

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

I. On Manometric Method for Accurate Kinetic Measurements

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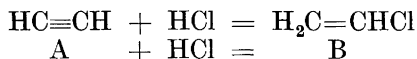
Submitted in honour of the ninetieth birthday of Professor *Hans von Euler*

The reaction



is quantitative at 25°C in aqueous solutions of cuprous chloride in hydrochloric acid. A manometric apparatus for study of the kinetics of this and similar reactions and for precise absorption measurements is described; its characteristics are: no "dead volume", mercury manometer for 0–2 atm, with device for quick reading, constant volume, magnetic stirring, nonfluctuating circulation thermostat. The conditions for accurate measurements are formulated and immanent methodological problems are discussed. It is pointed out *i.a.* that the diffusion resistance at mass transfer can become a noticeable source of error although the main reaction is slow and stirring good; test methods for different kinds of diffusion resistance are indicated. Starting from new measurements of the compressibility and solubility of gaseous vinyl chloride and previous measurements of the corresponding data for acetylene we have investigated the effect of the non-ideal behaviour of the gases, how the absorption coefficients change during the experiment, and the mutual dependence of the absorptions. Methods for the determination of P_0 and P_∞ are discussed. It is possible to compute from the time-pressure curve: conversion degree, acetylene partial pressure, and other quantities necessary for a kinetic analysis. Required formulas are given for two different sets of experimental conditions (a) homogeneous catalyst solution with constant CuCl_2 , (b) catalyst solution in equilibrium with $\text{CuCl}(s)$.

The hydrochlorination of acetylene in aqueous solution catalyzed by cuprous complexes according to



was observed in 1929 by Nieuwland¹. Some technical reports^{2,3} have been devoted to the reaction, though in the plant it could not compete with the dry mercury salt catalyst, but no theoretical studies have been published. For several reasons we are interested in the kinetics and mechanism of the reaction, *i.a.* in trying to find out if some special effect can be attributed to any of the dissolved compounds $C_2H_2Cu^+$, C_2H_2CuCl , $C_2H_2CuCl_2^-$ and $C_2(CuCl)_8^{2-}$, which we have previously⁴⁻⁷ shown to exist in equilibrium with acetylene in solutions of this kind. We have found that a distinction between kinetic alternatives often requires very accurate measurements. The reaction occurs already at 25°, at what temperature equilibrium data for the species mentioned are known. The yield is very good and the reaction rather slow, which is an advantage in the attempt to attain high precision.

The principle of the measurement is simple. A certain amount of acetylene is introduced into an evacuated reaction flask containing known amounts of cuprous chloride, hydrochloric acid and possibly other catalyst components. The main portion of the gas, *e.g.* 75 % is immediately absorbed in the liquid. The vinyl chloride forming has a markedly lower solubility and is mainly accumulated in the gas phase, only a small amount, *e.g.* 15 %, remains in the liquid. The course of the reaction can thus be followed by observing the rising pressure-time curve. The volume of the closed system is kept constant, not being influenced by manometer displacements.

When studying a catalyst recipe at a given temperature the amount of acetylene can be arbitrarily chosen (up to the point where solid acetylene compounds precipitate). The pressure limits, P_0 and P_∞ , of the reaction are then displaced approximately proportionally. There is also an extra degree of freedom characteristic of two-phase experiments of this type, *viz.* the gas/liquid ratio in the apparatus. A change in this ratio brings about a non-proportional displacement of the pressure limits and a shift in the conversion rate, which can become arbitrarily low. In most cases it has been appropriate so to regulate the batch that the initial pressure will fall within the interval 175–400 mm Hg and the final pressure within the interval 550–1300 mm.

The basis of the method thus is the considerable difference between the solubilities of acetylene and vinyl chloride in the catalyst solution. Both substances have a certain "physical" solubility of 0.04–0.05 m.atm⁻¹ (for definition of m, *cf.* *Symbols* below), but for acetylene is added an absorption which depends on the formation of Cu^I-complexes and which can reach 0.8 m.atm⁻¹ (in 10 m HCl saturated with CuCl at 25°). The importance of the complex formation for the measuring method must not be confused with their possible role in the catalytic reaction.

If the premises are idealized (ideal gases and gas mixture, quantitative yield, constant absorption coefficients) the capacity quantities

$$\begin{aligned}\varphi_A &= A/P_A \\ \varphi_B &= B/P_B\end{aligned}\quad (1)$$

— which stand for the total acetylene and vinylchloride contents resp. per unit amount of catalyst and pressure unit — can be regarded as constants and computed from the start condition $P_A = P_\infty$, when $A = A_\infty$ and $B = 0$,

and the end condition $P_B = P_\infty$, when $A = 0$ and $B = A_\infty$. (For indices cf. *Symbols* below.)

One will then find a simple linear relation between conversion degree and pressure:

$$Y \equiv \frac{B}{A_\infty} = \frac{P - P_\infty}{P_\infty - P_\infty} \quad (2)$$

and between acetylene partial pressure and total pressure:

$$P_A = P_\infty \frac{P_\infty - P}{P_\infty - P_\infty} \quad (3)$$

How these and similar functions are to be applied will of course depend on which kinetic assumption one wishes to try out. If the aim is to determine whether the reaction is of the first order in P_A according to $dB/dt = k \cdot P_A$ it is to be stated whether (idealized premises still implied) the quantity

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

is a linear t -function. If this is the case the value of k is given by the constant slope dI_1/dt .

As usual the end value P_∞ , here used for computing the vinyl chloride capacity, φ_B , is an indispensable quantity. But the initial value, P_∞ , also is important, though in a different manner, connected with the "extra" degree of freedom. The quantity $\varphi_A^\circ = A_\infty/P_\infty$ enters as an independent factor in (4) and occurs in all corresponding non-approximate formulas for the calculation of kinetic constants. The measurement of the start pressure thus is not only a determination of that P -value which corresponds to $t = 0$, in itself of minor interest, but essentially gives information on the "reaction-free" equilibrium pressure P_∞ which corresponds to the acetylene amount A_∞ .

The precision of the primary data obtainable by a manometric method is most satisfactory, as has been pointed out by several authors, especially DeTar⁸. Without difficulty the pressures can be read with a dispersion of ± 0.2 mm, or less, and the total pressure difference (in our experiments) reaches 300–900 mm. The time readings can be regarded as errorless since the half life of the reaction is as long as 10 h or more. However, the measurements will be relevant to the homogeneous catalytic reaction in the liquid phase only provided a sufficiently rapid mass transfer between the phases and a rapid equilibration between the different dissolved compounds.

Exact expressions for the calculation of conversion degree, acetylene partial pressure and on the whole for the computation of kinetic constants will often become very complicated. Therefore it will be essential to find suitable approximations resulting in more handy expressions, without losing too much of the potential accuracy of the measurements. Primarily it will have to be stated whether the gases are sufficiently ideal for a reasonable application of partial pressure and capacity quantities according to (1). Even if that is so it is evident that the acetylene capacity φ_A only by a crude approximation is a constant quantity; it shows a P_A -dependence and also changes due to the HCl-consumption (2–4 %) which occurs during the experiments.

Symbols. The amount of vinyl chloride formed B , acetylene remaining A , the formation velocity dB/dt etc. should be stated per unit amount of catalyst solution or catalyst component. We have chosen $m = \text{mole}/1000 \text{ g H}_2\text{O}$, *i.e.* the same concentration unit as has been used for the catalyst components: CuCl_2 , HCl_t etc. (We thus use formal molalities which do not correspond to actual concentrations in the liquid phase.) Other extensive quantities — especially the φ -values below — will have to be treated analogously.

