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Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and Bacteria

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Abstract

Thermophilic and hyperthermophilic Archaea and Bacteria have been isolated from marine hydrothermal systems, heated sediments, continental solfataras, hot springs, water heaters, and industrial waste. They catalyze a tremendous array of widely varying metabolic processes. As determined in the laboratory, electron donors in thermophilic and hyperthermophilic microbial redox reactions include H_2, Fe^{2+}, H_2S, S, $S_2O_3^{2-}$, $S_4O_6^{2-}$, sulfide minerals, CH_4, various mono-, di-, and hydroxy-carboxylic acids, alcohols, amino acids, and complex organic substrates; electron acceptors include O_2, Fe^{3+}, CO_2, CO, NO_3^-, NO_2^-, NO, N_2O, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and S. Although many assimilatory and dissimilatory metabolic reactions have been identified for these groups of microorganisms, little attention has been paid to the energetics of these reactions. In this review, standard molal Gibbs free energies (ΔG_r^0) as a function of temperature to 200°C are tabulated for 370 organic and inorganic redox, disproportionation, dissociation, hydrolysis, and solubility reactions directly or indirectly involved in microbial metabolism. To calculate values of ΔG_r^0 for these and countless other reactions, the apparent standard molal Gibbs free energies of formation (ΔG^0) at temperatures to 200°C are given for 307 solids, liquids, gases, and aqueous solutes. It is shown that values of ΔG_r^0 for many microbially mediated reactions are highly temperature dependent, and that adopting values determined at 25°C for systems at elevated temperatures introduces significant and unnecessary errors. The metabolic processes considered here involve compounds that belong to the following chemical systems: H–O, H–O–N, H–O–S, H–O–N–S, H–O–$C_{inorganic}$, H–O–C, H–O–N–C, H–O–S–C, H–O–N–S–$C_{amino\ acids}$, H–O–S–C–metals/minerals, and H–O–P. For four metabolic reactions of particular interest in thermophily and hyperthermophily (knallgas reaction, anaerobic sulfur and nitrate reduction, and autotrophic methanogenesis), values of the overall Gibbs free energy (ΔG_r) as a function of temperature are calculated for a wide range of chemical compositions likely to be present in near-surface and deep hydrothermal and geothermal systems. © 2001 Federation of European Microbiological Societies. Published by Elsevier Science B.V. All rights reserved.

Keywords: Metabolic reaction; Energetics; Thermodynamics; Thermophile; Hyperthermophile; High temperature

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1. Introduction

In the late 1970s, with the discovery of the Archaea, Woese and coworkers rang in the most recent biological revolution by proposing that gene sequences could be used to divide all life on Earth into three distinct groups which are taxonomically above the level of kingdom. These groups later became known as domains and include the Eucarya, Bacteria (formerly Eubacteria), and Archaea (formerly Archaebacteria) [1]. Partial ribosomal RNA sequences from countless organisms have now been determined and employed to establish phylogenetic relationships. In addition, approximately 30 complete genomes, including those of several Archaea, have been deciphered, and having as many as 100 microbial genomes in the very near future no longer seems unrealistic [2]. Although phylogenetic trees built upon this ever-increasing wealth of partial and complete genomic data may differ, in some cases significantly [3], these data provide the cornerstone for investigating life's phylogenetic diversity, the Earth's evolutionary history, and the universal ancestor [4].

Beyond genetic relations, molecular phylogeny can also be used to interpret the evolutionary progression of metabolic and consequently microbial diversity [5]. A striking feature of global phylogenetic trees that cannot be overlooked is that thermophiles, organisms that favor elevated temperatures, represent the deepest and shortest branches of these trees, both in the Bacteria and particularly the Archaea domains. It follows that the origin and evolution of many metabolic reactions and pathways may be rooted in thermophiles. At the same time, discoveries about thermophiles are continuously being made and many reactions known only from mesophiles at present may also be conducted by unknown thermophiles.

Perhaps the most fundamental characteristic dictating the progression of a metabolic reaction, in fact any chemical reaction, is the amount of energy required or released. A quantitative assessment of the energy budget at the appropriate temperature, pressure, and chemical composition of the system of interest is an essential prerequisite for determining which of a large array of metabolic reactions may be energy-yielding (exergonic). Energy conservation in microorganisms living at ambient conditions (mesophiles) is well documented [6], but the counterpart for organisms at elevated temperatures is not. The purpose of this study is to calculate the energetics as a function of temperature and pressure for numerous known metabolic reactions and determine which of these may provide an energetic drive for thermophilic microorganisms. For reasons discussed below, the emphasis is placed on overall metabolic reactions rather than the stepwise reactions which constitute assimilatory processes. These overall reactions, such as the reduction of elemental sulfur by H_2 to yield H_2S, or the oxidation of methane (CH_4) by O_2 to yield CO_2 and H_2O, generally consist of several electron transfer steps, each of which may be catalyzed by a different enzyme. Therefore, the organism containing the appropriate enzymes is viewed as mediating the sum of stepwise reactions in overall metabolic processes.

2. Thermophiles and hyperthermophiles

2.1. Life at high temperature

An alkaline hot spring in the Lower Geyser Basin of Yellowstone National Park, USA hosts *Thermocrinis ruber*, an aerobic, facultatively chemolithotrophic Bacterium that grows in the laboratory between 44 and 89°C by oxidizing hydrogen, elemental sulfur, thiosulfate, formate, or formamide. Deep-sea hydrothermal systems at a depth of 2600 m near 21°N on the East Pacific Rise support anaerobic autotrophic methanogens such as *Methanococcus jannaschii* which grows optimally in the laboratory at ~85°C. Meanwhile, acid solutions generated by the interaction of volcanic gases and seawater at Vulcano in the Aeolian Islands and the solfatara fields of Naples, Italy are the habitats of acidophilic Archaea, including *Acidianus infernus*, *Thermoplasma volcanium*, and *Metallosphaera sedula*, which grow optimally at a pH near 2. The enormous genetic and metabolic diversity present in high temperature environments reflect the ranges of pH, oxidation/reduction states, solute concentrations, gas compositions, and mineralogy that characterize these environments.

Microorganisms which inhabit these high temperature environments are defined as thermophilic if their optimum growth temperatures are $>45°C$ [7]. If an organism has optimum and maximum growth temperatures of at least 80 and 90°C, respectively, it is further defined as a hyperthermophile [8]. The current maximum growth temperature of a pure isolate is 113°C [9], but microbiologists are willing to speculate that the upper temperature limit for life may be closer to 150°C [10,11]. Circumstantial evidence obtained from mixed culture experiments [12], particulate DNA concentrations in black smoker fluids [13,14], direct cell counts on sediment samples [15], and fluid inclusion studies [16] suggests that even this estimate appears conservative. Regardless of what the maximum growth temperature of life on Earth may be – if such a temperature does in fact exist – it is safe to say that it remains unknown.

Although extreme temperatures attract considerable attention in the discussion of hyperthermophiles [10,11], biomolecule stability [17–20], and the universal ancestor [21–23], they are less relevant than the availability of energy. All chemosynthetic organisms gain energy by catalyzing oxidation/reduction (redox) reactions that are slow to equilibrate on their own. These reactions have to be thermodynamically favored but kinetically inhibited to serve as energy sources. As temperature increases, reaction rates also increase, and at some elevated temperature, abiotic reaction rates are so fast that there is no benefit to an organism if it catalyzes the reaction. Therefore, at high temperatures, it is the rapid unassisted approach to equilibrium that places a limit on life and not temperature itself.

2.2. Natural host environments

Easily accessible natural biotopes of thermophilic microbes include shallow and deep marine hydrothermal vent environments, heated beach sediments, continental solfataric areas, and hot springs. The in situ temperatures and pressures of these habitats vary considerably, but more than cover the range to which known organisms have adapted. The majority of these systems are characterized by extremely low oxygen concentrations. Consequently, most of the known species of thermophiles are classified as obligate or facultative anaerobes, though aerobic and microaerophilic isolates are also known. As noted by Brock [24], the majority of continental hot spring fluids exhibit a bimodal distribution with respect to pH with average values either in the acidic region (pH 1–3) or near neutral to slightly alkaline (pH 7–9). It should thus come as no surprise that a preponderance of thermophiles is either acidophilic or neutrophilic.

Although many thermophile biotopes have in situ pressures significantly greater than atmospheric, researchers are only starting to realize the effects of pressure on cell growth. For example, the survival of the deep-sea hyperthermophile *Pyrococcus* strain ES4 at super-optimal temperatures was enhanced by elevated pressure (220 bar) relative to low pressure (30 bar) [25]. On the other hand, the hyperthermophile *Pyrolobus fumarii* isolated from a depth of 3650 m from a hydrothermally heated black smoker fragment at the Mid Atlantic Ridge showed no growth enhancement when incubated at 250 bar relative to experiments at 3 bar [9]. In contrast, earlier experiments on *M. jannaschii*, an autotrophic methanogen from submarine hydrothermal systems, showed a decrease in doubling time from 83 min at 86°C and 7.8 bar to 18 min at the same temperature but 750 bar [26]. At 90°C, in the same study, the doubling time of *M. jannaschii* decreased from 160 min at 7.8 bar to 50 min at 750 bar. Owing to the wide range of temperature, pressure, fluid chemistry, and mineralogy of host environments, the metabolic strategies of thermophiles are, accordingly, highly diverse.

2.3. Deep biosphere

It is increasingly apparent that surface thermal features and the organisms they support are giving researchers a glimpse of what life may be like in the deep subsurface [27,28]. Indeed, numerous studies have shown that a subsurface biosphere exists in coastal plain sediments, sedimentary basins, and granitic and basaltic aquifers (see Table 1). For example, autotrophic methanogens and SO_4^{2-} and Fe^{3+} reducers have been identified at depths

Table 1
Direct observations of microorganisms in the deep subsurface

Location	Rock or fluid type	Max. depth (m)	T_{MAX} (°C)	Laboratory metabolism	References
Cerro Negro, NM, USA	Sandstone, shale	247		Heterotrophy, SO_4^{2-} reduction, acetogenesis	[163]
Savannah River, Aiken, SC, USA	Sediments of sand and clay	260		Aerobic and anaerobic heterotrophy, SO_4^{2-} reduction, methanogenesis, nitrification, N_2-fixation	[164,165]
Rainier Mesa, NV, USA	Volcanic ashfall tuff	400	18	Aerobic chemoheterotrophy	[166,167]
Lac du Bonnet batholith, Man., Canada	Granite	420		Fe^{3+} and SO_4^{2-} reduction, Fe^{2+} oxidation	[168,169]
Japan Sea, Peru Margin, Eastern equatorial Pacific, Juan de Fuca Ridge, Lau Basin, Philippine Trench, Kermadec-Tonga Trench, Soenda Deep, Weber Deep	Marine sediments	518[a]	80	SO_4^{2-}-reducing methanotrophy[b], NO_3^- and SO_4^{2-} reduction, obligate and facultative barophily	[28,39]
Äspö, Sweden	Granite	860	20.5	Heterotrophic Fe^{3+} and SO_4^{2-} reduction, autotrophic methanogenesis and acetogenesis	[40–43]
Great Artesian Basin, Australia	Thermal aquifer	914	88	Heterotrophic and autotrophic SO_4^{2-} reduction	[170–172]
Stripa mine, Sweden	Granite	1240	26	Heterotrophy and autotrophy	[173]
Hanford Reservation, Washington, USA	Basalt	1300		Autotrophic methanogenesis, SO_4^{2-} and Fe^{3+} reduction	[29,30]
Madison Formation, MT, USA	Aquifers in dolomitic limestone	1800	50	SO_4^{2-} reduction, methanogenesis	[174]
Piceance Basin, CO, USA	Sandstone and shale	2100	85	Heterotrophic and autotrophic Fe^{3+} reduction	[175,176]
Paris Basin, France	Oil field brine, geothermal water	2500	85	Heterotrophic and autotrophic SO_4^{2-} reduction, autotrophic methanogenesis	[35,38,177,178]
Taylorsville Basin, VA, USA	Siltstone and shale	2800	85	Heterotrophic SO_4^{2-} and Fe^{3+} reduction	[175,179]
Witwatersrand, South Africa	Carbonate, sandstone, shale	3200	60	Heterotrophic Fe^{3+}, Mn^{4+}, S, NO_3^-, O_2 reduction	[31,32,173]
Gravberg, Siljan Ring, Sweden	Granite	3500	60	Heterotrophy	[33,34]
Northsea oil fields: Statfjord and Beatrice fields, East Shetland basin	Oil field waters	4000	110	Heterotrophic SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and S reduction, autotrophic SO_4^{2-} reduction, Heterotrophic Mn^{4+}, Fe^{3+}, and NO_3^- reduction	[36,37,180,181]

[a] This refers to the depth below the sediment–water interface, not the depth below sea level.

[b] Although methanotrophs able to use SO_4^{2-} as their electron acceptor have not been isolated, other lines of evidence strongly suggest their existence.

up to 1300 m in basaltic rock in Washington, USA [29,30]. In addition, sedimentary rocks, such as sandstone, shale, and limestone at depths up to 3200 m and temperatures > 80°C are hosts to a variety of autotrophs and heterotrophs, including aerobes and SO_4^{2-}, S, Fe^{3+}, Mn^{4+}, and NO_3^- reducers [31,32]. In the granitic aquifers at Gravberg, Sweden, heterotrophic metabolism has been documented at a depth of 3500 m at 60°C [33,34]. Furthermore, thermophiles and hyperthermophiles have been cultured at temperatures up to $\sim$100°C from oil field waters in the Paris Basin and the North Sea [35–38], and obligate and facultative barophiles (organisms that favor elevated pressures) thrive in marine sediments hundreds of meters below the sediment–water interface [28,39].

The metabolic diversity already examined in the deep biosphere shows that chemosynthetic organisms can take advantage of many forms of energy that are sufficient to support life [40–43]. These energy sources can be linked to photosynthesis at the surface, as in the case of heterotrophs that use organic compounds in sediments that are the residue of photosynthetic organisms, or they can be completely independent of photosynthesis, as in the case of autotrophs that gain energy and fix carbon by reacting CO_2 and H_2 provided by geologic processes [30,44,45]. These observations lead inescapably to the proposition that microorganisms can live in the subsurface wherever there are sources of geochemical energy and where the system is open to mass exchange on at least the timescale of microbial processes.

3. Metabolism of thermophiles and hyperthermophiles

3.1. *Energy-yielding substrates for autotrophs and heterotrophs*

More than 200 species of thermophiles and hyperthermophiles belonging to circa 100 genera (Table 2) are cur-

Table 2
Taxonomy and metabolic features of thermophiles and hyperthermophiles

Genus	Species	T_{MAX} (°C)	Hetero/auto	Aerobe/anaerobe	References
Thermophilic Bacteria					
Acidimicrobium	*ferrooxidans*	57	FA	FAN	[182,183]
Alicyclobacillus	*acidocaldarius*	70	H	AE	[184–186]
	acidoterrestris	60	H	AE	[184]
	cycloheptanicus	53	H	AE	[184]
Ammonifex	*degensii*	77	FA	AN	[187]
Anaerobranca	*horikoshii*	66	H	AN	[188]
Bacillus	*infernus*	61	H	AN	[116]
	schlegelii	79	FA	AE	[189]
	thermoantarcticus	65	H	AE	[190,191]
	thermoleovorans	78	H	FAN	[192]
	thermosphaericus	64	H	AE	[193]
	tusciae	55[a]	FA	AE	[194]
Calderobacterium	*hydrogenophilum*	82	A	AE	[195]
Caldicellulosiruptor	*lactoaceticus*	78	H	AN	[196]
	owensensis	80	H	AN	[197]
	saccharolyticus	80	H	AN	[198]
Caloramator	*indicus*	75	H	AN	[199]
	proteoclasticus	68	H	AN	[200]
Chloroflexus	*aurantiacus*	65	H	FAN	[201]
Clostridium	*paradoxim*	63	H	AN	[202]
	thermosuccinogenes	65	H	AN	[203]
Coprothermobacter	*proteolyticus*	75	H	AN	[204]
Deferribacter	*thermophilus*	65	H	AN	[181]
Deinococcus	*geothermalis*	55	H	AE	[205]
	murrayi	52	H	AE	[205]
Desulfacinum	*infernum*	65	FA	AN	[206]
Desulfotomaculum	*australicum*	74	FA	AN	[170]
	geothermicum	57	FA	AN	[35]
	kuznetsovi	85	FA	AN	[207]
	luciae	70	FA	AN	[175,208]
	nigrificans ssp. *salinus*	70	H	AN	[209]
	putei	65	FA	AN	[175]
	thermoacetoxidans	65	FA	AN	[210]
	thermobenzoicum	70	H	AN	[211]
	thermocisternum	75	FA	AN	[180]
	thermosapovorans	60	FA	AN	[212]
Desulfurella	*acetivorans*	70	H	AN	[213]
	kamchatkensis	70	FA	AN	[214]
	multipotens	77	FA	AN	[215]
	propionica	63	FA	AN	[214]
Desulfurobacterium	*thermolithotrophum*	75	A	AN	[216]
Dictyoglomus	*turgidus*	86	H	AN	[217]
Fervidobacterium	*islandicum*	80	H	AN	[218]
	nodosum	79	H	AN	[219]
	pennavorans	80	H	AN	[220]
Flexistipes	*sinusarabici*	53	H	AN	[221]
Geotoga	*petraea*	55	H	AN	[222]
	subterranea	60	H	AN	[222]
Halothermothrix	*orenii*	68	H	AN	[223]
Hydrogenobacter	*acidophilus*	65	A	AE	[224]
	halophilus	75	A	AE	[225]
	thermophilus	79	A	AE	[226,227]
Hydrogenophilus	*thermoluteolus*	52	FA	AE	[228,229]
Isosphaera	*pallida*	55	H	AE	[230]
Meiothermus	*cerbereus*	60	H	AE	[231]
	chliarophilus	60	H	AE	[232]
	ruber	65	H	AE	[232]
	silvanus	65	H	AE	[232]
Methylococcus	*thermophilus*	62	H	AE	[233]
Moorella	*glycerini*	65	H	AN	[234]
	thermoaceticum	65	H	AN	[235,236]

Table 2 (*continued*)

Genus	Species	T_{MAX} (°C)	Hetero/auto	Aerobe/anaerobe	References
Petrotoga	*miotherma*	65	H	AN	[222]
	mobilis	65	H	AN	[237]
Rhodothermus	*marinus*	77	H	AE	[238]
	obamesis	85	H	AE	[239]
Rubrobacter	*xylanophilus*	70	H	AE	[240]
	radiotolerans	48[a]	H	AE	[241]
Sphaerobacter	*thermophilus*	60	H	AE	[242]
Spirochaeta	*caldaria*	52[a]	H	AN	[243]
	thermophila	73	H	AN	[244]
Sulfobacillus	*acidophilus*	50	FA	FAN	[183,245]
	thermosulfidooxidans	55	FA	FAN	[183,246,247]
Thermaerobacter	*marianensis*	80	H	AE	[248]
Thermoanaerobacter	*acetoethylicus*	79	H	AN	[204,249]
	brockii	85	H	AN	[250–252]
	ethanolicus	78	H	AN	[252,253]
	kivui	72	FA	AN	[236,254]
	mathranii	75	H	AN	[255]
	sulfurophilus	75	H	AN	[256]
	thermohydrosulfuricus	78	H	AN	[252]
	wiegelii	78	H	AN	[257]
Thermoanaerobacterium	*aotearoense*	66	H	AN	[258]
	saccharolyticum	70	H	AN	[252]
	thermosulfurigenes	75	H	AN	[252]
	xylanolyticum	70	H	AN	[252]
Thermoanaerobium	*lactoethylicum*	75	H	AN	[259]
Thermobrachium	*celere*	75	H	AN	[260]
Thermocrinis	*ruber*	89	FA	AE	[261]
Thermocrispum	*agreste*	62	H	AE	[262]
	municipale	62	H	AE	[262]
Thermodesulfobacterium	*commune*	85	H	AN	[263]
	mobile	85	H	AN	[264,265]
Thermodesulforhabdus	*norvegicus*	74	H	AN	[266]
Thermodesulfovibrio	*yellowstonii*	70	H	AN	[267]
Thermohalobacter	*berrensis*	65	H	AN	[268]
Thermohydrogenium	*kirishiense*	75	H	AN	[269]
Thermoleophilum	*album*	70	H	AE	[270]
Thermomicrobium	*roseum*	85	H	AE	[271]
Thermonema	*rossianum*	65	H	AE	[272]
Thermosipho	*africanus*	77	H	AN	[273]
Thermosyntropha	*lipolytica*	70	H	AN	[274]
Thermoterrabacterium	*ferrireducens*	74	H	AN	[275]
Thermothrix	*azorensis*	87	A	AE	[276]
	thioparus	77	FA	FAN	[277,278]
Thermotoga	*elfii*	72	H	AN	[279]
	hypogea	90	H	AN	[280]
	subterranea	75	H	AN	[281]
	thermarum	84	H	AN	[282]
Thermus	*aquaticus*	79	H	AE	[283]
	oshimai	70	H	AE	[284]
	thermophilus	85	H	AE	[285]
Thiobacillus	*thermophilica*	80	A	AE	[286]
Hyperthermophilic Bacteria					
Aquifex	*pyrophilus*	95	A	FAN	[82]
Thermotoga	*maritima*	90	H	AN	[287]
	neapolitana	90	H	AN	[288]
Thermophilic Archaea					
Acidianus	*ambivalens*	87	A	FAN	[289–291]
	brierleyi	75	FA	FAN	[292–294]
Archaeoglobus	*lithotrophicus*	89	A	AN	[37]
	veneficus	85	FA	AN	[295]
Metallosphaera	*prunae*	80	FA	AE	[296]
	sedula	80	FA	AE	[293,297]

