-1</sup> ·h <sup>-1</sup>
	HCl <sub>t</sub> <sup>o</sup> m	A <sub>oo</sub> m	$\kappa_3^o$ m·atm <sup>-1</sup> ·h <sup>-1</sup>	$-d\kappa_3/dY$ m·atm <sup>-1</sup> ·h <sup>-1</sup>	
5	9.05	0.2193	0.0475 <sub>5</sub>	0.0016	0.0013
6	9.05	0.3966	0.0477 <sub>5</sub>	0.0026	0.0024
7	7.94	0.2983	0.0345 <sub>5</sub>	0.0019	0.0018

The result of a comparison between the computed and observed slope can be seen in Table 3. The derivate  $d\kappa_3/dY$  has been computed as  $\sigma A_{oo}/2$  with  $\sigma = 0.0119 \text{ atm}^{-1} \cdot \text{h}^{-1}$ , attained as  $\Delta\kappa_3^o/\Delta \text{HCl}_t$  from the values of  $\kappa_3^o$  and HCl<sub>t</sub>. The value of  $d\kappa_3/dY$  in the third column corresponds to the slope of the straight lines in Figs. 4 and 5.

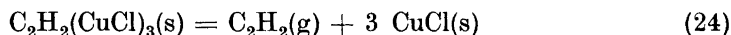
Taking into consideration that the whole  $\kappa_3$  variation here discussed lies within a few percent the agreement between computed and measured slopes must be regarded as very good. The conclusion will be that in these experiments there is no other  $\kappa_3$  variation than that which is caused by HCl-changes and that the function  $f_p$  is thus independent of  $P_A$ .

It is likely that the conclusion can be generalized to cover both a wider HCl-interval and to hold for solutions not saturated with cuprous chloride also, provided that the thermodynamic cuprous chloride activity {CuCl} is used as a variable.

Of immediate interest is, however, to study how  $f_p$  depends on HCl<sub>t</sub> at {CuCl} = 1. The only information on this matter which can be derived from the present material is found in the comparison (Table 3) between the  $\kappa_3$ -values from experiments 5–6 (9.05 m HCl) and from experiment 7 (7.94 m HCl), which shows that  $f_p$  in this interval increases very rapidly with HCl<sub>t</sub>, proportionally almost to HCl<sub>t</sub><sup>2.5</sup>.

#### CATALYST SOLUTION IN CONTACT WITH SOLID CUPROUS CHLORIDE AND SOLID ADDITION COMPLEX

The solid addition compound  $C_2H_2(CuCl)_3$ , according to previous investigations,<sup>1</sup> stays in equilibrium with its components:



and the equilibrium pressure (in atm.) depends on the temperature as follows:

$$\log P_3 = \log 0.377 - 2.68 \times 10^3 \left( \frac{1}{T} - \frac{1}{298.2} \right) \quad (25)$$

Thus, at 25.0°C the equilibrium pressure is  $0.377 \pm 0.001 \text{ atm.}$

This solid addition compound, as well as the analogous compound  $C_2H_2(CuCl)_2(s)$  and others that may exist,<sup>2</sup> can be utilized as a means of experimental aid in several different ways at the study of the behaviour of acetylene in cuprous chloride solutions. In a system where an addition compound forms the single solid phase the  $CuCl$ -activity can be adjusted with high precision by the acetylene pressure; we have previously<sup>2</sup> used this method for analysis of other equilibria. For synthetical purposes the addition compounds have been utilized, perhaps quite unintentionally, in making both divinylacetylene<sup>3</sup> and acrylonitrile<sup>4</sup> in the original batch processes, where the catalyst solution holds an excess of solid cuprous chloride which is partially transformed into addition compound upon the introduction of acetylene. This means that a considerable amount of acetylene is stored at a moderate pressure and the consumption due to the irreversible reaction in the solution is continuously compensated for.

In the case here discussed the aim is of course to keep the catalyst solution in equilibrium with *two* solid phases so that both the cuprous chloride and the acetylene activities remain constant during the reaction; a most appealing type of experiment for kinetical studies of the vinyl chloride formation. It is assumed that the solid addition compound does not as such enter into any noticeable chemical reaction or gas adsorption.

