A GRAND SALE:
$12 For A Dozen Experiments In CRE

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WE HAVE NOTICED THAT undergraduate chemical engineering laboratories in the United States commonly make use of experiments in unit operations, instrumentation and control; but that experiments in chemical reaction engineering (CRE) are very rare. This is understandable because such experiments usually require an advanced level of understanding, are rather complex in set up, and more involved to operate.

We would like to introduce a whole class of experiments which require very simple and inexpensive equipment and which illustrate one of the basic problems of chemical reaction engineering: the development of a kinetic rate equation from laboratory data. In essence, the student takes laboratory data, guesses a kinetic equation, tests its fit to the data and, if this is satisfactory, determines the corresponding rate constants.

Basically, we use a hydraulic analog. We will illustrate this with the simplest case; the fitting of a first order decomposition, A→R.

Connect an ordinary glass capillary to a burette as shown in Fig. 1. Fill the burette with water, at time zero let the water flow out, and record the change in volume as time progresses.

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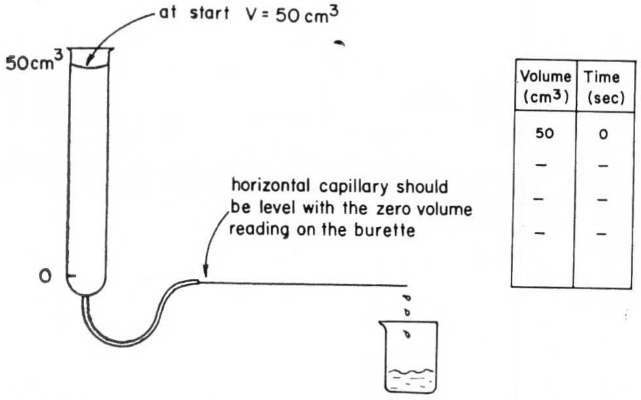

Volume (cm³)	Time (sec)
50	0
–	–
–	–
–	–

FIGURE 1. Experimental set up to represent the first order decomposition of reactant A, or A → R.

The student is told to view the experiment of Fig. 1 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 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 reactant concentration (actually the volume of water in the burette) versus time the student is to determine the order of reaction and the value of the rate constant. If the experiment is set up properly, one will find that the data fits first order kinetics.

The student sooner or later guesses first order kinetics, integrates the rate equation to give $ln(C_o/C) = kt$, plots the logarithm of concentration versus time, and from this evaluates the rate constant. Thus he learns how to test kinetic models. Of course, the length and diameter of capillary will determine the value of the rate constant.

The experiment is so simple and quick to do one can incorporate a lesson in statistical analysis with it. Ask the student to repeat the experiment

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a number of times, find the rate constant, and also the 95% confidence interval for the rate constant.

This is the simplest of a whole class of experiments that can be done with burettes and capillaries. Fig. 3 shows some of the many other reaction schemes that may be used.

There may be more than one way to test a rate form and fit the rate constants. It challenges the student's initiative and ingenuity to see how he approaches his particular problem. For example: for reactions in series, A→R→S he can try to follow the concentrations directly, he may follow concentration ratios and fit them to charts as shown in Levenspiel [1], or he may try to use the conditions when the intermediate hits its maximum value. He soon finds that some approaches are much more discriminating than others.

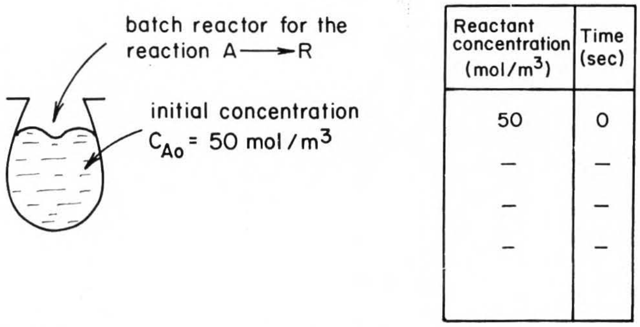
SUGGESTIONS FOR SETTING UP THE EXPERIMENTS

WE HAVE TESTED ALL THE experimental variations of Fig. 3 in the laboratory ourselves, and we have found that observation of the following simple precautions will result in excellent agreement of experiment with theory.

- Be sure that the capillary outlet is level with the zero line of the burette. Check this by filling the burette and letting water run out until equilibrium is achieved.
- Do not have any restriction between burette and capillary comparable with that of the capillary itself.
- Verify that laminar flow exists in the capillary. For an ordinary capillary and burette this condition is well satisfied.
- Before starting an experiment pour water through the burettes so as to wet them. Also see that water does not flow back along the bottom of the capillary. Use a rubber band or a Chinese teapot spout dripper at the capillary outlet.
- If the capillary is not long enough then the run time will be awkwardly short; if too long, a lot of time is wasted: The following suggestions are convenient time scales and capillary lengths.