- φ_A Total acetylene capacity of the system, mole/pressure unit and unit amount of catalyst. Unit: $\text{m}\cdot\text{atm}^{-1}$, or $\text{m}\cdot\text{mm}^{-1}$.
- φ_g Capacity of gas phase, for ideal gas. Unit: $\text{m}\cdot\text{atm}^{-1}$.
- φ_B Total vinyl chloride capacity. Unit: $\text{m}\cdot\text{atm}^{-1}$.
- α_A, α_B Absorption coefficients. Unit: $\text{m}\cdot\text{atm}^{-1}$.
- α_w Absorption coefficient, corresponding to "physical" solubility of acetylene. Unit: $\text{m}\cdot\text{atm}^{-1}$.
- k_c Equilibrium constant for acetylene absorption in homogeneous solution, as defined in (21)
- γ Equilibrium constant, rendering HCl_t -dependence of the acetylene absorption acc. to (18).
- k_A, k_B Boyle coefficients, defined in (10).
- P "Dry" total pressure, $P_{\text{tot}} - P_v$. Unit: atm or mm Hg uncorr. ($= 760.7^{-1} \text{ atm}$). $P_v =$ vapour pressure of catalyst solution.
- Index o of $P_o, \varphi_A^o, \text{HCl}_t^o$ etc. marks value at $t = 0$. P_∞ stands for pressure at $B = 0$, *i.e.* "reaction-free" equilibrium pressure corresponding to the acetylene amount A_∞ . P_∞ stands for end pressure.

APPARATUS AND PROCEDURE

The manometric apparatus, sketched in Fig. 1, has an exchangeable, thick-walled reaction vessel b , which is immersed in the water thermostat c . The evacuation is carried out portion-wise by the gas pipette a , connected to the vacuum line at E . This results in small evaporation losses, which can also be approximately estimated. The gas-burette has a mercury differential manometer h (*cf.* also Fig. 2 b) which can be closed by a stopcock and used also for venting the burette. The duct between $S 1, S 4$ and $S 5$ can be evacuated through B . The gas source is connected at D and after reading an appropriate amount is introduced through $S 4$.

The inner branch of the manometer has its upper part d enclosed in the thermostat; the outer branch consists of an 1.5 m glass tube mounted in front of a mirror glass scale. The mercury vessel m is connected via a glass cock $S 9$ of a special type (for details *cf.* Fig. 2 a). (This "inverted" stopcock is very expedient, feasible up to approx. 10 atm.) The bellows k , for precise adjustment, is filled with air-free water, as is the upper part of the cylinder n . When $S 8$ and $S 9$ are closed the manometer system contains no observable elastic element. At p have been inserted two tested capillaries, which have the effect of damping oscillations and rendering the meniscus' movements simultaneous. If necessary the mercury amount is coarsely adjusted by moving m and alternately manipulating $S 8$ and $S 9$; the shift of the meniscus in d is kept small. With $S 9$ closed and $S 8$ open the bellows are then used for a fine adjustment where the meniscus in d is slowly approaching the zero-line from below. When coincidence occurs $S 8$ is quickly closed, which marks the time of the reading, a time which will thus be rather exactly defined even at a rapid pressure change. Not until the time has been noted the outer meniscus is read. The pressure unit is mm "uncorr." (which according to scale calibration, local g -value and an assumed mercury temperature of 20° corresponds to 760.7^{-1} atm). The air pressure is read on an aneroid gauge, System Paulin. If the precision of the manometer readings is tested by comparison with a water manometer, connected to a freshly assembled empty appara-

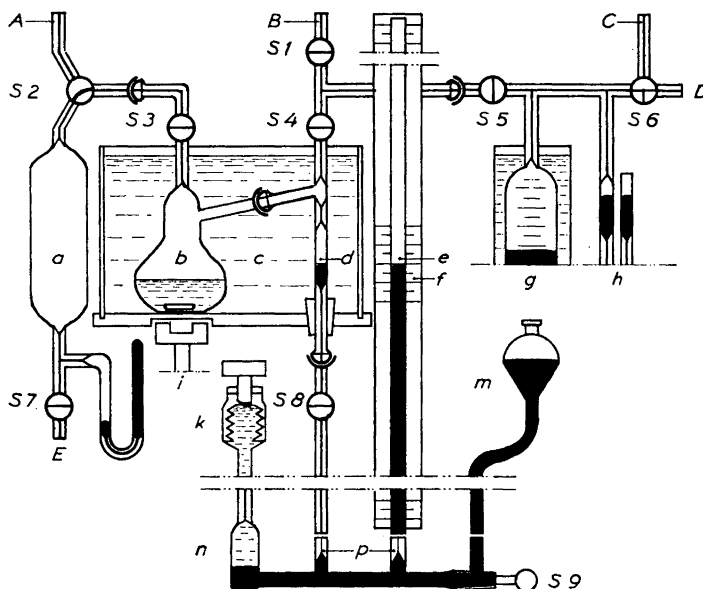


Fig. 1. Sketch of manometrical apparatus for accurate kinetical measurements, scale 1:6. *a*: Evacuation pipette, approx. 250 ml, with manometer. *b*: Reaction vessel, approx. 150 ml, glass walls 2–2 1/2 mm thick, magnetic stirrer in thick glass coating. *c*: Water thermostat. Glass cylinder diam. 20 cm, bottom of Perspex. *d*: Inner arm of manometer, caliber 10 mm. *e*: Mirror glass scale 150 cm, graduation in mm. *f*: Gas burette (or other measuring vessel) in water jacket. *g*: Differential manometer for burette pressure; *cf.* Fig. 2 *b*. *h*: Permanent magnet. *i*: Waterfilled tombak bellows with compression screw for manometer adjustment. *k*: Levelling bulb of manometer. *l*: Glass cylinder, filled with water over mercury. *m*: Capillaries for oscillation damping. *n*: Inverted glass stopcock; *cf.* Fig. 2 *a*.

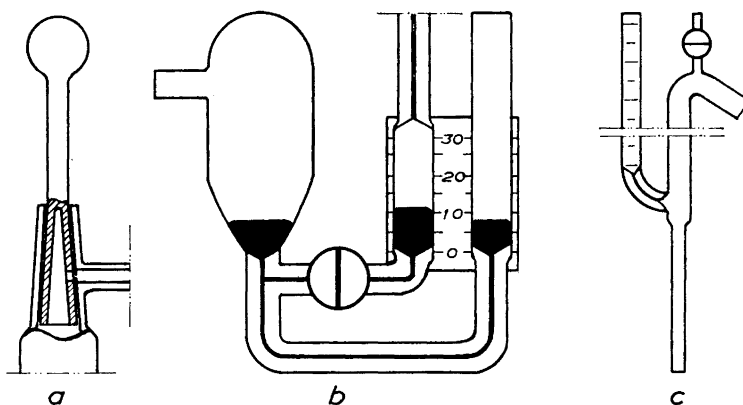


Fig. 2. Details of apparatus. *a*: Pressure-safe glass stopcock, scale 1:2. *b*: Differential manometer, scale 1:2. *c*: Entrance tube for circulation liquid, with flow-meter, length 32 cm, scale 1:5.

tus, the standard deviation will be approx. ± 0.1 mm, *i.e.* not exceeding the estimation error. In the kinetic experiments the scatter is definitely larger, for unknown reasons. Towards the end of each experiment, when the pressure is almost constant, a great number of readings is therefore made, whose scatter can be graphically determined; the dispersions resulting lie between ± 0.2 and ± 0.4 mm.

The temperature constancy must be good. A ballast flask or similar device cannot be used. To eliminate periodic fluctuations the glass cylinder *c* is only a circulation vessel, connected to a commercial precision thermostat (Ultrathermostat Höppler NB). The water is introduced at the bottom of the cylinder *via* a tube acc. to Fig. 2 c; this tube is also a calibrated flow meter whose reading is the difference between the water levels in- and outside the graded portion. From the glass cylinder the liquid flows freely over the brim of an internal funnel tube passing the bottom of the cylinder.

At a given working temperature (here 25°) the behaviour of the outer thermostat depends on the relation *w* between the heating and total periods, changeable at will by adjusting the flow of the cooling water. The mean temperature T_i changes approximately linearly with *w*, and in the best interval $0.1 < w < 0.5$ the derivate dT_i/dw is -0.4° . When *w* exceeds 0.25 the oscillation frequency ν remains fairly constant at $2.2-2.5 \text{ min}^{-1}$, but at a lower *w* the frequency decreases markedly. The amplitude A_i is ± 0.03 to $\pm 0.06^\circ$ and shows no definite dependence of *w*.

