SIMULATION OF REACTION KINETICS USING EQUIVALENT HYDRODYNAMIC MODELS

Modeling and Laboratory Experiment

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Laboratory work is an important segment of chemical engineering instruction that cannot be overemphasized. It reinforces the theoretical foundation of courses laid out during lectures, and it is a way to help students develop vital experimental skills (*e.g.,* planning, observation, analysis, communication, etc.) to succeed in their future careers.[1,2] Learning skills through "doing," however, is not always an easy task because of budgetary constraints and the high costs incurred by equipment maintenance and safety requirements. These shortcomings can be countered by resorting to the simulation tool. That is, expensive and/or hazardous experiments can be simulated by simple *analogous* physical concepts.

An interesting example offered by this approach is the analogy that exists between the hydrodynamics of nonviscous liquids and chemical reaction kinetics. The idea is that the mathematical models describing the velocity as a function of the hydrostatic height of free-falling liquids in ducts, with appropriate shapes, are similar in form to models expressing the rate of simple chemical reactions as a function of species concentrations.

This paper describes a safe and inexpensive experiment to simulate the kinetics of simple chemical reactions by analogous hydrodynamic models. Among the advantages of such simulation work is the possibility of studying the rate of chemical reactions in a hazard-free environment necessary for an experimenter, to avoid unnecessary generation of hazardous waste, and to lower the cost of experimental runs that involve large quantities of chemicals. The proposed approach is not intended to be a substitute for real kinetic measurements, but the breadth of the analogy is valuable from the pedagogical point of view, and the data analysis is an excellent exercise for a student taking a class in chemical reaction kinetics.

MODELING

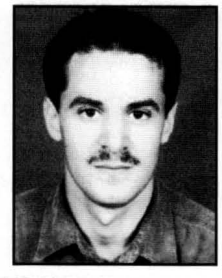
Figure 1 shows a cylindrical duct within which a fluid flows. The duct holds some volume of a nonviscous liquid, which drains through a small area or orifice. The hydrostatic height, H, of the liquid decreases with time as the volume of the liquid in the system decreases; the flow is clearly unsteady. From the macroscopic expressions of the energy and mass balances within the boundaries of an isothermal system, assuming frictional losses to be negligible and the liquid density, ρ, to be constant, it is easy to establish the following relationship (Torricelli's law) between the velocity of the liquid, v_o, at the outlet of the cylinder, the velocity, v, of the falling liquid at the liquid-free surface, and the hydrostatic height, H,[3]

$$v_o^2 - v^2 = 2gH \tag{1}$$

The macroscopic mass balance within the boundaries of the system states that

$$-\rho A\frac{dH(t)}{dt} = \rho v_o A_o = \rho v A = q \tag{2}$$

where A, A_o, and q are the cylinder cross-sectional area, outlet orifice area, and mass flow rate of the falling liquid, respectively. If the outlet orifice area is much smaller than the area of the liquid-free surface, the velocity of the liquid in



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the duct is a small fraction of the velocity of the liquid leaving the duct. Under this condition, the term v^2 can be neglected in Eq. (1). This assumption holds as long as the liquid-free surface is far from the outlet (*i.e.,* for values of z large enough).

A substitution of v_o obtained from Eq. (2) into Eq. (1) leads to the final differential form of Eq. (1) as

$$-\frac{dH(t)}{dt} = \kappa H(t)^{\frac{1}{2}} \tag{3}$$

with

$$\kappa = \frac{A_o}{A}\sqrt{2g} \tag{4}$$

Equation (3) expresses the dependence of the velocity of the falling liquid on the hydrostatic height and has a similar mathematical form to the equation of mass balance for a reactive system in a closed well-stirred reactor wherein a simple reaction of order one-half takes place.[4,5] In Eq. (3), the hydrostatic height mimics a species concentration in the equation giving the rate of a chemical reaction. On the other hand, noticing that the velocity, -dH/dt, of the falling liquid decays with decreasing hydrostatic height, H, with time is a valuable exercise from the practical and instructional viewpoints. It is exactly the same as the variation of the rate of a simple chemical reaction of order one-half with concentration. Finally, by judiciously choosing the geometry of the duct, it is possible to simulate the kinetics of simple chemical reactions of various orders.

For simplification, let us consider a duct with the geometry illustrated in Figure 2. The hydrostatic height, H, and width, x, of the liquid inside the duct are assumed to be related by a simple equation of the form

$$H = ax^n \tag{5}$$

where n can be an integer or a fractional number, and a is a constant.