  Let T_1 be the time required for the water in the first burette to drop to half its initial height and let the corresponding length of capillary be L_1.

  For the first experiment of Fig. 3 we find that T_1 = 30—40 sec is about right. For other experiments the appropriate time scales and capillary lengths are shown in Table 1.
- By preparing a number of capillaries and by using

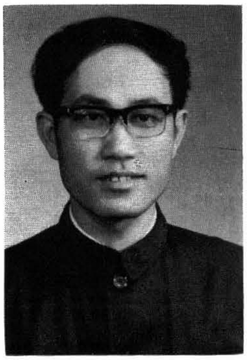


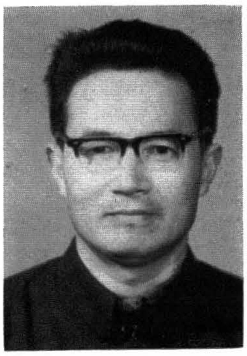
Reactant concentration (mol/m^3)	Time (sec)
50	0
–	–
–	–
–	–

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

TABLE 1
Recommended experimental conditions

Reaction Scheme Shown in Fig. 3	T_1 (sec)	Capillary length
Case 1	30—40	L_1
Case 2	20—30	L_2 = 2—6 L_1
Case 3	30—40	L_3 = 2—4 L_1
Case 4	20—30	L_2 = 4 L_1, L_3 = 2—4 L_1
Case 5	30—40	L_3 = 2—4 L_1, L_4 = 2 L_1
Case 6	20—30	L_2 = 4—5 L_1, L_3 = 2—4 L_1
Case 7	20—30	L_2 = 4 L_1, L_3 = 2—4 L_1, L_4 = 8—10 L_1
Case 8a,b	30—40	L_1
Case 9	20—30	L_3 = 4 L_1
Case 10	30—40	L_3 = 4 L_1
Case 11a,b	30—40	L_3 = 3—4 L_1
Case 12	30—40	L_2 = 2—4 L_1, L_3 = 6—8 L_1





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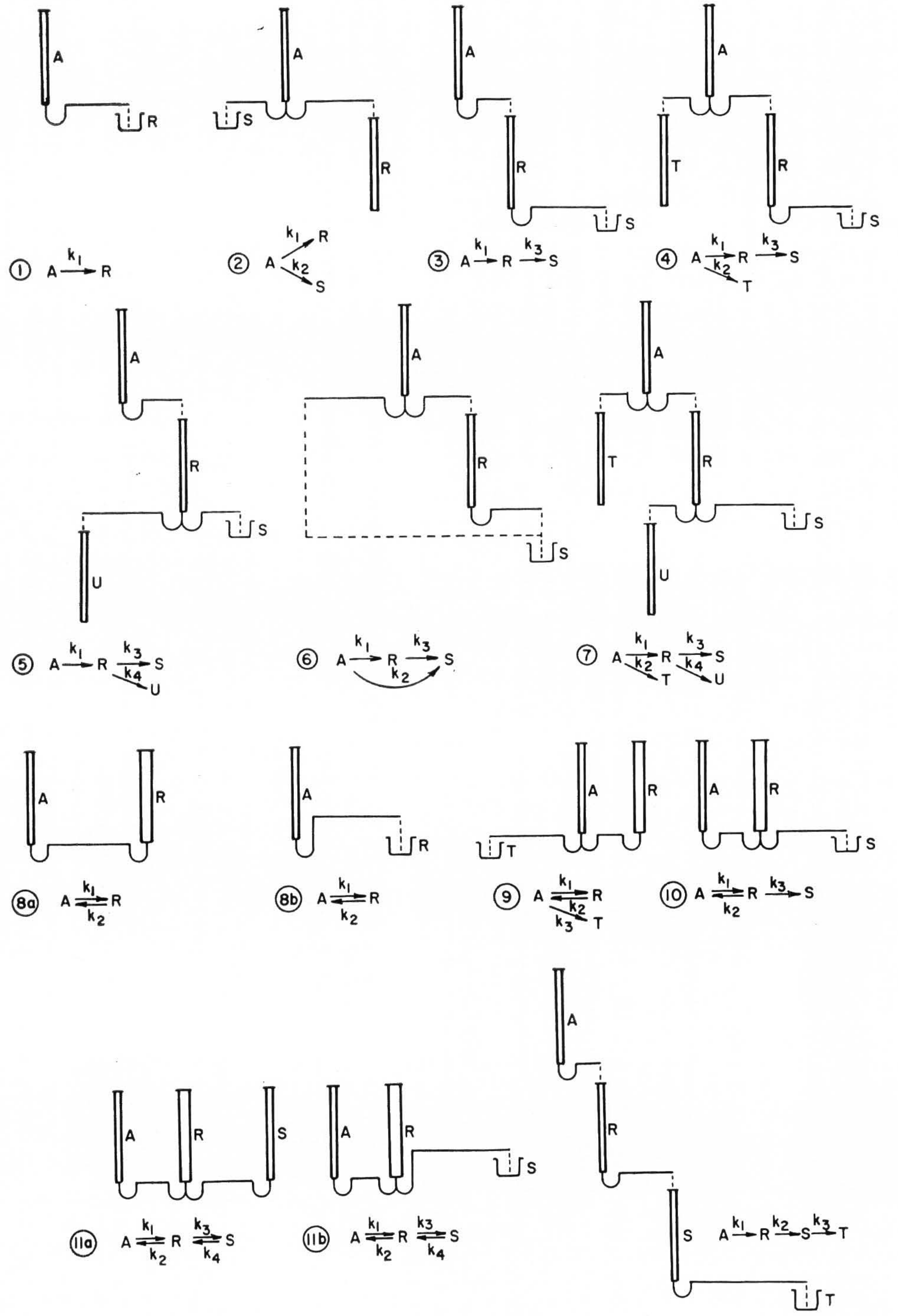