The uninsulated glass cylinder has a heat exchange with the surroundings which amounts to $k = 25 \text{ cal/degree} \times \text{min}$ according to cooling curves and temperature differences at stationary states. The equilibrium temperature T_e in the glass cylinder is determined by room temperature T_o , inlet temperature T_i and the flow velocity *v* acc. to

$$T_e = \frac{k T_o + v T_i}{k + v} \quad (5)$$

The damping quotient can be approximately calculated acc. to

$$A_i/A_e = 2 \pi \nu V/v \quad (6)$$

where *V* is the water content (4000 ml) of the cylinder. With decreasing flow *v* the damping is improved but the dependence on the room temperature T_o increases. Generally the flow rate has been $v = 2000 \text{ ml/min}$, which gives $\partial T_e/\partial T_o = 0.01$ and $A_i/A_e \approx 25$. The damping is thus satisfactory, the amplitude of the oscillations will be far less than $\pm 0.01^\circ$. There is, however, a definite dependence on the room temperature, whose long-range changes will be reproduced in the scale 1:100, if no adjustment is undertaken. But the room temperature can easily be controlled or compensated for by changes in *w*, so that the variations will be smaller than $\pm 0.01^\circ$ during the more critical phase of the reaction (up to 90–95 % conversion) when the accumulated effect of the temperature variations on the reaction rate will still be of importance. During the lengthy final period, when only the momentary temperature effects (VTP and liquid absorption) are important, the temperature need be checked only at the readings; reasonable variations inbetween are tolerable. Temperature equilibration at the start will demand 1–2 h.

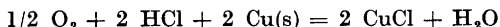
The lubrication of stop cocks and joints, especially the cocks *S 3* and *S 4* and the spherical joint between the flask and the manometer, is problematic since the vapour contains both hydrocarbons, chlorinated hydrocarbons and water. For some kinetical experiments (*e.g.* Nos. 7 and 8 of Part II) and for the vinyl chloride compressibility determinations (Fig. 4) we have used a special lubricant prepared by grinding silica of the finest grain (rubber filler quality) with a completely fluorinated "lube oil fraction", described by Davis⁹. There is practically no absorption of vinyl chloride or other gas components but the mechanical reliability is not quite satisfactory. Commercial silicon lubricants have a perceptible vinyl chloride absorption, but a rapid equilibration so that the effect will be insignificant in the kinetical experiments, although the uncorrected figures of the vinyl chloride solubility will be somewhat too high. A recently marketed lubricant based on chlorotrifluoroethylene-polymer has a similar vinyl chloride absorption but a slower equilibration. Silicon lubricant has therefore been used in most experiments — sparingly. For ground joints and stopcocks which contact mercury only Ramsay lubricant is preferable. The shortest possible tube connections of polyvinylchloride-vinylacetate tubing are used in those parts of the manometer which are filled with mercury or water.

The stirring is effected by an external permanent magnet mounted on a constant speed worm gear motor. In the flask there is a permanent magnet rod covered by teflon or thick-walled glass. If the solution contains solid substances it is advantageous to add glass beads which will prevent caking.

The surface movements of the liquid and splashes have some stirring effect in the gas phase. Moreover, after most manometer readings the gas filled portion of the manometer tube d is "vented" by a rapid displacement of the mercury meniscus between the capillary sections of the tube, afterwards the surface is again reset to zero.

The composition of the catalyst is computed directly from the weights of hydrochloric acid (titrated against standard sodium carbonate) and cuprous chloride, without subsequent analysis. A prerequisite for this is a cuprous chloride of analytical grade, free from Cu^{II} . Commercial CuCl can hardly be used, satisfactory results are obtained with a coarse-crystalline cuprous chloride prepared acc. to the following principle (for details cf. Ref. 4): Ingredients are metallic copper of high purity, atmospheric oxygen and hydrochloric acid; recrystallization from strong hydrochloric acid whereto has been added an amount of Cu^{II} which prevents formation of photohalides; washing procedure which prevents formation of basic Cu^{I} - or Cu^{II} -compounds.

If CuCl of this quality is dissolved in an air-free flask in practically oxygen-free hydrochloric acid the resulting solutions will contain no more Cu^{II} than tallies with the low concentration quotient $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ corresponding to the dismutation equilibrium $2 \text{Cu}^{\text{I}} = \text{Cu} + \text{Cu}^{\text{II}}$ in a strong solution of a dissociating chloride. However, it is more convenient to use hydrochloric acid in equilibrium with the atmosphere, *i.e.* with an oxygen content of approx. 3×10^{-4} m. The Cu^{II} formed must then be reduced with metallic copper to prevent acetylene losses in a side reaction where acetylene acts as a reducing agent. The contents of both CuCl and HCl will be changed acc. to



but the concentrations will be displaced at the utmost by 1×10^{-3} m, which is stoichiometrically negligible.

Addition of metallic copper to the reaction mixture is appealing since it will bring about a more exact adjustment of the dismutation equilibrium. It should however be pointed out that metallic copper should not be used for the reduction of Cu^{II} resulting from an uncontrolled air oxidation of CuCl or solution.

The strong colour in the scale yellow — brown — black which Cu^{II} causes in a highly concentrated solution of Cu^{I} in a dissociating chloride can be used for a check. The strength of the colour can be gauged by eyesight, if one first makes some simple comparisons, *e.g.* tries out what colour (definitely yellow, but not brown) corresponds to the oxygen concentration of air saturated hydrochloric acid.

It is to be expected that metallic copper should have to be added after the solution has been prepared, but this has not proved necessary since the reduction is somewhat slow and requires stirring.

The solution consequently is prepared acc. to the following scheme:

(a) In a well dried reaction flask are weighed first metal copper and then cuprous chloride.

(b) The spherical joint is closed and the flask with its solid contents is evacuated for 2 h to ≤ 0.01 mm.

(c) After weighing hydrochloric acid is added from a burette connected to the flask via a three-way stopcock which permits evacuation of the connection; the flask is again weighed.

(d) The reaction vessel is mounted — *cf.* type experiment — and is filled with nitrogen. After some few revolutions the stirrer is stopped and the Cu^{II} -colouration is checked.

(e) Brisk stirring, and the reduction will render the solution colourless.

TYPE EXPERIMENT

Experiment 1: 2.753 m CuCl; 8.92 m HCl; $P_0 = 342.7$ mm; 25.0°C.

Batch: 4.605 g CuCl ^a, 1.99 g Cu ^b and, after evacuation, 22.45 g hydrochloric acid (8.93 m) are introduced into the reaction flask.

Determination of vapour pressure: The reaction vessel is joined to the pipette *a*, the connection is evacuated and the vessel filled with oxygen-free nitrogen *c*) from A. Under a continuous stream of nitrogen the mounting is completed by connection to the spherical joint of the manometer. The thermostat is filled up and set to work. Then the vessel is evacuated through the gas pipette, stopcocks *S* 3 and *S* 7 being opened alternately, stirring is going on. A constant vapour pressure $P_v = 13.3$ mm is attained after six evacuations. Reading after 16 h, for check of leakage, gives the same figure.

Nitrogen calibration: Nitrogen is added in portions, without stirring, and the pressure which becomes constant almost immediately is read after each addition, resulting in the following values of *n* and P_N (units: millimoles and mm Hg uncorr): 1.656–333.6; 2.853–575.8; 3.849–776.3; 4.731–954.2; 6.251–1260.4. A quotient $(n/P_N) = 4.958 \times 10^{-3}$ millimoles/mm constant within the experimental errors *d*) is attained, *cf.* Fig. 6 c.

Vinyl chloride calibration: After evacuation to vapour pressure, requiring 5 operations under stirring, gaseous vinyl chloride *e*) is added in portions. After each addition a pressure-time curve is observed, *acc.* to Fig. 3 a, and an equilibrium pressure is reached after 1 to 1 1/2 h. The following values of n and P_N (units as above) are obtained: 2.180–359.8; 3.883–637.6; 5.771–939.0; 6.457–1048.1. In Fig. 6 a the P/n quotients have been plotted against *n* and in Fig. 6 b the quotients n/P against *P* – in both cases the relations can be regarded as linear – within the experimental errors *d*). The vessel is left for 18 h with vinyl chloride, a check then shows a decrease of the pressure from 1048.1 to 1047.6 mm.

Acetylene experiment: Evacuation to vapour pressure, which demands 8 operations interluded each time by stirring periods of 10 min, is followed by addition of 6.482 (± 0.008) *s*) millimoles of acetylene *h*). The acetylene is added in two approx. equal portions with 5 min interval, and each addition takes 20 sec. Halfway of the later addition timing is started. The measurements are grouped in a "start period" for determination of P_0 , Fig. 7, a "main period", utilized for the kinetical computations, and a "final period" for determination of P_{∞} , Fig. 5 b.