In *experiment 8* the 8.5 m  $HCl$  solution is saturated with cuprous chloride; the undissolved amount can be estimated at 6.67 millimoles per g of water. An amount of acetylene is introduced, formally corresponding to 0.85 m,

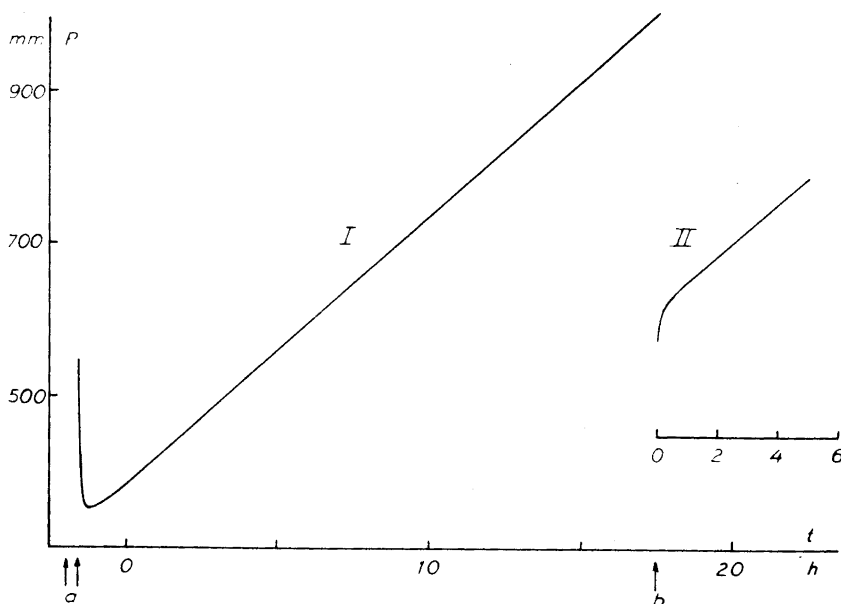


Fig. 7. Pressure-time curve from experiment (No. 8) with two solid phases, general survey. At *a* acetylene is introduced, at *b* gas is sucked out.

and about 22 % of the solid  $\text{CuCl}$  is transformed into  $\text{C}_2\text{H}_2(\text{CuCl})_3$ . A characteristic supersaturation phenomenon is observed: the acetylene pressure rises to 1 1/2 atm. before the crystallization begins. Afterwards acetylene is quite rapidly absorbed at a pressure slightly above the equilibrium pressure 0.377 atm. As is seen in Fig. 7 a slow, almost linear pressure rise then sets in, which can be observed for a long time. If gas is sucked out from the vessel the system soon returns to a stationary state and the almost linear pressure increase continues — curve II in Fig. 7. An examination of the  $P-t$  relation in a larger scale shows that there is a faint downward bend.

Empirically it is possible to treat the  $P-t$  relation as an expression of second order in  $t$ . With constants determined by the least square method we get an amazing agreement between the computed and the measured  $P$ -values; cf. Table 4. The accuracy of the computed constants also is very good. The primary aim of the statistical treatment, however, is to calculate the velocity derivate  $U = dP/dt$ , its dependence on  $t$  (or  $P$ ) and its accuracy. From these  $U$ -values it will then be possible to compute  $dB/dt$  and  $f_p$ .

Fig. 8 shows that in both curves there are initial periods before the stationary state is reached, more markedly in curve I where possibly it is connected with a crystal growth. To avoid a systematic error early points have been rigorously excluded, only the last one in each figure has been included in the calculations.

*Statistical treatment of the pressure-time curve I.* The first task is to determine, by the least square method, the best constants of the function

