

# **pH measurements at high temperatures and pressures: Standardization of pH phthalate buffer (0.05m KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) to 200°C and 5000 bars.**

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pH is one the most important parameters which control the processes related to the short and long term effects of carbon dioxide sequestration. Both for experimental and natural pH measurements it is necessary to have reliable pH values of buffer solutions at high temperature and pressure. This study is devoted to standardization of phthalate NBS buffer (pH at 25°C and 1 bar is equal to 4.01).

pH values of this buffer have been adopted as NBS standard (Bates, 1964) in temperature range 0-95°C and 1 bar. To attest the pH as a function of pressure the pressure dependence of the first and second dissociation constants for phthalic acid were defined using the potentiometric method. Measurements were performed in the isothermal electrochemical cells with a liquid junction at 25, 50 and 70±0.3°C as a function of pressure from 1 to 1000 bars. The uncertainty of measured values of  $\Delta\text{pH} = \text{pH}_{1000\text{bars}} - \text{pH}_{1\text{bar}}$  lies in the range 0.002 to 0.007 pH unit.

Based on these experimental data for pressure dependence of two-step dissociation constants together with the reliable data for their temperature dependence from 0 to 60°C (Hamer et al., 1945; Hamer and Acree, 1945) and thermodynamic properties of phthalic acid ( $\text{H}_2\text{C}_8\text{H}_4\text{O}_4, \text{aq}$ ) the best fit of the standard thermodynamic properties and HKF parameters  $\text{HC}_8\text{H}_4\text{O}_4^-$  and  $\text{C}_8\text{H}_4\text{O}_4^{2-}$  were derived using the UT-HEL optimization procedure (Shvarov, 1995).

At the final stage the direct pH measurements of phthalate buffer (0.05m KHC<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) at 60-150°C (Bower and Bates, 1957; Kryukov et al., 1966) and pressure to 1000 (Kryukov and Zarubina, 1982 and our data) and 6000 bars (Kryukov et al., 1977) were supplementary involved into optimization.

Recommended pH values of phthalate buffer are given as a function of temperature and pressure. Deviation of these values from the NBS data does not exceed 0.005 pH. At higher temperatures (100-150°C) and pressures (1000-6000 bars) the difference between recommended and experimental values is less than 0.01-0.02 pH.