Readings: $t(h) - P$ (mm Hg uncorr.) during start period: 0.05–432.9; 0.11–356.2; 0.1889–348.9; 0.2458–349.8; 0.3250–351.4; 0.4139–353.6; 0.5000–355.9; 0.5861–358.1; 0.7486–362.1; 0.9167–366.5; 1.0833–370.6; 1.3306–376.7. Main period: 1.581–382.4; 1.839–388.7; 2.093–394.9; 2.525–404.6; 5.210–465.0; 6.526–492.6; 14.347–637.1; 14.861–645.1; 18.953–706.0; 19.888–718.4; 23.908–767.2; 24.44–773.6; 26.81–797.6; 26.98–799.3; 38.48–893.1; 45.13–931.9; 47.68–943.9; 48.10–945.8; 65.53–1000.3; 67.94–1005.3; 68.52–1006.3; 71.26–1011.0. Final period: 86.7–1029.7; 90.7–1031.9; 94.2–1034.2; 99.3–1037.3; 110.7–1041.5; 114.7–1042.5; 118.7–1043.2; 134.6–1044.9; 138.5–1045.2; 142.7–1045.6; 166.8–1047.3; 186.6–1046.9.

Computed values: Correction for evaporation losses *i*) gives 16.89 g H_2O and HCl , $\rho = 8.92$ m, both values referring to start of acetylene experiment. The amount of $CuCl$ will then correspond to $CuCl_t = 2.753$ m and the amount of acetylene to $A_{\infty} = 0.3838$ m, the capacity of the gas phase will be $\varphi_g = 2.935 \times 10^{-4}$ m/mm. End pressure of acetylene experiment is 1047.3 mm *acc.* to Fig. 5 b. Theoretical end pressure 1051.5 ± 2.0 *acc.* to vinyl chloride calibration *h*). The start pressure $P_0 = 342.7$ mm *acc.* to Fig. 7 b and the equilibrium pressure *h*) $P_{\infty} = 341.6$.

Comments: *a*) Coarse-crystalline and of high purity, preparation described previously ⁴. *b*) Electrolytic copper powder is boiled with 0.5 M HCl , washed in nitrogen atmosphere with 0.1 M HCl , acetone and ether and dried *in vacuo*. *c*) Prep. *acc.* to Wartenberg,¹ oxygen content less than 0.001 vol%. *d*) The uncertainty in *n* can be estimated to ± 0.004 for the two first values and to ± 0.008 for the later ones, and in *P* it can be estimated to ± 0.3 mm. *e*) From AB Fosfatbolaget, Ljungaverk, distilled. *f*) $P = P_t - P_v$. *g*) At the volumetric measurement (20–25°, 1 atm.) the mole volume of acetylene is 0.70 % smaller than for ideal gas, of vinyl chloride vapour 1.70 % smaller. *h*) Of fair purity in cylinder with normal filling (AGA) but without acetone. *i*) The loss of HCl at each evacuation operation can be estimated to 0.029 millimoles (checked by trapping and titration) and the water loss to 2.7 mg. *k*) *Acc.* to Fig. 6 a the quotient $(p/n) = 162.20 \pm 0.20$ holds for a number of moles equivalent to the acetylene amount of the experiment. Thus $P_{\infty c} = (162.2 \pm 0.2) \times (6.482 \pm 0.008) = 1051.5 \pm 2.0$ mm. *l*) During the pause (0.083 h) between the two acetylene additions the reaction velocity can be estimated to one half of the velocity which according to Fig. 7 a corresponds to $(dP/dt)_0 = 25.6$ mm/h. Thus $P_{\infty} = P_0 - (1/2) \times 0.083 \times 25.6 = P_0 - 1.1$ mm.

MASS TRANSFER

At the mathematical treatment of the experiments it is desirable to be able to presuppose a thermodynamic equilibrium between the phases both regarding acetylene and vinyl chloride, and also an equilibrium between the solution and a possible solid phase. Since there is a mass transfer between the phases certain differences in activity are necessary, but provided sufficiently low diffusion resistances these can of course become negligible. If the experiment does not fulfill these conditions it will still be possible — though difficult — to draw some conclusions on the homogeneous kinetics, provided the size of the diffusion barrier and its effect on the over-all kinetics can be reasonably well estimated.

Delayed mass transfer is a general methodological problem in kinetical experiments with multi-phase system which has often been disregarded; *cf.* however, Pedersen¹¹ who has described such experimental errors. The problem has two sides: to arrange the experiment in such a way that the diffusion resistances become low and to find a method of checking this. The risk of disturbances of this kind is of course decreased by a low reaction velocity, large phase boundary and brisk stirring. In these experiments the reaction rate is low, not exceeding 0.02 m.h^{-1} , and the stirring is lively. The surface of the liquid is often split, but the enlargement is not very considerable. It is possible to attain a far larger phase boundary, *e.g.* in a shaking flask, where the liquid is dispersed by collisions with the walls, but considering the build up of our apparatus we have refrained from such an arrangement. However, the stirring in the apparatus can be kept constant, so that one dares rely upon a check-result as valid for a continuous period of experiment.

The main difficulty is caused by the phase boundary diffusion of the vinyl chloride, which is strikingly slow. For a check it is possible to use the pressure-time curves from the calibration with pure vinyl chloride. In Fig. 3b $\log(P - P_\infty)$ has been plotted against t for the first readings after addition of vinyl chloride to the evacuated reaction flask. The dot at $t = 0$ does not correspond to a read P_0 -value but has been computed from φ_g and the measured amount of vinyl

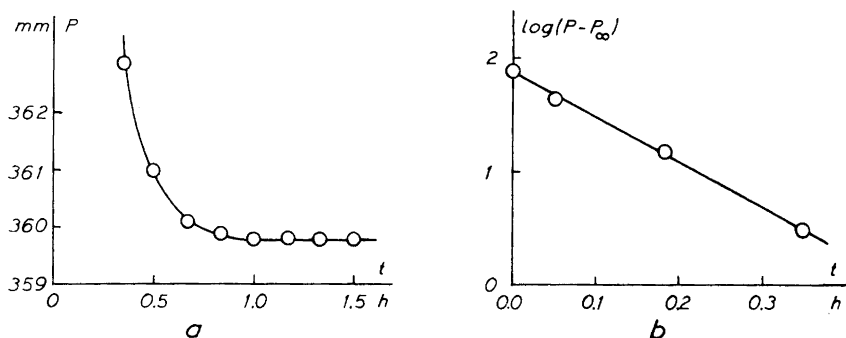


Fig. 3. Pressure-time curve from absorption of gaseous vinyl chloride in catalyst solution; experiment 1. *a*: Determination of equilibrium pressure (359.8 mm). *b*: Estimation of half life.

chloride, assumed to exist entirely in the gas phase at the start. The absorption is approximately of the first order and the half-life periods observed at the experiments vary between 2 and 5 min, depending on stirring *etc.* Desorption experiments give corresponding results.

Since the half-life period of the absorption does not exceed 5 min, the primary impression is that the mass transfer would hardly cause significant disturbances of a process whose half-life is 10 to 20 h — but it does.

If the phase boundary diffusion is treated as an idealized liquid film case¹², the relation between the driving force and the transport rate can be expressed by:

$$P' - P = \psi \cdot dB_g/dt \quad (7)$$

P denotes the vinyl chloride pressure in the gas phase, while P' is the activity in the liquid phase; P' can be replaced by B_d/α_B , *i.e.* the concentration of dissolved vinyl chloride divided by the absorption coefficient. The transport rate liquid \rightarrow gas is expressed here by the derivate dB_g/dt , where B_g stands for the vinyl chloride content, [m], of the gaseous phase. The quantity ψ denotes the film resistance in a unit of the dimension [pressure \cdot m⁻¹·t]. Starting from this expression it is easy to show that the pressure drop in the calibration experiment will be of the first order and that the film resistance, both at absorption and desorption, can be computed from the half-life acc. to:

$$\psi = 1.443 \frac{\varphi_B}{\varphi_g \alpha_B} \cdot t_{1/2} \quad (8)$$

If the stirring is not changed the same ψ -value should be applicable to the main experiment and the driving force $P' - P$ required for a given reaction rate can be computed. However, it is not this difference which is of interest primarily, but the actual pressure error, *i.e.* the difference between the pressure observed and that which were to be measured at an instantaneous equilibration of the vinyl chloride between the phases. Assuming the the transport rate dB_g/dt at a stationary state to approach the fraction φ_g/φ_B of the total formation rate dB/dt , and neglecting the diffusion resistance for acetylene, we deduct the following relation:

$$P_e - P_{\text{obs}} = \frac{\varphi_g \cdot \alpha_B}{\varphi_B^2} \cdot \psi \cdot \frac{dB}{dt} \quad (9)$$

If this estimate is carried through utilizing data from the type experiment the result will be a pressure error as large as 4 mm. In spite thereof the experiment can be accepted; other experiments have been discarded because the diffusion barrier has caused still larger errors.