$$P = a + bt + ct^2 \quad (26)$$

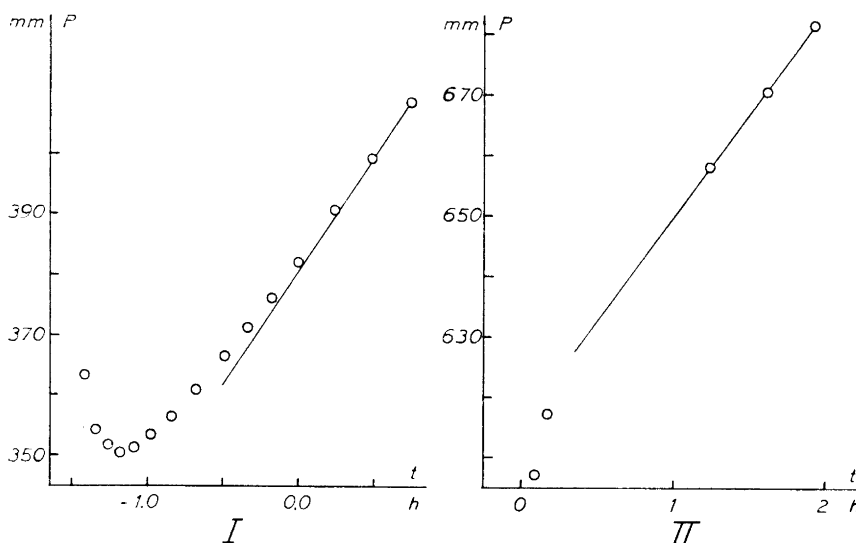


Fig. 8. Initial periods in experiment with two solid phases. I: after acetylene addition, II: after suction. The straight lines are extrapolations from the later linear course, outside the range of the figure.

Approximate constants are graphically determined with the result:  $a' = 380.60$ ,  $b' = 37.190$  and  $c' = -0.0900$ . Then are computed the differences  $y = P - a' - b't - c't^2$  (with one more decimal place than  $P$ ) and graphically studied as a function of  $t$ . It is estimated that  $|dy/dt|$  for a fitted second order curve surely is small enough to permit a shortening of  $t$ ; the numerical accuracy of the first decimal place in  $t$  seems sufficient to make a computed  $y$ -value reliable in the second decimal place. Such abbreviated  $t$ -values are denoted  $x$  and used for calculation of the best constants in

$$y = \Delta a + \Delta b x + \Delta c x^2 \quad (27)$$

by means of the normal equations

$$\begin{cases} \Delta a n + \Delta b (1) + \Delta c (2) = (y) \\ \Delta a (1) + \Delta b (2) + \Delta c (3) = (y1) \\ \Delta a (2) + \Delta b (3) + \Delta c (4) = (y2) \end{cases} \quad (28)$$

where we have used the abbreviations (1) =  $\Sigma x$ , (2) =  $\Sigma x^2$ , (3) =  $\Sigma x^3$ , (4) =  $\Sigma x^4$ , (y) =  $\Sigma y$ , (y1) =  $\Sigma yx$  and (y2) =  $\Sigma yx^2$ . In these numerical calculations the  $y$ - and  $x$ -values have been regarded as exact numbers and no shortening has been accepted, apart from the one already mentioned and those which at the end of the calculation (evaluation of the determinants) are found permissible. From the  $\Delta$ -values attained is calculated  $a = a' + \Delta a$  etc. and by means of these constants the function values  $P_{\text{comp}}$  for all occurring  $t$ -values. As is evident from Table 4 the differences between computed and measured  $P$ -values are very small. The dispersion, computed according to (29) is

Table 4. Experiment with two solid phases,  $P-t$  readings and  $P_{\text{comp}} = a + bt + ct^2$ .

Curve I			Curve II			
$t$	$P$	$P_{\text{comp}}$	$t$	$P$	$P_{\text{comp}}$	
					Alt. 1	Alt. 2
0.754	408.6	408.41	1.927	681.9	681.94	682.04
1.021	418.6	418.31	2.294	694.4	694.48	694.50
1.245	426.5	426.61	2.667	707.3	707.18	707.14
1.495	435.8	435.86	3.000	718.5	718.47	718.41
1.745	445.1	445.10	3.502	735.6	735.43	735.36
2.004	454.5	454.66	4.000	751.9	752.17	752.12
2.499	472.7	472.89	4.500	768.9	768.89	768.90
2.995	490.9	491.12	5.000	785.6	785.53	785.64
3.244	500.1	500.25				
5.129	569.3	569.01				
5.559	584.8	584.60				
15.859	947.5	947.79				
16.429	967.4	967.31				
16.809	980.2	980.28				
17.479	1003.3	1003.11				

$\sigma(P) = \pm 0.22$  mm and thus hardly larger than the reading error. For computation of the errors of the constants the following expressions have been applied:

$$\left\{ \begin{array}{l} \sigma^2(P) = \frac{\Sigma(P - P_{\text{comp}})^2}{n-3} ; \sigma^2(b) = \left| \begin{array}{c} n(2) \\ (2)(4) \end{array} \right| \cdot \frac{\sigma^2(P)}{D} \\ \sigma^2(a) = \left| \begin{array}{c} (2)(3) \\ (3)(4) \end{array} \right| \cdot \frac{\sigma^2(P)}{D} ; \sigma^2(c) = \left| \begin{array}{c} n(1) \\ (1)(2) \end{array} \right| \cdot \frac{\sigma^2(P)}{D} \end{array} \right. \quad (29)$$

where  $D$  is the main determinant of the equation system (28).

