Hydraulic Simulation of n*th*-Order Reaction Kinetics

M. A. DAOUS

Department of Chemical & Materials Engineering, Faculty of Engineering,
King Abdulaziz University, Jeddah, Saudi Arabia

ABSTRACT. This note provides some necessary corrections for the concept and design of the hydraulic analog method introduced by Zhang and Hau to simulate n*th*-order reaction kinetics. It attempts to show that Zhang and Hau have made a basic mistake in the design of the hydraulic analog of non-linear reactions and consequently in the simulated kinetic data interpretations, and to provide the proper hydraulic analog design to simulate these types of reacitons.

1. Introduciton

Zhang and Hau[1,2] (hereafter called Z&H) have introduced a hydraulic analog method to simulate various linear and non-linear reaction schemes. The method is thought to be useful to illustrate the development of kinetic rate equations from laboratory data which is one of the basic problems in chemical reaction engineering.

The hydraulic analog introduced has a modular design and can be composed, in its simplest form, of a burette (to simulate linear reactions) or a funnel (to simulate non-linear reactions) connected to a horizontally positioned capillary tube as shown in Fig. 1. Z&H, however, have failed to show the right parameters of the funnel that influence the order of the simulated non-linear reactions. This is probably due to an over look in the basic principle on which the hydraulic analog method is based, which in any case, was not explicated in Z&H papers.

2. Principle of the Hydraulic Analog Method

Consider the burette and ordinary glass capillary-tube system shown in Fig. 1-a, where the horizontal cappilary is levelled with the zero volume reading on the burette. If the burette is filled with a Newtonian fluid (water for example) and the liquid discharge-rate from the capillary is maintained low (in the form of drops which can be controlled by the diameter and length of the capillary), then this discharge rate is described by the Hagen-Poiseulle equation.

$$Q = \Delta P \pi D^4 / 128\mu L \tag{1}$$

where

Q	=	Liquid flow rate out of the capillary, cm^3/s.
ΔP	=	Pressure drop in capillary, dyne/cm^2.
D	=	Capillary diameter, cm.
μ	=	Liquid viscosity, gm/cm.s.
L	=	Capillary length, cm.

The mass balance equation for the fluid in the burette-capillary system is given by

$$\frac{dv}{dt} = -Q \tag{2}$$

(a)

(b)   (c)
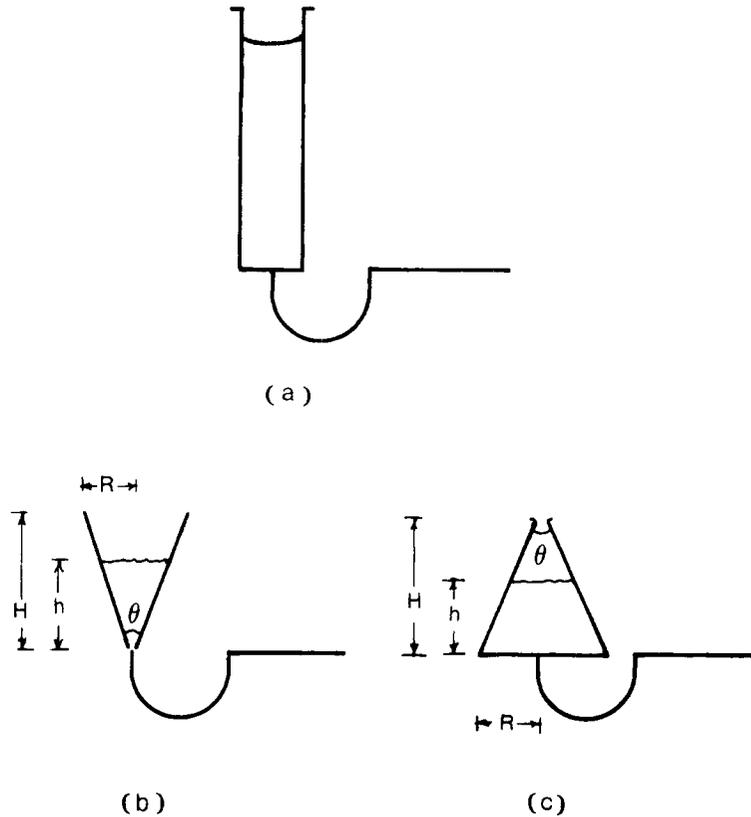
FIG. 1. The basic modules of the hydraulic analog of Z & H.

where v is the fluid volume in the system, which is practically equal to that in the burette. Combining equations (1) and (2) gives

$$\frac{dv}{dt} = -\frac{\pi D^4}{128\mu L}\,\Delta P \tag{3}$$

The change in fluid kinetic energy between the inlet and outlet of the capillary is negligible. Thus, ignoring this term in the mechanical energy balance then gives

$$\Delta P = \rho g h \quad \text{(Static pressure head in burette)} \tag{4}$$

where

h =   Liquid level in burette measured from the horizontal capillary level, cm.

g =   Gravitational acceleration, cm/s^2.