Fortunately the enrichment of vinyl chloride in the liquid phase does not in itself influence the reaction rate dB/dt , nor the derivate $d \ln (P_\infty - P)/dt$ of the main process and related kinetical constants. As is evident from (9) the pressure error ($P_e - P_{\text{obs}}$) is proportional to the reaction velocity and consequently approximately proportional to $(P_\infty - P)$. In a diagram where $\log(P_\infty - P)$ has been plotted against t the diffusion resistance of the vinyl chloride thus will only cause a parallel displacement of the curve. More im-

portant is the effect of the error upon the computation of P_{∞} , which is required for the determination of the acetylene capacity φ_A° ; cf. below.

The *phase boundary diffusion of acetylene* takes place more easily. In experiments with a homogeneous catalyst solution the rate of the initial acetylene absorption can be used as a test. Immediately after the addition of acetylene one observes (cf. Fig. 7a) a rapid pressure drop during the first minutes (estimated start pressure in the figure approx. 850 mm). From a minimum the pressure rises, rather soon following an approximately linear curve. The initial absorption is so rapid that no proper measurement of the diffusion resistance can be made. But a fair estimate is that ψ_A is less than 1/10 or 1/20 of ψ_B . Also the transfer rate ($-dA_g/dt$) is smaller than dB_g/dt . The driving force $P-P'$ can then hardly be larger than some tenths of a mm.

The *complex formation* in the solution is so rapid that its duration is insignificant in comparison to the delay caused by the phase boundary resistance. This is evident from equilibrium measurements,⁶ where the absorption is even more rapid, due to a more intense shaking.

Cuprous chloride is swiftly dissolved in strong hydrochloric acid, even if coarse crystalline. In a series of accurate solubility determinations, using the same CuCl, the concentration reached its equilibrium value already after a few minutes of shaking, provided a suitable excess and a rapid heat transfer; the same holds for crystallization from a supersaturated solution. At the kinetic experiments with a CuCl-saturated catalyst solution the speed of the initial acetylene absorption can be used as a test in this respect also, since the equilibrium is not reached until further CuCl has been dissolved. In comparison to experiments without CuCl there is no significant delay.

THE NON-IDEAL BEHAVIOUR OF THE GASES

Acetylene's deviation from ideal compressibility can be rendered by a Boyle-coefficient according to

$$VP = n RT (1 + kP) \approx n RT (1 - kP^{-1}) \quad (10)$$

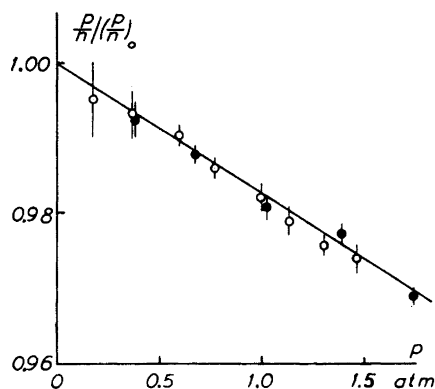


Fig. 4. Compressibility of gaseous vinyl chloride at 25°C. Two independent series.

From previous measurements¹³ we know that for acetylene k_A is -0.0070 atm^{-1} at 25°C . An analogous determination of the compressibility of vinyl chloride vapour (performed in the apparatus described) is illustrated by Fig. 4, where the slope of the line corresponds to $k_B = -0.0170 \text{ atm}^{-1}$ at 25°C .

In a solution of constant cuprous chloride activity and constant HCl, it seems most probable that the acetylene absorption is proportional to the fugacity, which depends on P acc. to $f_A = P(1 + k_AP)$. For a system of both gaseous and liquid phases thus holds

$$n_A = \frac{VP}{RT}(1 - k_AP) + a \alpha_A P(1 + k_AP) \quad (11)$$

where a is the amount of water and α_A the absorption coefficient. The two ideality corrections counteract each other. If the dissolved and gaseous quantities of acetylene are approximately equal it is impossible to discover any variation in the quotient n_A/P , when n_A is changed at constant V and a . This pseudo-ideality is the reason why compressibility corrections have not been required in earlier absorption measurements^{6,7}, although the accuracy has been sufficient to demonstrate clearly the n_A/P variation in an empty vessel. This compensation effect is observed for acetylene in pure water also and for vinyl chloride in water and in hydrochloric acid; it is probably a common phenomenon at the absorption of nearly ideal gases in liquids where their solubility is rather low.

A gaseous mixture of acetylene and vinyl chloride of a given composition has a compressibility which can be rendered by a (10)-expression with a coefficient k_m which approaches k_A when x_A goes towards 1, and approaches k_B when x_A decreases. The detailed shape of the $k_m(x_A)$ -function has not been definitely settled by our measurements. It seems probable that the following expression

$$k_m = k_A x_A + k_B x_B \quad (12)$$

holds with a fair approximation, but that the corresponding expression where x_A and x_B have been substituted by their squares (which would be the nearest equivalent to an application of Dalton's law) is excluded.

There is much in favour of Lewis' and Randall's¹⁴ assumption on gas mixtures as ideal solutions, implying that the fugacity is proportional to the mole fraction at a given T and P . From this assumption the following two sentences can be derived: (a) the partial mole volumes are independent of x ; (b) for binary mixtures expressions (10) and (12) hold, provided that the components follow (10). Reversedly holds that Lewis' assumption can be derived from the sentences (a) and (b) — as empirically verified — if one is able to prove also that there exists some definite pressure (e.g. a very low one) where f_i is proportional to x_i , which in this case seems almost self-evident.

The liquid absorptions are independent of each other since the vinyl chloride absorption is purely a water solubility (*cf.* below) while acetylene is mainly absorbed due to the formation of cuprous complexes.

Under these premises and with the introduction of the denotations $A = n_A/a$ and $\varphi_g = V/RT \cdot a$ we get

$$A = \varphi_g x_A P(1 - k_m P) + \alpha_A x_A P(1 + k_A P) \quad (13)$$

where x_A is the mole fraction of acetylene in the gaseous phase. A corresponding expression for the vinyl chloride B is obtained by exchanging the indices. According to (12) k_m is symmetrical and remains unchanged.

From these two equations and the equalities $A_{\infty} = A + B$ and $x_A + x_B = 1$ it is possible to eliminate x_A and x_B . The result will be a complicated expression which can be used for computation of the conversion degree $Y = B/A_{\infty}$ corresponding to a given P . By an analogous operation it is possible to calculate the acetylene fugacity by application of

$$f_A = x_A \cdot P(1 + k_A P) \quad (14)$$

An exemplifying numerical comparison between this more exact Y -value and the approximate value of $Y_p = (P - P_{\infty}) / (P_{\infty} - P_{\infty})$ acc. to (2) is given in Table 1. The constants utilized for the computations have been borrowed from an experiment (No. 7) of Part II with a CuCl-saturated catalyst. (The data of the type experiment could also have been used, but for experiments in the absence of CuCl(s) the assumption of a constant α_A becomes unrealistic.) The absorption coefficients α_A and α_B have been computed from start and end pressures by means of the equations:

$$\begin{cases} \varphi_A^{\circ} = \frac{A_{\infty}}{P_{\infty}} = \varphi_g(1 - k_A P_{\infty}) + \alpha_A(1 + k_A P_{\infty}) \\ \varphi_B^{\infty} = \frac{A_{\infty}}{P_{\infty}} = \varphi_g(1 - k_B P_{\infty}) + \alpha_B(1 + k_B P_{\infty}) \end{cases} \quad (15)$$

which are expressions of the (13)-type with $x_A = 1$ and $x_B = 1$. The difference between Y and Y_p will not be more than 0.4 %, as is evident from the table. This is a rather small figure considering the Boyle-correction of vinyl chloride, which amounts to 1.7 % already at 1 atm. The explanation is both the "compensation effect" mentioned and the circumstance that the φ -quantities when set constant in the approximate calculus have been given favourable numerical values acc. to (15).