The requested pressure-time derivate can be written:

$$U \equiv \frac{dP}{dt} = b + 2ct \quad (30)$$

For an estimate of its uncertainty one will have to study how  $U$  depends on the individual  $P$ - (or  $y$ -) values by summing up the squares of the partial derivatives. This expression can be simplified to:

$$\Sigma \left( \frac{\partial U}{\partial y} \right)^2 = \frac{1}{D} \left( \left| \begin{array}{c} n(2) \\ (2)(4) \end{array} \right| - 4t \left| \begin{array}{c} n(2) \\ (1)(3) \end{array} \right| + 4t^2 \left| \begin{array}{c} n(1) \\ (1)(2) \end{array} \right| \right) \quad (31)$$

from which is computed

$$\sigma(U) = \sigma(P) \cdot \Sigma^{1/2}$$

This expression, where  $t$  enters as a parameter, has a minimum and in its vicinity  $\sigma(U)$  is rather small in comparison to the individual terms; their coefficients must therefore be calculated with fair numerical accuracy.

In the  $U$ -function (30) the  $t$ -term is so small in comparison with the constant term that  $U$  can be interpreted as an approximately linear function of  $P$  also. If related  $U$ - and  $P$ -values are computed according to (26) and (30), respectively, for a series of arbitrarily chosen  $t$ -values, it will be easy to choose graphically a linear  $U(P)$ -function which renders the  $U$ -values with deviations smaller than  $\sigma(U)$ .

For curve I the final result is

$$\left\{ \begin{array}{l} a = 380.37 \pm 0.14 \\ b = 37.257 \pm 0.063 \\ c = -0.0932 \pm 0.0033 \end{array} \right. \\ \left\{ \begin{array}{l} U = 37.257 - 0.1864 t \\ \sigma(U) = \pm 0.063 (1 - 0.2116 t + 0.01142 t^2)^{1/2} \end{array} \right.$$

In Fig. 9 the quantity  $2\sigma(U)$  has been plotted on each side of the straight line which represents  $U = b + 2ct$  for curve I; the dotted lines thus give proximately a 95 % confidence band.

*Statistical treatment of pressure-time curve II.* An analogous treatment starting from the data of Table 4 and the approximate constants  $a' = 616.00$ ,  $b' = 34.410$  and  $c' = -0.0960$  gives a final result which we have called *alternative 1*:

$$\begin{cases} a = 615.3 \pm 0.7 \\ b = 34.89 \pm 0.45 \\ c = -0.170 \pm 0.064 \end{cases} \quad \sigma(P) = \pm 0.16$$

The  $P$ -values computed with accepted constants are given in Table 4.

$$\begin{cases} U = 34.89 - 0.340 t \\ \sigma(U) = \pm 0.45 (1 - 0.571 t + 0.0825 t^2)^{1/2} \end{cases}$$

That the constants for curve II are less accurate than the corresponding ones for curve I is of course explained by the fact that the  $P$ - and  $t$ -intervals are narrower and the readings fewer. The difference between the  $c$ -constants is not significant and there is every reason to assume that the true values coincide. Under these conditions it is justified to study curve II in such a way (denoted *alternative 2*) that the value  $c = -0.0932$  is borrowed from curve I, while the two other constants are computed. The same approximate values as above are used for  $a'$  and  $b'$ . The normal equations then simplify into:

$$\begin{cases} \Delta a n + \Delta b (1) = (y) \\ \Delta a (1) + \Delta b (2) = (y1) \end{cases} \quad (32)$$