If the duct has a constant depth, D, and using Eq. (5), the expression for the area of the falling liquid-free surface becomes

$$A = Dx = D\left(\frac{H}{a}\right)^{\frac{1}{n}} \tag{6}$$

Using the same approach described previously, the term v^2 is neglected in Eq. (1) provided that A_o is much smaller than A. By substituting A obtained from Eq. (6) into Eq. (1), the differential form of Eq. (1) takes the form

$$-\frac{dH(t)}{dt} = \kappa' H(t)^{\frac{n-2}{2n}} \tag{7}$$

with

$$\kappa' = \frac{A_o a^{\frac{1}{n}}}{D}\sqrt{2g} \tag{8}$$

The analogy between the hydrodynamics of draining a duct and the kinetics of simple chemical reactions is now established. Let us examine some simple cases.

Model of order 0 • A nonviscous liquid falling through a duct whose lateral boundary (see Figure 2) is parabola-like (n = 2) simulates a chemical reaction or order zero.

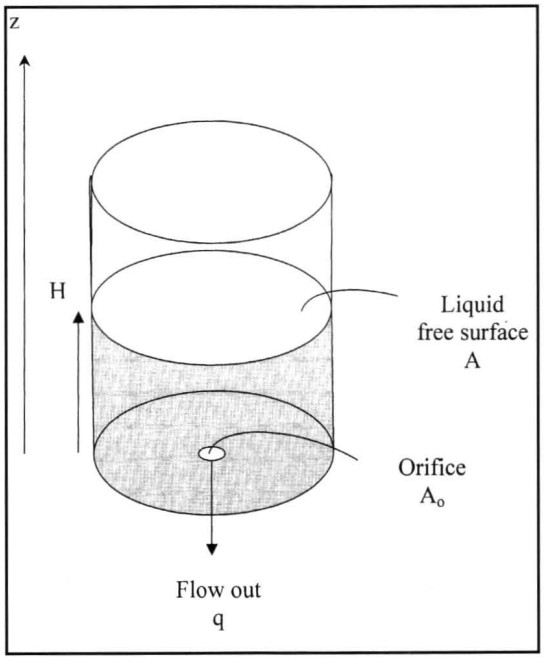

Figure 1. *Schematic of the physics of a cylindrical duct.*

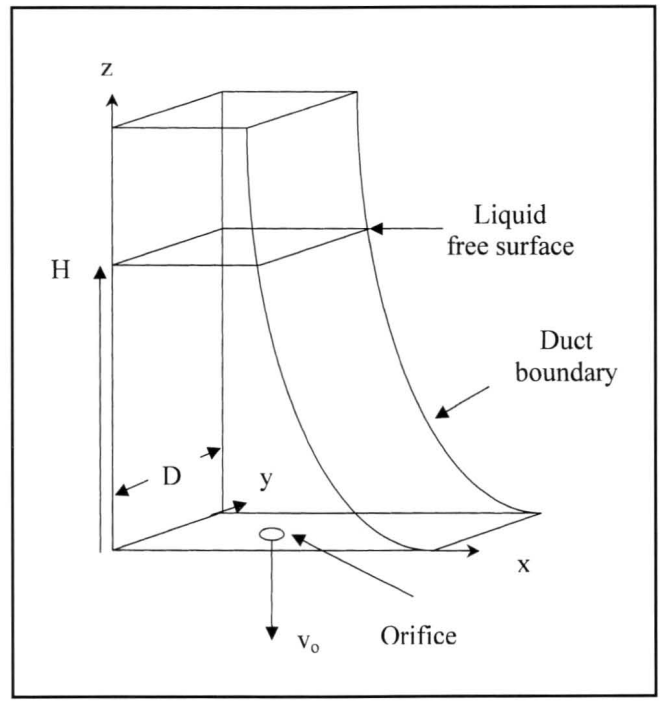

Figure 2. *Schematic of an arbitrary-shaped duct.*

Model of order 1/2 • This is the situation for which the parameter n must be very large. The lateral boundary of the duct is parallel to z-axis (n >> 1, x = const). The draining of a cylindrical duct is a special case simulating a chemical reaction of order one-half.

Model of order 3/2 • By equating the exponent in the hydrostatic height in Eq. (7) to 3/2, the boundary of the duct takes the form of a hyperbola, with n = -1.

Model of order -1/2 • A chemical reaction of this order can be simulated by an analogous hydrodynamic model for which n = 1. The lateral boundary of the duct for this case is linear in form.