That quantity P_A which is defined by (3) has also been computed in Table 1 and is compared with the fugacity, the partial pressure P_A' (classical defini-

Table 1. Numerical comparison between different methods for computation of conversion degree and acetylene partial pressure. Constants: $\varphi_g = 2.651 \times 10^{-4}$ m.mm⁻¹; $P_{\infty} = 260.0$ mm; $P_{\infty} = 908.0$ mm; $A_{\infty} = 0.2983$ m.

P mm	Y %	Y_p %	f_A mm	P_A' mm	P_A mm	$x_A P$ mm
300	6.08	6.17	243.5	244.5	244.0	244.2
400	21.32	21.60	203.9	205.5	203.8	204.6
500	36.64	37.04	164.0	166.0	163.7	164.8
600	52.05	52.47	124.0	126.0	123.6	124.7
700	67.52	67.90	83.9	85.7	83.5	84.5
800	83.08	83.33	43.7	44.7	43.3	44.0
850	90.94	91.05	23.4	24.0	23.3	23.5

tion) and the partial pressure $x_A P$, all these three computed acc. to exact formulas. The comparison shows that P_A is actually a good approximation for f_A but not so good for the other quantities. However, we shall stick to the term "partial pressure" for P_A .

A ΔY of 0.4 % is not entirely negligible at this high accuracy in the measurements; neither is the $P_A - f_A$ difference, and consequently it would be justified to utilize the more exact calculus. But computation acc. to (1)–(3), including the partial pressure conception and constant capacity quantities will give so much simpler expressions, that we have stuck to this method as long as the kinetic conclusions cannot reasonably be influenced by the approximations.

Above have been treated only cases where the absorption coefficients α_A and α_B (definition based on activities) are constants, which for acetylene requires constant $\{\text{CuCl}\}$ and HCl_t . Where these conditions are not fulfilled and where α_A is varying it will of course be impossible to apply (2) and (3). It should, however, be feasible to utilize the partial pressure conception acc. to (1), but with a variable φ_A and possibly φ_B .

DETERMINATION OF START AND END PRESSURES AND CAPACITY VALUES OF THE SYSTEM

Determination of the end pressure P_∞ , which has importance both for yield control and for computation of the vinyl chloride capacity, requires that the pressure-time curve is followed for a considerable time. In a process of the first order with a pressure change of 700 mm totally 0.1 mm remains even after 13 half lives. Fig. 5 (data from the type experiment) shows in part *a* a survey of the entire pressure-time curve and in part *b*, where the pressure scale has been

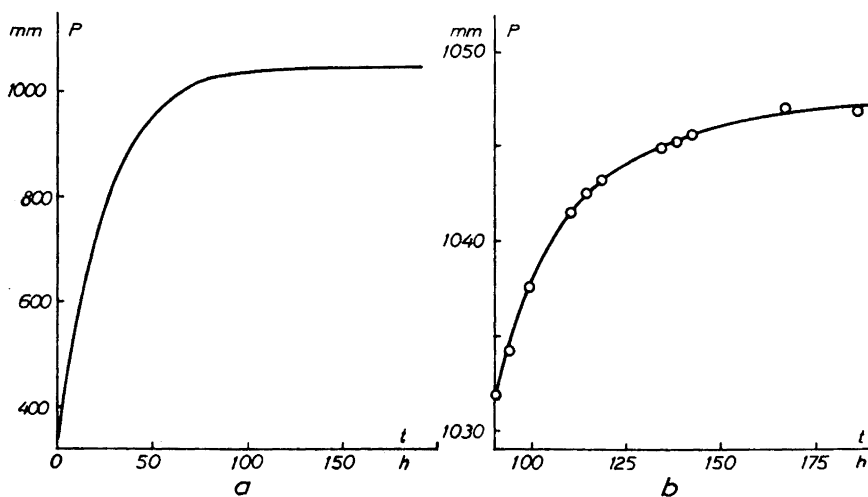


Fig. 5. Pressure-time curves from experiment 1. *a*: Entire experiment. *b*: End period, covering 98–100 % conversion.

enlarged, the end period from 98 to 100 % conversion. The long time of observation of course involves considerable risk of errors caused by imperfections of the apparatus, consecutive side reactions *etc.* In Fig. 5 b it is thus a little bit difficult to cover the two last points by a smooth curve, but the deviation can be interpreted as a random variation. From other experiments with a longer end period it is however clear that there is a slow pressure decrease amounting to 0.01–0.03 mm·h⁻¹, after the pressure curve has passed a flat maximum. The same slow pressure drop is observed when pure vinyl chloride is added in substance — the effect is obviously independent of acetylene and the main reaction on the whole. It is not a leakage, possibly some kind of vinyl chloride reaction, but more probable is an out-diffusion of such small quantities of vinyl chloride as are absorbed in the stop cock grease. The result is that the maximum pressure read will be somewhat low, but the error in earlier readings will be very small. Lacking data for correction we accept the uncorrected highest pressure reading — or the vertex of the fitted curve — as the measured end pressure of the reaction, $P_{\infty m}$, but assign to this value a greater uncertainty than to the pressure readings of the main period.

The yield of the reaction at 25°C seems quantitative except at $HCl_t < 6$ m where acetaldehyde is found in the liquid and at $HCl_t > 11$ m where traces of an easily hydrolysed chlorine compound, probably dichloroethane, can be traced in the gas formed.

A check of the yield is made by comparing the measured end pressure $P_{\infty m}$ and that end pressure $P_{\infty c}$, which can be computed from the calibration with pure vinyl chloride. The couples of values $n - P_B$ are graphically treated in a diagram as in Fig. 6 a, where the quotient P/n has been plotted against n . Within the primary experimental errors the relation will be linear, and it is possible to read, with good accuracy, the quotient value $(P/n)_A$ which holds for an amount of vinyl chloride equivalent to the acetylene amount n_A ; finally is achieved the computed end pressure $P_{\infty c} = n_A \cdot (P/n)_A$. The accuracy is essentially limited by the accuracy in n_A , whose relative error is $1 - 2 \times 10^{-4}$.

As is evident from Table 2 the comparison is on the whole satisfactory. In no case is the difference greater than 0.4 %; the amount of a

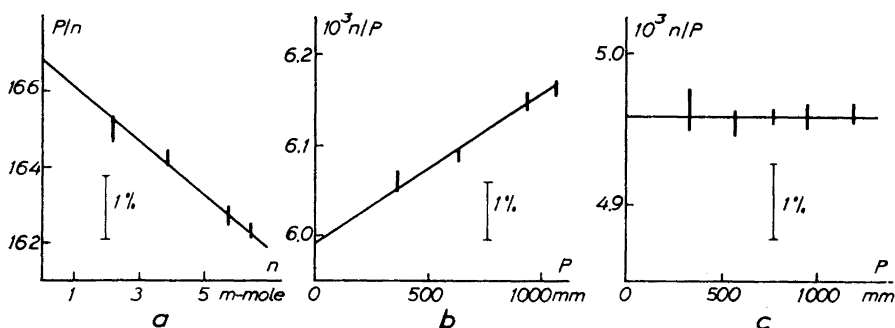


Fig. 6. Result from vinyl chloride and nitrogen calibrations of experiment 1, n in millimoles, P in mm Hg, uncorr. (Vertical lines denote errors derived from uncertainty of read data.) a and b: Vinyl chloride. c: Nitrogen.

Table 2. Comparison between computed $P_{\infty c}$ and measured $P_{\infty m}$ end pressures.

Experiment No.	HCl _t m	CuCl _t m	$P_{\infty m}$ mm	$P_{\infty c}$ mm	Diff. %
1	8.92	2.75	1047.3	1051.5 ± 2.0	-0.4 ± 0.2
3	9.05	2.02	1071.7	1071.0 ± 2.0	+ 0.1 ± 0.2
4	9.96	2.01	945.3	947.5 ± 2.0	-0.2 ± 0.2
5	9.05	(s)	534.9	537.8 ± 1.7	-0.5 ± 0.4
6	9.05	(s)	955.9	957.5 ± 1.7	-0.2 ± 0.2
7	7.94	(s)	908.1	908.0 ± 2.1	± 0.0 ± 0.3

dissolved by-product, *e.g.* acetaldehyde, thus can be no larger. (At Experiment 2 in Part II, where the pressure-time curve has not been pursued, we have therefore used a computed end pressure for the kinetical calculations.) However, the table shows a clear trend to let the measured end pressure become somewhat lower, as is to be expected.