Table 2 (*continued*)

Genus	Species	T_{MAX} (°C)	Hetero/auto	Aerobe/anaerobe	References
Methanobacterium	*defluvii*	65	A	AN	[298]
	thermoaggregans	75	A	AN	[299]
	thermoalcaliphilum	69	A	AN	[300]
	thermophilum	57	A	AN	[301]
	thermoflexum	70	A	AN	[298]
Methanococcus	*thermolithotrophicus*	70	A	AN	[302]
	vulcanius	89	A	AN	[303]
Methanoculleus	*thermophilicum*	60	H	AN	[304]
Methanohalobium	*evestigatus*	60	H	AN	[305]
Methanosarcina	*thermophila*	50	H	AN	[128]
Methanothermobacter	*thermoautotrophicus*	75	A	AN	[306]
	wolfeii	74	A	AN	[307]
Methanothrix	*thermophila*	60[a]	H	AN	[308]
Palaeococcus	*ferrophilus*	88	H	AN	[309]
Picrophilus	*oshimae*	65	H	AE	[310,311]
	torridus	65	H	AE	[310,311]
Stygiolobus	*azoricus*	89	A	AN	[312]
Sulfolobus	*acidocaldarius*	80	FA	FAN	[293,313–315]
	hakonensis	80	FA	AE	[316]
	metallicus	75	A	AE	[317]
	shibatae	86	FA	AE	[293,318,319]
	solfataricus	87	FA	AE	[293,320]
Sulfurococcus	*mirabilis*	86	FA	AE	[321]
	yellowstonii	80	FA	AE	[322]
Thermocladium	*modestius*	82	H	FAN	[259]
Thermococcus	*zilligii*	85	H	AN	[323,324]
Thermoplasma	*acidophilum*	63	H	FAN	[325,326]
	volcanium	67	H	FAN	[325]
Hyperthermophilic Archaea					
Acidianus	*infernus*	96	A	FAN	[292,293]
Aeropyrum	*pernix*	100	H	AE	[327]
Archaeoglobus	*fulgidus*	95	FA	AN	[328–330]
	profundus	90	A	AN	[331]
Caldivirga	*maquilingensis*	92	H	FAN	[332]
Caldococcus	*litoralis*	100	H	AN	[333]
	noboribetus	96	H	AN	[334,335]
Desulfurococcus	*amylolyticus*	97	H	AN	[336]
	mobilis	97	H	AN	[337]
	mucosus	97	H	AN	[337]
Ferroglobus	*placidus*	95	FA	AN	[84]
Hyperthermus	*butylicus*	108	H	AN	[338]
Methanococcus	*fervens*	92	A	AN	[303,339]
	igneus	91	A	AN	[340]
	infernus	91	A	AN	[341]
	jannaschii	94	A	AN	[126,304]
Methanopyrus	*kandleri*	110	A	AN	[94,342]
Methanothermus	*fervidus*	97	A	AN	[343]
	sociabilis	97	A	AN	[344]
Pyrobaculum	*aerophilum*	104	FA	FAN	[345]
	islandicum	102	FA	AN	[346]
	organotrophum	102	H	AN	[346]
Pyrococcus	*abyssi*	108	H	AN	[347]
	endeavori (ES4)	110	H	AN	[348]
	furiosus	103	H	AN	[349]
	horikoshii	102	H	AN	[350]
	woesei	104	H	AN	[351]
Pyrodictium	*abyssi*	110	H	AN	[347]
	brockii	110	A	AN	[352,353]
	occultum	110	A	AN	[352,353]
Pyrolobus	*fumarii*	113	A	FAN	[9]
Staphylothermus	*marinus*	98	H	AN	[354]
Stetteria	*hydrogenophila*	102	H	AN	[355]
Sulfophobococcus	*zilligii*	95	H	AN	[356]

Table 2 (*continued*)

Genus	Species	T_{MAX} (°C)	Hetero/auto	Aerobe/anaerobe	References
Sulfurisphaera	*ohwakuensis*	92	H	FAN	[357]
Thermococcus	*acidaminovorans*	93	H	AN	[358]
	aggregans	94	H	AN	[359]
	alcaliphilus	90	H	AN	[360]
	barophilus	100	H	AN	[361]
	barossi	92	H	AN	[362]
	celer	93	H	AN	[363]
	chitonophagus	93	H	AN	[364]
	fumicolans	103	H	AN	[365]
	gorgonarius	95	H	AN	[366]
	guaymasensis	90	H	AN	[359]
	hydrothermalis	100	H	AN	[367]
	litoralis	98	H	AN	[368,369]
	pacificus	95	H	AN	[366]
	peptonophilus	100	H	AN	[370]
	profundus	90	H	AN	[371]
	siculi	93	H	AN	[372]
	stetteri[b]	98	H	AN	[373]
Thermodiscus	*maritimus*	98	H/A[c]	AN	[374,375]
Thermofilum	*pendens*	100	H	AN	[376]
Thermoproteus	*neutrophilus*	85[a]	A	AN	[375]
	tenax	96	FA	AN	[375,377]
	uzoniensis	102	H	AN	[378]
Thermosphaera	*aggregans*	90	H	AN	[261]

A: autotroph; H: heterotroph; FA: facultative autotroph (or facultative heterotroph); AN: anaerobe; AE: aerobe; FAN: facultative anaerobe (or facultative aerobe).

[a] This represents the optimum growth temperature; the maximum growth temperature is not given.

[b] Some strains are thermophilic with a temperature optimum of 73–77°C and a maximum of 94°C, but others are hyperthermophilic with optimum and maximum growth temperatures equal to 88 and 98°C, respectively [373].

[c] Fischer et al. (1983) [375] describe *Thermodiscus maritimus* as an obligate autotroph, but Stetter et al. (1990) [374] list it as a heterotroph.

rently known. These microorganisms can carry out a wide variety of metabolic processes featuring a multitude of electron donors and acceptors. To date, 12 genera are known within the Archaea, both aerobes and anaerobes, autotrophs as well as heterotrophs, which catalyze metabolic reactions at temperatures ≥100°C. Although the metabolic pathways used by thermophiles and hyperthermophiles are still largely unresolved, several dominant characteristics of energy-yielding redox reactions are apparent. Only approximately 25 known genera of thermophiles and hyperthermophiles contain obligate aerobes; most are obligate anaerobes, but some are facultative anaerobes. Therefore, the common electron acceptors used by these organisms include, for example, sulfate, nitrate, carbon dioxide, and ferric iron rather than oxygen. This directly reflects the geochemical nature of the biotopes discussed above.

Furthermore, the majority of known thermophiles and hyperthermophiles are obligately heterotrophic, preferentially using complex mixtures of polypeptides and/or carbohydrates as energy and carbon sources in laboratory growth experiments. Others are strict autotrophs that assimilate CO_2, and yet others are able to grow hetero- or autotrophically depending on the availability of carbon sources. It should be noted that the actual carbon compounds metabolized by thermophilic or hyperthermophilic heterotrophs in natural ecosystems are generally not resolved [46].

In addition, all hyperthermophiles and many species of thermophiles are chemosynthetic rather than photosynthetic, deriving energy by the oxidation or reduction of dissolved organic and inorganic compounds rather than by harnessing solar energy. This fact also correlates directly with the geochemistry and geophysics of high temperature ecosystems. These environments are almost exclusively at depths greater than those penetrable by sunlight.

Finally, the majority of thermophiles and hyperthermophiles in culture take advantage of electron transfer among species in the sulfur redox system. Anaerobes commonly reduce sulfate, sulfite, thiosulfate, or elemental sulfur to sulfide, while aerobes may oxidize sulfide or elemental sulfur to sulfate. Of these, perhaps the most common energy-yielding process used by hyperthermophiles is the reduction of elemental sulfur represented by:

$$H_2(g) + \text{Sulfur} \rightarrow H_2S(g) \tag{1}$$

This experimentally-verified reaction [47] is believed to be the sole energy-yielding process in numerous autotrophs, although it has been shown [48] that the energy release in hot spring systems is rather moderate relative to other known autotrophic and heterotrophic metabolic reactions.

3.2. Comparisons with mesophiles

Thermophiles, and in particular hyperthermophiles, are relatively recent discoveries in microbiology. If the volume of Earth where life may exist is indeed as vast as recently estimated [27], most of the habitable subsurface can only be inhabited by thermophiles and hyperthermophiles. Although considerable progress has already been made in identifying their required substrates for growth in the laboratory, significant gaps still exist in (1) understanding the actual carbon sources of thermophilic heterotrophs in natural biotopes, (2) evaluating the impact of solid phases on metabolism, both as substrates and products, (3) elucidating the pathways of intracellular anabolism and catabolism, and (4) quantifying the energetics of metabolic reactions at the temperature, pressure, and chemical composition of natural systems. In all four cases, the plethora of information and data gathered from studies of mesophilic organisms may provide some useful constraints.

It is the objective of this study to calculate the energetics as functions of temperature and pressure of 'overall' metabolic reactions known to be mediated by thermophiles and hyperthermophiles. We have included reactions that are unfamiliar to thermophily if they are experimentally verified energy-yielding processes in mesophiles. In addition, we supply thermodynamic properties of 307 individual aqueous solutes, gases, liquids, and minerals, which permit calculations for thousands of additional reactions that may be of interest as research progresses. Calculations of this sort may aid in identifying likely thermophilic and hyperthermophilic metabolisms not yet observed, as well as in the selection of potential habitats for discovering novel isolates. In a step toward reaching these goals, we present a thermodynamic approach to evaluate quantitatively the energetics of overall metabolic reactions in microorganisms as functions of temperature and pressure.

4. Thermodynamic framework

4.1. Energetics of metabolic reactions at 25°C and 1 bar

Prior to the discovery of thermophiles, energetic calculations at 25°C and 1 bar for metabolic reactions were sufficient for most applications in microbiology. It can be seen in tables and figures presented here that the energetics of the chemical reactions of interest show very little change over a narrow temperature range near 25°C. In other words, applying a thermodynamic value for a specific reaction at 25°C to the same reaction at 15 or 37°C introduces only minimal error. Thauer et al. (1977) [6] published a compilation of thermodynamic calculations at 25°C for energy conservation in chemotrophic anaerobes that is still useful today. However, accurately determining the energetics of metabolic reactions carried out, for example, by *P. fumarii* at 113°C and 250 bar requires accurate thermodynamic properties at this temperature and pressure. Recent developments of theoretical equations of state permit the calculation of standard partial molal thermodynamic properties of aqueous, liquid, solid, and gaseous organic and inorganic compounds over wide ranges of temperature and pressure. In the present study, we evaluated standard state[1] thermodynamic properties at temperatures up to 200°C, which is well within the range of temperature covered by experimental data and equations of state, and should be sufficient for metabolic energy calculations for even the most optimistic microbiologists.

4.2. Internally consistent thermodynamic data at elevated temperatures and pressures

There is always uncertainty in thermodynamic calculations, but some sources can be minimized or even eliminated. Systematic and experimental uncertainties can not be overcome through data interpretation. Mixing of thermodynamic data from various sources can introduce inconsistencies that can cripple the accuracy of calculations. On the other hand, inconsistencies among various sets of thermodynamic data can be resolved by careful analysis. The result is usually called an internally consistent database, which means that thermodynamic properties of a network of reactions have been used to extract corresponding properties of individual compounds. The data and equations used in this study represent one of the most comprehensive internally consistent data sets available for biochemical and geochemical calculations.

The revised Helgeson–Kirkham–Flowers (HKF) equations of state have been combined with experimental calorimetric, densimetric, and sound velocity measurements as well as solubility and dissociation data available in the literature to generate parameters required to calculate standard molal thermodynamic properties at elevated temperatures and pressures for hundreds of aqueous compounds. The classes of compounds for which internally consistent thermodynamic data are now available include aqueous inorganic ions and neutral solutes [49–56], aqueous organic compounds including hydrocarbons, carboxylic acids, ketones, alcohols, aldehydes, amines, amides, chlorinated compounds, amino acids, and peptides [57–67], and metal–organic complexes [68–70]. Discussions of the theoretical foundation for the HKF equations in their original form are given by Helgeson et al. (1981) [71], and in their revised forms by Tanger and Helgeson [72], Shock and Helgeson [49,57], Shock et al. (1989, 1992) [50,51], Johnson et al. (1992) [73], and Sverjensky et al. (1997)

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[1] Standard states used in these calculations are as follows: for solids and water, unit activity of the pure compound at any temperature and pressure; for gases, unit fugacity of the pure gas at any temperature and 1 bar; and for aqueous solutes, unit activity of a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure.

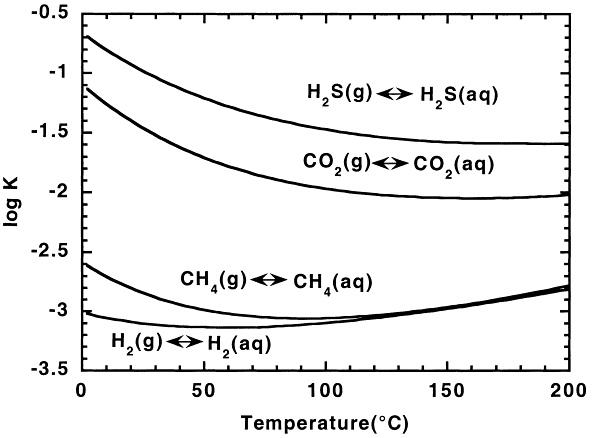

Fig. 1. Log K plotted against temperature at P_{SAT} for the solubility of gaseous H_2S (reaction G8), CO_2 (reaction G9), CH_4 (reaction G10), and H_2 (reaction G1).

[55], and relevant equations are presented in the Appendix. In addition, internally consistent data for solid, liquid, and gaseous organic compounds [74,75] and numerous inorganic gases and rock-forming minerals [56,76] can be included in these calculations. To underscore the variability of thermodynamic data as functions of temperature and pressure, it seems appropriate to show a few examples of the effects of temperature and pressure on the thermodynamic behavior of gases and aqueous species involved in microbial metabolic reactions.

4.3. Gas solubilities

Molecular hydrogen (H_2) is a common electron donor (reductant) in thermophilic and hyperthermophilic metabolism. Therefore, the equilibrium constant for H_2 dissolution in water as a function of temperature, shown in Fig. 1, is of direct significance[2]. It can be seen in this figure that the logarithm of the equilibrium constant (K) for the $H_2(g)$ dissolution reaction minimizes with increasing temperature at constant pressure, (P_{SAT})[3]. The key point to note is that the solubility of $H_2(g)$ is moderately temperature dependent. In fact, at P_{SAT}, $H_2(g)$ is more than twice as soluble at 200°C than at 50°C.

The solubility of CO_2 plays an important role in the metabolism of autotrophs that use it as a carbon source, as well as heterotrophs that produce it as a metabolite. Values of log K for the $CO_2(g)$ solubility reaction are also shown in Fig. 1. In contrast to H_2, log K for CO_2 minimizes at a temperature well above 100°C. In fact, the solubility at P_{SAT} of $CO_2(g)$ is nearly eight times higher near 0°C than at 200°C.

CH_4 serves as a carbon source for methanotrophs, but it is metabolically produced by methanogens. Its solubility at P_{SAT} is quite temperature dependent at low temperature, but only moderately so above ~50°C. It can be seen in Fig. 1 that the values of log K for the CH_4 solubility reaction minimize at ~100°C and P_{SAT}, and that $CH_4(g)$ is approximately twice as soluble at 2 and 200°C than at 100°C.

Many hyperthermophilic heterotrophs currently in culture depend on the reduction of sulfur to H_2S for optimum growth [8]. Therefore, the solubility of H_2S as a function of temperature may be useful for understanding their metabolisms. Not unlike that of CO_2 discussed above, the solubility of H_2S decreases significantly with increasing temperature. This can be interpreted from the values of log K for the H_2S solubility reaction shown in Fig. 1. In fact, like CO_2, the solubility of $H_2S(g)$ at P_{SAT} is approximately eight times higher near 0°C than at 200°C.

4.4. Neutrality

The temperature and pH dependencies of dissociation reactions affect many microbial metabolic processes. Many bioenergetic calculations are carried out at $pH = 7$ (see below), because this denotes neutrality at 25°C and 1 bar. However, because neutrality is defined as the pH where activities of H^+ and OH^- are equal, and the dissociation constant for H_2O is temperature dependent, the pH representing neutrality also varies with temperature. It can be seen in Fig. 2 that neutral pH, depicted by the curve, decreases at P_{SAT} from ~7.4 at 0°C to ~5.6 at 200°C. A pH of 7 carries no special significance at temperatures and pressures other than 25°C and 1 bar. The consequences of this fact can not be ignored when describing metabolic reactions written in terms of species such as CO_2, H_2S, SO_4^{2-}, NH_3, and organic acids.

At neutral pH, as shown by the dashed curve in Fig. 3a, dissolved CO_2 is the dominant species in the carbonic acid system only above ~80°C; below this temperature, HCO_3^- dominates at neutrality[4]. It can be inferred from this figure that the equilibrium concentration of CO_3^{2-} is only significant in highly alkaline solutions, regardless of the temperature. Note in Fig. 3b that at neutral pH the activity of H_2S exceeds that of HS^- to an increasing degree with increasing temperature. In the sulfuric acid system (Fig. 3c), SO_4^{2-} is the dominant species at alkaline and

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[2] There are many ways to write this reaction and to describe its thermodynamic properties. The dissolution equilibrium refers to the reaction $H_2(g) = H_2(aq)$, and the corresponding equilibrium constant is given by $K = a_{H_2(aq)}/f_{H_2(g)}$ where a and f refer to activity and fugacity, respectively. Therefore, K is related to the Henry's constant K_H, which refers to the reaction $H_2(aq) = H_2(g)$ by $K = a_{H_2(aq)}/K_H X_{H_2(aq)}$, because $K_H = f_{H_2(g)}/X_{H_2(aq)}$ where X stands for mol fraction.

[3] P_{SAT} is used in this study to denote saturation pressures for H_2O, in other words the P–T boiling curve for water.

[4] Although carbonic acid is often represented as H_2CO_3, this molecule is only present as a reactive intermediate between HCO_3^- and dissolved CO_2. The latter is the molecular form that >99% of carbonic acid takes at pH values $< pK_1$, and H_2CO_3 is a conventional species with properties equal to the sum of the properties of H_2O and $CO_2(aq)$ [77]. Therefore, we do not use H_2CO_3 in our calculations, tables, or figures.

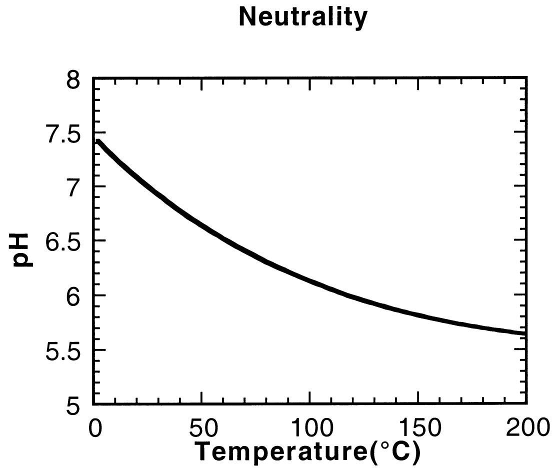

Fig. 2. Neutral pH depicted by the curve as a function of temperature at P_{SAT}.

neutral pHs and well into the acid region over the entire temperature range considered here. However, with increasing temperature in highly acid environments, the activity of HSO_4^- may rival and even surpass that of SO_4^{2-}. In the ammonia system (Fig. 3d), NH_4^+ is the dominant species at neutral pH between 0 and 200°C, although to a lesser degree with increasing temperature.

4.5. pK_a values

Changes in temperature have variable effects on pK_a values for inorganic and organic acids involved in microbial metabolism, as illustrated with the examples shown in Fig. 4. In some cases, these changes are dramatic, and, as a result, the speciation of metabolites differs considerably between environments at various temperatures even though pH values may be quite similar. For example, at neutral pH, acetate will dominate the speciation of acetic acid solutions at all temperatures from 0 to 200°C as shown in Fig. 4a. On the other hand, acetic acid acting as a buffer can hold the pH between 4.8 and 5.5 over this temperature range. Speciation of succinic acid (Fig. 4b) is dominated by succinate^{2-} at neutral pH and temperatures $< \sim 110$°C, and by the monovalent anion, H–succinate$^-$, at neutral pH and higher temperatures. Aspartic acid (Fig. 4c) exhibits only the slightest variation in pK_a from 0 to 200°C, and that of lysine (Fig. 4d) is not significantly more pronounced. In the three dissociation reactions of phosphoric acid (Fig. 4e), the pH values of the equal activity curves vary only slightly as functions of temperature. $H_2PO_4^-$ dominates at and near-neutral pH, and HPO_4^{2-} dominates at slightly alkaline pH. H_3PO_4 and PO_4^{3-} are only significant in highly acidic ($< \sim 2$) or highly alkaline ($> \sim 12$) solutions, respectively. The speciation of vanadic acid (Fig. 4f) shows five different protonated and deprotonated forms with $H_2VO_4^-$ being the dominant one at neutral pH over the entire temperature range.

