

Estimating the effect of pressure on the TRIS buffer system for in-situ pH measurements



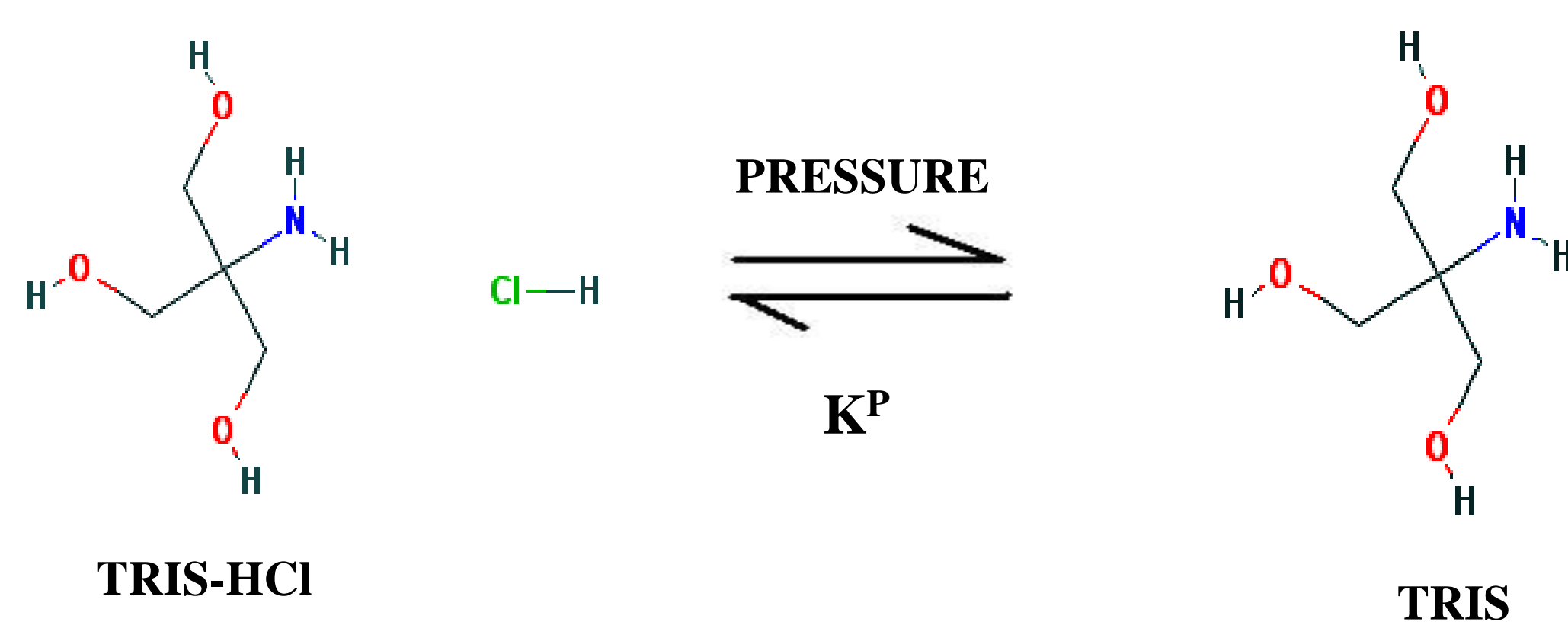
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Introduction and aims

Autonomous pH sensors provide extensive, long-term data of the in-situ chemistry of a water column, and shed light on changes in oceanic pH.¹ Results obtained from these sensors should account for physical parameters on chemical equilibria. TRIS-HCl buffers are often used to calibrate pH measuring systems.²⁻⁴ The effect of pressure on its dissociation equilibrium is thought to be small, but has not yet been characterized.

The effect of pressure on a weak acid can be estimated from its volume and compressibility taken at atmospheric pressure. We have evaluated these properties for TRIS and TRIS-HCl to estimate the effect of pressure on its equilibrium constant (K^P). The results will be useful in calibrations of sensors measuring pH in-situ.



Methods and materials

All measurements were made at 1atm. Separate solutions of TRIS and TRIS-HCl were prepared in water and 0.725m NaCl, and diluted gravimetrically. The densities were measured with an Anton Paar vibrating tube densimeter (Figure 1) and the sound speeds were measured with a Nusonics sing-around sound velocimeter (Figure 2). The measurements were used to calculate Apparent Molal Volumes (ΦV) and Apparent Molal Compressibilities ($\Phi \kappa$).