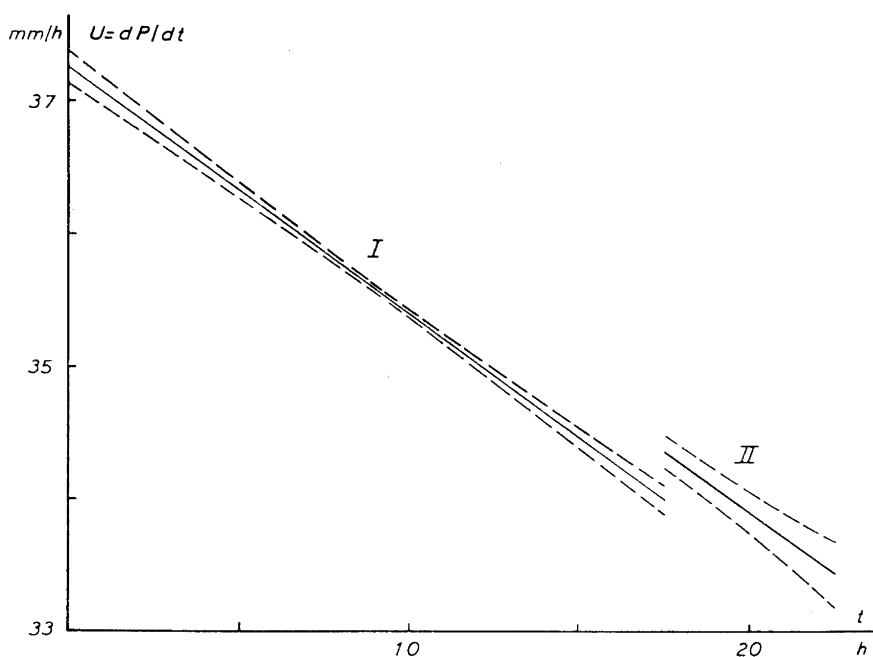


Fig. 9. Rate of pressure increase,  $U$ , as function of  $t$  in experiment with two solid phases. Computed functions with 95 % confidence band.

$P$ -values computed by means of accepted constants are found in Table 4. For estimation of the errors of the constants and the uncertainty in  $U$  we have applied:

$$\begin{cases} \sigma^2(P) = \frac{\Sigma(P - P_{\text{comp}})^2}{n-2} ; \sigma^2(b) = \frac{n}{D} \cdot \sigma^2(P) \\ \sigma^2(a) = \frac{(2)}{D} \cdot \sigma^2(P) ; \sigma^2(U) = \sigma^2(b) + 4 t^2 \sigma^2(c) \end{cases} \quad (33)$$

In  $\sigma(U)$  there is of course a contribution from the borrowed  $c$ -constant, however, almost negligible. The final result at an interpretation according to *alternative 2* is

$$\begin{cases} a = 616.17 \pm 0.21 \\ b = 34.36 \pm 0.06 & \sigma(P) = \pm 0.17 \\ c = -0.0932 \pm 0.0033 \\ U = 34.36 - 0.1864 t \\ \sigma(U) = \pm 0.06 (1 + 0.0121 t^2)^{1/2} \end{cases}$$

The standard deviation  $\sigma(P) = \pm 0.17$  is practically the same as in *alternative 1* ( $\pm 0.16$ ), which indicates that *alternative 2* can be accepted. Fig. 9 shows  $U(t) \pm 2\sigma$  according to *alternative 2*.

*Computation of  $f_p$  from  $U = dP/dt$ .* The kinetic function  $f_p$ , defined in (14) can be computed from

$$f_p = \frac{U}{P_3} \cdot \frac{dB}{dP} \quad (34)$$

provided the solution is in equilibrium with both solid phases.

To get a sufficiently accurate value for the derivate  $dB/dP$  we have started from the discussion on the non-ideal behaviour of the gases in Part I, using expression (I-13), the analogous  $B$ -expression, and (I-14). If the acetylene activity  $f_A \approx P_3$  is regarded as a constant,  $x_A$  and  $x_B$  can be substituted by  $P$ -functions, which results in an explicit  $B(P)$ -expression. After derivation and reduction, neglecting corrections of a higher order, we get:

$$\frac{dB}{dP} = \alpha_B [1 + (k_A + k_B) \cdot P_3 + 2 k_B (P - P_3)] + \varphi_B [1 - 2 k_B (P - P_3)] \quad (35)$$

If the "differential capacity" is calculated from the vinyl chloride calibration it should, in accordance with the expressions mentioned, applied with  $x_A = 0$ ,  $x_B = 1$ , satisfy the equation:

$$D_B(P) \equiv \left( \frac{dB}{dP} \right)_{\text{cal}} = \alpha_B (1 + 2 k_B P) + \varphi_B (1 - 2 k_B P) \quad (36)$$