Similarly, further simple chemical reactions can be simulated using the hydrodynamic analogy described above.

DESCRIPTION OF EXPERIMENT

The equipment required for this experiment is rudimentary and inexpensive. It consists of ducts that were made from Plexiglass wherein water flows and leaves through an orifice. Duct surfaces have been tailored after a precise large-format drawing of the function defining the shape of the duct as expressed by Eq. (5). Pieces of Plexiglass were then carefully cut according to the drawing, and the resulting surfaces were assembled using chloroform as a gluing agent. Four ducts with shapes as described in the previous section were designed so as to simulate the rates of four simple chemical reactions. The suggested experimental procedure is:

1. *Fill the duct with a nonviscous liquid (e.g., water) until the zero reading of the scale.*
2. *Make sure all air bubbles in the duct are eliminated.*
3. *Refill the duct with the liquid until the zero reading after elimination of air bubbles.*
4. *Open the orifice and start reading the height of the liquid as a function of time using a stopwatch. Either a time or liquid height increment can be fixed during the experiment.*
5. *Take frequent readings and tabulate the results as time vs. height.*
6. *Repeat steps 1 through 5 a number of times for a statistical analysis of the results.*

RESULTS AND DISCUSSION

The results obtained for models -1/2(n=1), 1/2(n=∞), and 3/2(n=-1) considered in this study are shown in Figures 3a,b,c, respectively. All figures depict values of log(-dH/dt) as a function of log(H). Data relative to the order (n-2)/2n and constant κ' for a given model can be estimated from the corresponding curve slope and intercept, respectively. These model parameters are summarized in Table 1. The ex-

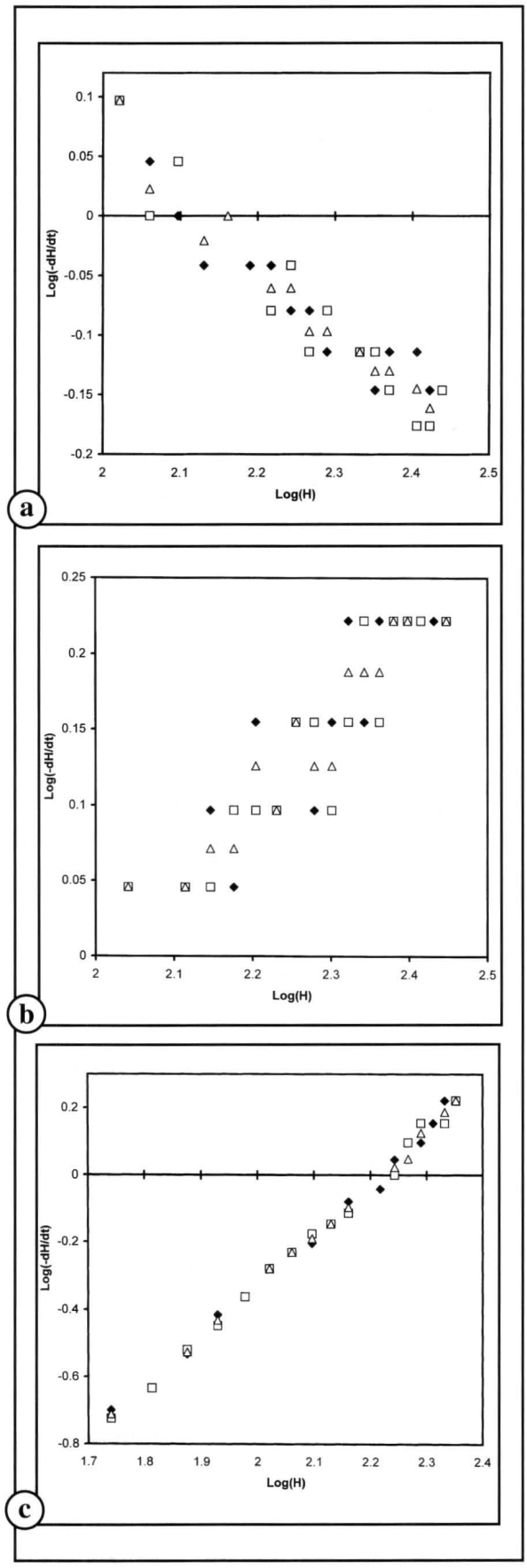

Figure 3.
Log (-dH/dt) as a function of log (H) for (a) model -1/2, (b) model 1/2, and (c) model 3/2. Different markers correspond to different experimental runs.

perimental results, at least those relative to the parameter (n-2)/2n, are in good accordance with theoretical predictions, discussed earlier, within experimental errors. The latter are mainly attributed to inaccuracies in readings done by human operators. For this reason, automation of the experimental procedure is desirable as it allows for flexibility in data collection and it yields more precise data.