Figure 1: Schematic of densimeter

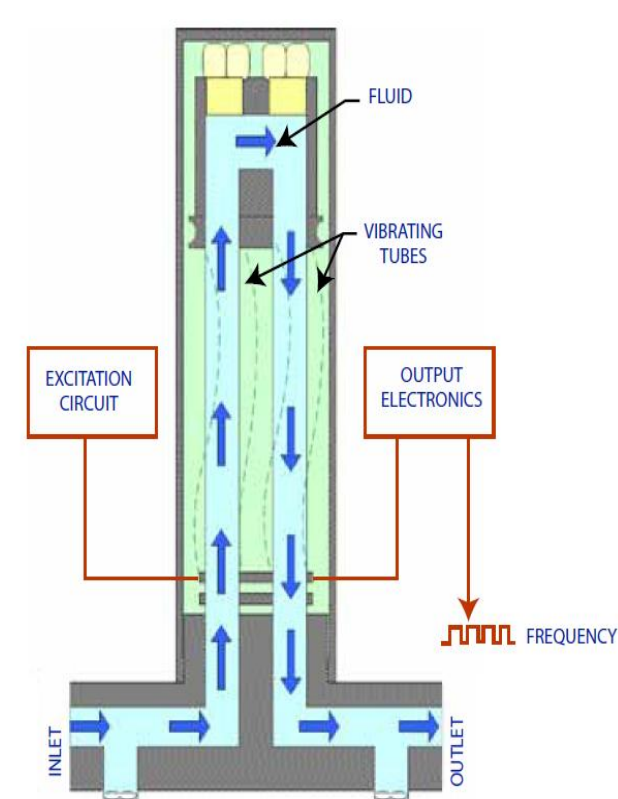
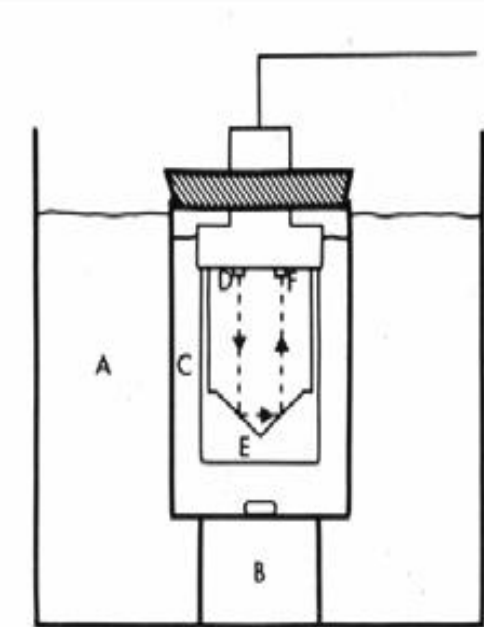


Figure 2: Schematic of velocimeter



A Constant Temp. Bath
B Magnetic Stirrer
C Solution Cell
D Transmitting Transducer
E Reflector
F Receiving Transducer

Apparent molal properties

Apparent molal volumes (ΦV) and apparent molal compressibilities ($\Phi \kappa$) were measured as functions of temperature and concentration.

