Appendix 1

Thermodynamics and calculation of energy yields of metabolic processes

Understanding which bacterial processes predominate under a given set of circumstances requires an understanding of the energetics of dissimilatory metabolism and growth. There are two aspects involved: (i) considerations based on chemical thermodynamics; and (ii) kinetic constraints on chemical reactions and the coupling of those reactions to growth. Thermodynamics provides a framework for predicting whether or not a specific reaction can occur spontaneously, and the magnitude of energy exchanges (production or consumption) between reactants and their environment; thermodynamics also predicts whether a reaction may be usefully coupled to biological work and the extent of disorder (entropy change) associated with a reaction. However, thermodynamics does not directly predict the kinetic characteristics or mechanisms of reactions.

In contrast, the analysis of kinetics deals exclusively with mechanism and rate. Lacking a suitable mechanism, a thermodynamically permissible reaction may proceed only slowly, if at all. Reaction rates also depend on the proportion of reactants that are sufficiently energetic to participate in a given reaction. This proportion is a function of temperature and "activation energy" as specified by the Boltzmann distribution law. Activation energy, E_a, refers to a minimum or threshold molecular energy state that is required in order for colliding molecules to undergo a specified reaction. Reaction rates (or rate constants) are related to temperature and activation energy according to: $k = A e^{-E_a/RT}$ where A and E_a are characteristic reaction constants, R is the gas law constant and T is temperature in K. In general, the higher the activation energy, the slower the reaction.

Enzymes, which function as catalysts, act by lowering activation energies, thereby enhancing reaction rates. Enzymes provide reaction mechanisms that facilitate processes that might not occur otherwise. For example, hydrogen and oxygen can coexist in a gas or liquid without reacting, even though reduction of oxygen by hydrogen to form water should occur spontaneously according to thermodynamic calculations. Addition of bacterial hydrogenases to a stable hydrogen and oxygen mixture promotes rapid activity. There are numerous other examples in which microbial enzymes greatly accelerate chemical reactions, the energy from which supports growth and maintenance. It has become almost axiomatic that, if a proposed reaction is thermodynamically permissible, there is an enzyme or microbe to exploit it.

The repertoire of microbial catalysts or enzymes is not unlimited, however. Although oxidation of N_2 by O_2 to produce nitrate should occur spontaneously and provide energy for growth, the reaction is extremely slow due to a high activation energy and the absence of suitable catalytic enzymes. Likewise, reduction of N_2 by H_2 to form ammonia is favourable thermodynamically, but does not proceed at all under standard abiological conditions, again as a result of a high activation energy. A complex microbial enzyme, nitrogenase, catalyses ammonia production from N_2 and H_2, but this is an energetically expensive rather than energy-producing process. Even so, the microbial process is considerably more efficient than the commercial chemical process used for industrial ammonia production. Such limitations notwithstanding, microbes are remarkable chemists that fully exploit their environment, extracting the chemical energy from numerous reactions for use in an extraordinary array of biological processes.

The principles of equilibrium thermodynamics can be applied readily to understand the energetics of metabolic processes and the biogeochemical behaviour of micro-organisms. The origins of life, metabolic diversity, microbial competition, and mass and energy cycles can and should be understood in the context of thermodynamics.

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