

ANALYSIS OF CHEMICAL REACTIONS AND REACTORS WITH HIGH SPEED DATA PROCESSING AND RECORDING SYSTEM

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The rate of chemical reactions vary over a wide range. There are several physical and chemical testing methods, referring to the reaction rate.

By the help of both chemical and physical methods it is the reactions carried out from a few minutes to some hours that can most simply be tested. Still more rapid reactions are tested with difficulty, requiring complicated and expensive testing instruments; but even then recording of the results is rather uneasy.

Here a relatively simple measuring and recording instrument will be presented, likely to suit testing reactions of seconds to minutes order duration. Utilization is illustrated on two examples.

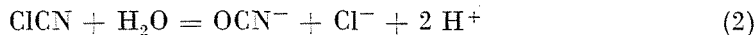
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The chemical purification of cyanide wastes is an important industrial problem. The best method known to-day is to oxidate the cyanide by hypochlorite, into carbon dioxide and nitrogen. The process involves the following subsequent stages:

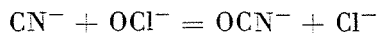
First the hypochlorite reacts with the cyanide to form chlorine cyanide:



chlorine cyanide undergoes hydrolysis with water:



Thus the overall process is:

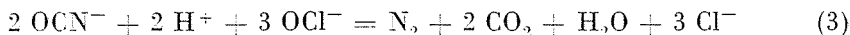


The first partial process is an instantaneous one, the rate of the second one depends on the reaction of the solution. In alkaline agent the hydrolysis goes

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on rapidly: it is slower in acidic medium; but even then the process takes 1 to 2 minutes above $\text{pH} = 7$.

As the cyanate is also poisonous, it must be further oxidated into carbon-dioxide and nitrogen according to the following equation:



This process is very slow in acidic agent; its rate can only be measured in the range below $\text{pH} = 8$. Besides the quantitative oxidation of cyanate requires at least 4 times the stoichiometric hypochlorite quantity. Thus the process is done in two steps, with a high hypochlorite excess. The first step is made in a medium of $\text{pH} = 12$, when the cyanide is oxidated into cyanate. In the second step the pH value of the solution is set to about 6.5 to 7 inducing the oxidation of the cyanate into nitrogen and carbon dioxide.

Our experiments aimed at catalysing oxidation and making it in one step.

Therefore, classical kinetic methods were applied first to test the homogeneous reaction in liquid phase, on compounds of $\text{pH} = 11.5$. Analysis of the reaction led to the following conclusions:

1) The reaction goes on quickly, 95% of the cyanide is oxidated into cyanate in one minute. The developing cyanate is stable under the circumstances of the reaction, it can only be oxidated at a high chlorine excess in a relatively slow reaction.

2) By modifying the initial concentrations of the reagents the dependence on concentration of the original rates, i.e. the partial orders of the hypochlorite and the cyanide were determined. Both resulted in orders of $2/3$, thus the phenomenological rate equation of the reaction is:

$$w = k[\text{CN}^-]^{2/3} [\text{OCl}^-]^{2/3} \quad (4)$$

the overall order of the reaction being $4/3$. This shows that the reaction is a composed process of subsequent steps.

The first step of the homogeneous reaction can be made instantaneously by applying a mixture-oxide catalyst. Thus the pH optimum for oxidizing the cyanide into cyanate in homogeneous medium can be reduced from 12 to 8.2. In this medium even the developing cyanate oxidizes quickly.

The reaction process was followed by measuring the quantity of the generated carbon dioxide. The carbon dioxide was carried by airflow into absorptive solution, and the conductance of the solution was continuously measured.

The measuring equipment and the data processing system will be illustrated on the second example.

The overall process in our intermittent tank reactor has been explained as a mechanism consisting of 14 elementary procedures. The circumstances of the experiment are so chosen that the elementary steps should be treated as primary kinematic reactions. The self-decomposing of the hypochlorite is also taken into consideration.