A comparison between (35) and (36) shows that  $D_B$  for the argument  $\Delta P = P - P_3$  is a good approximation for  $dB/dP$ . The quantity  $D_B(\Delta P)$  will be somewhat larger than  $(dB/dP)_p$ , the difference however, being small and constant. Finally  $f_p$  is calculated according to

$$f_p = \frac{U}{P_3} \cdot D_B(\Delta P) \quad (37)$$

If we insert into (37) the following numerical values referring to curve I at  $t = 0$ :  $D_B = 4.009 \times 10^{-4} \text{ m}\cdot\text{mm}^{-1}$ ,  $U = 37.26 \text{ mm}\cdot\text{h}^{-1}$ ,  $P_3 = 0.377 \text{ atm}$ , the result will be  $f_p = 0.0396 \text{ m}\cdot\text{atm}^{-1}\cdot\text{h}^{-1}$ . This figure is several percent lower than can be anticipated for 8.51 m HCl from experiments where cuprous chloride is the single solid phase. It seems likely that this difference is real and that either type of experiments should be preferred. The case with two solid phases seems more suspect, the dissolution rate of the addition complex may be insufficient. Anyway the experiment lacks a test which would tell if the dissolution is sufficiently rapid. (A closer examination of a start period as in Fig. 8 II, *i.e.* after partial evacuation of the gas phase, might give material for checking this transfer resistance.)

The drop in the reaction rate during the run, appropriately measured by the derivate  $\text{dln } U/\text{d}P = 2c/U^2$ , agrees very well with the slope which can be expected as a result of the HCl-consumption and the non-ideal behaviour of the gases.

The effect of the vinyl chloride pressure on the reaction velocity is an important question, which can be elucidated by experiments of this kind, even if the problem of the dissolution rate remains unsolved. In curve I the  $U$ -value falls to  $U_I = 33.99 \pm 0.05$  at  $t = 17.52 \text{ h}$ , which time coincides with  $t = 0$  for curve II, where the start value is  $U_{II} = 34.36 \pm 0.06$  (alternative 2). At a comparison between these values it can be taken for granted that there is no other differences in the conditions than the higher partial pressure of vinyl chloride (and a somewhat larger quantity of solid addition compound) in I while stirring, HCl, acetylene activity, *etc.* are identical.

If we start from the hypothesis that the reaction rates  $\text{d}B/\text{d}t$  are the same we find:

$$\frac{U_{II}}{U_I} = \frac{(\text{d}B/\text{d}P)_I}{(\text{d}B/\text{d}P)_{II}} \quad (38)$$

Starting from (35) it is easy to form:

$$\left(\frac{\text{d}B}{\text{d}P}\right)_I = \left(\frac{\text{d}B}{\text{d}P}\right)_{II} \left[ 1 + \frac{2 k_B(\alpha_B - \varphi_g)}{(\text{d}B/\text{d}P)_{II}} (P_I - P_{II}) \right] \quad (39)$$

In the denominator of the correction term the quantity  $(\text{d}B/\text{d}P)_{II}$  can, with sufficient accuracy, be substituted by  $(\alpha_B + \varphi_g)$  and  $\alpha_B$  can then be eliminated by means of  $\varphi_B^{\infty}$ , *i.e.* the limes value of  $B/P$  (when  $P$  approaches zero) in the vinyl chloride calibration. For the relative  $U$ -difference the theoretical value will then be:

$$\frac{U_{II} - U_I}{U_I} = 2 k_B \cdot \frac{\varphi_B^{\infty} - 2 \varphi_g}{\varphi_B^{\infty}} (P_I - P_{II}) \quad (40)$$

Insertion of  $P_I = 1000 \text{ mm}$  and  $P_{II} = 600 \text{ mm}$ ,  $\varphi_B^{\infty}$  and  $\varphi_g$  according to "Experiment" and  $k_B = -0.0170 \text{ atm}^{-1}$ , will give the figure  $+1.26 \%$ . The experiment gives the difference  $+(1.09 \pm 0.24) \%$  if curve II is interpreted according to alternative 2. Alternative 1 — with independent determination of constants — gives  $+(2.6 \pm 1.4) \%$ .

The conclusion is thus that there is no other change in  $\text{d}P/\text{d}t$  when the vinyl chloride partial pressure is changed from *ca.* 700 to *ca.* 300 mm than



that which can be explained by the non-ideal compressibility of the gases. The hypothesis that the reaction rate is independent of the vinyl chloride pressure thus is confirmed.

