

COMMENTARY

Anomalous energy yields in thermodynamic calculations: importance of accounting for pH-dependent organic acid speciation

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Introduction

Methanogenic ecosystems function close to oxidation–reduction equilibrium with change in Gibbs free energy (ΔG) values in the range of -10 to -20 kJ mol^{-1} (Hoehler *et al.*, 1998; Jackson and McInerney, 2002). With such small margins, attention to detail when making free energy calculations becomes exceedingly important. A pervasive source of confusion, if not error, when making free energy calculations is the fact that organic acids and their anions occur simultaneously (Mazur *et al.*, 2003; Mun *et al.*, 2008). Here, we point out that such confusion is not necessary, as weak acids and their conjugated bases are in thermodynamic equilibrium in anaerobic ecosystems. This equilibrium implies that Gibbs free energy values for redox reactions are to be calculated by G_f values of either the acid, with the formula $G_f = G_f^\circ + RT \ln \alpha$, or the conjugated base with the formula $G_f = G_f^\circ + RT \ln(1-\alpha)$, where $\alpha = 10^{-\text{pH}} / (10^{-\text{pH}} + 10^{-\text{pK}_a})$; by incorporating either the acid or its conjugated base the counterpart is incorporated implicitly.

Energetic implications

Thermodynamic equilibrium between weak acids and their conjugated bases implies that ΔG values are $(RT \ln 10) (\log \alpha - (1-\alpha) \text{pK}_a + (1-\alpha) \text{pH}) \text{ kJ}$ different from a situation where simultaneous occurrence of both species would not occur. Conceptually, this can easily be appreciated. For example, at $\text{pH} = \text{pK}_a$ in a nominally 1 mM solution of acetic acid, 0.5 mM occurs as acetate and 0.5 mM as acetic acid. Thus, acetoclastic methanogens experience an acetic acid potential corresponding to 0.5 mM rather than to the 1 mM that would be expected if dissociation of acetate did not occur. This dissociation effect is maximal when the pH is equal to the pK_a value of a reactant or a product

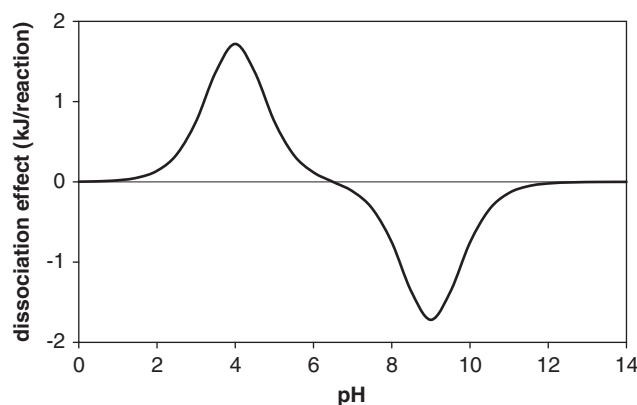


Figure 1 Dissociation of weak acids affects the energy yield of microbial reactions in anaerobic ecosystems. For a reaction $\text{AH} + \text{B} \rightarrow \text{CH} + \text{D}$ with $\text{pK}_a(\text{AH}) = 4$ and $\text{pK}_a(\text{CH}) = 9$, the effect is maximal at pH values of 4 and 9; at $\text{pH} = 4$ dissociation has a positive effect on ΔG and hence a negative effect on the energy available to the microbes, whereas at $\text{pH} = 9$ the effect is the opposite. The curve is based on the formula $\Delta G = (-RT \ln 10) (\log \alpha - (1-\alpha) \text{pK}_a + (1-\alpha) \text{pH})$, where $\alpha = 10^{-\text{pH}} / (10^{-\text{pH}} + 10^{-\text{pK}_a})$, $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, and T is temperature in K.

(Figure 1). Thermodynamic equilibrium between weak acids and their conjugated bases also implies that in a given environment ΔG for, for example, the reaction $\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$ is identical to ΔG for the reaction $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{CH}_4$ in that environment.

Implications for ΔG calculations

The error made by neglecting speciation is relatively minor as long as the proper (that is, the dominant) species is used for ΔG calculations. Speciation of a weak acid is thermodynamically most significant at pH values close to its pK_a value. The maximum error of neglecting speciation is $RT \ln 0.5$, at 25°C , that is 1.72 kJ mol^{-1} . Given the low amounts of energy at which many anaerobic ecosystems function values of that order of magnitude are not necessarily negligible.

Figure 2 illustrates the effect of pH on the energetics of methanogenesis from acetic acid/

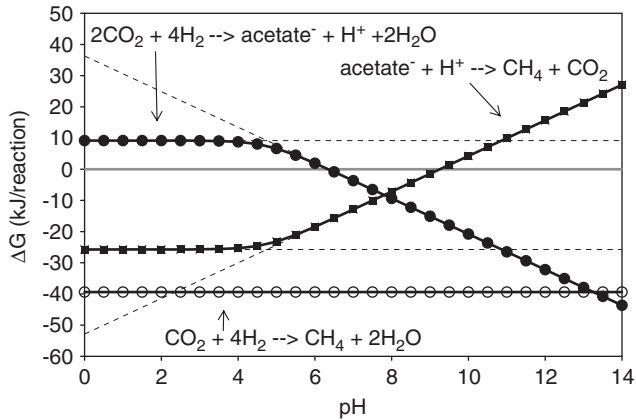


Figure 2 Effect of pH on ΔG values for methanogenesis from acetic acid/acetate (filled squares), for methanogenesis from $H_2 + CO_2$ (open circles) and for acetogenesis from $H_2 + CO_2$ (closed circles) at low concentrations of H_2 (10 Pa) and acetic acid/acetate (100 μM) under otherwise standard conditions (CO_2 and CH_4 at 1 atm; $T = 25^\circ C$).

acetate and from $H_2 + CO_2$, and on the energetics of acetogenesis from $H_2 + CO_2$ at low concentrations of H_2 (10 Pa) and acetic acid/acetate (100 μM). At constant partial pressures of CO_2 and CH_4 ΔG for methanogenesis from $H_2 + CO_2$ is independent of pH. Production or consumption of acetic acid/acetate changes this pattern. At pH values below the pK_a for acetic acid, ΔG values for H_2 -based acetogenesis and acetoclastic methanogenesis are essentially independent of pH, while at pH values above this pK_a these ΔG values are a linear function of pH.

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