The variations in speciation shown in Fig. 4 help to explain why various solutes behave differently in natural high temperature environments. As an example, in one

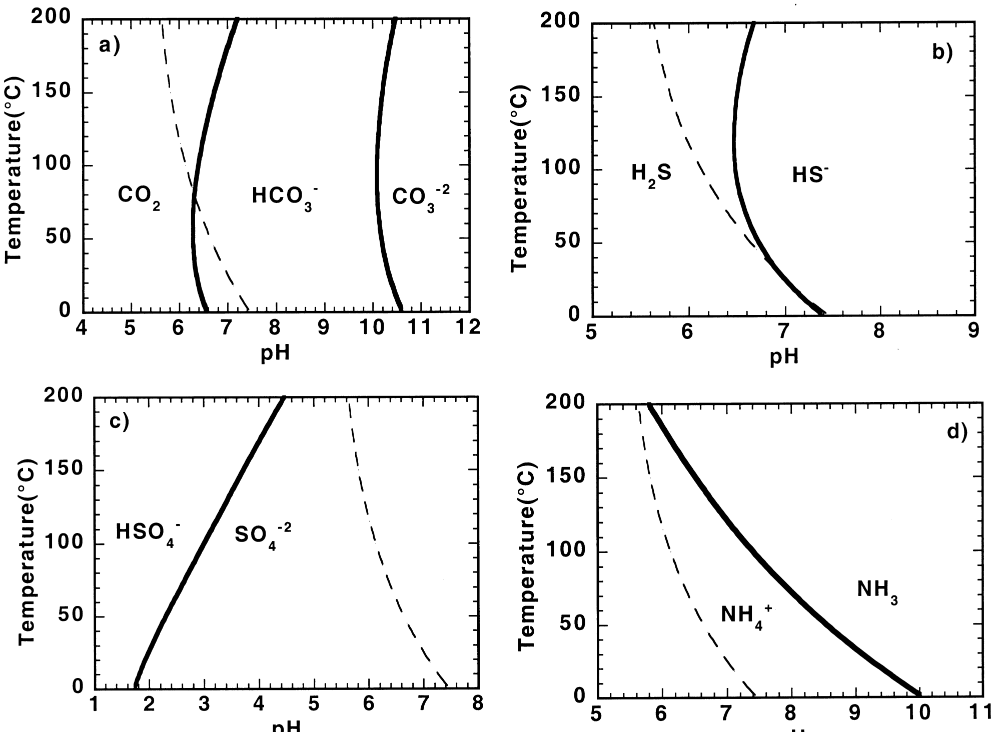

Fig. 3. Temperature–pH diagrams at P_{SAT} for the dissociation of (a) CO_2(aq) (reactions H9 and H10); (b) H_2S(aq) (reaction H8); (c) HSO_4^- (reaction H7); (d) NH_4^+ (reaction H2). The solid curves represent equal activities of the species that predominate on either side of the curves. The dashed lines depict neutral pH (see Fig. 2).

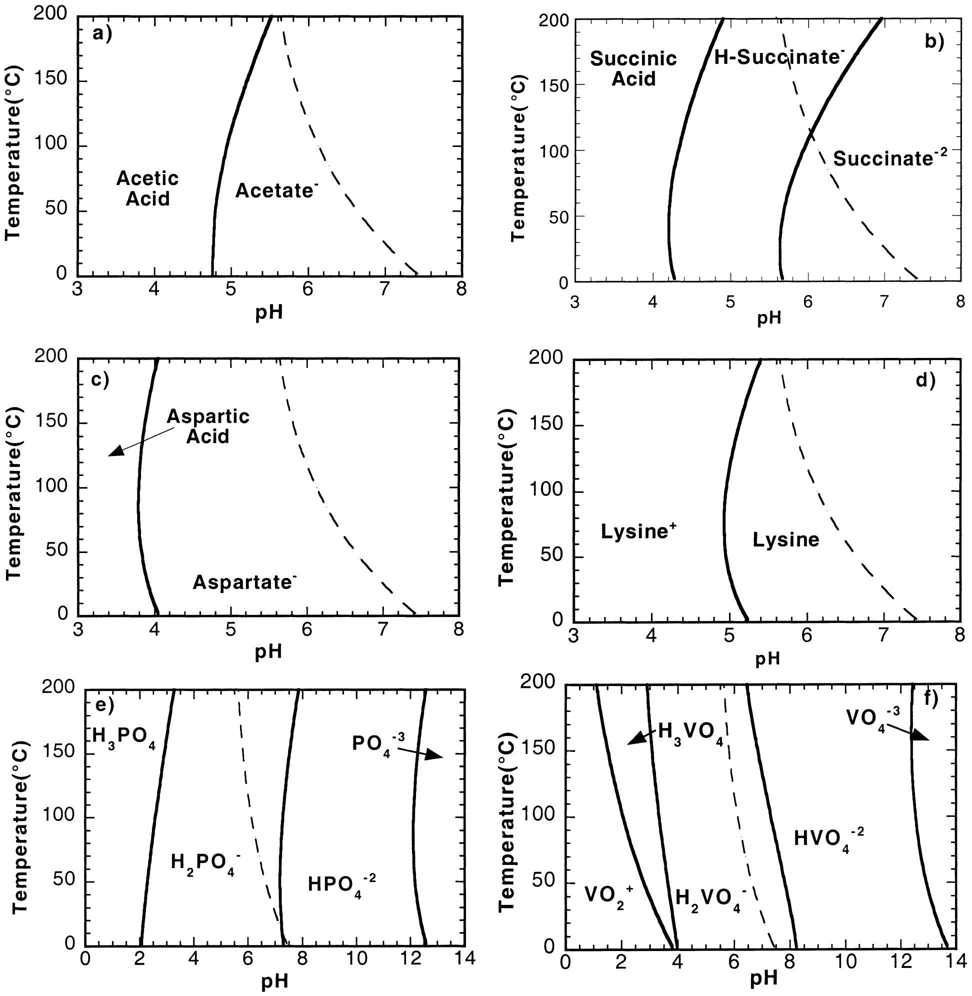

Fig. 4. Temperature–pH diagrams at P_{SAT} for the dissociation of (a) acetic acid (reaction H12); (b) succinic acid (reactions H23 and H24); (c) aspartic acid (reaction H28); (d) lysine$^+$ (reaction H31); (e) H_3PO_4 (reactions H45-H47); (f) VO_2^+ (reactions H32–H35). The solid curves represent equal activities of the species that predominate on either side of the curves. The dashed lines depict neutral pH (see Fig. 2).

outflow channel of Octopus Spring at Yellowstone National Park, populated by *T. ruber*, the pH is 7.88 at 88°C [78]. In contrast, we measured pH as low as 2.12 at only slightly lower temperature in thermal waters from Pozzo Vasca at Vulcano in the Aeolian Islands, southern Italy. At Octopus Spring, the predominant forms of the compounds shown in Fig. 4 would be acetate$^-$, succinate^{2-}, aspartate$^-$, lysine, $H_2PO_4^{2-}$, and HVO_4^{2-}, while at Vulcano, the speciation would be dominated by acetic acid, succinic acid, aspartic acid, lysine$^+$, H_3PO_4, and VO_2^+.

4.6. Pressure effects

Many thermophiles and hyperthermophiles are also barophiles and may employ metabolic processes that are affected by pressure. In general, the effect of pressure on values of the standard molal Gibbs free energy of formation (ΔG^0) between P_{SAT} and 1 kbar is significantly less than the effect of temperature from 0 to 100°C. To illustrate this point, values of ΔG^0 of aqueous glycine are plotted in Fig. 5 as a function of temperature at various pressures from P_{SAT} to 5 kbar (depicted as contours). It can be

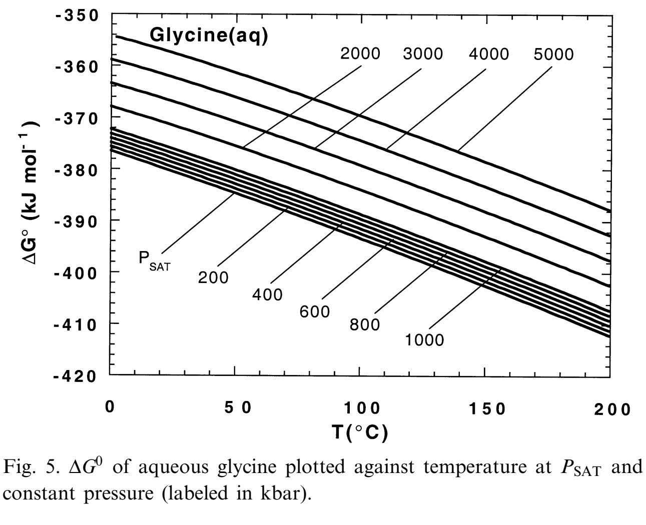

Fig. 5. ΔG^0 of aqueous glycine plotted against temperature at P_{SAT} and constant pressure (labeled in kbar).

seen in this figure that at constant temperature and pressures between P_{SAT} and 1 kbar, values of ΔG^0 differ by <5 kJ mol^{-1}. Conversely, at constant pressure and temperatures between 0 and 100°C, ΔG^0 decreases by ~ 17 kJ mol^{-1}. A change of this magnitude in ΔG^0 for aqueous glycine would require a decrease in pressure from 4 kbar to P_{SAT} at constant temperature. In other words, at most conditions of biological interest, the effect of pressure on ΔG^0 is secondary to that of temperature. Therefore, most thermodynamic properties tabulated in the present communication are calculated as a function of temperature at P_{SAT} rather than as a function of pressure. Nevertheless, in certain environments, the effect of pressure should not be ignored. Indeed, there is no need to make assumptions about pressure effects on the thermodynamic properties of aqueous species or reactions because they can be calculated explicitly with the revised HKF equations of state by integrating the volume with respect to pressure (see below).

Some further examples of the effects of pressure are shown in Fig. 6 for reactions that are introduced above. It can be seen in Fig. 6a that increasing pressure to 1000 bar (approximately equal to the pressure at a depth of 10 km in seawater) has a slight effect on the pH of neutrality. At 100°C, neutral pH decreases from just above 6.1 to just below 6.0 as pressure increases from 1 to 1000 bar. At 100°C, values of ΔG_r^0 for the CO_2 solubility reaction (Fig. 6b) change by ~ 3 kJ mol^{-1} over this same pressure range; those for H_2S (Fig. 6c) and acetic acid (Fig. 6d) dissociation change by ~ 1.5 and ~ 1.0 kJ mol^{-1}, respectively.

This set of examples is included here to emphasize the point that the effects of temperature and, to a lesser degree, pressure on the thermodynamic behavior of compounds involved in metabolic processes are often considerable. Calculating the energetics of metabolic processes such as methanogenesis, sulfur reduction, and acetic acid catabolism, to name only a few, can be accomplished with the standard molal thermodynamic properties of all reactants and products at the temperature and pressure of interest, together with their activities in natural or laboratory systems. Traditionally, bioenergetic calculations are conducted at reference conditions which are misleading at best when attempting to evaluate reaction energetics in high temperature/pressure systems.

4.7. Moving out of the conventional bioenergetic reference frame

Many bioenergetic calculations are carried out with thermodynamic data at reference conditions of 1 atmosphere (atm), 25°C, and with the additional constraint that pH = 7. Although few organisms actually require these environmental conditions, these data are useful when considering the metabolic energy demands of organisms living in near-surface environments where no pressure extrapolation is required, where the variability of temperature has a minimal effect on standard thermodynamic properties,

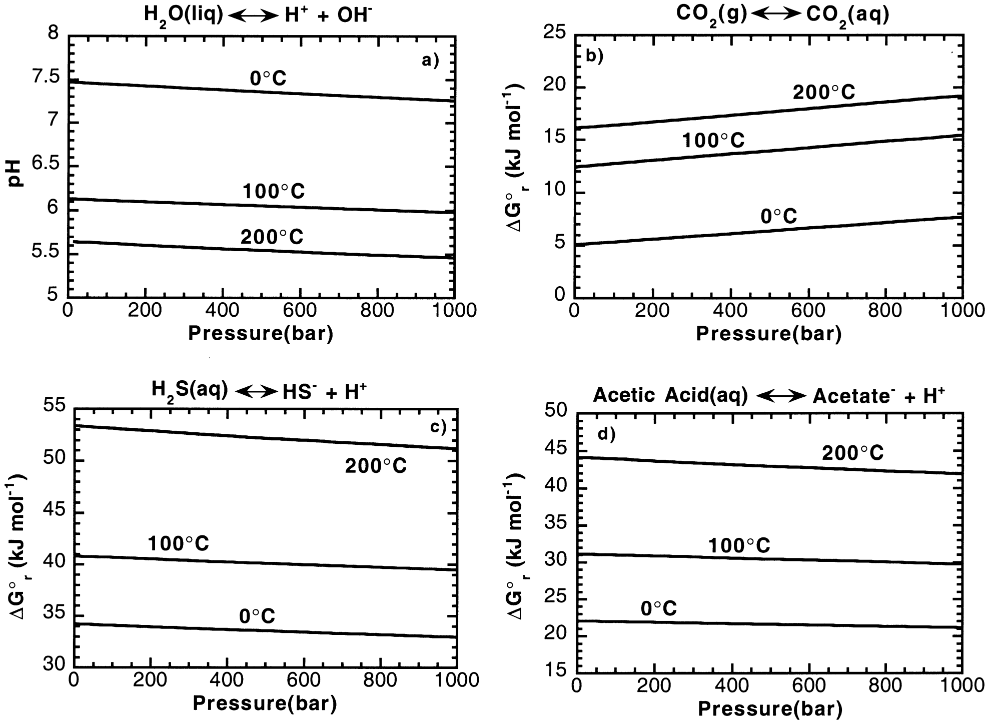

Fig. 6. ΔG_r^0 (or pH) plotted against pressure at 0, 100, and 200°C for the dissociation of H_2O, H_2S, and acetic acid as well as for the solubility of $CO_2(g)$.

and where near-neutral pH can often be assumed for intracellular fluids owing to homeostasis. On the other hand, acidophilic, barophilic, and thermophilic microorganisms require low pH or high pressures or high temperatures, and some require combinations of these factors. From a geochemical, ecological, or environmental perspective, the conventional biological reference frame for energetic calculations can inhibit meaningful insights into how these organisms live.

The problems introduced by the conventional bioenergetic reference frame are far from trivial. As shown above, direct application of 25°C data to the elevated temperatures that many microorganisms require can introduce enormous errors. In addition, many bioenergetic calculations also convert the standard partial molal Gibbs free energy of reaction (ΔG_r^0) into a revised version at pH = 7, indicated as $\Delta G_r^{0\prime}$. This is done by removing the hydrogen ion (H^+) from the standard state adopted for all other aqueous species in the calculation (corresponding to unit activity in a hypothetical 1 molal solution referenced to infinite dilution) and evaluating the free energy contribution of H^+ at an activity of 10^{-7}. This conversion is useful for studying processes inside mammalian cells, as well as comparative studies based on well-controlled laboratory conditions. Arguments in defense of this approach are presented by other investigators [79,80]. However, the adoption of the revised biologic standard state unnecessarily complicates thermodynamic evaluation of the effects of existing natural or laboratory constraints on the bioenergetics of microorganisms. Furthermore, as illustrated above, the pH which corresponds to neutrality depends on pressure and temperature. Therefore, although neutrality may be a useful constraint for applying thermodynamic data in bioenergetic calculations, pH = 7 is not.

Values of neutral pH as a function of temperature are determined from values of the equilibrium constant (K) for the reaction:

$$H_2O(l) \leftrightarrow H^+ + OH^- \quad (2)$$

which in turn are calculated with the relation:

$$\Delta G_r^0 = -2.303RT \log K \quad (3)$$

Values of ΔG_2^0 and neutral pH as a function of temperature are given in Table 3. To facilitate the conversion from ΔG_r^0 to $\Delta G_r^{0\prime}$ and vice versa, the contribution of a_{H^+} to ΔG_r^0 (denoted as G_n) as a function of temperature is explicitly listed in Table 3. This conversion, expressed as:

$$\Delta G_r^{0\prime} = \Delta G_r^0 + \upsilon_{H^+} G_n \quad (4)$$

requires accounting for the stoichiometry of H^+ in the reaction (υ_{H^+}). A sample calculation of the interconversion from the standard state adopted in this study and its biological counterpart is presented in the Appendix.

Another problem which plagues bioenergetic calculations does not involve the adoption of standard states, but rather confusion about the difference between standard state properties and the overall thermodynamic properties of reactions. It appears to be fairly common practice to use standard state Gibbs free energies to argue whether a reaction can provide energy without bringing in any other environmental constraints. These arguments contravene thermodynamics. It is impossible to tell from the sign of ΔG_r^0 which way a reaction will proceed, unless all of the chemical species in the chemical process of interest are already in their standard states. This can be the case for pure solids, but is generally not the case for aqueous solutes or gases. The direction in which a reaction involving aqueous solutes or gases will proceed can only be determined from the overall Gibbs free energy after evaluating the activities of all of the chemical species in the reaction. If this was not the case, then there would be no need to make chemical analyses of natural or laboratory aqueous systems. The overall Gibbs free energy of a reaction (ΔG_r) can be calculated from the familiar expression:

$$\Delta G_r = \Delta G_r^0 + RT \ln Q_r \quad (5)$$

where ΔG_r^0 is as defined above, R and T represent the gas constant and temperature (K), respectively, and Q_r denotes the activity product. Values of Q_r required to evaluate ΔG_r with Eq. 5 can be determined from the relation:

$$Q_r = \prod a_i^{\upsilon_{i,r}} \quad (6)$$

where a_i stands for the activity of the ith species, and $\upsilon_{i,r}$ represents the stoichiometric reaction coefficient of the ith species in reaction r, which is negative for reactants and positive for products. In the case of gases, activity is replaced by fugacity of the species, f_i.

It is the term on the left hand side of Eq. 5, ΔG_r, which determines how a reaction will proceed. Indeed, relying on the sign of the first term on the right hand side of this expression, ΔG_r^0, can be very misleading as illustrated by the example of anaerobic acetic acid oxidation represented by:

$$CH_3COOH(aq) + 2H_2O(l) \rightarrow 2CO_2(g) + 4H_2(g) \quad (7)$$

At 100°C and P_{SAT}, ΔG_7^0 is positive, and equal to 35.9 kJ mol^{-1}. In shallow hot spring systems, such as those in the Aeolian Islands of Italy, the activity product, Q_7, at the

Table 3
The values of ΔG_r^0, $pH_{neutral}$, and G_n for the water dissociation reaction $H_2O(l) = H^+ + OH^-$

T (°C)	2	18	25	37	45	55	70	85	100	115	150	200
ΔG_r^0	78.25	79.34	79.89	80.90	81.63	82.59	84.13	85.78	87.55	89.42	94.22	102.21
$pH_{neutral}$	7.43	7.12	7.00	6.82	6.70	6.58	6.41	6.26	6.13	6.02	5.82	5.64
G_n	−39.13	−39.67	−39.95	−40.45	−40.82	−41.30	−42.07	−42.89	−43.78	−44.71	−47.11	−51.11

prevailing environmental conditions ($a_{CH_3COOH} = 3\times10^{-6}$; $f_{CO_2} = 2.8\times10^{-2}$; $f_{H_2} = 4.8\times10^{-5}$ [46,81]) is equal to 1.39×10^{-15}. These values of ΔG^0_7 and Q_7 combined in Eq. 5 yield a negative value of ΔG_7 equal to -70.2 kJ mol^{-1}. Therefore, at the actual environmental conditions, Reaction 7 is energy-yielding (exergonic); i.e., the value of ΔG_7 is negative, even though that of ΔG^0_7 is positive.

The energetics of overall autotrophic and heterotrophic reactions discussed below are grouped by chemical system starting with simple systems such as H–O and H–O–N and proceeding to more complex systems involving organic compounds, metal ions, minerals, and multiple oxidation states of sulfur. In each system, we tabulate values of ΔG^0 at various temperatures (T) for individual solids, gases, and aqueous species, which are calculated from:

$$\Delta G^0 = \Delta G^0_f - S^0_{T_rP_r}(T-T_r) + \int_{T_r}^{T} C^0_P \mathrm{d}T - T\int_{T_r}^{T} C^0_P \mathrm{d}\ln T + \int_{P_r}^{P} V^0 \mathrm{d}P \quad (8)$$

where ΔG^0_f stands for the standard partial molal Gibbs free energy of formation from the elements at the reference temperature (T_r) and pressure (P_r) of 298.15 K and 1 bar, $S^0_{T_rP_r}$ represents the standard partial molal entropy at the reference conditions, and $C_P{}^0$ and V^0 designate the standard partial molal isobaric heat capacity and volume, respectively. Evaluating the integrals in Eq. 8 is accomplished with the revised-HKF equation of state (see Appendix). The advantage of this approach is that values of ΔG^0 can be summed directly to obtain ΔG^0_r without having to evaluate thermodynamic properties of the elements as functions of temperature and pressure (besides, they cancel across any balanced chemical reaction).