One point worthy of notice in Figure 3 is related to the distributions of experimental data depicted in Figures 3a and 3b. A careful analysis of the data indicates that the values of -dH/dt are not sensitive to the hydrostatic height, H, within many (between 2 and 4) successive readings for the models with n=1 and n=∞. These results are attributed to two factors: first, in order to have a good approximation of -dH/dt by -ΔH/Δt, a small height increment ΔH has been chosen so that within the time elapsing between two successive readings, the velocity of the liquid has not changed significantly; second, both sets of data (in Figures 3a and 3b) correspond to models with "weak" orders, *i.e.,* -1/2 and 1/2, respectively. The parameters of the different models were also estimated by an optimization technique, namely the simplex method,[6] using the commercial software MATLAB 5.3. The computed values are in good agreement with those estimated from the plots (Figure 3) and are shown in Table 1.

TABLE 1
Parameters of Hydrodynamic Models 1/2, 3/2, and -1/2
(G)-graphical estimation: (M)-MATLAB results

Model	(n-2)/2n (G)	(n-2)/2n (M)	κ' (G)	κ' (M)
1/2	0.529	0.537	$8.71\ 10^{-2}$	$8.34\ 10^{-2}$
3/2	1.535	1.525	$4.67\ 10^{-4}$	$4.15\ 10^{-4}$
-1/2	-0.541	-0.535	14.79	13.59

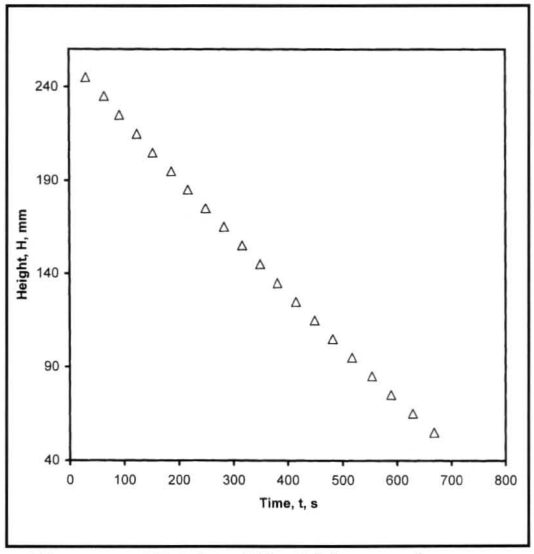

Figure 4. *Height of liquid-free surface as a function of time.*

Figure 4 depicts the hydrostatic height, H, of the liquid-free surface as a function of draining time, t, for model 0 with n = 2. It can be seen that the height, H, varies linearly with time so that the liquid velocity, -dH/dt, which is the opposite of the slope of the curve H vs. t shown in Figure 4, of the freely falling liquid has a constant value of ~0.3 mm/s- and is independent of H.

CONCLUSIONS

I have reported on a novel experiment for the simulation of the kinetics of simple chemical reactions by analogous hydrodynamic models. The experiment is safe and was set up with normal laboratory glassware and fittings. It exposes students to the power of simulation and to the tools of model parameter identification. The analogy between the hydrodynamics of non-viscous liquids and chemical reaction kinetics can be extended to any reaction order provided the duct shape is adequately chosen. The obtained experimental data for the different models considered in this study are in good agreement with the theory and numerical calculations.

ACKNOWLEDGMENTS

Thanks are due to Mr. A.R. Killani for helping in setting up the equipment and to two undergraduate students for the experimental results and model parameter estimation.

NOMENCLATURE

A	cross-sectional area for flow in duct, m^2
A_o	cross-sectional area for flow leaving duct, m^2
a	constant, m^{1-n}
D	depth of duct, m
g	constant of gravitation, m/s^2
H	height of liquid in duct, m
n	number
q	mass flow rate of liquid, kg/s
t	time, s
v	liquid velocity, m/s
v_o	liquid velocity at the outlet, m/s
x	width of liquid, m
x,y,z	Cartesian system of coordinates
κ	constant, $m^{1/2}/s$
κ'	constant, $m^{(n+2)/2n}/s$
ρ	liquid density, kg/m^3

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