

M	= molecular weight
M_{ai}	= local isothermal Mach number
$\overline{M_{ai}}$	= average isothermal Mach number for cross section
N_{Re}	= Reynolds number
P	= pressure
R	= perfect gas law constant
r	= radial distance
T	= absolute temperature
U	= local axial velocity
\overline{U}	= average axial velocity for cross section
$\overline{U^2}$	= mean square axial velocity for cross section
V	= radial velocity
μ	= viscosity
ρ	= density
τ_w	= local wall shear stress
$\overline{\tau}_w$	= average wall shear stress for given length of tube

Subscripts

0	= at center line
1	= upstream tap
2	= downstream tap

LITERATURE CITED

1. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 211, Wiley, New York (1960).
2. Dodge, B. F., "Chemical Engineering Thermodynamics," p. 350, McGraw Hill, New York (1944).
3. Dushman, S., "Scientific Foundations of Vacuum Technique," 2 ed., p. 82, Wiley, New York (1962).
4. Kuo, Y. H., *J. Math Phys.*, **22**, 13-30 (1943).
5. Langhaar, H. L., *Trans. Am. Soc. Mech. Engrs.*, **64**, A-55 (1942).
6. Shang, J., and M. H. Bloom, *Polytechnic Inst. of Brooklyn Aeronautical Lab. Rept. No. 749* (May 1962); N62-13611 Ad278 128.

Manuscript received October 22, 1968; revision received January 31, 1969; paper accepted February 3, 1969.

A New Technique for Chemical Kinetics at High Pressures

R. A. GRIEGER and C. A. ECKERT

University of Illinois, Urbana, Illinois

Information about the transition state of a chemical reaction is quite useful for the determination of mechanisms and for design of solvents for the reaction. High pressure kinetic studies, if sufficiently accurate, provide the required data. This work reports a new technique developed for measuring rates of chemical reactions in solution at high pressure. This method involves in situ mixing of reactants under pressure and direct sampling for analysis, eliminating large errors of temperature equilibration and time measurement inherent in existing techniques, and thus yielding more accurate results. Experimental results for the Diels-Alder reaction of isoprene and maleic anhydride are reported at pressures up to more than 6,000 atm.

A new technique for high pressure chemical kinetics has been developed for very precise determinations of volumes of activation. By eliminating two sources of significant uncertainty inherent in previous methods, errors in time and temperature, activation volumes may be measured with an accuracy better than 1 cc./g.-mole. The technique proposed here includes the first reported application of in situ initiation of the reaction, avoiding errors in temperature due to the heat of compression or the thermal lag of a heavy steel vessel. Analyses were carried out by continual sampling, at pressures more than twice as high as those at which previous high pressure sampling had been reported (7, 11), permitting much more accurate time measurements than would be obtained by the classical method of disassembly of the vessel for analysis.

The effect of pressure on the rate of a chemical reaction yields important information about the structure and properties of the transition state for the reaction. The activated

complex theory of Evans and Polyani (6) provides a theoretical basis for interpretation of high pressure kinetic data. Using this approach, and expressing the rate constant in pressure invariant concentration units (such as the rate constant in mole fraction k_x), one may show rigorously (8) that the measured effect of pressure gives the volume of activation ΔV^\ddagger , the difference in partial molal volume between the transition state for the reaction and the reactants:

$$\left(\frac{\partial \ln k_x}{\partial P} \right)_T = - \frac{\Delta V^\ddagger}{RT} \quad (1)$$

The volume of activation represents the second derivative of the actual physical measurement, concentration as a function of time. Thus it is essential that the data taken be as accurate as possible. Frequently, a relatively small difference in activation volume may have significant meaning. For certain reactions, such as the Diels-Alder reaction, a difference in activation volume of approximately

R. A. Grieger is at the University of Wisconsin, Madison, Wisconsin.

TABLE 1. FLOW CORRELATIONS

Run No.	P ₁ (μ Hg)	P ₂	N _{Re}	U ₂ (ft./sec.)	M _{ai2}	P ₁ ² - P ₂ ²	Right-hand sides			Percent deviation		
							Equation (4)	Modif. Equation (4)	Equation (12)	Equation (4)	Modif. Equation (4)	Equation (12)
1	1,855	941	385	381	0.312	2.556	2.472	2.515	2.530	-3.28	-1.61	-1.02
2	1,785	840	388.5	427	0.352	2.481	2.485	2.525	2.540	+0.16	+1.77	+2.38
3	1,348	815	195.5	222	0.183	1.153	1.179	1.186	1.192	+2.20	+2.80	+3.31
4	1,111	902	70.3	71.5	0.059	0.421	0.411	0.412	0.412	-2.37	-2.25	-2.14
5	2,577	1,500	702	427.5	0.352	4.391	4.560	4.665	4.695	+3.85	+6.24	+6.92
6	2,830	1,410	895	583	0.481	6.021	6.250	6.470	6.430	+3.66	+7.19	+6.55
7	3,315	1,760	1,150	571	0.477	7.892	7.770	8.080	8.010	-1.55	+2.51	+1.50
							Average (absolute)			2.43		
							Average (with sign)			+0.38		

At high velocities, the predicted and observed P₁² - P₂² values are significantly higher than those predicted by the Poiseuille-Meyer equation. At the highest flow rate tested, for example, Equation (4) predicts a P₁² - P₂² value which is 19% higher than the Poiseuille-Meyer value. For the same mass flow rate and exit pressure, the percentage increase will become greater as the pipe length decreases.

