USING HYDRAULIC ANALOG METHODS TO DEVELOP KINETIC RATE EQUATIONS FROM LABORATORY DATA

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IN A PREVIOUS paper (A Grand Sale: $12 for a Dozen Experiments in CRE [1]) we introduced a class experiment which employed the hydraulic analog to represent systems of first order reactions in batch reactors. These experiments require very simple and inexpensive equipment, and they illustrate one of the basic problems in chemical reaction engineering. In this paper we extend the hydraulic experiments to represent reaction systems with non-linear systems.

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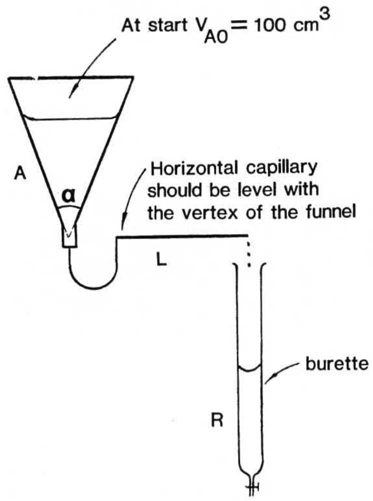

Volume (cm^3)	Time (sec)
100	0
-	-
-	-
-	-

FIGURE 1. Experimental set up to represent reactions (A → R) with orders smaller than one.

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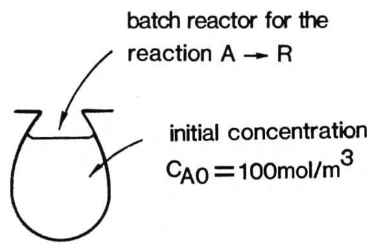


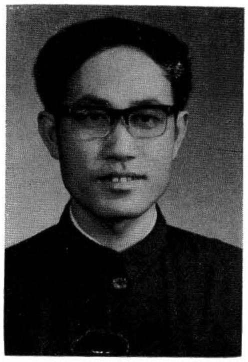
Reactant concentration (mol/m^3)	Time (sec)
100	0
-	-
-	-
-	-

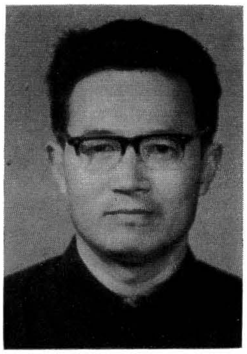
FIGURE 2. Reactor analog to the hydraulic experiment of Fig. 1.

CASE 1: Reaction orders $n < 1$

Let us first illustrate the experimental apparatus. Connect an ordinary glass capillary to a funnel as shown in Fig. 1. Fill the funnel with water. At time zero let the water flow out, and record the change in volume with time.

We tell the student that we view the experiment of Fig. 1 as a batch reactor in which reactant A disappears to form product R. The volume of water in the funnel in cm^3 is to be considered as a concentration of reactant in mole/m^3. Thus the experiment of Fig. 1 is to be treated as shown in Fig. 2. By following the volume of water in the funnel versus time the student is to determine





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the reaction order and the value of the rate constant.

One may guess, and it so happens, that this hydraulic experiment and its kinetic analog are reasonably represented by n^{th} order kinetics

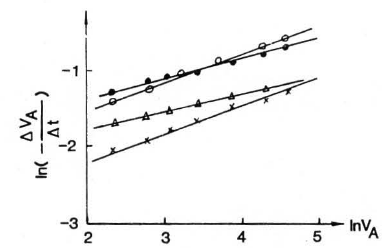
$$-\frac{dV}{dt} = k\,V^n$$

or

$$-\frac{dC_A}{dt} = k\,C_A{}^n$$

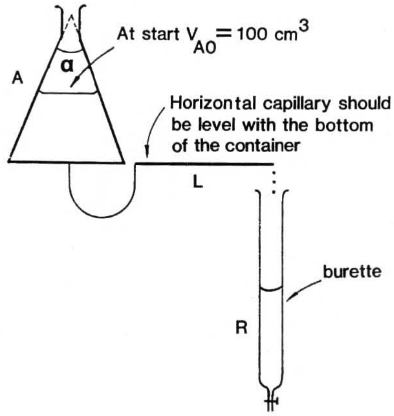
in which case a plot of $ln(-\Delta V/\Delta t)$ versus ln V should give a straight line of slope n. From this the reaction order and rate constant can be determined.