The absorption coefficient of vinyl chloride α_B can be computed from calibrations made in connection with the kinetical experiments. As has already been pointed out the absorption requires some time, the equilibrium pressure can be read after 0.5—1.5 h, *cf.* Fig. 3 a. Desorption experiments clearly demonstrate that it is a reversible absorption. If the gas phase capacity ϕ_g is known it is possible to compute α_B ; the accuracy will be low as the main portion of the vinyl chloride added remains in the gas phase — in accordance with the main aim of the experiment — and the dissolved amount must be computed as the difference between the measured total and the computed gaseous amounts.

Experiments 1, 3, 4, and 21 give values (*cf.* Table 3) between 0.048 and 0.051 m.atm⁻¹ with an uncertainty of one unit in the last figure and a systematic positive error of 2—3 units due to absorption in the lubricant. The values show no significant dependence on the pressure, nor on HCl_t or CuCl_t. Accurate solubility determinations with a more favourable quotient gas phase/

Table 3. Vinyl chloride absorption in homogeneous catalyst solution.

Expt. No.	HCl _t m	CuCl _t m	$10^{-4} \phi_g$ m.mm ⁻¹	B m	P_B mm	α_B m.atm ⁻¹
1	8.92	2.75	2.935	0.1291	359.8	0.048
				.2299	637.6	48
				.3417	939.0	50
				.3823	1048.1	50
3	9.05	2.02	1.768	0.1319	542.6	0.049
				.2512	1017.7	50
4	9.96	2.01	2.126	0.1550	553.2	0.050
				.2224	786.3	50
				.3013	1056.6	51
21	9.05	1.52	2.092	0.1220	447.1	0.048
				.2045	742.0	0.049

liquid phase have confirmed the conclusions regarding the pressure independence of α and its independence of CuCl_t at a constant HCl_t . HCl has a small salting-in effect, which at a concentration of 10 m increases the α -value by approx. 10 % as compared to pure water. No detailed account of these measurements is given here since the results in Table 2 clearly show that the absorption cannot appreciably depend on the formation of Cu^+ -complexes but essentially is just a water solubility.

The conclusion regards the vinyl chloride capacity φ_B will thus be that this quantity can be considered constant at all kinetic experiments, uninfluenced both by the acetylene absorption in the solution and by minor HCl_t -fluctuations. The reaction is sufficiently quantitative to allow application of the equality $B_\infty = A_\infty$, and the numerical value of the vinyl chloride capacity can thus be computed according to

$$\varphi_B = A_\infty/P_\infty \quad (16)$$

Determination of the start pressures P_0 and P_∞ and the acetylene capacity φ_A° . In each kinetical experiment it is possible to determine directly the initial value of the acetylene capacity:

$$\varphi_A^\circ = A_\infty/P_\infty \quad (17)$$

This requires an estimation of the "reaction free" equilibrium pressure P_∞ which corresponds to the acetylene amount A_∞ . In some cases the approximation: φ_A constant and equal to φ_A° may be accepted, but as a rule the φ_A -changes must be taken into consideration. These changes can be computed from empirical formulas which give the acetylene absorption as dependent on the composition of the solution etc. It seems best to utilize — in these cases as well — the φ_A° -value directly determined in the experiment and to compute the

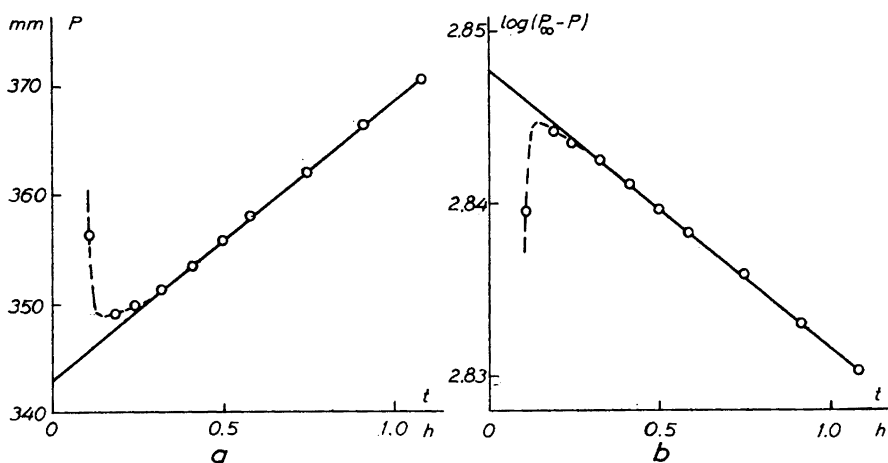


Fig. 7. Determination of P_0 in experiment 1 from pressure-time curve of start period, 0–4 % conversion. a: Linear extrapolation. b: "Logarithmic" extrapolation.

required corrections by means of the formulas mentioned as is described in the next section.

Due to the wide P -interval and the slow reaction it is possible to make a series of readings within such a narrow conversion interval that the $P-t$ relation becomes linear within the experimental errors. This holds for the initial phase of the experiments also and as can be seen from Fig. 7 a the linear portion is sufficient to allow a satisfactory determination of the start pressure P_0 by an extrapolation to $t = 0$. A larger scale diagram than that of Fig. 7 a should however be used. Errors, both from the initial deviation caused by delay in the acetylene absorption, and from the later downward bend caused by the exponentiality — not perceptible in the figure — must be avoided when fitting the extrapolation line.

Determination of P_0 by a linear extrapolation in a diagram according to Fig. 7 b, where $\log(P_\infty - P)$ is plotted against t — which for short we call "logarithmic extrapolation" — is of course to be preferred. The exponential curvature is eliminated in this case and the linear relation covers a far greater interval than required for an adequate extrapolation. If P_0 is to be determined with an accuracy of ± 0.1 mm one has to choose a larger scale than that of the figure for $\log(P_\infty - P)$.

In most experiments the acetylene amount, for practical reasons, is added in two or more portions with a certain time interval. The extrapolated P_0 -value is referred to the last addition ($t = 0$). For computation of the equilibrium pressure it is necessary to correct for the vinyl chloride formation between the additions; *cf.* comments to type experiment. Where all acetylene is added in one portion P_0 is equal to P_∞ . Different denotations are still justified, since errors occur which are of importance when P_∞ is to be utilized for the determination of the acetylene capacity φ_A° , but negligible when P_0 is regarded as a point on the pressure-time curve.

The amount of vinyl chloride formed during the initial phase is somewhat smaller than in an ideal experiment where a distribution equilibrium is reached momentarily at the acetylene addition. The difference is small, however, since the concentration of dissolved acetylene will approach that of an ideal experiment very rapidly. (In Fig. 7 a the first reading shows an "overpressure" of approx. 12 mm; the concentration of dissolved acetylene none the less has already reached 98.9 % of that of the ideal experiment.) The diffusion barrier against vinyl chloride (*cf.* above) is surely the main source of error; this also causes too low a P_∞ value. According to our previous estimate a P_∞ -error of up to 1 % could be expected, resulting in an equally large relative error in φ_A° .

Acetylene absorption and computation of φ_A changes. According to previous investigations⁶ the absorption of acetylene in hydrochloric acid solutions of cuprous chloride can be rendered fairly well by the empiric formula:

$$[C_2H_2]_t = \alpha_w \cdot P_A + \beta \{CuCl\} P_A + \gamma \{CuCl\} HCl_t P_A \quad (18)$$

where $\{CuCl\}$ denotes the thermodynamic activity of cuprous chloride. The constants at 25°C are $\alpha_w = 0.0372 \text{ m} \cdot \text{atm}^{-1}$, $\beta = 0.046 \text{ m} \cdot \text{atm}^{-1}$ and $\gamma = 0.0759 \text{ atm}^{-1}$.