ρ =   Fluid density gm/cm^3.

Combining equations (3) and (4) gives

$$\frac{dv}{dt} = -\frac{\pi D^4 \rho g}{128 \mu L} h \tag{5}$$

But, v and h of the liquid in the burette are related to each other linearly through the constant cross-sectional area, A, of the burette. Thus multiplying and dividing the right-hand side of equation (5) by A yields

$$\frac{dv}{dt} = -\frac{\pi D^4 \rho g}{128 \mu L A} v \tag{6}$$

or

$$\frac{dv}{dt} = -Kv \tag{7}$$

where K is a constant $= \dfrac{\pi D^4 \rho g}{128 \mu L A}$

equation (7) is of the same form as the rate equation of a constant volume first order reaction, $A \rightarrow R$, with a rate equation

$$\frac{dC_A}{dt} = -K C_A$$

Thus, one could view the burette and capillary set up of Fig. 1-a as a batch reactor in which reactant A disappears to form product R. The volume reading on the burette in cm^3 is to be viewed as a concentration of the reactant A in mol/m^3. By following the volume of water in the burette (*i.e.*, the reactant concentration) versus time, a student would generate data analogous to a kinetic data of a first order reaction which he could analyze by either the "integral" or the "differential" method of data analysis[3].

From equation (7), it can be noticed that for a given fluid system, the rate constant, $\dot{K}$, depends on the capillary length and diameter, and the burette cross sectional area. Thus, one could simulate a wide range of the value of the rate constant in a given experimental set-up by simply changing the length of the capillary tube or burette diameter.

By following the same principles, the basic hydraulic-simulator module shown in Fig. 1-a can be extended to simulate many multiple first order reaction schemes as shown by Z&H.

3. Extention to Non-Linear Reaction Orders

As can be seen from equations (5) and (6), the linear relationship between v and h in a burette makes the hydraulic simulation of first order reaction possible in the set up of Fig. 1-a. Thus, it is obvious then to simulate reactions of different orders, one has to replace the burette with containers in which the relationship between v and h is not linear, but can be expressed in the form $h = kv^n$, where $n \# 1$.

Z&H have used circular cones in place of the burette as shown in Fig. 1-b and 1-c to simulate reaction orders smaller and greater than unity, respectively. They have further claimed that large cone angles give large deviations from the first order kinetics. A closer look into the v-h relationship of these cones of different orientation reveals, however, that this claim is incorrect.

The volume-height relationship in the cone of Fig. 1-b is given by

$$v = \frac{1}{3} \pi \left(\frac{R}{H}\right)^2 h^3$$

or

$$h = [3/\pi \left(\frac{H}{R}\right)^2]^{1/3} \ v^{1/3} \tag{8}$$

where R and H are the radius and height of the circular cone respectively. Now equation (8) is of the form

$$h = m \ v^{1/3} \tag{9}$$

where m is constant $= [3/\pi \left(\frac{H}{R}\right)^2]^{1/3}$. Combining equations (5) and (9) gives

$$\frac{dv}{dt} = -Kv^{1/3} \tag{10}$$

where K is a constant $= \frac{\pi D^2 \rho g}{128 \mu L m}$. Equation (1) is the equation of the hydraulic analogue to a $\frac{1}{3}$ order reaction kinetics. Thus, one could use the set up of Fig. 1-b to simulate such a reaction. It should be further noticed that a change in the cone angle θ, i.e., H/R will only change the rate constant but not the reaciton order as claimed by Z&H. Thus, one could only simulate this uncommon reaction order using this set-up.