4.8. *Coupled and linked redox reactions*

Microorganisms have developed the means to take advantage of an enormous variety of redox energy sources. As a result, almost every conceivable combination of reduced and oxidized compounds are linked by organisms in overall metabolic processes. Although the biochemical pathways of electron transfer can be quite complicated, mediated by enzymes, and are in many cases unknown, it is useful to break down overall reactions into their constituent redox steps. This can be illustrated by writing half-cell reactions that explicitly include electrons (e^-) such as:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O(l) \quad (9)$$

which is a suitable thermodynamic representation of nitrate reduction to nitrite. This expression would be particularly useful when considering the process going on at an electrode (a cathode) where nitrate is reduced as electrons enter a solution. Half-cell reactions can be combined into coupled redox reactions by conserving electrons; in this case by combining Reaction 9 with:

$$H_2(aq) \rightarrow 2H^+ + 2e^- \quad (10)$$

to yield:

$$NO_3^- + H_2(aq) \rightarrow NO_2^- + H_2O(l) \quad (11)$$

Reaction 11 represents the coupled process of nitrate reduction to nitrite and H_2 oxidation to water, and does not explicitly involve electrons even though electrons are transferred in the actual overall reaction.

This sort of representation is particularly useful because the source of electrons in microbial reactions may or may not be known. For example, in the case of an autotroph that gains energy from the knallgas reaction:

$$H_2(aq) + 0.5O_2(aq) \rightarrow H_2O(l) \quad (12)$$

H_2 is the source of electrons used to reduce O_2 to water. However, in the case of a heterotroph, it may only be known that the organism reduces nitrate to nitrite with electrons provided by the oxidation of uncharacterized organic compounds in organic matter (either occurring naturally or from yeast extract or other commonly used constituents of laboratory media). In this case, it may still be useful to consider the energetics of nitrate reduction using Reaction 11 despite the fact that the source of the H_2 is unknown. In fact, H_2 may be a proxy for hydrogen obtained from organic compounds or, for that matter, electrons obtained through partial or complete oxidation of organic carbon. If the organic compound involved is known, then the coupled organic oxidation and nitrate reduction reactions can be obtained by combining Reaction 11 with the H_2-balanced organic oxidation reaction. As an example, oxidation of carbon in formic acid to CO_2:

$$HCOOH(aq) \rightarrow CO_2(aq) + H_2(aq) \quad (13)$$

can be combined with Reaction 11 to yield:

$$HCOOH(aq) + NO_3^- \rightarrow NO_2^- + CO_2(aq) + H_2O(l) \quad (14)$$

Note that this representation of the linked overall redox process of formic acid oxidation and nitrate reduction does not involve $H_2(aq)$ or electrons. Nevertheless, the mechanisms of actual biochemical redox pathways may use H_2, e^-, or both.

In our treatment of coupled and linked redox reactions, we have chosen to tabulate standard Gibbs free energies for reactions that are identified with the metabolism of specific microorganisms. If the actual stoichiometry of the reaction has been demonstrated, or is certain for that organism based on the description in the original literature, those reactions are indicated ‘as written’. ‘Inferred’ is used in cases where there is some ambiguity but a reasonable interpretation of the text leads to the conclusion that the reaction is appropriate. Finally, we also list organisms as using ‘hydrogen from an organic source’ if it is apparent that the source of reductant is

Table 4.1
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for compounds in the system H–O

Compounds	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
O_2(g)	4.69	1.44	0	−2.47	−4.12	−6.20	−9.33	−12.48	−15.64	−18.83	−26.33	−37.20
O_2(aq)	18.82	17.28	16.54	15.18	14.21	12.95	10.95	8.81	6.56	4.19	−1.74	−11.17
H_2O_2(aq)	−130.74	−133.01	−134.02	−135.75	−136.93	−138.40	−140.64	−142.91	−145.21	−147.54	−153.10	−161.31
HO_2^-	−66.61	−67.14	−67.32	−67.57	−67.71	−67.84	−67.96	−68.02	−67.99	−67.91	−67.40	−65.88
H_2O(l)	−235.64	−236.70	−237.18	−238.04	−238.63	−239.39	−240.57	−241.81	−243.08	−244.41	−247.66	−252.69
H_2O(g)	−223.86	−226.82	−228.13	−230.39	−231.90	−233.81	−236.69	−239.59	−243.12	−246.07	−253.04	−263.16
OH^-	−157.39	−157.36	−157.30	−157.14	−157.00	−156.80	−156.44	−156.02	−155.54	−154.99	−153.44	−150.48
H^+	0	0	0	0	0	0	0	0	0	0	0	0
H_2(g)	2.98	0.91	0	−1.57	−2.63	−3.96	−5.97	−8.00	−10.05	−12.12	−17.00	−24.12
H_2(aq)	18.89	18.11	17.72	16.99	16.46	15.76	14.62	13.39	12.08	10.68	7.11	1.33

chosen to be H_2 for convenience. These designations apply to coupled reactions involving H_2, such as Reaction 11, rather than fully linked redox reactions.

5. Energetics of microbial metabolic reactions

Is methanotrophy (the consumption of CH_4) or methanogenesis (the production of CH_4) a viable mode of metabolism in a particular environment? When attempting to isolate from a solfatara a microorganism that uses elemental sulfur, is one likely to find one that oxidizes sulfur to sulfate or one that reduces it to sulfide? In microbial metabolism, acetate is commonly produced as a metabolite, but also consumed as a carbon source; which of these processes is energy-yielding in a particular biotope or growth experiment? In order to answer questions of this type, the overall Gibbs free energies of the appropriate reactions need to be calculated at the temperature, pressure, and chemical composition that obtain in the system of interest. In this section, we present and discuss the standard and overall Gibbs free energies of compounds and reactions in autotrophic and heterotrophic microbial metabolism. Because some prefer to think of reaction energetics in terms of standard potentials, relations between standard Gibbs free energies and standard potentials for oxidation–reduction reactions are also discussed (see Appendix). The focus in this study is on thermophilic Archaea and Bacteria, and thus the thermodynamic properties are computed as a function of temperature. Although the thermodynamic properties for all compounds and reactions given in this review can also be calculated as functions of pressure, those included here are limited to P_{SAT}, unless mentioned otherwise.

In figures depicting solubility and dissociation reactions, temperature is continuous from 0–200°C. However, in most figures and tables, we report values of ΔG^0 and ΔG^0_r at representative temperatures, which were chosen as follows: 2°C, the average temperature of the world's oceans; 18°C, the average temperature of surface ocean waters; 25°C, the accepted standard reference temperature; 37°C, the average body temperature of humans and a temperature at which many thermodynamic properties are measured; 45, 55, and 70°C, three representative growth temperatures in thermophiles; 85, 100, and 115°C, three representative growth temperatures in hyperthermophiles, the last being near the current upper temperature limit for a pure isolate in the laboratory; 150 and 200°C, two temperatures at which hyperthermophilic life may be thriving, although clear laboratory results have yet to confirm this[5]. Values of ΔG^0 or ΔG^0_r at temperatures other than those listed in the present tables can be readily determined to high precision by interpolation. Using finite difference derivatives between the two points on either side of the desired temperature will introduce errors in ΔG^0 on the order of 250 J mol^{-1} or less, which is well within the uncertainties of the accepted values (see also Fig. 5). Extrapolation below 2°C or above 200°C should be avoided, however, as it may yield values of ΔG^0 that differ significantly from those computed with revised HKF equations of state. Thermodynamic calculations at temperatures < 2 or > 200°C can be carried out with the software package SUPCRT92 [73] or ORGANOBIOGEOTHERM[6].

This section is further divided into subsections. We start with the energetics of overall metabolic processes in the chemical system H–O and note some of the microbes known to catalyze these specific processes (Section 5.1). Section 5.2 deals with compounds and reactions in the chemical system H–O–N, followed sequentially in further subsections by the systems H–O–S, H–O–N–S, H–O–$C_{inorganic}$, H–O–C, H–O–N–C, H–O–S–C, H–O–N–S–$C_{amino\ acid}$, and H–O–S–C–metals/minerals. Section 5.8 covers the inorganic aqueous chemistry in the H–O–P system and demonstrates the need for thermodynamic data as a function of temperature for organo-phosphate compounds. Finally, although various microorganisms gain metabolic energy from Cl-redox reactions, we decided not to include a discussion in the main body of the text,

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[5] Calculations above 100°C are conducted at P_{SAT}, which for 115, 150, and 200°C correspond to 1.70, 4.76, and 15.54 bar, respectively.

[6] Both of these codes are available from Prof. Harold Helgeson at U.C. Berkeley.

Table 4.2
Hydrogen and oxygen metabolic reactions

A1	$H_2(aq)+0.5O_2(aq) \leftrightarrow H_2O(l)$
A2	$H_2O_2(aq)+H_2(aq) \leftrightarrow 2H_2O(l)$

because there are currently no known thermophiles that mediate these processes (J.D. Coates, 1999, personal communication). Instead, we provide standard Gibbs free energies for Cl-containing (and other halogen-containing) compounds and redox reactions, and identify mesophilic microorganisms responsible for their catalysis, in the Appendix.

5.1. The H–O system

Aquifex pyrophilus, a hyperthermophile isolated from hot marine sediments at the Kolbeinsey Ridge, Iceland [82], and other species among the Aquificales gain metabolic energy by reducing oxygen (or oxidizing hydrogen) and forming water via:

$$H_2 + 0.5O_2 \rightarrow H_2O \tag{15}$$

Values of ΔG_r^0 for this reaction can be calculated from those of ΔG^0 for O_2, H_2 and H_2O listed in Table 4.1 consistent with:

$$\Delta G_r^0 = \sum_i \upsilon_{i,r} \Delta G^0 \tag{16}$$

The value of ΔG_r^0 will depend on whether the reaction is written to include gases ($H_2(g)$, $O_2(g)$) or aqueous species ($H_2(aq)$, $O_2(aq)$), liquid H_2O ($H_2O(l)$), or water vapor ($H_2O(v)$). Values of ΔG^0 for all of these chemical species are given in Table 4.1. Other values of ΔG^0 from Table 4.1 allow evaluation of ΔG_r^0 with Eq. 16 for the dissociation of H_2O (Reaction 2), as well as reactions (A1)[7]and (A2) in Table 4.2, and other reactions that may be of interest in microbial metabolism. Values of ΔG_r^0 for the reactions in Table 4.2, calculated with Eq. 16 and consistent with data in Table 4.1 are listed in Table 4.3. These are followed, in Table 4.4, with an inventory of the microorganisms which are known to use these reactions in their overall metabolic processes. For example, besides *A. pyrophilus*, at least two dozen other species of microorganisms are known to gain metabolic energy by mediating Reaction 15.

Combining values of ΔG_r^0 from Table 4.3 with those of Q_r, calculated with compositional constraints on the reactants and products from natural systems or laboratory experiments, allows evaluation of ΔG_r in accord with Eq. 5, which corresponds to the amount of energy available from the environment for the overall reaction used in metabolism. In the case of *A. pyrophilus*, concentration data on H_2 and O_2 allow evaluation of ΔG_r for Reaction A1. If these data are from the gas phase, then values of ΔG_r^0 for the reaction involving gases will need to be calculated from data in Table 4.1, or values of ΔG_r^0 for the solubility reactions for H_2 and O_2 from Tables A.3 and A.4 in the Appendix will need to be included with the values of ΔG_r^0 for Reaction A1 in Table 4.3.

The following example should help to illustrate this point, which may be useful for converting values of ΔG_r^0 listed in these tables to values appropriate for a specific application. Converting ΔG_r^0 from Table 4.3 for Reaction A1:

$$0.5O_2(aq) + H_2(aq) \leftrightarrow H_2O(l) \tag{A1}$$

to that for:

$$0.5O_2(g) + H_2(g) \leftrightarrow H_2O(l) \tag{17}$$

is accomplished by adding $\frac{1}{2}\Delta G_r^0$ for:

$$O_2(g) \leftrightarrow O_2(aq) \tag{G2}$$

and ΔG_r^0 for:

$$H_2(g) \leftrightarrow H_2(aq) \tag{G1}$$

from Table A.4 in the Appendix. Therefore, using values of ΔG_r^0 from the tables in this review:

$$\Delta G_{17}^0 = \Delta G_{A1}^0 + \tfrac{1}{2}\Delta G_{G2}^0 + \Delta G_{G1}^0 \tag{18}$$

At 100°C, ΔG_{A1}^0 from Table 4.3 is -258.44 kJ mol^{-1}, those for Reactions G2 and G1 from Table A.4 are 22.13 kJ mol^{-1} and 22.20 kJ mol^{-1}, respectively, and the corresponding value for Reaction 17 is -225.2 kJ mol^{-1}, which can also be calculated directly with the values in Table 4.1 (thereby illustrating a point about internal consistency of data).

In continental or shallow submarine hot springs where species of *Aquifex* are found, concentrations of $H_2(aq)$ and $O_2(aq)$ can be at or below the equilibrium saturation values[8]. Activities consistent with these concentrations in near-surface environments are likely to fall in the ranges used to construct the plots in Fig. 7, which show contours of the overall Gibbs free energy for Reaction A1 (ΔG_{A1}) at 25, 55, 100, and 150°C. The slopes of these contours are dictated by the stoichiometry of Reaction A1. By comparing these four plots it can be seen that the value of ΔG_{A1} becomes less negative with increasing temperature if the activities of H_2 and O_2 are held constant[9].

As an example, we can calculate the value of ΔG_{A1} with Eq. 5 for a shallow hot spring in the Baia di Levante on the island of Vulcano, Italy, close to the site of isolation

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[7] Two different numbering systems for reactions are used throughout this review. Arabic numerals are used to denote reactions introduced in the text, and capital letters followed by Arabic numerals represent reactions listed in tables.

[8] In some cases supersaturation of aqueous solutions with gases is possible if they are rapidly cooled, but nucleation of gas bubbles is a relatively rapid process in natural systems.

[9] Methods for calculating activities from concentration data are summarized in the Appendix.

Table 4.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 4.2

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
A1	−263.94	−263.45	−263.17	−262.62	−262.20	−261.63	−260.67	−259.60	−258.44	−257.18	−253.90	−248.44
A2	−359.43	−358.50	−358.07	−357.31	−356.80	−356.14	−355.13	−354.10	−353.03	−351.95	−349.34	−345.40

for *Aquifex aeolicus* [83]. The reported temperature and partial pressure of hydrogen gas (P_{H_2}) of this spring are 98°C and 4.8×10^{-5} bar, respectively [81]. The corresponding activity of H_2 (3.80×10^{-8}), required to evaluate Q_{A1}, was computed from the equilibrium constant at 98°C and 1 bar of the H_2 dissolution Reaction G1; the activity of O_2 (1.64×10^{-4}) was assumed to be in equilibrium with $O_2(g)$ in the atmosphere. The value of Q_{A1} (2.05×10^9) determined with Eq. 6 was combined in Eq. 5 with the value of ΔG_{A1}^0 (−258.60 kJ mol^{-1}) at 98°C and 1 bar to yield ΔG_{A1} (−192.44 kJ mol^{-1}). This calculation shows that 192.44 kJ per mol of $H_2(g)$ consumed is the maximum amount of energy available to *A. aeolicus* or any other hyperthermophile catalyzing the knallgas reaction in this hot spring on Vulcano.

5.2. *The H–O–N system*

In the absence of sufficient free oxygen, denitrifiers, including the thermophiles *A. pyrophilus*, *Thermothrix thiopara*, and *Pyrobaculum aerophilum*, as well as other groups of facultative anaerobes may switch from aerobic to anaerobic respiration using NO_3^- as the terminal electron acceptor. Other microbes carrying out NO_3^- reduction are obligate anaerobes, unable to pursue aerobic respiration. However, NO_3^- is not the only *N*-bearing compound involved in microbial metabolism. The biochemical cycling of nitrogen among its various inorganic forms involves +5, +3, +2, +1, 0, and −3 oxidation states more familiar as NO_3^-, NO_2^-, NO, N_2O, N_2, and NH_3. Values of ΔG^0 at various temperatures between 0 and 200°C for these compounds as gases or dissolved ions and associated forms, as appropriate, are listed in Table 5.1. Eleven reactions known to be involved in microbial metabolism are listed in Table 5.2, and the locations of each of these reactions in the biogeochemical cycle of nitrogen are shown in Fig. 8. It can be seen in this figure that five of the overall reactions (B1, B4, B5, B7, and B8) involve the transfer of only one or two electrons, but the others involve the transfer of as many as three (Reactions B6, B9, and B11), five (Reaction B2), six (Reaction B10), and even eight electrons (Reaction B3). Values of ΔG_r^0 as a function of temperature for these reactions are listed in Table 5.3.

Among the thermophilic microbes, *A. pyrophilus*, which can gain metabolic energy from the knallgas reaction as discussed above, also mediates the reduction of NO_3^- and NO_2^- represented by Reactions (B1), (B2), and (B6) [82]. Similarly, the anaerobic hyperthermophile *Ferroglobus placidus*, isolated from a shallow submarine hydrothermal system on the island of Vulcano, Italy, catalyzes the conversion of NO_3^- to NO_2^- (Reaction B1) and NO_2^- to NO (Reaction B5) [84]. Several other microbes responsible for mediating the reactions given in Table 5.2 are listed in Table 5.4.

Analogous to the approach described for the H–O system above, values of ΔG_r in the H–O–N system can be evaluated by combining values of ΔG_r^0 from Table 5.3 with those of Q_r calculated with compositional data on the reactants and products in the geochemical or laboratory environment of interest. Activities of NO_3^-, NO_2^-, and H_2 likely to be encountered in hot springs where *A. pyrophilus* and *F. placidus* can be found are in the ranges depicted in Figs. 9–11. In order to accommodate the three compositional variables (H_2, NO_3^-, and NO_2^-) in two-dimensional plots, three sets of figures at four temperatures (25, 55, 100, and 150°C) were constructed, each set evaluated at a different value of H_2 activity (10^{-3} in Fig. 9, 10^{-5} in Fig. 10, and 10^{-7} in Fig. 11). In these figures, values of ΔG_{B1} at the four temperatures are shown as contours. As in the example for the knallgas reaction discussed above, the slopes of the contour lines in Figs. 9–11 are set by the stoichiometry of reaction (B1). It can be seen in these figures that ΔG_{B1} increases with increasing temperature at constant activities of NO_3^-, NO_2^-, and H_2.

