Syntrophic acetate oxidation coupled to hydrogenotrophic methanogenesis has been identified as a significant anaerobic pathway in high-temperature (55°C) oil fields (1, 2). In a paper on acetate production from oil under sulfate-reducing conditions, Callbeck et al. (3) took note of that observation, only to emphatically state that “syntrophic acetate oxidation coupled to hydrogenotrophic methanogenesis is not thermodynamically feasible at lower temperatures, as in the Medicine Hat Glauconitic C field” (MHGC field). This is not necessarily true. Syntrophic associations are known to metabolize at close to thermodynamic equilibrium (Gibbs free energy $\Delta G \approx 0$) (4). At the temperature of the MHGC field (22°C) (5) and under environmentally realistic conditions (acetate 5 mM, CO2 and CH4 at 1 atm, and pH 7) the amount of $\Delta G$ available from acetate oxidation coupled to H2-driven methanogenesis is $-22.0$ kJ/mol, which allows for a substantial window of opportunity in which both reactions are exergonic (Fig. 1A).

Molecular hydrogen is not the only electron shuttle compound potentially involved in syntrophic acetate oxidation: (i) formate-
based and (ii) direct interspecies electron transport (DIET) can also be envisaged (6, 7). (i) The $\Delta G$ for syntrophic acetate oxidation coupled to formate-driven methanogenesis is identical to the $\Delta G$ for syntrophic acetate oxidation coupled to $H_2$-driven methanogenesis; consequently, the window of opportunity for this route is also substantial (Fig. 1; note the log scales). (ii) A $\Delta G$ of $-22.0$ kJ/mol for acetate-driven methanogenesis translates into a potential of 28.5 mV/electron; part of this potential is needed for and dissipated in exocellular electron transport (8), while the remainder is available to drive the metabolism of the organisms involved. Thus, irrespective of the mechanism of interspecies electron transport, methanogenesis based on syntrophic acetate oxidation is thermodynamically feasible under the conditions prevailing in the Medicine Hat Glauconitic C field. Indeed, the prevalence and importance of this pathway in various man-made and natural environments under mesophilic conditions (9, 10), even at temperatures as low as 15°C (11), has been well documented. Accordingly, Schröder and coworkers have isolated and described a series of mesophilic organisms, including Clostridium ultunense, Syntrophaceticus schinkii, and Tepidanaerobacter acetatoxydans (12–14), which can grow as syntrophic acetate oxidizers in coculture with hydrogenotrophic methanogens.

Interestingly, the crux of the aforementioned paper by Callbeck et al. (3) is that in their sulfate-limited, oil-fed bioreactors, alkane oxidation per se is most likely a syntrophic process in which oil alkanes and water are metabolized to acetate and hydrogen by fermentative and syntrophic bacteria, with the hydrogen being used by sulfate-reducing bacteria (SRB) to reduce sulfate to sulfide. It is tempting to speculate that, if given extra sulfate, these reactors will develop complementary syntrophic communities that couple acetate oxidation to sulfate reduction. The hydrogenotrophic SRB are already in place (3).

Recent reports on direct interspecies electron transport in methanogenic ecosystems raise the question of how pH affects the thermodynamics of the reactions involved. DIET between acetate oxidizers and methanogens is associated with the production and consumption of eight protons per acetate metabolized (Fig. 2; see the legend). Consequently, pH strongly affects the energetics of the catabolic reactions of the organisms involved. Figure 2 shows that under otherwise standard conditions, the window of opportunity where acetate oxidation and electron-fueled methanogenesis are both exergonic is in the range of pH 1.9 to 2.9. At pH 7, methanogenesis would be strongly endergonic in this scenario. However, the standard conditions mentioned above encompass a standard Gibbs free energy value for electrons of zero. An electron activity (pE) diagram for DIET-facilitated, acetate-based methanogenesis shows that, at pH 7 and under otherwise standard conditions, the electron activity range where both reactions are exergonic is between pE $-4.1$ and $-4.9$ (Fig. 2B); the electron potentials at which both reactions are exergonic at pH 7 are in the range of 244 to 290 mV. Interspecies electron transport through nanowires or other conductive exocellular material between acetate oxidizers and methanogens implies that the electron potential at the site of the electron producer is different from the electron potential at the site of the electron consumer.

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