Figure 3: Apparent molal volume (ΦV) of TRIS in H_2O

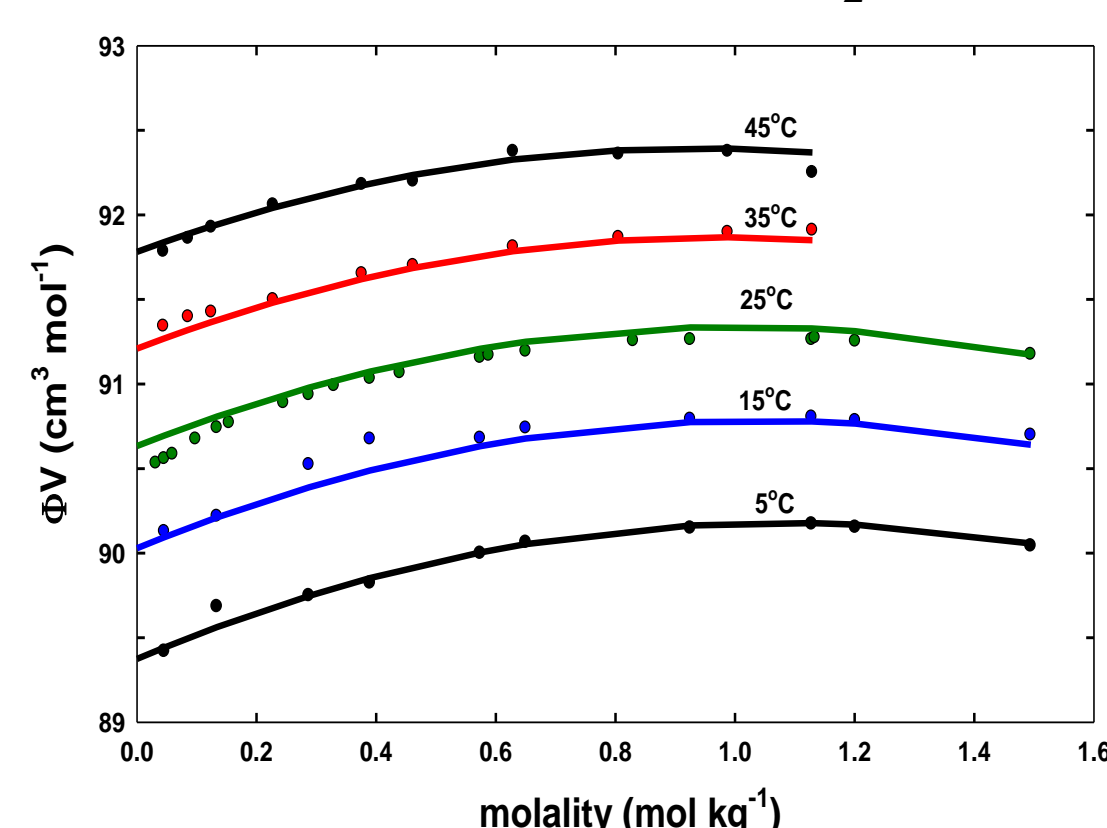
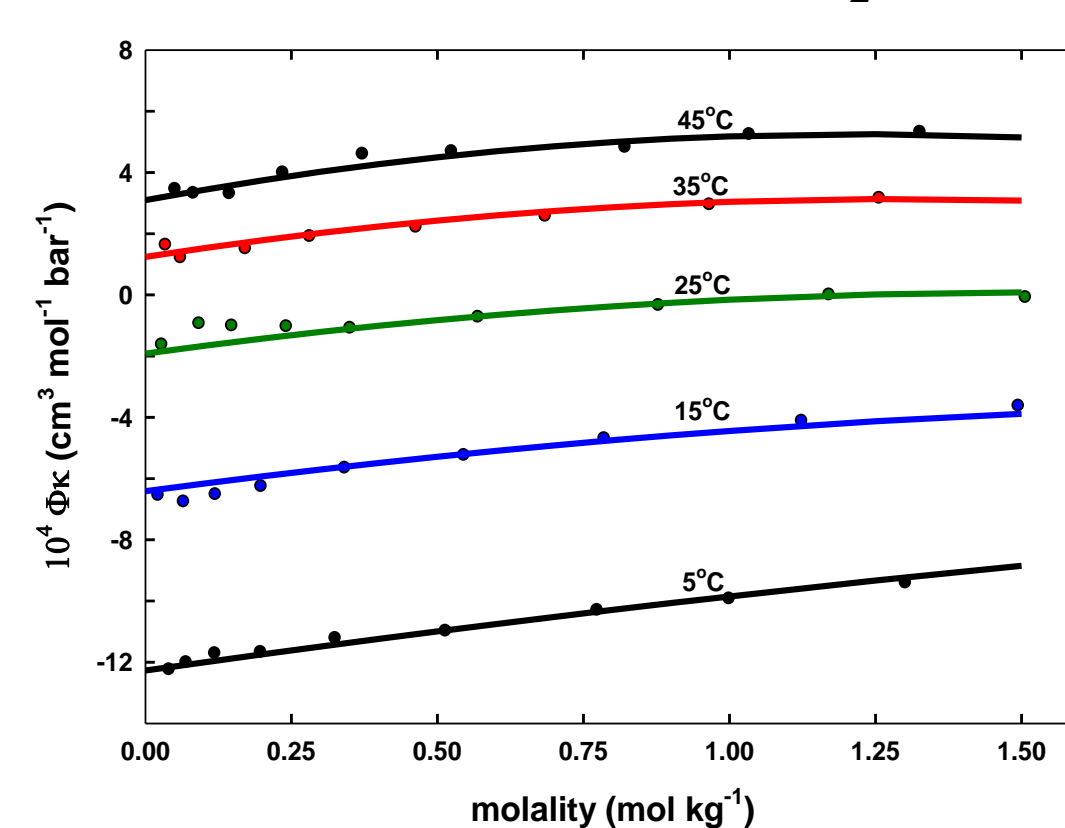