The reactions listed in Table 5.2 are limited to those that can be linked to specific microorganisms. Thus, this table is limited by our ignorance about novel metabolic pathways rather than by reactions that are thermodynamically and geochemically plausible as energy sources for thermophiles and hyperthermophiles. As an example, many hot springs have concentrations of ammonium and nitrate that

Table 4.4
Microorganisms that use the hydrogen and oxygen reactions specified in Table 4.2

Reaction	
A1	*Acidovorax delafieldii*, *Acidovorax facilis*, *Alcaligenes xylosoxidans*, *Ancylobacter aquaticus*, *Hydrogenophaga palleronii*, *Pseudomonas hydrogenovora*, *Xanthobacter autotrophicus* [379], *P. fumarii* [9] *Sulfolobus acidocaldarius*, *Sulfolobus solfataricus*, *Sulfolobus shibatae*, *A. brierleyi*, *A. infernus*, *M. sedula* [293] *Bacillus schlegelii* [189] *Hydrogenobacter halophilus* [225] *Hydrogenophilus thermoluteolus* [228,229] *Calderobacterium hydrogenophilum* [195], *M. prunae* [296], *Hydrogenobacter thermophilus* [226], *P. aerophilum* [345], *A. pyrophilus* [82], *Hydrogenobacter acidophilus* [224], *Sulfurospirillum arcachonense* [380]
A2	*Acetobacter peroxidans* [381]

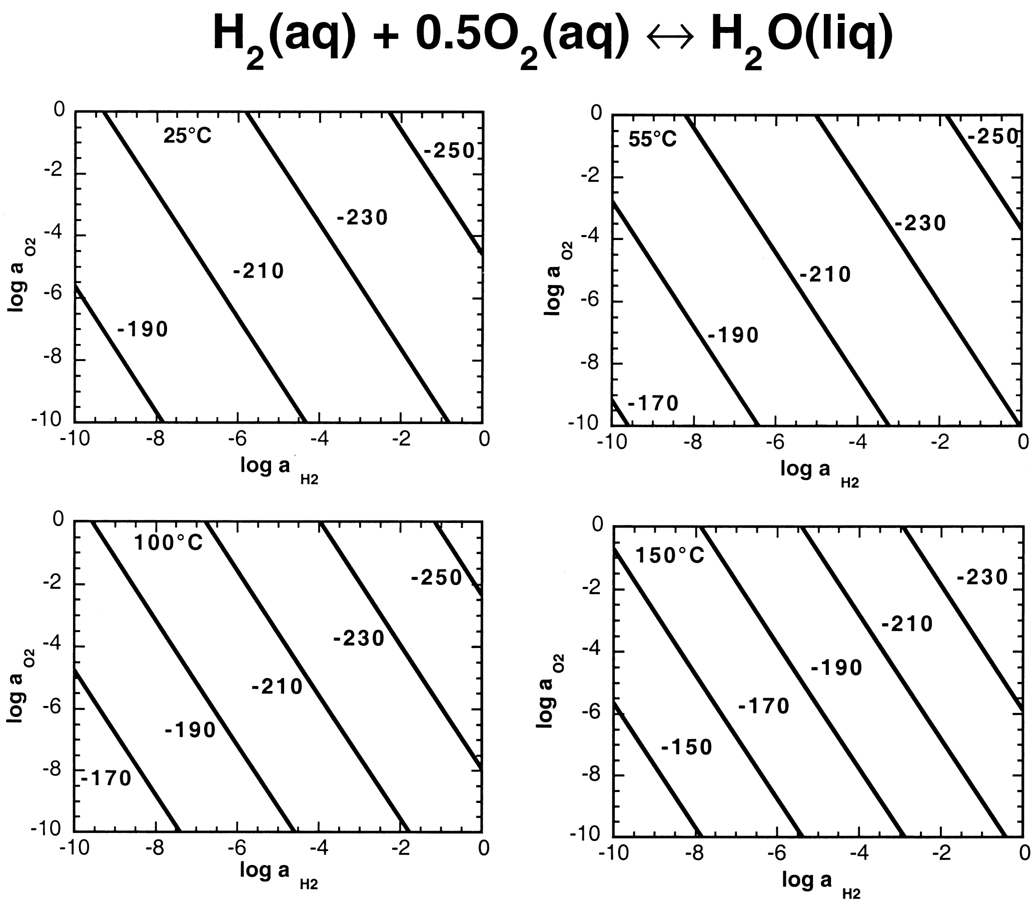

Fig. 7. Plots of ΔG_r (represented as solid contours) at P_{SAT} and 25, 55, 100, and 150°C for Reaction A1 as a function of log a_{O_2} and log a_{H_2}. The activity of $H_2O(l)$ is taken to be unity.

are out of equilibrium with respect to the reaction:

$$1.25NH_4^+ + 0.75NO_3^- \rightarrow N_2(aq) + 0.5H^+ + 2.25H_2O(l) \qquad (19)$$

It follows that it is plausible that an organism may exist that can obtain metabolic energy by combining ammonium and nitrate to form nitrogen. If so, this metabolism would also tend to acidify the environment, or be affected by changes in pH brought about by other coexisting organisms. In fact, Reaction 19 was proposed more than two decades ago as a metabolic process in chemosynthetic mi-

Table 5.1
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for compounds in the system H–O–N

Compounds	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
NO_3^-	−107.45	−109.87	−110.91	−112.66	−113.81	−115.24	−117.35	−119.44	−121.49	−123.52	−128.14	−134.30
$HNO_3(aq)$	−99.44	−102.23	−103.47	−105.64	−107.10	−108.94	−111.75	−114.61	−117.52	−120.47	−127.53	−138.03
NO_2^-	−29.28	−31.35	−32.22	−33.67	−34.62	−35.79	−37.49	−39.15	−40.77	−42.35	−45.84	−50.29
$HNO_2(aq)$	−47.53	−49.68	−50.63	−52.26	−53.36	−54.74	−56.84	−58.95	−61.09	−63.26	−68.40	−75.98
$NO(g)$[a]	91.39	88.04	86.57	84.03	82.33	80.20	76.99	73.75	70.50	67.23	59.53	48.38
$NO(aq)$[b]	104.56	102.87	102.06	100.58	99.53	98.15	95.98	93.67	91.25	88.72	82.46	72.77
$N_2O(g)$[a]	109.22	105.73	104.20	101.55	99.78	97.55	94.18	90.78	87.36	83.91	75.78	63.94
$N_2O(aq)$[c]	115.84	114.18	113.38	111.90	110.86	109.48	107.27	104.91	102.41	99.78	93.20	82.83
$N_2(g)$	4.38	1.34	0	−2.31	−3.85	−5.79	−8.72	−11.66	−14.63	−17.61	−24.63	−34.82
$N_2(aq)$	20.15	18.84	18.18	16.98	16.12	14.99	13.18	11.24	9.19	7.02	1.55	−7.19
$NH_3(g)$	−12.06	−15.11	−16.45	−18.77	−20.33	−22.28	−25.23	−28.20	−31.20	−34.23	−41.36	−51.76
$NH_3(aq)$	−24.30	−25.96	−26.71	−28.02	−28.92	−30.06	−31.82	−33.63	−35.50	−37.42	−42.08	−49.17
NH_4^+	−76.96	−78.68	−79.45	−80.81	−81.72	−82.89	−84.68	−86.50	−88.37	−90.28	−94.86	−101.70

[a] See Table A.2 in the Appendix for thermodynamic properties.

[b] Obtained using the ΔG_r^0 values for $NO(g) \leftrightarrow NO(aq)$ from Plyasunov et al. (2000) [382] together with the value of ΔG^0 for NO(g) tabulated here.

[c] Obtained using the ΔG_r^0 values for $N_2O(g) \leftrightarrow N_2O(aq)$ from Plyasunov et al. (2000) [382] together with the value of ΔG^0 for $N_2O(g)$ tabulated here.

Table 5.2
Inorganic nitrogen metabolic reactions

B1	$NO_3^- + H_2(aq) \leftrightarrow NO_2^- + H_2O(l)$
B2	$NO_3^- + 2.5H_2(aq) + H^+ \leftrightarrow 0.5N_2(aq) + 3H_2O(l)$
B3	$NO_3^- + 4H_2(aq) + H^+ \leftrightarrow NH_3(aq) + 3H_2O(l)$
B4	$NO_2^- + 0.5O_2(aq) \leftrightarrow NO_3^-$
B5	$NO_2^- + 0.5H_2(aq) + H^+ \leftrightarrow NO(aq) + H_2O(l)$
B6	$NO_2^- + 1.5H_2(aq) + H^+ \leftrightarrow 0.5N_2(aq) + 2H_2O(l)$
B7	$NO(aq) + 0.5H_2(aq) \leftrightarrow 0.5N_2O(aq) + 0.5H_2O(l)$
B8	$0.5N_2O(aq) + 0.5H_2(aq) \leftrightarrow 0.5N_2(aq) + 0.5H_2O(l)$
B9	$0.5N_2(aq) + 1.5H_2(aq) \leftrightarrow NH_3(aq)$
B10[a]	$NH_3(aq) + 1.5O_2(aq) \leftrightarrow H^+ + NO_2^- + H_2O(l)$
B11	$NH_3(aq) + NO_2^- + H^+ \leftrightarrow N_2(aq) + 2H_2O(l)$

[a] Drozd (1976) [383] and Suzuki et al. (1974) [384] note that NH_3, rather than NH_4^+, may be the substrate transferred across the cellular membranes.

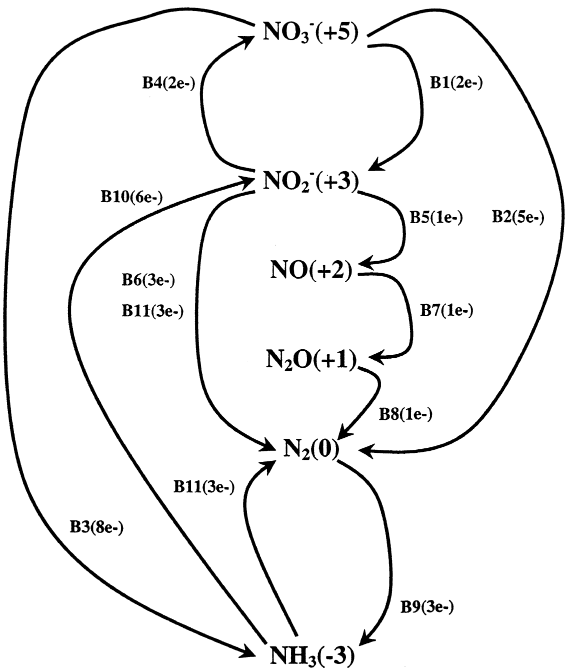

Fig. 8. Schematic of the microbial nitrogen redox cycle. The numbers in parentheses next to the species represent the oxidation state of N; the labels next to the reaction arrows denote the reaction listed in Table 5.2 and the number of electrons transferred in the process.

crobes [85], but it has never been observed. Recently, Strous et al. (1999) [86], described the cultivation of an organism able to metabolize a process very similar to Reaction 19, namely the anaerobic oxidation of ammonia to nitrogen using nitrite as the electron acceptor (reaction B11). This reaction too had been expected but went undetected for decades.

5.3. The H–O–S system

The ghastly stench of hydrogen sulfide is instantly familiar to anyone who has ever stepped foot on the island of Vulcano, north of Sicily or visited the Phlegrean solfatara near Naples, Italy. It is also unforgettable to anyone who has ever cultured a sulfur reducer such as *Pyrodictium, Acidianus, Thermococcus, Pyrococcus*, or *Desulfurococcus*, to name only a few. H_2S, in which sulfur is in the −2 oxidation state (S_{ox}), is only one of several familiar forms of inorganic sulfur. The others include SO_4^{2-}, SO_3^{2-}, and S, in which S_{ox} equals +6, +4, and 0, respectively. In addition, less common sulfur compounds exhibit a wide variety of other oxidation states. Of note in this regard are sulfur compounds with two or more S atoms, some of which have fractional nominal oxidation states. These compounds include the following, in decreasing order of S_{ox}, as well as their associated protonated forms: $S_2O_8^{2-}$ ($S_{ox} = +7$), $S_2O_6^{2-}$ ($S_{ox} = +5$), $S_2O_5^{2-}$ ($S_{ox} = +4$), $S_3O_6^{2-}$ ($S_{ox} = +3\frac{1}{3}$), $S_2O_4^{2-}$ ($S_{ox} = +3$), $S_4O_6^{2-}$ ($S_{ox} = +2\frac{1}{2}$), $S_2O_3^{2-}$ ($S_{ox} = +2$), $S_5O_6^{2-}$ ($S_{ox} = +2$), S_5^{2-} ($S_{ox} = -\frac{2}{5}$), S_4^{2-} ($S_{ox} = -\frac{1}{2}$), S_3^{2-} ($S_{ox} = -\frac{2}{3}$), S_2^{2-} ($S_{ox} = -1$). This wealth of oxidation state possibilities is represented by the 27 sulfur compounds for which values of ΔG^0 are listed in Table 6.1, and leads to a complex inorganic sulfur cycle much of which is mediated by microbes. As an example, 22 reactions known to be conducted by microbes are listed in Table 6.2, and corresponding values of ΔG_r^0 are given in Table 6.3. It should be recognized that hundreds of other sulfur redox reactions are possible.

In addition to simple redox reactions among pairs of compounds, several of the reactions listed in Table 6.2 involve disproportionation of sulfur among various oxida-

Table 5.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 5.2

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
B1	−176.36	−176.29	−176.21	−176.05	−175.90	−175.70	−175.34	−174.92	−174.44	−173.91	−172.49	−170.01
B2	−636.62	−636.09	−635.85	−635.45	−635.18	−634.84	−634.34	−633.84	−633.35	−632.88	−631.86	−630.69
B3	−699.32	−698.63	−698.23	−697.44	−696.85	−696.03	−694.68	−693.18	−691.56	−689.82	−685.39	−678.26
B4	−87.58	−87.17	−86.96	−86.57	−86.30	−85.92	−85.33	−84.68	−84.00	−83.27	−81.42	−78.43
B5	−111.24	−111.53	−111.76	−112.28	−112.71	−113.33	−114.41	−115.68	−117.10	−118.68	−122.92	−130.30
B6	−460.25	−459.80	−459.64	−459.40	−459.27	−459.14	−459.00	−458.92	−458.91	−458.97	−459.37	−460.68
B7	−173.90	−173.19	−172.82	−172.15	−171.65	−170.98	−169.95	−168.82	−167.63	−166.37	−163.25	−158.36
B8	−175.11	−175.08	−175.05	−174.98	−174.92	−174.82	−174.65	−174.44	−174.19	−173.92	−173.21	−172.02
B9	−62.70	−62.55	−62.38	−61.99	−61.67	−61.19	−60.34	−59.34	−58.21	−56.94	−53.53	−47.57
B10	−268.85	−268.01	−267.50	−266.46	−265.66	−264.55	−262.66	−260.54	−258.19	−255.63	−248.81	−237.06
B11	−397.55	−397.25	−397.25	−397.40	−397.60	−397.95	−398.66	−399.58	−400.71	−402.03	−405.85	−413.11

Table 5.4
Microorganisms that use the nitrogen reactions specified in Table 5.2

Reaction	
B1	**As written**: *F. placidus* [84], *A. pyrophilus* [82], *Veillonella alcalescens*, *Micrococcus denitrificans*, *Thiobacillus denitrificans* [6] **Inferred**: *B. schlegelii* [189] *C. hydrogenophilum* [195] **Hydrogen from an organic source:** *Pseudomonas* strain MT-1 [385], *Silicibacter lacuscaerulensis* [386], *P. aerophilum* [345], *Thermothrix thioparus* [277,278], *Clostridium perfringens*, *Aerobacter aerogenes*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Pseudomonas denitrificans*, *Spirillum itersoni*, *Selenomonas ruminantium* [6]
B2	**As written:** *A. pyrophilus* [82], *M. denitrificans*, *T. denitrificans* [6] **Hydrogen from an organic source:** *P. aerophilum* [345], *T. thioparus* [277,278], *C. perfringens*, *P. aeruginosa*, *P. denitrificans* [6]
B3	**As written:** *Ammonifex degensii* [187], *P. fumarii* ([9], *V. alcalescens* [6]
B4	**As written:** *Nitrobacter*, *Nitrospina*, *Nitrococcus* [387]
B5	**As written:** *F. placidus* [84], *M. denitrificans*, *T. denitrificans* [6] **Hydrogen from an organic source:** *T. thioparus* [277,278], *C. perfringens*, *P. aeruginosa*, *P. denitrificans* [6]
B6	**As written:** *A. pyrophilus* [82], *M. denitrificans*, *T. denitrificans* [6], **Hydrogen from an organic source:** *T. thioparus* [277,278], *C. perfringens*, *P. aeruginosa*, *P. denitrificans* [6]
B7	**As written:** *M. denitrificans*, *T. denitrificans* [6] **Hydrogen from an organic source:** *T. thioparus* [277,278], *C. perfringens*, *P. aeruginosa*, *P. denitrificans* [6]
B8	**As written:** *M. denitrificans*, *T. denitrificans* [6] **Hydrogen from an organic source:** *T. thioparus* [277,278], *C. perfringens*, *P. aeruginosa*, *P. denitrificans* [6]
B9	**As written:** *Methanosarcina barkeri* [388], *Desulfovibrio gigas*, *Desulfovibrio vulgaris*, *Desulfovibrio desulfuricans*, *Desulfovibrio salexigens* [389], *Desulfovibrio africanus* [389,390], *Desulfovibrio baculatus* [390]
B10	**As written:** *Nitrosococcus*, *Nitrosomonas*, *Nitrosospira*, *Nitrosovibrio* [387], *Nitrosolobus* [391]
B11	**As written:** *Planctomycete* [85,86,392]

tion states. As an example, thiosulfate, $S_2O_3^{2-}$, can disproportionate to SO_4^{2-} and H_2S (reaction C8). As long as the products are produced in equal proportions, the overall oxidation state of sulfur does not change during the reaction. However, the nominal oxidation state of each of the sulfur atoms in $S_2O_3^{2-}$ ($S_{ox} = +2$) changes to +6 (SO_4^{2-}) or −2 (H_2S) as the reaction proceeds. Although Reaction (C8) does not contain H_2 or O_2, both reduction and oxidation occur as the reaction proceeds. Other sulfur disproportionation reactions listed in Table 6.2 include (C2), (C4), (C6), (C7), (C9), (C11), (C13), and (C17). Many of the microorganisms known to catalyze the reactions listed in Table 6.2 are given in Table 6.4.

As noted above, numerous thermophiles and hyperthermophiles gain metabolic energy by oxidizing or reducing sulfur compounds. One of these is *Pyrodictium occultum*, a hyperthermophilic chemolithoautotrophic Archaeon isolated from shallow marine hot springs in the Baia di Levante on Vulcano, Italy [47]. *P. occultum* was the first organism in pure culture able to grow at temperatures above 100°C, gaining metabolic energy by reducing elemental sulfur with H_2 and producing H_2S (Reaction C19). Several other genera of thermophiles and hyperthermophiles (see Table 6.4), both autotrophic and heterotrophic, include species that are known to catalyze this reduction reaction, including *Acidianus*, *Thermococcus*, *Pyrococcus*, *Hyperthermus*, *Pyrobaculum*, *Thermoplasma*, and *Staphylothermus*.

Values of ΔG_{C19} as functions of a_{H_2} and a_{H_2S} representative of many hydrothermal systems are shown in Fig. 12. These values were calculated at 25, 55, 100, and 150°C with Eq. 5 as described above. It can be seen in Fig. 12 that at constant values of a_{H_2S}, values of ΔG_{C19} decrease with increasing values of a_{H_2} at any temperature investigated; the decrease of ΔG_{C19} is more precipitous at high rather than at low temperatures. In other words, values of ΔG_{C19} increase with increasing temperature at low values of a_{H_2}, but decrease with increasing temperature at higher values of a_{H_2}. Conversely, at constant values of a_{H_2}, values of ΔG_{C19} increase with increasing values of a_{H_2S} at any temperature investigated, increasing more dramatically at high than at low temperatures. The net effect of the complex dependence of ΔG_{C19} on temperature, a_{H_2}, and a_{H_2S} is that organisms such as *P. occultum* can obtain the most metabolic energy from Reaction (C19) at high temperatures, high activities of H_2, and low activities of H_2S. The lowest amount of energy is available at high temperatures, high activities of H_2S, and low activities of H_2. Observations of this type, coupled with appropriate chemical analyses, should help to explain the occurrence of *P. occultum* in some hydrothermal systems but not in others.

5.4. The H–O–N–S system

Metabolic processes are discussed above in which the reduction (by H_2) and oxidation (by O_2) of various nitrogen (Table 5.2) or sulfur compounds (Table 6.2) provide energy for microorganisms. Additional metabolic processes are known in which the oxidation of sulfur is coupled to the reduction of nitrogen. Five such reactions in which NO_3^- serves as the electron acceptor and thiosulfate, sulfur, or sulfide as the electron donor are listed in Table 6.5; the corresponding values of ΔG_r^0 as a function of temperature are reported in Table 6.6. All five of these reactions are known to be carried out by thermophiles or hyperthermophiles, including, for example, *T. thiopara*, a facultatively anaerobic facultative chemolithoautotroph isolated from a pH-neutral, sulfide-rich, 74°C hot spring in New Mexico. In the laboratory under anaerobic conditions at temperatures between 62 and 77°C, *T. thiopara* can gain metabolic energy from Reactions (C23) and (C25)–(C27). Other microbes experimentally verified to mediate the sulfur–nitrogen redox couples shown in Table 6.5 are listed in Table 6.7, including the hyperthermophiles

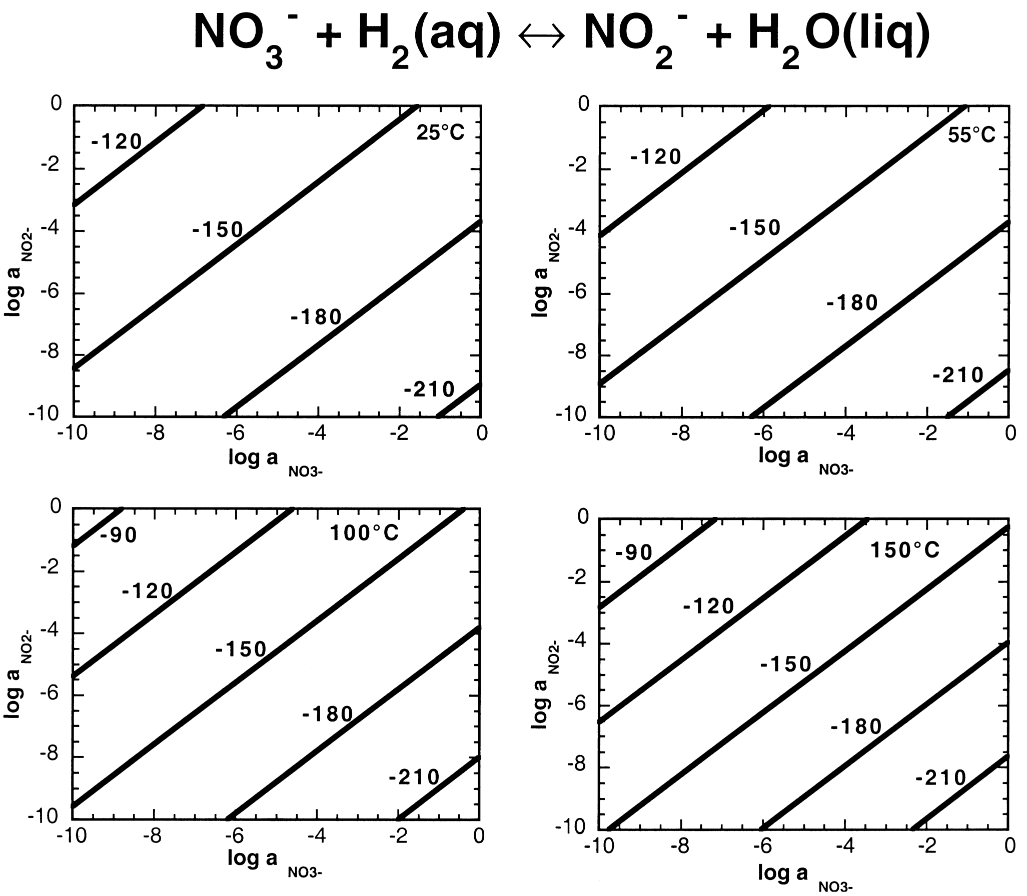

Fig. 9. Plots of ΔG_r (represented as solid contours) at P_{SAT} and 25, 55, 100, and 150°C for Reaction (B1) as a function of log $a_{NO_2^-}$ and log $a_{NO_3^-}$. The activity of $H_2(aq)$ is set at 10^{-3}, and the activity of $H_2O(l)$ is taken to be unity.