The v-h relationship in the cone of Fig. 1-c is give by

$$v = \pi R^2 H \left[\alpha - \alpha^2 + \frac{\alpha^3}{3}\right] \tag{11}$$

where α is the dimensionless liquid height in the cone, h/H. For given values of R and H, and therefore the cone angle θ, this equation can be substituted by an equation of the form $h = Kv^n$ through fitting numerical data from equation (11) into this equation. The fit is excellent for any given R, H, and range of h values. The value of n, however, is always greater than 1, and can be changed by changing the initial liquid height in the cone, h_0. Increasing h_0 in a cone with a given cone angle θ causes n to de-

crease. This allows for a multitude of reactions of order greater than one to be hydraulicly simulated by circular cones of the same angle similar to that of Fig. 1-c, but of different initial liquid heights.

Furthermore, the rate constant in a given simulated reaction order can be controlled by changing the cone angle θ, while using the same initial liquid height, h_0. For a given h_0, increasing θ causes the rate constant K to decrease.

Better results than those obtained by the circular cones, and which were not considered by Z&H, can be achieved by utilizing hemispherical containers such as those depicted in Fig. 2-a and 2-b. The v-h relationship in the hemisphere of Fig. 2-a is given by

$$v = \frac{1}{3} \pi R h^2 (3-\gamma)$$
(12)
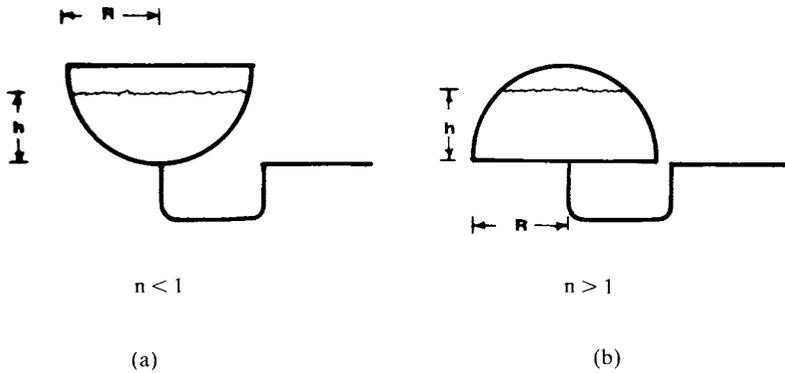
FIG. 2. Hemispherical modules for simulating non-linear reaction kinetics.

where R is the radius of the hemispherical container and γ is the dimensionless liquid level in the container, h/R. Again it can be shown that for a given R, equation (12) can be replaced by an equation of the form $h = Kv^n$ as before. The value of n, for any given radius, is always less than 1, and can be decreased by increasing the initial liquid level in container h_0.

On the other hand, the v-h relationship of the hemispherical container of Fig. 3-b is given by

$$v = \frac{1}{3} \pi R^2 h (3-\gamma^2)$$
(13)

when this equation is replaced by an equation of the form $h = Kv^n$ for a given container radius, R, n will always be greater than 1, and can be increased by decreasing the initial liquid level in the container h_0.

4. Conclusion

The simple and inexpensive experimental facilities introduced by Zhang and Hau,

in consultation with professor Levenspiel, to simulate n*th* order reactions are very instrumental in illustrating chemical reaction kinetics and the development of rate equations from laboratory data. The set-ups depicted in this note as well as many of those outlined by Z&H to simulate multiple reaction schemes have been experimentally verified by the author of this note. The discrepancy between these experimental findings and Z&H conclusions on their hydraulic analog set up for non-linear reactions has instigated this note.

References

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محـــاكاة هيـــدرولية لحركيـــة التفاعـــلات ذات الدرجـــة (ن)

محمد عبد الرحمن داعوس

قسم الهندسة الكيميائية وهندسة المواد ، كلية الهندسة ، جامعة الملك عبد العزيز

جـــــدة – المملكة العربية السعودية

المستخلص . تعطى هذه العُجالة بعض التعديلات الضرورية لمفهوم المحاكاة الهيدرولية لحركية التفاعلات الكيميائية ذات الدرجة ن ، وبالتالي تصحيح لتصميم النظير الهيدرولي الذي قدمه كل من زَنج وهيو لهذا الغرض . حيث تهدف هذه المذكرة إلى إيضاح الخطأ في تصميمها للمحاكي الهيدرولي للتفاعلات اللاخطية وفي تحليل البيانات الناتجة عنه ، كما تهدف إلى إعـطاء التصميم الصحيح لهذا النظير الهيدرولي لمحـاكاة هذه الأنـواع من التفاعلات الكيميائية .