The solution of the system of equations describing the whole procedure:

$$c_{14} = c_{1,0} \left\{ 1 - \sum_{i=1}^{14} \frac{\exp[-k_i t]}{\prod_{\substack{j=1 \\ i \neq j}}^{14} (k_j - k_i)} \right\} \quad (5)$$

This complicated and tedious expression has been substituted by the following simple equation:

$$w = \frac{dc_{\text{CO}_2}}{dt} \approx \frac{k_{\text{II}} e^{-k_{\text{II}} t} - k_{\text{I}} e^{-k_{\text{I}} t}}{\frac{1}{k_{\text{I}}} - \frac{1}{k_{\text{II}}}} \quad (6)$$

(where rate constants k_{I} and k_{II} are fictive values, to be calculated from the measured data; t is the reaction time referred to the induction time; it can be determined by experiments). On the basis of our measurements the induction time is:

$$T \approx 10 \text{ [s]}$$

Both rate constants are given by the following system of equations:

$$\max = \frac{\ln k_{\text{I}} - \ln k_{\text{II}}}{k_{\text{I}} - k_{\text{II}}} \quad (7)$$

$$\left(\frac{dw}{dt} \right)_{t=0} = k_{\text{I}} \cdot k_{\text{II}} (k_{\text{I}} + k_{\text{II}}) \quad (8)$$

the values on the left side being measured values.

To illustrate the capacity of our continuous concentration measuring and recording equipment another series of experiments will be described, i.e. the dynamic test of the isothermic tubular reactor in a model-reactor of our make.

The tested model reaction was a neutralization, where the product of the reaction is a salt. The rate equation of the reaction is:

$$-\frac{dc_1}{dt} = kc_1 c_2 \quad (9)$$

where c_1 and c_2 are the non-continuously and continuously fed reaction component concentrations, respectively. The concentration of the product is given by the following equation:

$$c(x; t) = \frac{k \frac{x}{v} c_{1b}^2 \left(t - \frac{x}{v} \right)}{1 + k \frac{x}{v} c_{1b} \left(t - \frac{x}{v} \right)} \quad (10)$$

where the subscript b denotes the input.

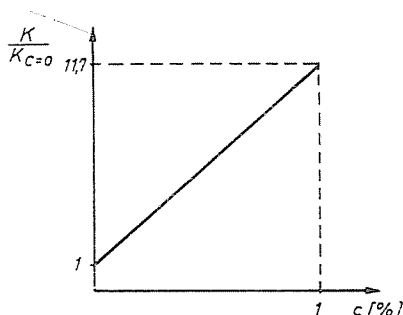


Fig. 1

Owing to the small reaction time the conversion is small, therefore the second term of the denominator of the above equation can be neglected, leading to the following equation:

$$c(x; t) \cong k \frac{x}{v} c_{1b}^2 \left(t - \frac{x}{v} \right) \quad (11)$$

The concentration of the product is determined by measuring the electric conductivity of the solution. The dependence of the electric conductivity of the solution on the concentration of the product is shown in Fig. 1. It can be stated that, although the characteristic curve does not represent a linearity, it is fully linear and the electric conductivity is highly dependent on the concentration of the product

$$\left(\sim 1070 \frac{\text{percentage change of conductivity}}{\text{percentage change of concentration}} \right)$$

which allows a very accurate measuring of the product concentration.

Owing to the small change of concentration during the reaction and to the small reaction heat, the change of the temperature over the whole length of the reactor (1340 mm) was less than 0.05 °C, thus the reactor could be considered isothermic.

From the point of view of isothermic operation the temperature differences of the continuously fed reaction component could also be neglected; it was less than 0.1°C during the test.

The applied measuring method required a flow speed in the reactor where the diffusion effect could be neglected (the input signal of the reactor is not distorted at the output signal). This speed was determined in preliminary tests; in our tests this rather high speed of $30\text{ cm}\cdot\text{sec}^{-1}$ has been applied. For this speed the pressure drop between the two ends of the reactor is 25 water mm: i.e. the flow does not undergo considerable damping.

Test apparatus

The equipment is shown in Fig. 2. The reactor is operated as non-continuous (pulse) reactor, therefore one of the components is fed continuously, (from the tank 1 through the charger 2), the other component non-continuously (of the pipette 3) to the mixing space 4, where the turbulent flow $\left(1.5 < \frac{\text{Re}}{\text{Re}_{\text{crit}}} < 15\right)$ produces a nearly homogeneous distribution of concentra-

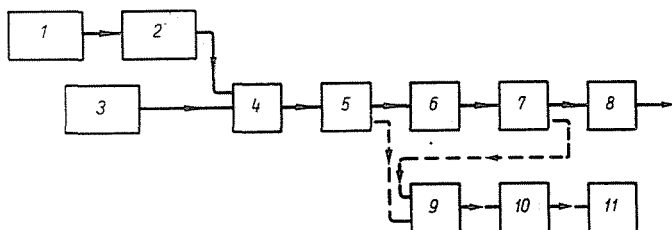


Fig. 2

tion. The reacting compound gets from the mixing space through the electric conductivity measuring cell 5 to the reactor 6 of 1340 mm length and 3 mm inner diameter. The reactor tube is made of aluminium, housed in a thermostatic cover. The compound leaves the reactor via the electric conductivity meter cell 7 through the spillway 8.