Pyrobaculum, *Aquifex*, and *Ferroglobus*. Given the substantial variety in oxidation states of inorganic sulfur and nitrogen compounds, it is very likely that the reactions listed in Table 6.5 are only a subset of the sulfur–nitrogen redox reactions used by microorganisms.

5.5. The H–O–C$_{inorganic}$ system

For the purpose of this review, we have grouped several carbon compounds that can have abiotic sources in the H–O–C$_{inorganic}$ system including CH_4 and hydrogen cyanide (HCN). Values of ΔG^0 as a function of temperature for 'inorganic' carbon species, including several containing N or S, are given in Table 7.1. Nine Reactions among these molecules known to be mediated by microorganisms and values of ΔG_r^0 as a function of temperature for these Reactions are given in Tables 7.2 and 7.3, respectively.

Under aerobic conditions, CO and CH_4 can be oxidized to CO_2 (reactions D4 and D9, respectively) by a variety of organisms including members of the genera *Bacillus*, *Pseudomonas*, *Alcaligenes*, and *Methylococcus*. Reduction (reaction D6) and disproportionation (Reaction D5) of CO producing CH_4 can be mediated by *Methanobacterium*. Some *Thiobacillus thioparus* and *Paracoccus* strains oxidize organosulfur compounds such as carbonyl sulfide or thiocyanate to sulfate and CO_2 (Reactions D2 and D7, respectively) to gain metabolic energy [87]. These strains can also hydrolyze carbonyl sulfide (Reaction D3) and thiocyanate (Reaction D8) yielding H_2S and either CO_2 or OCN^-, respectively [87]. It should be noted that values of ΔG_r^0 over the temperature range considered here (Table 7.3) for the two hydrolysis Reactions are much greater (less negative or even positive) than those of their oxidation counterparts.

Of the reactions listed in Table 7.2, autotrophic methanogenesis from CO_2 and H_2 (Reaction D1) is by far the most common and also one of the best characterized of all metabolic processes in thermophiles [8,88–93]. Species belonging to at least six genera are able to carry out this mode of autotrophic methanogenesis, including a significant number of thermophiles and hyperthermophiles. As an example, *Methanopyrus kandleri*, isolated from heated deep sea sediments in the Guaymas Basin and from a shallow marine hydrothermal system on Iceland [94], grows on metabolic energy gained from reaction (D1) at temperatures up to 110°C. Many microorganisms respon-

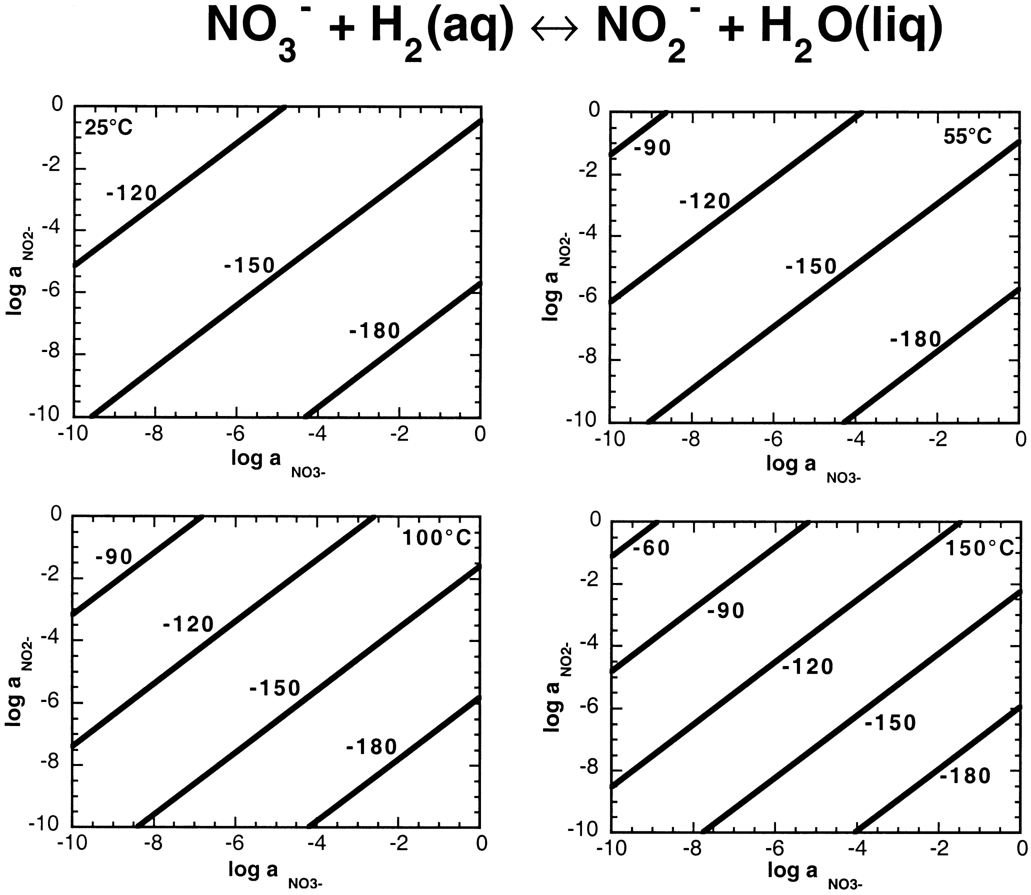

Fig. 10. Same as for Fig. 9, except that the activity of $H_2(aq)$ is set at 10^{-5}.

sible for conducting the reactions given in Table 7.2 are listed in Table 7.4.

Values of the overall Gibbs free energy for autotrophic methanogenesis from CO_2 (ΔG_{D1}) were calculated in accord with Eq. 5 at 25, 55, 100, and 150°C and are shown in Figs. 13–15. In these figures, constructed for activities of H_2 equal to 10^{-3} (Fig. 13), 10^{-5} (Fig. 14), and 10^{-7} (Fig. 15), values of ΔG_{D1} are depicted as contours relative to the activities of CH_4 and CO_2 that range from 10^{-10} to 0. It can be seen in these figures that ΔG_{D1} is negative at most conditions considered here, increasing towards less exergonic values with increasing temperature at constant activities of H_2, CO_2, and CH_4. Reaction (D1) is endergonic only at elevated temperatures in combination with high activities of CH_4 or low activities of CO_2 and H_2. For example, at representative activities of CH_4, H_2, and CO_2 in hydrothermal systems equal to 10^{-6}, 10^{-5}, and 10^{-4}, respectively, and at a temperature of 100°C (see Fig. 14), close to the optimum laboratory growth temperature of *M. kandleri*, ΔG_{D1} is equal to -55 kJ mol^{-1}. Although numerous obligately autotrophic thermophiles, including *M. kandleri*, have been isolated from hydrothermal ecosystems, the majority of thermophiles currently in culture are obligate heterotrophs [8].

5.6. The H–O–C, H–O–N–C, H–O–S–C, and H–O–N–S–C$_{amino\ acid}$ systems

In laboratory growth studies, thermophilic heterotrophs commonly utilize complex organic molecules such as proteinaceous materials and carbohydrates as carbon and energy sources. In nature, however, the molecular identities of the requisite organic compounds remain obscure. Owing to an incomplete data set for the thermodynamic properties of aqueous sugars, peptides, nucleic acid bases, and vitamins at elevated temperatures, together with an alarming shortage of organic analyses from hydrothermal systems where heterotrophic thermophiles are known to thrive, only a limited number of heterotrophic metabolic reaction types could be included in this study. It may seem at first glance that the plethora of organic compounds listed in Table 8.1 would be sufficient to characterize a significant fraction of overall heterotrophic metabolisms. This is not the case. Because of the dearth of thermodynamic and compositional data, we are limited to evaluating ΔG_r^0 for heterotrophic reactions which involve predominantly organic acids, alcohols, or amino acids. The reactions and values of ΔG_r^0 as a function of temperature in the system H–O–C are given in Tables 8.2 and 8.3,

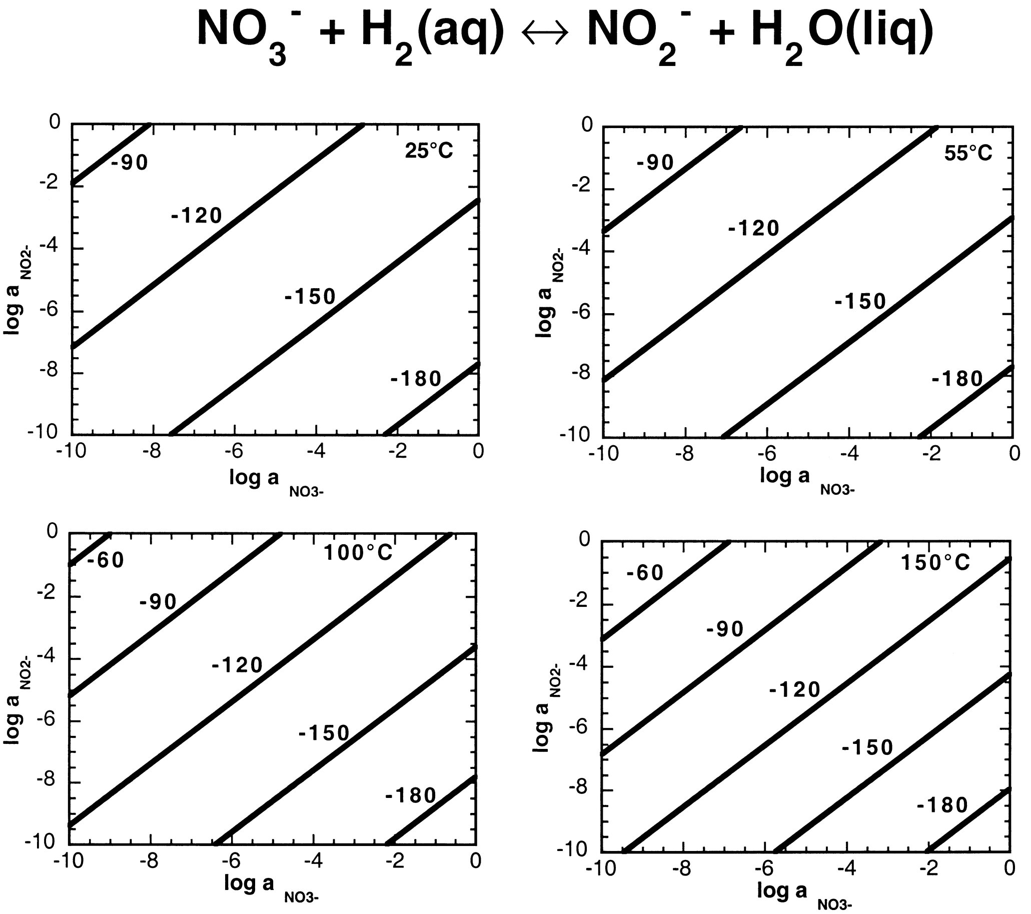

Fig. 11. Same as for Fig. 9, except that the activity of H_2(aq) is set at 10^{-7}.

respectively. Analogous data are also given for the systems H–O–N–C (Tables 8.5 and 8.6), H–O–S–C (Tables 8.8 and 8.9), and H–O–N–S–$C_{\text{amino acid}}$ (Tables 8.11 and 8.12). Organisms known to carry out the reactions listed in Tables 8.2, 8.5, 8.8 and 8.11 are listed in Tables 8.4, 8.7, 8.10 and 8.13, respectively.

Of the Reactions included in this section, only a few have been experimentally verified as overall metabolic processes in hyperthermophiles. For example, *Methanococcus thermolithotrophicus* is a methanogen able to disproportionate formic acid to CH_4 and CO_2 (Reaction E2). *P. aerophilum* can oxidize various carboxylic acids with O_2 as the electron acceptor under aerobic conditions (Reactions E3 and E5) or with NO_3^- under anaerobic conditions (Reactions E14, E15, E16, and E18). Several species of *Archaeoglobus* gain metabolic energy by catalyzing the oxidation of formic acid (Reactions E28-E30), acetic acid (Reaction E33), and lactic acid (Reactions E43, E45, and E47) in the presence of sulfate or sulfite. *Archaeoglobus veneficus* can also metabolize ethanol with sulfite as the electron acceptor (Reaction E69). The facultative autotroph *Thermoproteus tenax* can grow heterotrophically by using elemental sulfur to oxidize formic acid (Reaction E31), methanol (Reaction E66), or ethanol (Reaction E73).

The energetics of redox reactions involving organic carbon depend significantly on the type and amount of the organic species as well as the type and amount of the electron acceptor. To demonstrate this point, we compare, as examples, values of ΔG_r at 100°C for all known heterotrophic metabolic reactions in Table 8.8 in which sulfate is reduced to sulfide, and CO_2 is the resultant oxidized carbon compound (Reactions E27, E28, E32, E36, E43, E51, E57, E60, E63, E67, E74, E82, E88, E91–E96). To compute values of the activity product, Q_r, in these model calculations, the activities of SO_4^{2-} and H_2S are chosen to be 10^{-4} and 10^{-6}, respectively, the activities of CO_2 and each organic compound are 10^{-4}, and the pH is set equal to 6. Values of ΔG_r for all of these reactions were calculated with Eq. 5 using these activities along with appropriate values of ΔG_r^0 given in Table 8.9. The temperature and activities chosen here are not meant to represent a specific type of natural environment (although they are reasonable values for some hot springs), but rather these values are used to permit evaluation of ΔG_r and to show the direct effect of the specific organic substrate on ΔG_r at isochemical, isothermal, and isobaric conditions.

Values of ΔG_r^0 and ΔG_r at 100°C and the geochemical conditions noted above are given in Table 8.14 for a subset of coupled organic carbon/inorganic sulfur redox reac-

Table 6.1
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for compounds in the system H–O–S

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
SO_4^{2-}	−743.74	−744.30	−744.46	−744.63	−744.68	−744.68	−744.56	−744.32	−743.94	−743.44	−741.72	−737.75
HSO_4^-	−752.89	−754.88	−755.76	−757.27	−758.29	−759.56	−761.49	−763.43	−765.38	−767.33	−771.89	−778.22
SO_3^{2-}	−486.98	−486.78	−486.60	−486.18	−485.84	−485.35	−484.48	−483.47	−482.30	−481.00	−477.35	−470.48
HSO_3^-	−524.50	−526.75	−527.73	−529.41	−530.52	−531.92	−534.02	−536.12	−538.21	−540.31	−545.13	−551.79
SO_2(aq)	−297.64	−300.05	−301.17	−303.16	−304.53	−306.29	−309.03	−311.88	−314.83	−317.88	−325.32	−336.72
SO_2(g)	−294.52	−298.46	−300.19	−303.18	−305.19	−307.70	−311.49	−315.32	−319.17	−323.05	−332.19	−345.49
$S_2O_3^{2-}$	−520.79	−522.10	−522.59	−523.33	−523.78	−524.28	−524.92	−525.44	−525.83	−526.10	−526.21	−524.89
$HS_2O_3^-$	−529.28	−531.31	−532.21	−533.74	−534.77	−536.06	−538.01	−539.97	−541.93	−543.89	−548.46	−554.80
$H_2S_2O_3$(aq)	−531.33	−534.25	−535.56	−537.84	−539.39	−541.37	−544.38	−547.47	−550.61	−553.83	−561.55	−573.14
$S_2O_4^{2-}$	−598.07	−599.74	−600.41	−601.46	−602.12	−602.89	−603.96	−604.91	−605.76	−606.49	−607.74	−608.17
$HS_2O_4^-$	−611.17	−613.57	−614.63	−616.48	−617.73	−619.29	−621.68	−624.10	−626.54	−629.01	−634.80	−643.04
$H_2S_2O_4$(aq)	−611.97	−615.24	−616.73	−619.32	−621.09	−623.34	−626.80	−630.34	−633.97	−637.68	−646.64	−660.13
$S_2O_5^{2-}$	−788.16	−790.03	−790.78	−791.99	−792.75	−793.65	−794.91	−796.07	−797.13	−798.07	−799.83	−801.01
$S_2O_6^{2-}$	−963.42	−965.61	−966.51	−967.97	−968.91	−970.03	−971.62	−973.12	−974.52	−975.82	−978.41	−980.85
$S_2O_8^{2-}$	−1109.30	−1113.30	−1115.00	−1118.00	−1119.90	−1122.20	−1125.80	−1129.20	−1132.60	−1135.90	−1143.40	−1153.20
$S_3O_6^{2-}$	−954.77	−957.16	−958.14	−959.76	−960.79	−962.04	−963.84	−965.54	−967.15	−968.66	−971.76	−974.96
$S_4O_6^{2-}$	−1034.50	−1038.80	−1040.60	−1043.60	−1045.70	−1048.10	−1051.80	−1055.50	−1059.10	−1062.60	−1070.50	−1080.90
$S_5O_6^{2-}$	−954.12	−956.96	−958.14	−960.11	−961.39	−962.95	−965.21	−967.39	−969.48	−971.48	−975.77	−980.73
S(s)	0.71	0.22	0	−0.39	−0.65	−0.99	−1.51	−2.04	−2.59	−3.17	−4.70	−7.08
HS^-	13.63	12.45	11.97	11.17	10.66	10.04	9.16	8.33	7.55	6.82	5.33	3.85
H_2S(aq)	−25.21	−27.06	−27.92	−29.47	−30.55	−31.94	−34.12	−36.39	−38.76	−41.23	−47.30	−56.69
H_2S(g)	−28.86	−32.12	−33.56	−36.04	−37.70	−39.79	−42.93	−46.10	−49.30	−52.51	−60.10	−71.12
S_2(g)	84.52	80.89	79.30	76.55	74.71	72.40	68.92	65.42	61.90	58.35	50.00	37.90
S_2^{2-}	80.43	79.72	79.50	79.22	79.09	79.00	78.99	79.12	79.38	79.78	81.30	85.08
S_3^{2-}	75.41	74.12	73.63	72.90	72.46	71.97	71.35	70.85	70.47	70.22	70.16	71.56
S_4^{2-}	71.63	69.77	69.03	67.84	67.09	66.21	64.98	63.86	62.85	61.96	60.33	59.37
S_5^{2-}	69.11	66.68	65.68	64.04	62.98	61.71	59.87	58.13	56.49	54.94	51.76	48.44

tions. Each reaction is of the type

$$aC_{org} + bSO_4^{2-} + cH^+ = dCO_2 + eH_2S + fH_2O \qquad (20)$$

where a, b, c, d, e, and f represent the stoichiometric reaction coefficients for the balanced chemical reaction, and C_{org} stands for any organic compound of interest. It can be seen in Table 8.14 that the amount of metabolic energy (ΔG_r) released by these different heterotrophic reactions varies tremendously among the different organic substrates. Per mol of organic carbon species metabolized, values of ΔG_r at 100°C range from −60.15 kJ for the oxidation of aqueous formic acid (Reaction E28) to −1392.50 kJ for the oxidation of liquid hexadecane (Reaction E95). Per mol of sulfate reduced, values of ΔG_r at 100°C range from −63.05 kJ for the oxidation of CH_4 (Reaction E27) to −240.59 kJ for the oxidation of formic acid (Reaction E28). Note that Reaction (E28) yields the lowest amount of energy per mol of carbon species oxidized but the highest amount of energy per mol of sulfate reduced. It should perhaps be noted that environmental constraints determine the limiting reactants.

It may be useful to compare the energy yield from the oxidation of different organic species with the same number of carbon atoms such as, for example, propanoic acid, lactic acid, and propanol, each of which is a three-carbon compound. One might be tempted to assume that the energy yield is highest for oxidizing the most reduced compound, which is propanol with an average nominal oxidation state of each carbon equal to −2; similarly, that the lowest energy yield is for the oxidation of the least reduced species, which is lactic acid with an average nominal oxidation state of each carbon equal to 0. This, however, is incorrect. The oxidations of these three compounds, represented by Reactions (E36), (E43), and (E74), respectively, yield −208.50, −258.72, and −280.69 kJ per mol of carbon substrate. The oxidation of propanoic acid with an average nominal oxidation state of each carbon equal to −2/3, intermediate to propanol and lactic acid, yields the lowest amount of energy. It follows that propanoic acid is less unstable than the other compounds and may be more likely to be metastably preserved. This may explain the common occurrence of propanoic acid rather than lactic acid or propanol in geologic fluids [95–97]. It should be emphasized that the relative positions with respect to energy yield of these three reactions, and in fact all reactions considered here, may change considerably as temperature, pressure, and the chemical composition of the system change.