## DISCUSSION

At an *a priori estimate* of the accuracy in  $\kappa$  we apply the expression

$$\kappa = \frac{1}{t} \cdot \frac{A_{\infty}}{P_{\infty}} \ln \frac{P_{\infty} - P_0}{P_{\infty} - P} \quad (41)$$

not only for  $\kappa_1$  but also for  $\kappa_2$  and  $\kappa_3$ . When comparing the  $\kappa$ -values within one single run the common and constant errors arising from  $A_{\infty}$  and  $P_{\infty}$  are of no interest. The quantities  $P_0$  and  $P_{\infty}$  are also singular, but the error which they cause in  $\kappa$  is not constant. They will therefore have to be taken into consideration as of course the errors of the individual  $P$ -values. If (41) is differentiated with respect to these quantities an expression will result, which, after the introduction of the conversion degree  $Y \approx (P - P_0)/(P_{\infty} - P_0)$  can be reduced to:

$$d \ln \kappa = \frac{1}{\ln(1-Y)} \left( \frac{dP_0}{P_{\infty} - P_0} - \frac{1}{1-Y} \cdot \frac{dP}{P_{\infty} - P_0} + \frac{Y}{1-Y} \cdot \frac{dP_{\infty}}{P_{\infty} - P_0} \right) \quad (42)$$

In Table 5 the numerical values at different conversions have been computed for the three partial derivatives, all multiplied by  $(P_{\infty} - P_0)$ . The figures of columns 2-4 then directly state the percent change in  $\kappa$  caused by such a change in  $P$ ,  $P_0$ , and  $P_{\infty}$  as amounts to 1% of the entire interval  $P_{\infty} - P_0$ . The  $P$ -dependence is considerable both at high and low conversions but has a minimum at  $Y = 0.6$ . The dependence on  $P_0$  is largest at a low conversion

Table 5.  $P$ -,  $P_0$ - and  $P_{\infty}$ -dependence of  $\kappa$  at different conversion degrees  $Y$ . Estimation of the  $\kappa$ -uncertainty in Experiment 1.

Y	Partial derivatives acc. to (42) multiplied by $\Delta = (P_{\infty} - P_0)$			Experiment 1			
				Estimated error contribution (%) in $\kappa$			$\sigma_1(\kappa)$ %
	$\Delta \frac{\partial \ln \kappa}{\partial P}$	$\Delta \frac{\partial \ln \kappa}{\partial P_0}$	$\Delta \frac{\partial \ln \kappa}{\partial P_{\infty}}$	from $P$	from $P_0$	from $P_{\infty}$	
0.05	20.5	19.5	1.03	0.88	1.11	0.00	1.42
0.1	10.5	9.5	1.05	0.45	0.54	0.01	0.70
0.2	5.6	4.5	1.12	0.24	0.26	0.03	0.36
0.3	4.0	2.8	1.20	0.17	0.16	0.06	0.24
0.4	3.3	2.0	1.31	0.14	0.11	0.09	0.20
0.5	2.9	1.44	1.44	0.12	0.08	0.12	0.18
0.6	2.7	1.09	1.64	0.12	0.06	0.18	0.23
0.7	2.8	0.83	1.94	0.12	0.05	0.26	0.29
0.8	3.1	0.62	2.49	0.13	0.04	0.42	0.44
0.9	4.3	0.43	3.90	0.19	0.03	0.81	0.83
0.95	6.7	0.33	6.35	0.29	0.02	1.50	1.54

and rapidly disappears with increasing  $Y$ . The  $P_\infty$ -dependence of course culminates at high conversions; with a falling  $Y$  the derivate approaches a limes value, equal to unity in the tabulated quantity. This limes value actually should be subtracted from all values since it corresponds to an error which is constant in the whole series.

The separate error contributions in the Type experiment are computed from the primary uncertainties, which have been estimated at:  $\sigma(P) = \pm 0.3$ ,  $\sigma(P_0) = \pm 0.4$ ,  $\sigma(P_\infty) \pm 2.0$ , the resulting figures are found in columns 5–7 of the table; the constant share in the error from  $P_\infty$  has been excluded. If these anticipated uncertainties are to be considered at the interpretation of a  $\kappa$ – $Y$  diagram such as in Fig. 2, it has to be kept in mind that only the error derived from  $P$  appears as a random variation (symbolized by the vertical stretches of the diagram). The errors in  $P_0$  and  $P_\infty$  are constant (but unknown) quantities which cause displacements of the calculated  $\kappa$ -values. These derived errors also depend on  $Y$  according to individual functions — the derivatives of the table.