The concentration of the compound entering and leaving the reactor is a magnitude proportional to the signals of the 5 and 7 electric conductivity meter cells, respectively, passing through the amplifier and rectifier instrument 9 (containing a voltage source and an oscillator). These signals are measured by the digital voltmeter 10 and recorded by the 11 "Addo" electric recorder working at a speed of one data (a number of four digits) per second. Some

main characteristics of the digital voltmeter are: number of inputs: 20; maximum sampling rate: 0.05 sec/channel; accuracy: 0.01%, referred to the maximum value.

Our testing apparatus has the following characteristics: the reactor is of isothermic operation, diffusionless, the reacting compound flows at a constant speed, the electric conductivity of the compound is a linear function of the product concentration, which is, under these circumstances, directly proportional to the reaction time. The applied data processing system is able to record the high-rate process.

Experimental results

The following tests were carried out in our preliminary experiments:

a) Measurement of the occasional deviations of the flow speeds in case of different flow speed values.

These measurements were carried out only in case of small flow speeds by the following way: The flow-pulse results in steps of conductivity measured by the cells placed at the input and output of the tube.

The time of passing through between each pair of electrodes proved to vary by less than 2%.

b) Determination of the flow speed from the volumetric speed and the dead time. The flow speed (v):

$$v = \frac{4W}{d^2 \pi}$$

where W = the outflow speed of the reagent compound [ml/s]

d = the diameter of the reactor tube [cm].

According to our method:

$$v = \frac{X}{T_h}$$

where X = the length of the reactor as defined by the spacing of two cells [cm]

T_h = the pulse duration in the reactor [s].

Examples for determining the flow speed by each method:

In one measurement 50 ml reaction compound flows out of the reactor in 2 min 23 sec; thus the flow speed:

$$v = \frac{4.50}{143 \cdot 0.3^2 \cdot 3.14} = 4.95 \text{ [cm} \cdot \text{s}^{-1}\text{]}$$

The input pulse appeared on the first cell after 2 seconds, on the second one, after 30 seconds. Thus

$$v = \frac{136}{30 - 2} = 4.86 \text{ [cm} \cdot \text{s}^{-1}\text{]}$$

It is clearly seen that the deviation of the speed values calculated by the two methods is less than 2%.

c) Examination of the diffusion effect by pulse-distortion. These tests aimed at determining flow speeds where the influence of the diffusion on the operation of the reactor can be neglected.

In view of literature data it has been supposed (our reaction-product being a salt) that the diffusion constant of the reaction product was of the same order of magnitude as that of the NaCl in water at 20 °C, i.e. $D = 1.35 \cdot 10^{-5}$ [cm² · s⁻¹]. Besides the influence of the diffusion was negligible, if the following condition was met

$$Pe = \frac{v \cdot l}{D} > 500$$

where v = flow speed [cm/s]

l = length of the reactor tube [cm]

D = diffusion constant [cm²/s].

As the experiment was made in water at 20 °C with $v = 0.1$ cm · s⁻¹ flow speed in a reactor of 130 cm length, $Pe = 9.6 \cdot 10^5 \gg 500$, we supposed that the diffusion in the reactor had little influence even at this low speed.

Our tests, however, showed this supposition to be wrong. Namely the run-up time of the pulse was much higher at the reactor end at a speed of 1 cm/s than at the input, as seen by the pulse distortion due to diffusion. For instance in case of a flow speed of 1.03 cm/s the 6 sec run-up time at the input of the reactor increased to 32 sec at the output.

Our experiments demonstrated the influence of the diffusion to be rather unimportant in NaCl solution at 5 cm/s flow speed: the run-up time of the pulse is increased from 3 sec to 4 sec. In our test system, however, the diffusion effect is considerable as seen by the increase of the pulse run-up time from 3 sec to 15 sec.