5.7. The H–O–S–C–metals/minerals system

Sluggish redox reactions involving a host of other elements can serve as sources of energy for thermophiles and hyperthermophiles, and these reactions are often coupled

Table 6.2
Inorganic sulfur metabolic reactions

C1	$SO_4^{2-}+4H_2(aq)+2H^+ \leftrightarrow H_2S(aq)+4H_2O(l)$
C2	$4SO_3^{2-}+2H^+ \leftrightarrow 3SO_4^{2-}+H_2S(aq)$
C3	$SO_3^{2-}+3H_2(aq)+2H^+ \leftrightarrow H_2S(aq)+3H_2O(l)$
C4	$SO_2(aq)+H_2O(l)+S(s) \leftrightarrow H_2S_2O_3(aq)$
C5	$S_2O_3^{2-}+2O_2(aq)+H_2O(l) \leftrightarrow 2SO_4^{2-}+2H^+$
C6	$6S_2O_3^{2-}+5O_2(aq) \leftrightarrow 4SO_4^{2-}+2S_4O_6^{2-}$
C7	$5S_2O_3^{2-}+H_2O(l)+4O_2(aq) \leftrightarrow 6SO_4^{2-}+2H^++4S(s)$
C8	$S_2O_3^{2-}+H_2O(l) \leftrightarrow SO_4^{2-}+H_2S(aq)$
C9	$S_2O_3^{2-} \leftrightarrow SO_3^{2-}+S(s)$
C10	$S_2O_3^{2-}+2H^++4H_2(aq) \leftrightarrow 2H_2S(aq)+3H_2O(l)$
C11	$4S_2O_4^{2-}+4H_2O(l) \leftrightarrow 3H_2S(aq)+5SO_4^{2-}+2H^+$
C12	$S_3O_6^{2-}+2O_2(aq)+2H_2O(l) \leftrightarrow 3SO_4^{2-}+4H^+$
C13	$S_3O_6^{2-}+H_2O(l) = SO_4^{2-}+S_2O_3^{2-}+2H^+$
C14	$2S_4O_6^{2-}+6H_2O(l)+7O_2(aq) \leftrightarrow 8SO_4^{2-}+12H^+$
C15	$S_4O_6^{2-}+H_2(aq) \leftrightarrow 2S_2O_3^{2-}+2H^+$
C16	$S(s)+1.5O_2(aq)+H_2O(l) \leftrightarrow SO_4^{2-}+2H^+$
C17	$4S(s)+4H_2O(l) \leftrightarrow SO_4^{2-}+3H_2S(aq)+2H^+$
C18	$S(s)+O_2(aq)+H_2O(l) \leftrightarrow H^++HSO_3^-$
C19	$S(s)+H_2(aq) \leftrightarrow H_2S(aq)$
C20	$H_2S(aq)+2O_2(aq) \leftrightarrow SO_4^{2-}+2H^+$
C21	$2H_2S(aq)+2O_2(aq) \leftrightarrow S_2O_3^{2-}+H_2O(l)+2H^+$
C22	$H_2S(aq)+0.5O_2(aq) \leftrightarrow S(s)+H_2O(l)$

with redox reactions in the H–O–N–S–C system. Reactions involving iron and manganese are the most familiar, but natural redox disequilibria occur in geochemical processes involving V, Cr, Cu, As, Se, Ag, W, Mo, Au, Hg, and U as well. These elements are typically present at low concentrations in most natural settings, and locations where they are concentrated tend to be ore deposits. Redox disequilibria are a large part of the explanation for why these elements are concentrated in ore deposits to levels that are economically viable. As a consequence, there is an enormous scientific literature on geochemical processes involving oxidation, reduction, transport, and deposition of these elements, and numerous experimental investigations of phase equilibria, calorimetry, solubility, dissolution kinetics, crystal chemistry, aqueous speciation, adsorption, and ion exchange. As a result, there are thermodynamic data for numerous oxide, sulfide, carbonate, and silicate minerals containing these elements, as well as for their aqueous ions, hydrolysis products, and complexes.

Standard Gibbs free energies for minerals and aqueous solutes containing these elements are listed in Table 9.1. An enormous number of reactions can be written involving these minerals and aqueous species, but we have selected reactions that microorganisms have been shown to conduct, or which can be inferred from reports in the literature. Inorganic reactions are listed in Table 9.2, and corresponding values of ΔG_r^0 are given in Table 9.3. Many microbes known to catalyze the reactions in Table 9.2 are listed in Table 9.4. Reactions involving these metals or minerals and organic compounds are listed in Table 9.5, with values of ΔG_r^0 given in Table 9.6. Microbes associated in the literature with the metabolic processes represented in Table 9.5 are listed in Table 9.7. The following examples should help to illustrate the various types of processes involving these elements. In some cases, the distinctions between these processes are rather subtle.

Pyrite (FeS_2) oxidation is an energy-yielding process conducted by several species of aerobic thermophiles, with a subtle distinction of whether both the sulfur and

Table 6.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 6.2

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
C1	−299.58	−302.00	−303.08	−304.96	−306.24	−307.85	−310.33	−312.86	−315.46	−318.13	−324.67	−335.03
C2	−308.53	−312.86	−314.91	−318.62	−321.21	−324.58	−329.89	−335.49	−341.39	−347.55	−363.05	−388.02
C3	−301.82	−304.71	−306.04	−308.38	−309.98	−312.04	−315.22	−318.52	−321.94	−325.48	−334.27	−348.28
C4	1.23	2.28	2.79	3.74	4.42	5.31	6.73	8.26	9.90	11.63	16.13	23.35
C5	−768.68	−764.38	−762.23	−758.24	−755.38	−751.59	−745.53	−739.02	−732.09	−724.75	−706.09	−675.58
C6	−2013.30	−2008.60	−2006.20	−2001.70	−1998.40	−1994.10	−1987.10	−1979.70	−1971.70	−1963.30	−1941.90	−1907.60
C7	−1695.30	−1686.90	−1682.80	−1675.30	−1670.00	−1663.10	−1652.00	−1640.30	−1628.00	−1615.20	−1583.50	−1533.00
C8	−12.52	−12.57	−12.61	−12.72	−12.82	−12.95	−13.19	−13.47	−13.80	−14.16	−15.15	−16.87
C9	34.53	35.53	35.98	36.76	37.28	37.94	38.93	39.93	40.93	41.93	44.15	47.33
C10	−312.10	−314.57	−315.70	−317.69	−319.06	−320.80	−323.52	−326.33	−329.26	−332.29	−339.82	−351.90
C11	−459.50	−456.93	−455.71	−453.53	−452.01	−450.07	−447.05	−443.91	−440.65	−437.28	−428.89	−415.39
C12	−842.80	−836.93	−833.95	−828.40	−824.41	−819.11	−810.60	−801.42	−791.63	−781.22	−754.59	−710.57
C13	−74.12	−72.54	−71.72	−70.17	−69.03	−67.52	−65.07	−62.41	−59.54	−56.47	−48.51	−34.99
C14	−2598.70	−2577.70	−2567.20	−2547.80	−2533.80	−2515.50	−2486.00	−2454.40	−2420.80	−2385.30	−2294.60	−2145.90
C15	−25.94	−23.55	−22.32	−20.03	−18.37	−16.17	−12.62	−8.78	−4.68	−0.30	10.97	29.78
C16	−537.03	−533.75	−532.09	−528.97	−526.72	−523.73	−518.90	−513.69	−508.10	−502.14	−486.75	−461.23
C17	120.37	120.44	120.51	120.67	120.82	121.03	121.41	121.89	122.47	123.20	125.84	131.23
C18	−308.39	−307.55	−307.09	−306.16	−305.46	−304.49	−302.88	−301.08	−299.09	−296.91	−291.03	−280.86
C19	−44.81	−45.39	−45.64	−46.07	−46.35	−46.71	−47.23	−47.74	−48.25	−48.73	−49.71	−50.95
C20	−756.16	−751.81	−749.62	−745.51	−742.56	−738.64	−732.34	−725.54	−718.29	−710.59	−690.94	−658.72
C21	−743.64	−739.24	−737.00	−732.79	−729.74	−725.69	−719.15	−712.07	−704.49	−696.43	−675.79	−641.85
C22	−219.13	−218.06	−217.53	−216.55	−215.84	−214.92	−213.44	−211.86	−210.19	−208.45	−204.20	−197.48

Table 6.4
Microorganisms that use the sulfur reactions specified in Table 6.2

Reaction	
C1	**As written:** *Archaeoglobus lithotrophicus* [37], *Desulfotomaculum auripigmentum* [393], *Desulfacinum infernum* [206], *Desulfonatronum lacustre* [394], *Thermodesulfobacterium mobile* [265], *Thermodesulfobacterium commune* [263], *Desulfotomaculum putei* [175], *Desulfotomaculum luciae* [175,208], *Archaeoglobus profundus* [331], *Thermodesulfovibrio yellowstonii* [267], *Desulfotomaculum kuznetsovii* [207], *Desulfotomaculum geothermicum* [35], *Desulfonatronovibrio hydrogenovorans* [395], *Desulfotomaculum thermocisternum* [180], *Desulfotomaculum thermosapovorans* [212], *A. degensii* [187], *Desulfotomaculum australicum* [170], *Desulfotomaculum halophilum* [178], *Desulfobulbus rhabdoformis* [396], *D. desulfuricans* [381], *Desulfotomaculum thermoacetoxidans* [210] **Hydrogen from an organic source:** *Archaeoglobus fulgidus* [328–330], *Thermocladium modestius* [259]
C2	**As written:** *Desulfovibrio sulfodismutans* [397,398], *Desulfocapsa sulfoexigens* [399], *Desulfocapsa thiozymogenes* [400]
C3	**As written:** *D. desulfuricans* [381], *D. infernum* [206], *D. lacustre* [394], *A. veneficus* [295], *D. putei* [175], *A. profundus* [331], *T. yellowstonii* [267], *D. kuznetsovii* [207], *D. hydrogenovorans* [395], *D. thermocisternum* [180], *D. thermosapovorans* [212], *D. halophilum* [178], *D. rhabdoformis* [396], *Desulfurobacterium thermolithotrophum* [216], *Pyrodictium brockii* [352] **Hydrogen from an organic source:** *A. fulgidus* [328–330], *Pyrobaculum islandicum* [346]
C4	**As written:** *Thiobacillus thiooxidans*, *T. thioparus* [381]
C5	**As written:** *Thiobacillus novellus* [381], *A. pyrophilus* [82], *P. aerophilum* [345], *Thermothrix azorensis* [276], *T. thiopara* [277,278], *Thiobacillus hydrothermalis* [401], *Thiomicrospira crunogena* [402], *Thiomicrospira chilensis* [403]
C6	**As written:** *Thiobacillus neapolitanus* [381]
C7	**As written:** *T. thioparus* [381]
C8	**As written:** *D. sulfodismutans* [397,398], *D. sulfoexigens* [399], *D. thiozymogenes* [400], *D. hydrogenovorans* [395]
C9	**As written:** purple and green photosynthetic Bacteria [404]
C10	**As written:** *A. fulgidus* [329], *D. infernum* [206], *F. placidus* [84], *D. lacustre* [394], *P. occultum* [352], *A. veneficus* [295], *D. putei* [175], *D. luciae* [175,208], *A. profundus* [331],*T. yellowstonii* [267], *D. kuznetsovii* [207], *D. thermocisternum* [180], *D. thermosapovorans* [212], *D. thermolithotrophum* [216], *D. australicum* [178], *D. rhabdoformis* [396], *Thermotoga subterranea* [281] **Hydrogen from an organic source:** *T. modestius* [259], *P. islandicum* [346], *Pyrodictium abyssi* [352], *Thermotoga elfii* [279], *Thermotoga hypogea* [280]
C11	**As written:** *D. sulfodismutans* [397,398]
C12	**As written:** *Thiobacillus tepidarius*, *T. neapolitanus* [87]
C13	**As written:** *T. tepidarius*, *T. neapolitanus* [87]
C14	**As written:** *T. neapolitanus* [381], *T. chilensis* [403], *T. hydrothermalis* [401], *T. azorensis* [276], *Sulfolobus hakonensis* [316], *T. tepidarius* [87]
C15	**Hydrogen from an organic source:** *Bacterium paratyphosum* B [405]
C16	**As written:** *T. thioparus* [381], *T. thiooxidans*, *T. ferrooxidans* [387], *A. pyrophilus* [82], *A. infernus*, *A. brierleyi* [292], *Acidianus ambivalens* [289–291], *M. sedula* [297], *M. prunae* [296], *S. acidocaldarius* [313], *S. solfataricus* [320], *S. metallicus* [317], *Sulfolobacillus thermosulfidooxidans* [246], *Sulfobacillus acidophilus* [245], *S. shibatae* [318,319], *S. hakonensis* [316], *S. yellowstonii* [322], *Sulfurococcus mirabilis* [321], *T. thiopara* [277,278], *T. azorensis* [276], *T. prosperus* [406], *T. hydrothermalis* [401], *T. chilensis* [403], *T. crunogena* [402], *Beggiatoa* [407–409], *Thiovulum* [409]
C17	**As written:** *D. sulfoexigens* [399], *D. thiozymogenes*, *Desulfobulbus propionicus* [400]
C18	**As written:** *T. thiooxidans*, *T. thioparus* [381]
C19	**As written:** *P. occultum*, *P. brockii* [353], *A. infernus*, *A. brierleyi* [292], *A. degensii* [187], *T. tenax* [375,377], *Thermoproteus neutrophilus*, *T. maritimus* [375], *P. islandicum* [346], *A. pyrophilus* [82], *A. ambivalens* [289–291], *Desulfurella kamchatkensis*, *Desulfurella propionica* [214], *D. thermolithotrophum* [216], *Hyperthermus butylicus* [338], *Stetteria hydrogenophila* [355] *Stygiolobus azoricus* [312], *S. arcachonense* [380] **Hydrogen from an organic source:** *Thermococcus litoralis* [368,369], *Thermococcus zilligii* [323,324], *Thermococcus alcaliphilus* [360], *Pyrobaculum organotrophum* [346], *Thermoproteus uzoniensis* [378], *Thermoplasma acidophilum*, *T. volcanium* [325], *Thermofilum pendens* [376], *Pyrococcus woesei* [351], *Thermococcus profundus* [371], *Thermococcus celer* [363], *Desulfurococcus mucosus*, *Desulfurococcus mobilis* [337], *Thermococcus stetteri* [373], *Pyrococcus abyssi* [347], *Pyrococcus furiosus* [349], *Pyrococcus horikoshii* [350], *P. abyssi* [352], *T. modestius* [259], *Thermococcus acidaminovorans* [358], *Thermococcus guaymasensis*, *Thermococcus aggregans* [359], *Thermococcus chitonophagus* [364], *Thermococcus barossii* [362], *Thermococcus fumicolans* [365], *Thermococcus gorgonarius* [366], *Thermococcus hydrothermalis* [367], *Thermococcus pacificus* [214], *Thermococcus siculi* [372], *Thermosipho africanus* [273], *T. maritima* [287], *Thermotoga neapolitana* [288], *Desulfurococcus amylolyticus* [336], *Staphylothermus marinus* [354]
C20	**As written:** *Thiovulum*, *Beggiatoa* [409], *T. chilensis* [403], *T. hydrothermalis* [401], *Thiobacillus propserus* [406], *T. crunogena* [402], *T. azorensis* [276], *S. hakonensis* [316], *T. thioparus* [410]
C21	**As written:** *T. thioparus* [410]
C22	**As written:** *T. thioparus* [410], *Thiovulum* [409], *Beggiatoa* [407–409]

iron are oxidized as in:

$$2FeS_2 + 7.5O_2(aq) + H_2O(l) \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+ \tag{F5}$$

or whether only the sulfur is oxidized as in:

$$FeS_2 + 3.5O_2(aq) + H_2O(l) \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{F6}$$

In both cases, pyrite oxidation yields sulfate and protons which are capable of dissolving minerals and leaching many other elements from pyrite-containing rocks. In the case of the former reaction, the ferric ions produced are likely to precipitate as ferric hydroxide, oxide, or oxyhydroxide phases, and the variable thermodynamic properties of these possible products will influence the total amount of energy available.

Thiobacillus ferrooxidans has been shown to use Reaction (F5) to completely oxidize the sulfur and iron in pyrite, as implied by its name. Other organisms such as *M. sedula* and *Metallosphaera prunae* and *Sulfolobus metallicus* are

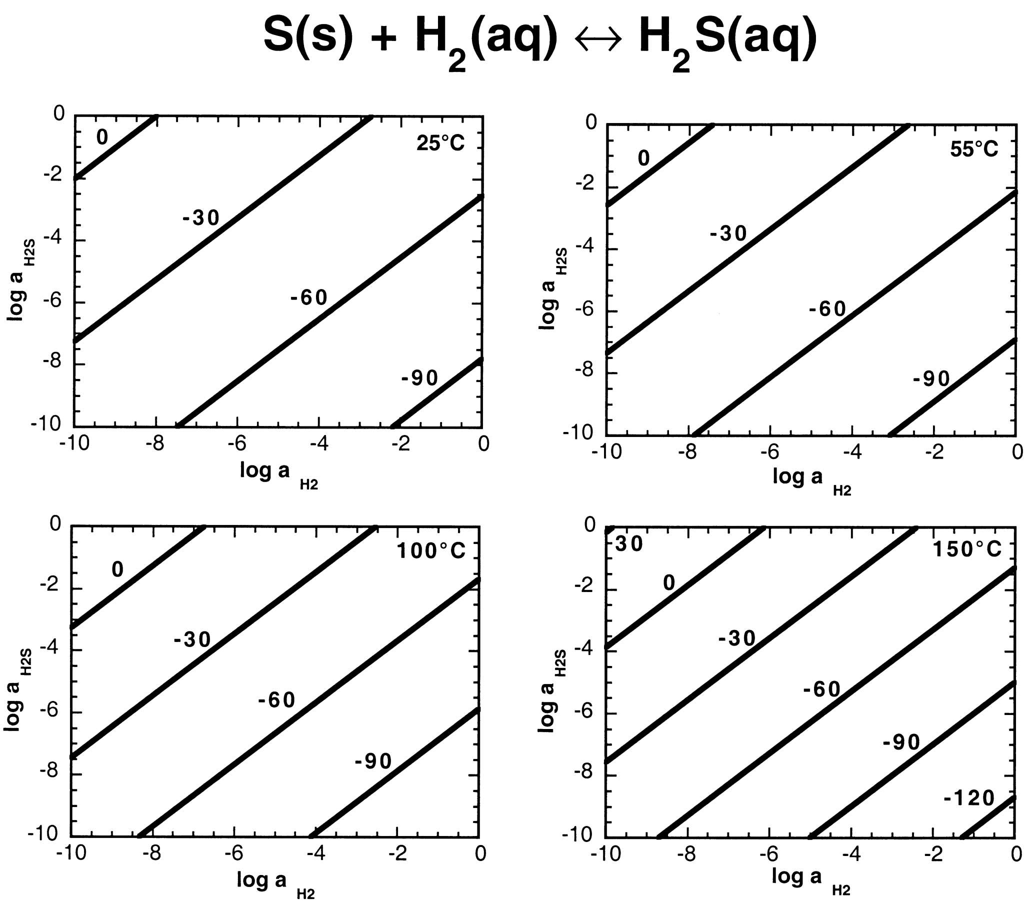

Fig. 12. Plots of ΔG_r (represented as solid contours) at P_{SAT} and 25, 55, 100, and 150°C for Reaction (C19) as a function of log a_{H_2S} and log a_{H_2}. The activity of $H_2O(l)$ is taken to be unity.

all known to use reaction Reaction (F6), and have not been shown to oxidize iron in pyrite. On the other hand, *Sulfurococcus yellowstonii*, *Thiobacillus prosperus*, and *Sulfobacillus thermosulfidooxidans* will use either reaction Reaction (F5) or Reaction (F6) as energy sources. All of these organisms, and no doubt many others, are likely to be the agents of pyrite oxidation and acid generation that leads to metal leaching and contamination of ground water near mine dumps and tailings piles [98–102]. This same microbially driven leaching process is also the foundation of modern methods to extract copper and other metals from ore which is subsequently removed from solution through electrolysis in an overall process that is considerably less costly economically and environmentally than smelting [103,104].

In contrast to pyrite oxidation, several other microbially mediated sulfide oxidation reactions are either pH independent or proceed with the consumption of H^+. Reactions (F7), (F9), (F10), and (F11) are examples of the oxidation of pyrrhotite (FeS), covellite (CuS), sphalerite (ZnS), and galena (PbS) in which the sulfide is oxidized to sulfate without generation of sulfuric acid. Members of the thermophilic genera *Sulfolobus*, *Metallosphaera*, *Sulfurococcus*, *Sulfolobacillus*, and *Thiobacillus* conduct these reactions, and reaction (F10) can also be inferred for *Acidianus brierleyi*. Chalcopyrite ($CuFeS_2$) oxidation, corresponding to Reaction (F8), requires the consumption of H^+. Many organisms capable of other sulfide oxidation reactions are capable of oxidizing chalcopyrite. Because this reaction has H^+ as a reactant, it would be enhanced by the simultaneous oxidation of pyrite in which H^+ is a product.

The heterotrophic reactions in Table 9.5, in which organic compounds and metals or semi-metals are coupled, all involve reduction of the inorganic compounds. Inorganic redox couples for which specific heterotrophic Reactions are identified include Fe^{III}–Fe^{II}, Co^{III}–Co^{II}, As^{V}–As^{III}, Se^{VI}–Se^{0}, Se^{VI}–Se^{IV}, Se^{IV}–Se^{0}, and U^{VI}–U^{IV}, but inferences about many other couples including V^{V}–V^{III}, Cr^{VI}–Cr^{III}, Mn^{VI}–Mn^{III}, Mn^{III}–Mn^{II}, Cu^{II}–Cu^{I}, Cu^{II}–Cu^{0}, Ag^{I}–Ag^{0}, and Au^{III}–Au^{0}, can be drawn from the microbiological and geochemical literature [105–115].