The deviations from Equation (4) are of the order of the ascribable sources of experimental error. Slight drifts in the reference pressure and in the micromanometer zero setting were observed and may account for a 1 to 2% error in pressure measurements.

It is curious that Equation (4) fits the experimental data somewhat better than either of the equations which take profile flattening and increased wall drag into account. In part this may be due to Equation (4), on the basis of a constant parabolic profile, somewhat overaccounting for the momentum changes due to expansion.

Nonisothermal conditions may account for part of the success of Equation (4). For adiabatic flow at the maximum velocity tested, the average temperature of the gas would decrease 6.3°K. due to its increase in kinetic energy. Rough analysis indicates that heat transfer, under the con-

ditions used, would have limited this temperature drop to about 2.9°K. below ambient. Such a temperature drop, when averaged over the test section, would produce a 1% lowering of the right-hand sides of the tested equations, an effect which could not be reliably detected. The temperatures measured at the entrance to the test section, the portion nearest the steam generator, were a few degrees above ambient and 2° to 5°K. higher than the temperatures at the middle and far end of the test line, indicating rapid equilibration of the temperature of the flowing steam and the environment.

While the adiabatic temperature drop at the maximum velocity tested would average only 6.3°K., if no conduction occurred, the temperature at the axis of the pipe would drop 25°K. This region is least accessible to heat transfer to the outside, and significant gradients in T and μ might therefore exist. If such gradients did exist, they would help preserve a near parabolic profile and favor greater conformity with Equation (4).

The entrance effect correction had an effect of roughly 4% on the pressure drop equations at the highest velocity tested. Because of the flattening profile, the entrance effect correction should be somewhat smaller than for normal parabolic flow. A reduced entrance effect correction would somewhat improve the fit between the experimental data and modified Equation (4) or Equation (12).

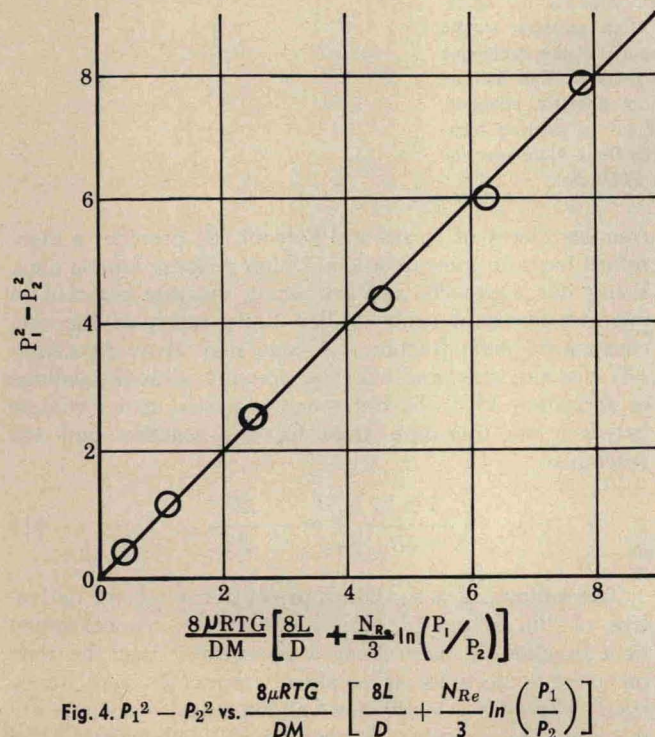
Because of the reasons just cited and the smallness of the difference of the computed results, 4% at the highest velocity tested, it is difficult to conclude that Equation (4) is preferable to the equations which account for profile flattening. In order to resolve this question, further tests at higher M_{ai} values and in pipes of various sizes are planned. Because of the marked flattening in the velocity profile indicated by Figure 2 at M_{ai} greater than 0.5, Equation (4) is not recommended for use above the range for which it has been tested to date.

ACKNOWLEDGMENT

The authors are grateful for a grant from the Maxwell House Division of the General Foods Corporation which made possible the purchase of test equipment used in this study.

NOTATION

- A = tube radius
- D = tube diameter
- (dP/dL)_f = pressure gradient due to friction
- (dP/dL)_i = pressure gradient for flow with negligible momentum change due to expansion
- G = mass flux, flow per unit area per unit time
- L = tube length, axial distance



Units: 10⁶ (Microns Hg)².