On the basis of these experiments we turned to the range of the high flow speeds (30 cm/s), where the influence of the diffusion is negligible.

Pulses of different extent were fed into the input and the concentration of the output product was measured. The main data of the experiments:

speed of the carrier: 28.2 ± 0.56 [cm/s]

extent of the pulses: 37 — 111 [%]

length of the pulses: 2 ± 0.1 [sec]

reactor temperature: 20.4 — 20.8 [d]

Table I

| | |
|--------------|--------------|
| 00-0403 · 01 | 00-0408 · 01 |
| 00-0404 · 01 | 00-0409 · 01 |
| 00-0401 · 01 | 00-0410 · 01 |
| 00-0402 · 01 | 00-0406 · 01 |
| 00-0405 · 01 | 00-0408 · 01 |
| 00-0408 · 01 | 00-0410 · 01 |
| 00-0414 · 01 | 00-0420 · 01 |
| 00-0417 · 01 | 00-0415 · 01 |
| 00-0429 · 01 | 00-0410 · 01 |
| 00-0439 · 01 | 00-0406 · 01 |
| 00-0450 · 01 | 00-0408 · 01 |
| 00-0459 · 01 | 00-0406 · 01 |
| 00-0466 · 01 | 00-0408 · 01 |
| 00-0469 · 01 | 00-0406 · 01 |
| 00-0476 · 01 | 00-0408 · 01 |
| 00-0478 · 01 | 00-0406 · 01 |
| 00-0479 · 01 | 00-0408 · 01 |
| 00-0478 · 01 | 00-0407 · 01 |
| 00-0469 · 01 | 00-0405 · 01 |
| 00-0459 · 01 | 00-0406 · 01 |
| 00-0439 · 01 | 00-0408 · 01 |
| 00-0417 · 01 | 00-0407 · 01 |
| 00-0414 · 01 | 00-0406 · 01 |
| 00-0408 · 01 | 00-0405 · 01 |
| 00-0406 · 01 | 00-0407 · 01 |
| 00-0408 · 01 | 00-0406 · 01 |
| 00-0405 · 01 | 00-0406 · 01 |
| 00-0402 · 01 | 00-0406 · 01 |
| 00-0401 · 01 | 00-0407 · 01 |
| 00-0404 · 01 | 00-0405 · 01 |
| 00-0406 · 01 | 00-0406 · 01 |

The extent of the pulse values is defined as the increase percentage of the carrier speed: Such not too high pulses were applied to disturb the flow as little as possible (owing to the high sensitivity of the concentration measurement this permitted a close evaluation). The length of the pulses was measured by a timing watch. Both the basis in the carrier and the acid in the pulse were the same in dissolver and in one normal solution.

Four digits following the sign (after deducing the zero-point voltage) on the recorded diagram (shown partly in Table I) confronted with the calibration

diagram furnish the conductivity of the solution, i.e. the product concentration. The last two digits mean the sampling place in order to accelerate the recording, however, the 20 inputs had been connected to the signals from the two cells and the channel-counter was blocked.

The product concentration *vs.* time curve shown in Fig. 3 helped to determine the rate constant of the salt-producing reaction for 20.4 °C:

$$k = (3.32 \pm 0.15) \cdot 10^{-4} [\text{mol}^{-1} \cdot \text{liter} \cdot \text{s}^{-1}]$$

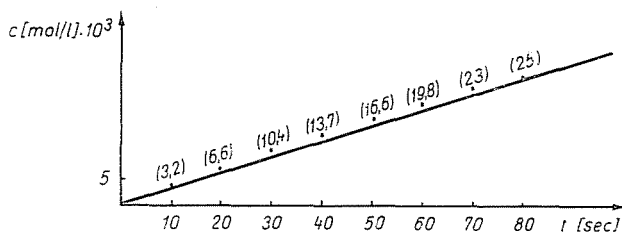


Fig. 3

The obtained reaction rate constant deviates by 7.5–15% from that calculated by Eq. (11). This deviation is rather slight, with due regard to the inaccuracies of timing and of the reaction rate constant determination.

Summary

An equipment has been designed for analysing various chemical reactions (oxidation of cyan, neutralisation) and various chemical reactors (tank reactor, tubular reactor). Details of the processes of seconds to minute duration, not detectable by the classical methods, can also be evaluated by utilizing this equipment.

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