Figure 4: Apparent molal compressibility ($\Phi \kappa$) of TRIS in H_2O



Infinite dilution values

Values of the apparent molal properties were fit to functions of the concentration (m) and the **infinite dilution values** (X^0 , where $X = V$ or κ) were obtained through extrapolation.

- TRIS (neutral species): $\Phi X = X^0 + Am + Bm^2$
- TRIS-HCl (electrolyte): Pitzer Equation
 $\Phi X = X^0 + \text{Debye-Huckel Term} + \text{Ionic Interaction Parameters}$

Fig. 5: Infinite dilution volumes (V^0)

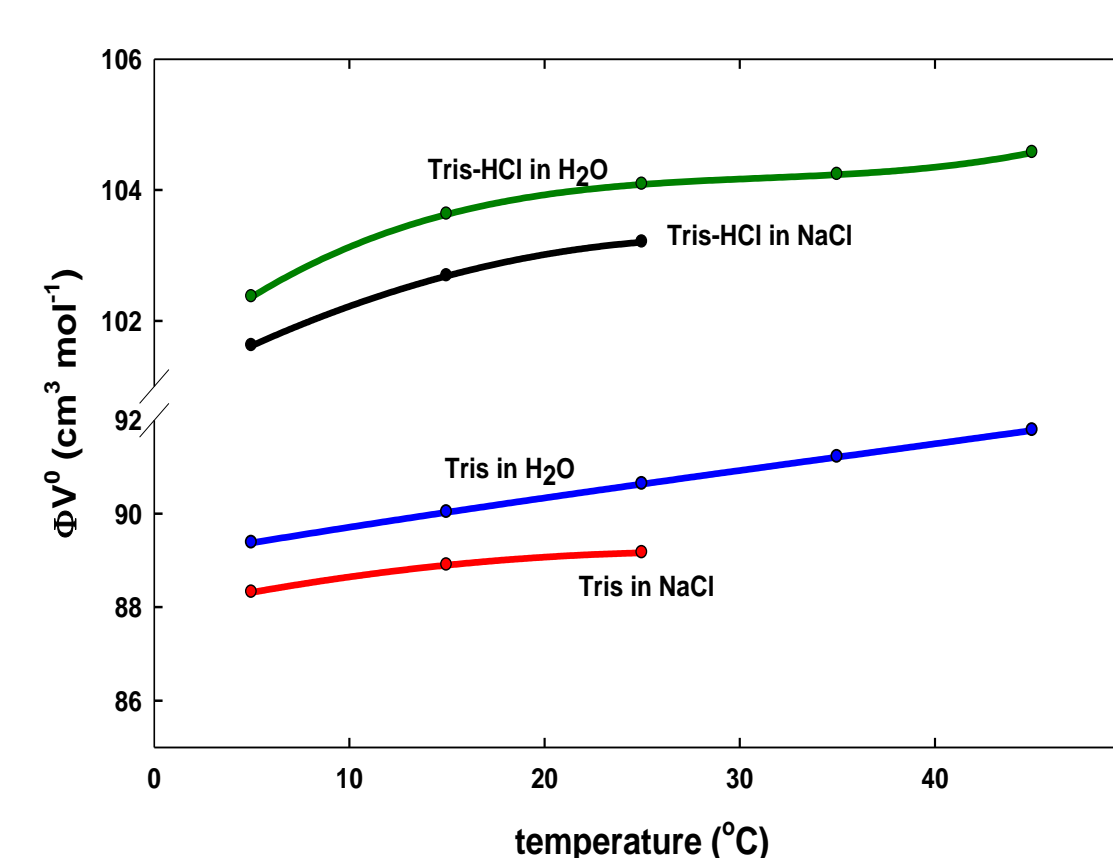
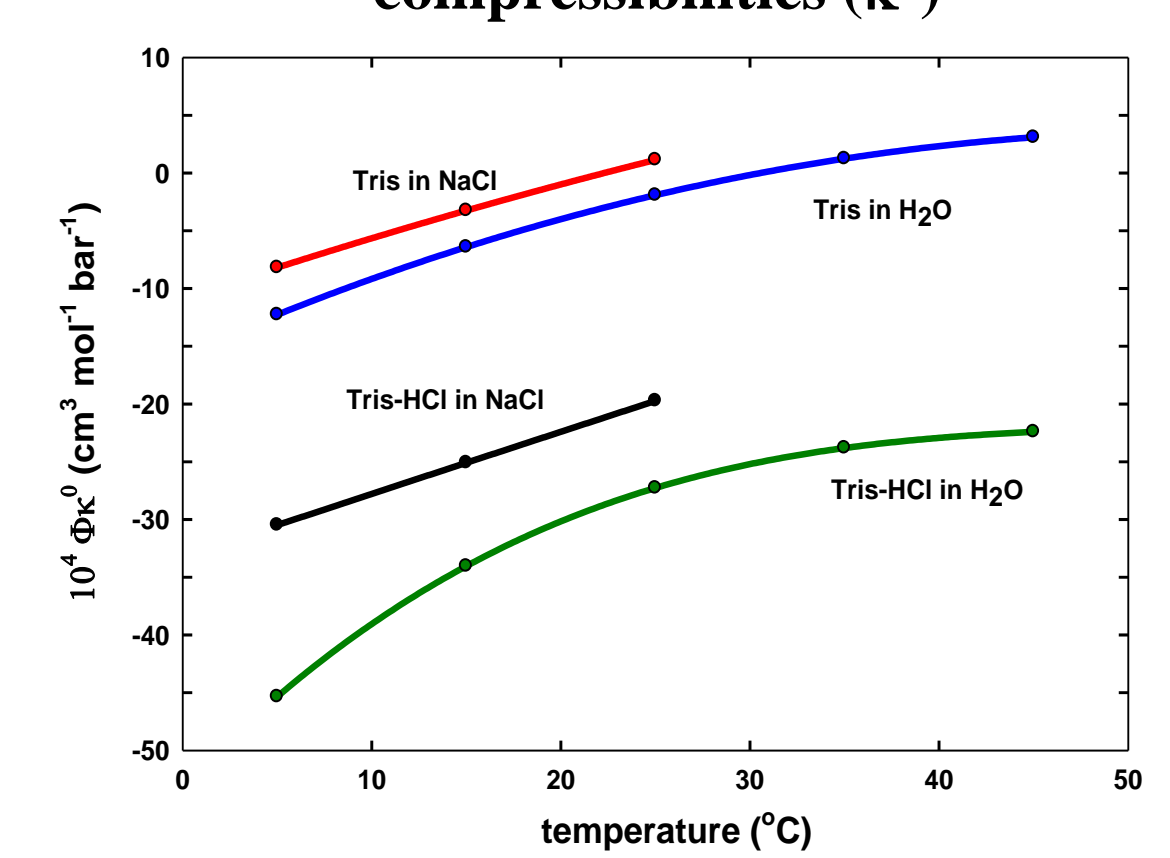