In cases where $\{\text{CuCl}\}$ and HCl_t are constant the concentration of dissolved acetylene is proportional to the partial pressure and a closed vessel holding both gaseous and liquid phases has a constant acetylene capacity.

However, in the experiments there is a HCl-consumption, equivalent to the amount of vinyl chloride formed. Then holds:

$$\begin{cases} \varphi_A = \varphi_A^\circ - \gamma B \\ \varphi_A^\circ = A_{\infty}/P_{\infty} \end{cases} \quad \begin{array}{l} \text{Condition: } \{\text{CuCl}\} \text{ constant} \\ \text{HCl}_t = \text{HCl}_t^\circ - B \end{array} \quad (19)$$

In a homogeneous solution with a constant total concentration of dissolved cuprous chloride the cuprous chloride activity will vary according to

$$\{\text{CuCl}\} = \frac{\text{CuCl}_t - [\text{C}_2\text{H}_2\text{Cu}]}{S} \quad (20)$$

where $[\text{C}_2\text{H}_2\text{Cu}]$ is the sum of the two last terms of (18) and S stands for the solubility of cuprous chloride in hydrochloric acid (in the absence of acetylene), regarded here as an empiric HCl_t -function.

If (20) is inserted into (18), the reduced equation will be:

$$\begin{cases} [\text{C}_2\text{H}_2]_t = \alpha_w P_A + \frac{\text{CuCl}_t k_c P_A}{1 + k_c P_A} \\ k_c = \frac{\beta + \gamma \text{HCl}}{S} \end{cases} \quad (21)$$

The acetylene capacity of the entire system can then be written:

$$\varphi_A = \varphi_g + \alpha_w + \frac{\text{CuCl}_t}{k_c^{-1} + P_A} \quad \text{Condition: } \text{CuCl}_t \text{ constant} \quad (22)$$

In this case the capacity will thus not be independent of P_A . The formula can be applied to kinetical experiments with a homogeneous catalyst solution, and k_c can be regarded as constant if the HCl consumption during the reaction is neglected. The constant k_c should then be determined by applying (22) on the start condition: $\varphi_A = A_{\infty}/P_{\infty}$ when $P_A = P_{\infty}$; the constant φ_g is obtained from the nitrogen calibration, CuCl_t from the recipe and for α_w is inserted the numerical value given above.

The effect of the change in P_A on the acetylene capacity will not be large; if (22) is applied to the type experiment — where P_A goes from 342 mm to zero — the decrease in φ_A will be approx. 5 %. On the computed Y -value the effect will be even smaller, but in some cases (22) will have to replace the approximation $\varphi_A = \varphi_A^\circ$.

If the k_c -dependence on HCl_t — the latter decreasing equivalently with B in the experiments — is to be included into (22) we use the empirical function $S = 0.464 (\text{HCl}_t - 2.63)$ which according to our measurements well renders the solubility of cuprous chloride in the interval $5 < \text{HCl}_t < 10$ m. However, the system of equations resulting becomes complicated and should, if possible, be avoided.

A fair approximation gives the expression:

$$\begin{cases} \varphi_A = \varphi_g + \alpha_w + \frac{\text{CuCl}_t}{(k_c^{-1})_o - \Delta(P_{\infty} - P_A) + P_A} \\ \Delta = \left(\frac{dk_c^{-1}}{d\text{HCl}} \right)_o \cdot \varphi_A^o \end{cases} \quad (23)$$

The general validity of (23) is difficult to judge. The factor Δ , which is positive, amounts to 0.1–0.2 in the experiments.

COMPUTATION OF CONVERSION DEGREE AND ACETYLENE PARTIAL PRESSURE

Above we have shown that acetylene and vinyl chloride are sufficiently ideal to enable a description of the relations between the total pressure P and the quantities A and B by the formulas:

$$\begin{cases} A = \varphi_A \cdot P_A \\ B = \varphi_B \cdot P_B \\ P = P_A + P_B \end{cases} \quad (24)$$

This presumes, however, that the capacities φ_A and φ_B are defined empirically so that the non-ideality is at least partially compensated for. It has also been shown that, within the interval $6 < \text{HCl}_t < 11$ m, the reaction is sufficiently quantitative for the application of

$$A_{\infty} = A + B \quad (25)$$

and finally that the vinyl chloride capacity φ_B of the system can be regarded as constant for a given manometric experiment:

$$\varphi_B = \varphi_B^{\infty} = A_{\infty}/P_{\infty} \quad (26)$$

These equations give the following *general* expressions for computation of the conversion degree $Y = B/A_{\infty}$ and the acetylene partial pressure:

$$\begin{cases} Y = \frac{P - A_{\infty}/\varphi_A}{P_{\infty} - A_{\infty}/\varphi_A} \\ P_A = \frac{A_{\infty}(1 - Y)}{\varphi_A} \end{cases} \quad (27)$$

In these expressions — besides Y , P_A and $P - \varphi_A$ can also be a variable. For φ_A there are four main alternatives:

(a) $\{\text{CuCl}\}$ and HCl_t constant, which implies:

$$\varphi_A = \varphi_A^o = A_{\infty}/P_{\infty} \quad (28)$$

and leads to those simple $Y-P$ - and P_A-P -functions, which are found in expressions (2) and (3). These can be utilized as rather good approximations in experiments with a CuCl -saturated catalyst, less good at the condition " CuCl_t constant".

(b) $\{CuCl_t\}$ constant and $HCl_t = HCl_t^\circ - B$, which implies

$$\varphi_A = \frac{A_{oo}}{P_{oo}} - \gamma \cdot B \quad (29)$$

and leads to the following relations between Y and P , P_A and Y resp.:

$$\left\{ \begin{array}{l} \frac{P - P_{oo}}{P_{oo} - P_{oo}} = Y \left(1 + \psi \frac{1 - Y}{1 - \gamma P_{oo} Y} \right) \\ \psi = \gamma P_{oo}^2 / (P_{oo} - P_{oo}) \\ P_A = \frac{P_{oo}(1 - Y)}{1 - \gamma P_{oo} Y} \end{array} \right. \quad (30)$$

The $Y-P$ -function thus is of the second order in Y . The expressions are valid for experiments with a $CuCl$ -saturated catalyst. (Like in many other instances in these papers the premises for the formulae have been given in full, but all elementary algebraic reductions have been excluded.)

(c) $CuCl_t$ and HCl_t constant, which implies

$$\varphi_A = \varphi_g + \alpha_w + \frac{CuCl_t}{k_c^{-1} + P_A} \quad (31)$$

If the start condition $\varphi_A = A_{oo}/P_{co}$ at $P_A = P_{oo}$ is used for elimination of k_c , we get:

$$\left\{ \begin{array}{l} \varphi_A = \frac{A_{oo}}{P_{oo}} + \frac{CuCl_t}{P_{oo}} \cdot \frac{\pi^2 y}{1 - \pi y} \\ y = \frac{P_{oo} - P_A}{P_{oo}} \\ \pi = \frac{A_{oo} - (\varphi_g + \alpha_w) P_{oo}}{CuCl_t} \end{array} \right. \quad (32)$$

Together with (27) this forms a system of three equations with φ_A , Y , P and P_A (or y) as variables. If φ_A is eliminated we get an $Y-P$ -function which is of the second order in both variables and a P_A-P -function which is of the second order in P_A . The expressions can be numerically applied by an iteration process or as you like it.

These expressions are quite good approximations also at the condition " $CuCl_t$ constant and $HCl_t = HCl_t^\circ - B$ ", *i.e.* in experiments with a homogeneous catalyst solution.

(d) $CuCl_t$ constant and $HCl_t = HCl_t^\circ - B$, which implies that the φ_A -variations can approximatively be rendered by (23). Elimination of k_c by means of the start condition gives

$$\varphi_A = \frac{A_{oo}}{P_{oo}} + \frac{CuCl_t}{P_{oo}} \cdot \frac{\pi^2 y(1 + \Delta)}{1 - \pi y(1 + \Delta)} \quad (33)$$

where y and π have the same meaning as in (c). This formula is applied as the c -formulas for computation of Y and P_A from a given P -value and gives a somewhat better approximation.

This work has been supported by the *B. F. Goodrich Co.* and at a later stage by grants to research on catalytical chemistry at the Stockholm University by *Swedish Technical Research Council*, *Swedish Natural Science Research Council* and *Knut and Alice Wallenberg Foundation*.

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Received December 6, 1962.