Fig. 3 shows the results of experiments under the following conditions



Symbol	α	L(cm)	n(slope)
o	23°	10	0.37
x	23°	20	0.37
•	30°	10	0.28
Δ	60°	10	0.25

FIGURE 3. Experimental results for Case 1.



Volume (cm^3)	Time (sec)
100	0
–	–
–	–
–	–

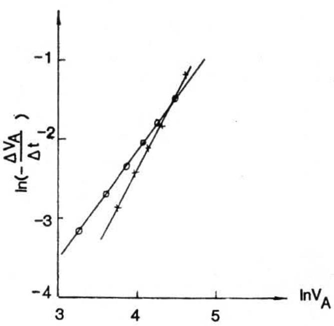
FIGURE 4. Experimental set up to represent reactions (A → R) with orders larger than one.

$V_{Ao} = 100\ cm^3$
L (length of capillary) $= 10$ cm, 20 cm
$\Delta V_A = 5\ cm^3$
d (diameter of capillary) $= 0.124$ cm

Clearly, n^{th} order kinetics with $n < 1$ well represents the results, the smaller the cone angle α the larger the value of n. Also note that the length of capillary does not affect the reaction order, however, it will affect the reaction rate constant.

CASE 2: Reaction orders $n > 1$

When the conical container is turned upside down, as shown in Fig. 4, the results of Fig. 5 are



Symbol	α	L(cm)	n(slope)
o	23°	10	1.35
×	30°	10	1.91

FIGURE 5. Experimental results Case 2.

obtained.

In this case the reaction order is found to be greater than unity. Again the larger the cone angle α the greater is the reaction order.

FINAL REMARKS

1. Experiments with hydraulic analogs to the batch reactor, reported in [1] and here show

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pean Committee for the Use of Computers in Chemical Engineering Education) in Europe [5, 6].

We are in very close contact with EURECHA, which makes possible a continuous interchange of experiences and computer programs and visits by experts. Together, we have worked out a standard of writing chemical engineering computer programs which is widely used both in Hungary and in other countries joined by EURECHA. We believe that the realization of the CHEMISYS system represents a significant advance since it represents a unified system; the projects organized earlier by CACHE and EURECHA are characterized by the lack of any common system. In order to promote the foreign applications of the CHEMISYS subroutines, an agreement has been signed between the ETH (Eidgenössische Technische Hochschule, Zurich, Switzerland) which is the Secretariat of EURECHA, and the Institute for Science Management and Informatics.

AVAILABILITY

The CHEMISYS algorithm is available as a collection of computer programs. They have been written in FORTRAN and run on RJAD-22, 32, and 40 series computers in Hungary. Of course, the programs can also run on larger computers without any difficulty as well as on IBM 360 or other computer in the same size range.

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that reaction orders smaller, equal or greater than unity are obtained with various shaped containers, as shown in Fig. 6. Large cone angles give large deviations from first order kinetics, and as cone angles approach zero the reaction order approaches unity.

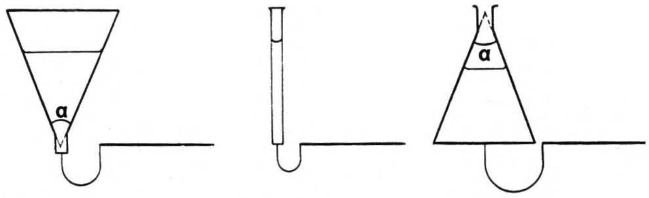

FIGURE 6. The relationship between shape of the container and reaction order.

2. Capillary length does not affect the reaction order. However, for ease in running the experiment it is suggested that the length be chosen such that the half life of the reaction is between 2 and 3 minutes.
3. In order to get accurate data it is better to measure ΔV from the outlet of the capillary with a burette (as shown in Fig. 1) instead of reading water levels on the funnel directly.
4. One can combine the set up here with additional burettes and funnels to give multiple reactions of various types as outlined in our previous paper [1], such as

$$A \rightleftharpoons R, A \rightarrow R \rightarrow S, \text{etc}$$

Interpretation of such systems with non-linear kinetics is not easy and provides a challenge to the brighter students and practice on the computer.

5. The large variety of combinations of set-ups and capillary lengths will allow each student in the laboratory to run his own experiment, even in China with its huge student population.

ACKNOWLEDGMENTS

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