If we disregard the differing nature of these error contributions and calculate the mean error "within the experiment" of  $\kappa$  as the root of the sum of squares, the values denoted  $\sigma_1(\kappa)$  in Table 5 are obtained. They can be accepted as a coarse estimate of the predictable accuracy and show that the  $\kappa$ -values have an uncertainty of  $\pm 0.2\%$  in a favourable conversion interval of 30 to 70% and that the measurements can be extended down to 5% and up to 95% conversion without the error rising to more than 1.5%. The general impression from the experiments is that these claims of accuracy are well met.

At a comparison between different experiments the error in  $\varphi_A^\circ = A_{\infty 0}/P_{\infty 0}$  must also be considered. As a rule it is of no interest to compare two individual  $\kappa$ -values from different experiments; the comparison should be directed to some epitomizing function. In this paper there is a function of such a type, viz.  $\kappa^\circ$ , determined by graphical extrapolation by means of  $\kappa$ – $Y$ - or  $\kappa$ – $Z$ -diagrams. This quantity will be rather independent of the error in  $P_\infty$  and of the random error in the  $P$  readings. The main source of error, apart from the uncertainty inherent in the extrapolation method as such, will be the  $\varphi_A^\circ$ -error, which according to Part I must be estimated to  $\pm 1\%$ , as long as we stick to a determination which is based on the  $P_{\infty 0}$ -value of a single run.

It is impossible to draw any more far-reaching conclusions regarding the reaction mechanism from these tentative experiments. If we, for a simplification of the results, imagine two idealized experiments ( $\text{HCl}_t$  constant) which represent the two types:

- (a) catalyst solution with constant  $\text{CuCl}_t$
- (b) catalyst solution with constant  $\{\text{CuCl}\}$

the quantity  $f_p$ , i.e. the reaction rate per  $P_A$ -unit, would show a rising trend in the  $a$ -experiment but remain constant in the  $b$ -experiment. That a noticeable difference at all occurs between these conditions is unambiguously connected with the existence of addition complexes; the experiments would otherwise be identical. When during the experiment the concentration of addition

complexes decreases an increase of  $\{\text{CuCl}\}$  occurs at a constant  $\text{CuCl}_t$ , and at a constant  $\{\text{CuCl}\}$  there is a decrease in  $\text{CuCl}_t$ .

A constant  $f_p$  in the *b*-experiment means that a velocity function which has  $P_A$ ,  $\{\text{CuCl}\}$  and  $\text{HCl}_t$  as variables has such a form that  $P_A$  can be "detached". This can be interpreted by a unimolecular hypothesis, implying that the reaction velocity is determined by a substance, whose concentration is proportional to  $P_A$  at constant  $\{\text{CuCl}\}$  and constant  $\text{HCl}_t$ . But it would seem equally justified to apply a bimolecular hypothesis with physically dissolved acetylene as the one and an inorganic cuprous complex as the other part in the rate determining step. Under all circumstances the result definitely indicates that the catalytic effect of the monovalent copper can be traced back to a reactive equilibrium complex — or several.

A plain *unimolecular decomposition* of any one of the known addition compounds  $\text{C}_2\text{H}_2\text{CuCl}_2^-$ ,  $\text{C}_2\text{H}_2\text{CuCl}$ , or  $\text{C}_2\text{H}_2\text{Cu}^+$  is an impossible mechanism, however, inconsistent with the observed dependence on both  $\text{HCl}_t$  and  $\text{CuCl}_t$ .

It seems very likely that *two atoms of copper* are involved in a rate determining step. In experiments 1 and 3, with identical  $\text{HCl}_t^0$  and  $P_0$  but with different  $\text{CuCl}_t$ , the  $\kappa^0$ -values can be used also for an estimate of the importance of the *CuCl-activity* at a constant  $\text{HCl}_t$ , since at a given acetylene partial pressure the *CuCl-activity* is proportional to  $\text{CuCl}_t$ . As pointed out before the ratio between the  $\kappa^0$ -values agrees well with the square of the ratio between the  $\text{CuCl}_t$ -values. An unimolecular hypothesis will thus have to reckon with a binuclear acetylene complex, whose concentration at a given  $\text{HCl}_t$  is proportional to  $\{\text{CuCl}\}^2 P_A$ , and a bimolecular hypothesis with a reaction between a simple addition complex (*e.g.*  $\text{C}_2\text{H}_2\text{CuCl}_2^-$ ) and a mononuclear inorganic  $\text{Cu}^+$ -compound.

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