

CONCLUSION

In summary it can be concluded that: (1) A quadratic polynomial is generally the best representation of the pressure dependence of a logarithmic rate constant regardless of the reaction type; (2) it appears *necessary* and *sufficient* to allow for the non-zero pressure dependence of activation volumes, and *this dependence is measurable*; and (3) differentiation of the appropriate function gives rise to a precise measurement of activation parameters.

ACKNOWLEDGMENTS

General financial assistance by the National Research Council and in particular a studentship to H. S. G. is gratefully acknowledged. The authors wish to thank the staff of the University of Calgary Computing Centre for writing the FORTRAN programs used in this study.

REFERENCES

1. J. B. HYNE and R. E. ROBERTSON. *Can. J. Chem.* **33**, 1544 (1955).
2. E. WHALLEY. *In* Advances in physical organic chemistry. Vol. 2. Edited by V. Gold. Academic Press, New York, N.Y. 1964.
3. C. WALLING and J. PEISACH. *J. Am. Chem. Soc.* **80**, 5819 (1958).
4. S. W. BENSON and J. A. BERSON. *J. Am. Chem. Soc.* **84**, 152 (1962).
5. J. B. HYNE, H. S. GOLINKIN, and W. G. LAIDLAW. *J. Am. Chem. Soc.* **88**, 2104 (1966).
6. M. G. EVANS and M. POLANYI. *Trans. Faraday Soc.* **31**, 875 (1935).
7. S. D. HAMMAN. *Trans. Faraday Soc.* **54**, 507 (1958).
8. C. T. BURRIS and K. J. LAIDLER. *Trans. Faraday Soc.* **51**, 1497 (1955).
9. C. WALLING and D. D. TANNER. *J. Am. Chem. Soc.* **85**, 612 (1963).
10. H. S. HARNED and B. B. OWEN. *The physical chemistry of electrolytic solutions*. 3rd ed. Reinhold Publishing Corp., New York, N.Y. 1958, p. 379.
11. B. T. BALIGA, R. J. WITHEY, D. POULTON, and E. WHALLEY. *Trans. Faraday Soc.* **61**, 517 (1965).
12. B. T. BALIGA and E. WHALLEY. *Can. J. Chem.* **43**, 2453 (1965).
13. P. W. BRIDGMAN. *The physics of high pressure*. G. Bell and Sons, Ltd., London, England. 1958. Chaps. V and VI.
14. F. DANIELS *et al.* *Experimental physical chemistry*. 5th ed. McGraw-Hill Book Co., New York, N.Y. 1956, p. 326.
15. K. R. BROWER. *J. Am. Chem. Soc.* **85**, 1401 (1963).
16. H. G. DAVID and S. D. HAMMAN. *Trans. Faraday Soc.* **50**, 1188 (1954).
17. S. W. BENSON and J. A. BERSON. *J. Am. Chem. Soc.* **86**, 259 (1964).