Fig. 6: Infinite dilution compressibilities (κ^0)



Estimating the effect of pressure

The change in the volume (ΔV) and compressibility ($\Delta \kappa$) for the dissociation of TRIS-HCl:

$$\text{TRIS-HCl} = \text{TRIS} + \text{H}^+ + \text{Cl}^- \quad (1)$$

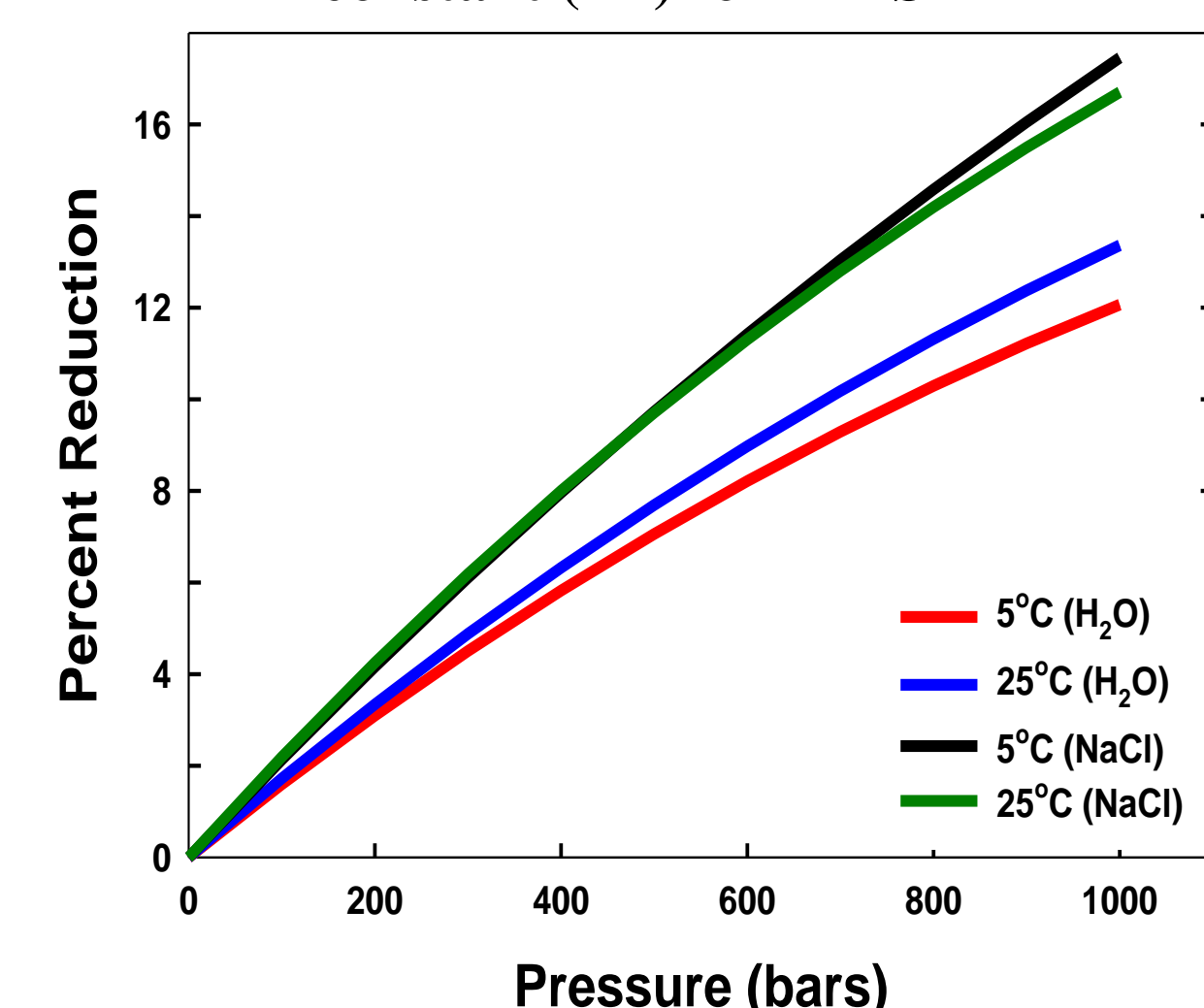
$$\Delta V^0 = V^0(\text{H}^+) + V^0(\text{Cl}^-) + V^0(\text{TRIS}) - V^0(\text{TRIS-HCl}) \quad (2)$$

$$\Delta \kappa^0 = \kappa^0(\text{H}^+) + \kappa^0(\text{Cl}^-) + \kappa^0(\text{TRIS}) - \kappa^0(\text{TRIS-HCl}) \quad (3)$$

The effect of pressure (P) on the dissociation constant (K) of TRIS-HCl can be estimated from these changes by the thermodynamic relationship:

$$\ln(K^P/K^0) = (\Delta V/RT)P - 0.5(\Delta \kappa/RT)P^2 \quad (4)$$

Figure 7: Effect of pressure on the dissociation constant (K^P) for TRIS- H^+



Conclusions

Our volume and compressibility studies made at atmospheric pressure have been used to estimate the effect of pressure on the dissociation equilibrium of the TRIS buffer system. We find that the **dissociation of the TRIS buffer (K^P) can be reduced by as much as 18%** at pressures of 1000 bars. The effect of pressure is greater in concentrated mediums such as NaCl solutions and seawater than it is in pure water. These new equations will be useful for improving the calibration of autonomous pH sensors as they are called upon more frequently to profile aquatic waters. Direct pressure measurements on the TRIS equilibrium are recommended to verify these findings.

References

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Acknowledgments

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