FIGURE 3. Some reaction schemes.

NOTES: In 8a, 9, 10, 11, use different diameter burettes to obtain different rate constants for the forward and reverse reactions. Be sure to take the volumetric burette reading, not height.

8b. One can use just one burette if one locates the capillary at a height above the zero reading on the burette.

11b. One can use 2 burettes if one locates the second capillary somewhat above the zero reading on the burettes.

various combinations of burettes the laboratory instructor can insure that no two laboratory groups will have the same experiment to perform, even in the giant classes which are now being processed.

Finally, a nice feature of this set of experiments is that the student most likely will be led to perform an integration of the performance equation for the batch reactor before he can test his guess with experiment.

CONCLUSION

WE HAVE SHOWN HOW A FEW burettes and capillaries, properly connected, can be the basis for a large number of simple experiments to teach the principles of data fitting in chemical reaction engineering. These experiments may be simple but they are not trivial. ☐

REFERENCES

1. O. Levenspiel, Chemical Reaction Engineering, 2nd Ed., Figure 15, page 191, Wiley, 1972.

APPENDIX

1. Many of the kinetic models of Fig. 3 (cases 1 to 6) are special cases of the Denbigh reaction scheme (case 7). The integrated form for this kinetic model, after appropriate manipulation is found to be

$$\frac{C_A}{C_{A,o}} = \exp(-K_1 t)$$

$$\frac{C_R}{C_{A,o}} = \frac{k_1}{K_2 - K_1}[\exp(-K_1 t) - \exp(-K_2 t)]$$

$$\frac{C_T}{C_{A,o}} = \frac{k_2}{K_1}[1 - \exp(-K_1 t)]$$

$$\frac{C_S}{C_{A,o}} = \frac{k_1 k_3}{(K_2 - K_1)}\left[\frac{1 - \exp(-K_1 t)}{K_1} - \frac{1 - \exp(-K_2 t)}{K_2}\right]$$

$$\frac{C_U}{C_{A,o}} = \frac{k_1 k_4}{(K_2 - K_1)}\left[\frac{1 - \exp(-K_1 t)}{K_1} - \frac{1 - \exp(-K_2 t)}{K_2}\right]$$

where

$K_1 = k_1 + k_2$

$K_2 = k_3 + k_4$

The conditions when the intermediate is at its maximum value are then

$$\frac{C_{R,max}}{C_{A,o}} = \frac{k_1}{K_1}\left[\frac{K_1}{K_2}\right]^{K_2/(K_2-K_1)}$$

and

$$t(\text{for } C_{R,max}) = \frac{\ln(K_2/K_1)}{K_2 - K_1}$$

These expressions may be useful for the instructor as a check of the students work.

2. All the kinetic equations in Fig. 3 involve systems of first order reactions and are conveniently solved, either by integration or by computer simulation for those who know how to talk to these machines. In a later paper we will consider non-linear systems and reaction orders different from unity. ☐

ACKNOWLEDGMENTS

We would like to thank our advisor, Professor Levenspiel for suggesting that we develop this series of experiments, and we would like to recognize Professor Jodra of the University of Madrid for indirectly bringing this type of experiment to our attention.