



Fig. 11. pH changes recorded from the Bathyscaphe FNRS III between 0 and 2350m in the Mediterranean Sea. Curves 1, 2, 3 give $E_1 - E_p = f(P)$, E_1 corresponding to the pH values at the surface (S_1, S_2, S_3). Curve 4 gives $E_1 - E_p = f(P)$ for sea water of constant composition. Curve 0 represents the simultaneous temperature record. From Distèche and Dubuisson (25).

the lower end of a pressure resisting steel cylinder containing a d-c amplifier with cathode follower output, driving a pen recorder, on which the pH shifts are observed as the distance between two traces, one of which represents the zero drift of the apparatus. The error on ΔpH is certainly less than 0.01 pH unit and very close to 0.005 pH unit.

The curves on Fig. 11 were obtained during two dives. They represent direct manual measurements (large dots) with a precision potentiometer circuit and the data taken from the recorded curves (small dots). After a small increase near the surface, the pH is seen to decrease exponentially (~ 0.15 pH unit) from 0 to 400m. From 400m to 2350m, the bicarbonate/ CO_2 ratio remains constant since the observed pH change corresponds to the effect of pressure on water of constant composition. A slight acid gradient is found near the bottom. The results obtained from the surface to the sea bottom agree with those recorded during the return to the surface, and there is a distinct correlation between the temperature curve and the pH curve.

Conclusion

The author is fully aware that his investigations on the behavior of a glass electrode at high pressure in various electrolytes cover only an extremely small portion of a very wide field. The important fact is that the reproducibility and the precision of the pH measurements with a glass electrode are affected by pressure but little or not at all. This statement is not a proof that the electrode gives, under all circumstances, the value of the hydrogen ion activity, but considering as a whole the results which have been obtained so far, makes one feel

confident, since many results agree well with what is known from conductance and density data.

Further instrumental development is possible. A bright gold electrode can be added to the glass electrode cell for rH measurements¹ and it is planned to try glass electrodes sensitive to Na^+ and K^+ (26, 27).

The use of multielectrode cells, including a conductivity cell, would certainly broaden the field of electrochemical investigation at high pressures (properties of electrolytes, protein chemistry, kinetics, oceanography, and industrial technology).

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REFERENCES

1. J. C. Jamieson, *Chem. Phys.*, **21**, 1385 (1953).
2. S. D. Hamann, "Physico-chemical Effects of Pressure," Butterworths Scientific Publication (1957).
3. H. G. David and S. D. Hamann, *Trans. Faraday Soc.*, **55**, 72 (1959).
4. H. G. David and S. D. Hamann, *ibid.*, **56**, 1043 (1960).
5. A. J. Ellis, *J. Chem. Soc.*, **1959**, 3689.
6. R. J. H. Clark and A. J. Ellis, *ibid.*, **1960**, 247.
7. S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).
8. R. Schall, *Z. angew. Physik*, **2**, 252 (1950).
9. A. H. Ewald and S. C. Lim, Unpublished experiments, see ref. (2).
10. K. Hayashi and I. Kono, *Japan J. Physiol.*, **8**, 246 (1958).
11. B. B. Owen and S. R. Brinkley, *Chem. Rev.*, **29**, 461 (1941).
12. E. Cohen and K. Piepenbroek, *Z. Physik. Chem.*, **170A**, 145 (1934).
13. W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes, *J. Am. Chem. Soc.*, **46**, 1437 (1924).
14. A. Distèche, *Rev. Sci. Instruments*, **30**, 474 (1959).
15. M. Le Peintre, *Bull. soc. franc. elec.*, 8ième série, **1** [9], 1 (1960).
16. W. H. Marburger, K. Anderson, and G. L. Wigle, A.N.L. 5298 Tech. Inf. Serv., Oak Ridge, Tenn. See ref. (15).
17. T. C. Poulter, *Phys. Rev.*, **40**, 860 (1932).
18. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corp., New York (1958).
19. O. Redlick and J. Bigeleisen, *Chem. Rev.*, **30**, 171 (1942), see ref. (18).
20. S. Harned and B. B. Owen, *J. Am. Chem. Soc.*, **52**, 5079 (1930).
21. J. S. Smith, Dissertation, Yale University (1943), see ref. (18).
22. F. K. Johnson, H. Eyring, and M. J. Polissar, "The Kinetic Basis of Molecular Biology," John Wiley & Sons, New York (1954).

¹The potential of the cell $Au-FeSO_4$ 0.05M, $Fe_2(SO_4)_3$ 0.025M, HCl 0.1M, AgCl-Ag changes very little with pressure in the range 0-1000 atm, and it might be interesting to replace the internal Ag-AgCl electrode of the glass electrode by a redox half cell; for the use of a glass electrode and an external redox half cell for rH determinations in oceanographic research, see ref. (28) and (29).

23. R. G. Bates, *J. Res. Nat. Bur. Standards*, **47**, 127 (1951).
24. J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).
25. A. Distèche and M. Dubuisson, *Bull. Inst. Océanogr. Monaco*, No. 1174, p. 1-8 (1960).
26. S. H. Friedman and C. L. Friedman, *Anat. Rec.*, **138**, 129 (1960).
27. C. H. Townes, Cation Selective Glasses. Internat. Biophysics Congress, Stockholm, 1961.
28. A. Riviere, *C. R. Acad. Sci. France*, **248**, 717 (1959).
29. F. Manheim, *Acta Univ. Stockholmiensis*, Stockholm Contributions in Geology, **VIII:3**, 27 (1961).