Table 6.5
Mixed metabolic reactions involving S, N, H and O compounds

C23	$5S_2O_3^{2-}+8NO_3^-+H_2O(l) \leftrightarrow 10SO_4^{2-}+4N_2(aq)+2H^+$
C24	$5S(s)+6NO_3^-+2H_2O(l) \leftrightarrow 5SO_4^{2-}+3N_2(aq)+4H^+$
C25	$NO_3^-+H_2S(aq) \leftrightarrow NO_2^-+H_2O(l)+S(s)$
C26	$2NO_3^-+5H_2S(aq)+2H^+ \leftrightarrow N_2(aq)+5S(s)+6H_2O(l)$
C27	$8NO_3^-+5H_2S(aq) \leftrightarrow 4N_2(aq)+5SO_4^{2-}+4H_2O(l)+2H^+$

Table 6.6
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 6.5

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
C23	−3657.59	−3641.55	−3634.49	−3622.38	−3614.29	−3604.17	−3588.98	−3573.76	−3558.52	−3543.23	−3507.25	−3454.68
C24	−2545.80	−2533.47	−2527.93	−2518.22	−2511.64	−2503.29	−2490.51	−2477.45	−2464.06	−2450.32	−2416.33	−2363.73
C25	−131.56	−130.90	−130.57	−129.98	−129.55	−128.99	−128.11	−127.17	−126.19	−125.18	−122.78	−119.06
C26	−1049.22	−1045.22	−1043.48	−1040.52	−1038.60	−1036.14	−1032.50	−1028.97	−1025.48	−1022.12	−1015.15	−1006.61
C27	−3595.02	−3578.69	−3571.40	−3558.75	−3550.24	−3539.43	−3523.02	−3506.42	−3489.54	−3472.43	−3431.48	−3370.35

Among the organisms that mediate the reactions listed in Table 9.5 only *Bacillus infernus* is a thermophile, able to grow in the laboratory between 45 and 60°C. *B. infernus*, isolated from ~2700 m below the surface in the Taylorsville Triassic Basin, VA, USA [116], is a strict anaerobe that can grow by mediating reactions (F14) and (F20). The other Reactions are known from mesophiles, but there is no obvious thermodynamic reason that precludes thermophiles from their use. We have included these reactions and their values of ΔG_r^0 in Table 9.6 in the hope that these data may help in the design of growth media for isolating thermophilic heterotrophs that use these energy sources in natural systems. Recent work from Hot Creek, California [117] suggests that microbial arsenic oxidation occurs at elevated temperatures, and ΔG_r^0 values for reactions such as (F22), (F23), and (F28) at high temperatures may help to design media for isolating these organisms. It should be noted that combining data from Tables 8.1 and 9.1 allows calculation of ΔG_r^0 for thousands of heterotrophic reactions involving inorganic redox couples.

Also listed in Table 9.1 are data for aqueous species and minerals containing Mg, Ca, Co, Ni, Zn, and Pb, which are involved in reactions that can affect microbial energetics although these elements do not exhibit redox changes in natural processes. For example, the availability of HCO_3^- in a natural environment is often a function of carbonate equilibria involving calcite ($CaCO_3$) and other carbonate minerals, through reactions such as:

$$Ca^{2+} + HCO_3^- \rightarrow \text{calcite} + H^+ \tag{21}$$

Autotrophic reactions dependent on HCO_3^- or CO_2(aq) may be regulated by the presence of carbonate minerals, and heterotrophic reactions that produce HCO_3^- or CO_2(aq) can be responsible for the precipitation of these minerals. Indeed, there are numerous examples of carbonate minerals in sedimentary rocks with carbon isotopic compositions indicative of an organic source for the carbon [118–122]. The extent to which this oxidation of carbon is microbially mediated is typically unknown. As another example, the concentration of Pb in a solution will affect the availability of energy from the dissolution of galena (PbS)

$$\text{Galena} + 2O_2(aq) \rightarrow Pb^{2+} + SO_4^{2-} \tag{F11}$$

even though the energy is obtained through oxidation of sulfide to sulfate.

5.8. The H–O–P system

Phosphorus is an essential nutrient not only in microbial metabolism, but in the metabolic processes of all life. However, the P involved in metabolic reactions generally does not undergo oxidation or reduction; by far the most dominant redox state of P in organic and inorganic phosphorus-containing compounds is +5, as in phosphate and pyrophosphate. Perhaps because phosphates make up the majority of phosphorus-containing compounds in metabolic reactions, the thermodynamic properties of phosphorus molecules in other redox states have not received much attention. In addition to the various protonated and deprotonated forms of phosphate and pyrophosphate, values of ΔG^0 as a function of temperature can be calculated only for a few P-compounds in which P is in the +3 or +1 oxidation state, as in phosphite and hypophosphite (Table 9.8).

Thermodynamic properties at elevated temperatures of organo-phosphates are extremely sparse although these compounds are central to numerous metabolic pathways, including known and proposed pathways in thermophiles and hyperthermophiles. For example, glucose 6-phosphate, glyceraldehyde 3-phosphate, and phosphoenolpyruvate are merely three of the numerous P-containing intermediates in the Entner–Doudoroff pathway in halophiles [123] and in the Embden–Meyerhof pathway in the anaerobic hyperthermophilic Bacterium *Thermotoga maritima* [124]. 2-Phosphoglycerate, phosphoenolpyruvate, and acetyl-CoA are P-containing intermediates in the proposed pyrosaccharolytic pathway of carbohydrate metabolism in hyperthermophilic Archaea [8]. In the oxidative and reductive tricarboxylic (or citric) acid (TCA) cycle used by heterotrophic and autotrophic microbes, respectively,

Table 6.7
Microorganisms that use the reactions specified in Table 6.5

Reaction	
C23	*T. denitrificans* [381], *P. aerophilum* [345], *A. pyrophilus* [82], *T. thioparus* [277,278]
C24	*T. denitrificans* [381], *A. pyrophilus* [82], *Thioploca chileae*, *Thioploca araucae* [411]
C25	*F. placidus* [84], *T. thioparus* [277,278]
C26	*T. chileae*, *T. araucae* [411], *T. thioparus* [277,278]
C27	*T. chileae*, *T. araucae* [411], *T. thioparus* [277,278]

Table 7.1
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for inorganic compounds in the system H–O–N–S–C$_{\text{inorganic}}$

Compounds	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
CO_2(g)	−389.48	−392.87	−394.36	−396.93	−398.66	−400.83	−404.10	−407.40	−410.73	−414.08	−421.99	−433.51
CO_2(aq)	−383.51	−385.17	−385.98	−387.44	−388.48	−389.84	−391.99	−394.26	−396.66	−399.17	−405.42	−415.22
CO_3^{-2}	−528.83	−528.31	−527.98	−527.32	−526.81	−526.10	−524.91	−523.56	−522.07	−520.43	−515.98	−507.92
HCO_3^-	−584.63	−586.25	−586.94	−588.12	−588.89	−589.86	−591.29	−592.71	−594.11	−595.49	−598.61	−602.71
COS(g)	−160.36	−164.03	−165.64	−168.43	−170.30	−172.65	−176.20	−179.77	−183.38	−187.01	−195.59	−208.07
CO(g)	−132.65	−135.79	−137.17	−139.55	−141.14	−143.14	−146.16	−149.19	−152.25	−155.32	−162.56	−173.04
CO(aq)	−117.91	−119.31	−120.01	−121.30	−122.23	−123.45	−125.42	−127.52	−129.76	−132.13	−138.11	−147.70
CN^-	174.63	173.04	172.38	171.26	170.54	169.65	168.34	167.06	165.82	164.62	161.95	158.65
HCN(aq)	122.36	120.52	119.66	118.12	117.06	115.68	113.54	111.30	108.97	106.57	100.65	91.55
OCN^-	−94.88	−96.65	−97.41	−98.67	−99.50	−100.52	−102.04	−103.52	−104.96	−106.38	−109.55	−113.62
SCN^-	96.08	93.73	92.71	90.99	89.85	88.43	86.32	84.22	82.14	80.08	75.36	68.97
CH_4(g)	−46.47	−49.42	−50.72	−52.97	−54.47	−56.36	−59.22	−62.10	−65.02	−67.95	−74.89	−85.01
CH_4(aq)	−32.71	−33.87	−34.46	−35.57	−36.38	−37.47	−39.23	−41.12	−43.17	−45.34	−50.87	−59.83

as well as in the partial TCA cycle in methanogens, acetyl– and succinyl–CoA, both of which contain several phosphate groups, serve as intermediates. Nicotinamide adenine dinucleotide phosphate in its protonated (NADPH) and deprotonated (NADP$^+$) forms serve as electron donor and acceptor, respectively, in a number of microbes that use the Entner–Doudoroff and Embden–Meyerhof pathways, the TCA cycle, glycine, sarcosine, or betaine reduction reactions, and the fermentation of peptides [8,123–125]. Cleavage of the terminal phosphate group from adenosine triphosphate (ATP) to yield adenosine diphosphate (ADP) and inorganic phosphate (P$_i$) supplies the requisite energy in otherwise endergonic intracellular reactions.

The thermodynamic properties of many organo-phosphate compounds are not only limited at elevated temperatures but even at 25°C. This is particularly true for solutes with complex structures including acetyl– and succinyl–CoA, NADP$^+$, NADPH, and compounds in the AMP, ADP, and ATP series. For example, although values of ΔG_r^0 at 25°C and 1 bar are known for the hydrolysis reactions of ATP, ADP, and AMP, represented by:

$$\text{ATP} + H_2O = \text{ADP} + P_i \tag{22}$$

$$\text{ADP} + H_2O = \text{AMP} + P_i \tag{23}$$

$$\text{AMP} + H_2O = \text{adenosine} + P_i, \tag{24}$$

values of ΔG_f^0 for the individual nucleosides and nucleotides are not. In fact, to permit calculating values of ΔG_r^0 for reactions among the different protonated and deprotonated forms and metal complexes of ATP, ADP, and AMP, an arbitrary convention is usually adopted in which ΔG_f^0 and ΔH_f^0 of aqueous adenosine are set equal to zero [79]. As a result of adopting this convention, values of ΔG_f^0, ΔH_f^0, and $S_{T_rP_r}^0$ for both adenosine(aq) and H$^+$ are all assigned zero. As a consequence, ΔG_r^0 at 25°C or at elevated temperature can not be calculated for the synthesis from environmental carbon sources of any nucleic acid base, nucleoside, nucleotide, or nucleic acid. Because organo-phosphates are ubiquitous in assimilatory and dissimilatory metabolic processes, the dearth of ΔG^0 values as a function of temperature for this class of compounds currently prohibits the quantitative evaluation of the energetics for many stepwise reactions in metabolic pathways of thermophiles and hyperthermophiles. Consequently, we are limited in this review to tabulating values of ΔG^0 as a function of temperature for P$_i$, phosphite, and hypophosphite (Table 9.8). Because redox reactions among these compounds cannot currently be linked to specific microorganisms, these reactions and corresponding values of ΔG_r^0 as a function of temperature are listed in Tables A.10 and A.11 in the Appendix.

6. Concluding remarks

Even organisms that branch deeply in the global phylogenetic tree are intensely complex living systems. One of these organisms embedded very near the root of the tree is the autotrophic, hyperthermophilic, methanogenic Archaeon *M. jannaschii*. This organism was originally isolated from a sediment sample collected at a depth of ~2600 m at 21°N on the East Pacific Rise [126]. Its complete 1.66-Mb pair genome has been sequenced, and 1738 predicted protein-coding genes have been identified; however, of these, only about 38% could be confidently linked

Table 7.2
Inorganic carbon metabolic reactions

D1	$CO_2(aq)+4H_2(aq) \leftrightarrow CH_4(aq)+2H_2O(l)$
D2	$COS(g)+2O_2(aq)+H_2O(l) \leftrightarrow SO_4^{2-}+CO_2(aq)+2H^+$
D3	$COS(g)+H_2O(l) \leftrightarrow CO_2(aq)+H_2S(aq)$
D4	$CO(aq)+0.5O_2(aq) \leftrightarrow CO_2(aq)$
D5	$4CO(aq)+2H_2O(l) \leftrightarrow CH_4(aq)+3CO_2(aq)$
D6	$CO(aq)+3H_2(aq) \leftrightarrow CH_4(aq)+H_2O(l)$
D7	$SCN^-+2O_2(aq)+2H_2O(l) \leftrightarrow SO_4^{2-}+CO_2(aq)+NH_4^+$
D8	$SCN^-+H_2O(l) \leftrightarrow H_2S(aq)+OCN^-$
D9	$CH_4(aq)+2O_2(aq) \leftrightarrow CO_2(aq)+2H_2O(l)$

Table 7.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 7.2

Reaction	*T* (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
D1	−196.02	−194.53	−193.73	−192.17	−191.01	−189.45	−186.87	−184.04	−180.98	−177.69	−169.22	−155.32
D2	−768.89	−763.32	−760.69	−755.96	−752.66	−748.38	−741.67	−734.62	−727.25	−719.57	−700.41	−669.86
D3	−12.72	−11.51	−11.07	−10.44	−10.10	−9.73	−9.33	−9.08	−8.96	−8.98	−9.47	−11.15
D4	−275.01	−274.50	−274.24	−273.73	−273.36	−272.86	−272.04	−271.14	−270.17	−269.13	−266.44	−261.93
D5	−240.31	−238.73	−237.99	−236.62	−235.65	−234.38	−232.36	−230.21	−227.92	−225.51	−219.35	−209.28
D6	−207.10	−205.59	−204.79	−203.28	−202.17	−200.68	−198.25	−195.59	−192.72	−189.64	−181.75	−168.81
D7	−866.64	−863.06	−861.32	−858.14	−855.90	−852.95	−848.28	−843.31	−838.06	−832.52	−818.55	−795.92
D8	19.47	19.26	19.14	18.91	18.73	18.50	18.11	17.68	17.22	16.72	15.45	13.40
D9	−859.72	−859.28	−858.97	−858.31	−857.79	−857.05	−855.80	−854.36	−852.77	−851.03	−846.39	−838.43

to a specific cellular function [127]. Since a majority of the intracellular catabolic and anabolic processes remain obscure, even in relatively simple organisms such as *M. jannaschii*, it follows that evaluation of the energetics of most metabolic reactions is similarly problematic. This situation is compounded in the case of thermophiles by the paucity of thermodynamic data at elevated temperatures for aqueous organic and inorganic species. However, all is not lost! Although calculating values of ΔG_r^0 as a function of temperature for most stepwise redox reactions in metabolic pathways, including those in electron transport chains, may remain a formidable challenge for some time to come, values of ΔG_r^0 at elevated temperatures can be readily computed for a staggering array of known, putative, and hypothesized overall metabolic processes in thermophilic microorganisms. In this review, values of ΔG_r^0 as a function of temperature are given for 188 established metabolic redox reactions plus an additional 182 reactions that chemically link metabolic processes to the composition of artificial and natural systems. In addition, thousands of ΔG_r^0 values can be calculated with the tabulated values of ΔG^0. We hope that these data prove useful in designing culture media, quantifying microbial energetics, and placing thermophiles and hyperthermophiles in their geochemical and ecological contexts.

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Appendix

Many topics mentioned in passing in the text are assembled in this appendix where proper attention can be given to the details that might have derailed other discussions. These topics include the interconversion of ΔG_r^0 and $\Delta G_r^{0'}$, the relation between ΔG_r^0 and standard potentials, methods for calculating activities from concentration data, and a review of the revised HKF equations of state. We have also included in this appendix tables of auxiliary reactions and corresponding ΔG_r^0 values. Some of these reactions are generally so rapid in their abiotic form (gas solubility, acid dissociation, cation hydrolysis, etc.) that microbial mediation is not directly involved. Nevertheless, these reactions will have indirect effects on microbial me-

Table 7.4
Microorganisms that use the carbon reactions specified in Table 7.2

Reaction	
D1	**As written:** *Methanococcus vannielii*, *M. barkeri* [387] *Methanobacterium wolfei*, *Methanobacterium alcaliphilum* [391], *M. thermolithotrophicus* [302], *M. jannaschii* [126] *M. kandleri* [94], *Methanococcus* CS-1 [165], *Methanococcus fervens* (AG86)[303,339], *Methanobacterium thermoautotrophicus* [306], *Methanothermus fervidus* [343], *Methanothermus sociabilis* [344], *Methanococcus igneus* [340], *Methanobacterium thermoalcaliphilum* [300], *Methanobacterium thermoaggregans* [299], *Methanocalculus halotolerans* [412], *Methanobacterium thermoflexum*, *Methanobacterium defluvii* [298], *Methanobacterium subterraneum* [43], *Methanococcus infernus* [341], *Methanococcus vulcanius* [303], *Methanoplanus petrolearius* [413]
D2	**As written:** *T. thioparus*, *Paracoccus* [87]
D3	**As written:** *T. thioparus*, *Paracoccus* [87]
D4	**As written:** *B. schlegelii*, *Pseudomonas carboxydovorans*, *Alcaligenes carboxydus* [387]
D5	**As written:** *Methanobacterium thermoautotrophicum* [387]
D6	**As written:** *Methanobacterium formicicum* [381]
D7	**As written:** *T. thioparus*, *Paracoccus* [87]
D8	**As written:** *T. thioparus*, *Paracoccus* [87]
D9	**As written:** *Methylococcus thermophilus* [233]

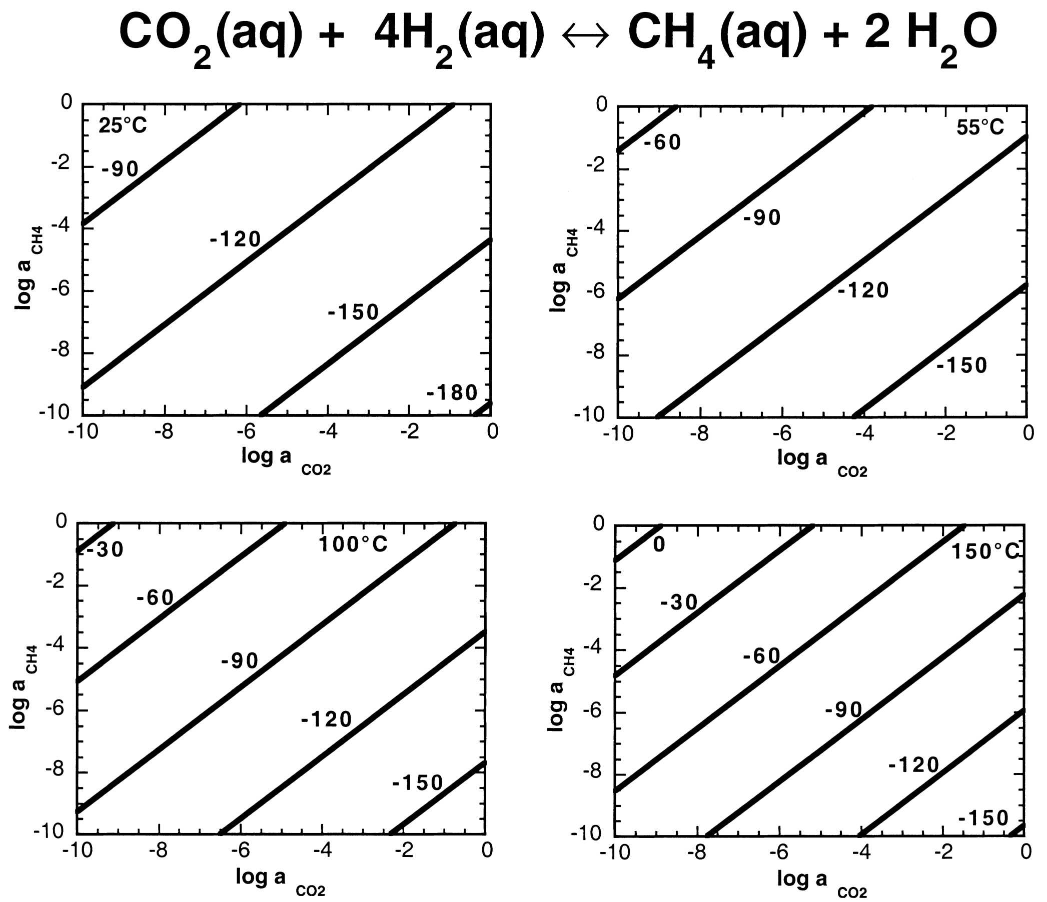

Fig. 13. Plots of ΔG_r (represented as solid contours) at P_{SAT} and 25, 55, 100, and 150°C for Reaction (D1) as a function of log a_{CH_4} and log a_{CO_2}. The activity of $H_2(aq)$ is set at 10^{-3}, and the activity of $H_2O(l)$ is taken to be unity.

tabolism. In addition, we include here redox and disproportionation reactions that have not, to our knowledge, been shown to be microbially mediated, but may be. Many of these auxiliary reactions are also required to connect known microbial processes with the larger realm of geochemical processes that support life at high temperatures and pressures.

A.1. Interconversion of ΔG_r^0 and $\Delta G_r^{0'}$

As stated in the text, differences in the conventional and biologic standard states can be accounted for explicitly (see Eq. 4). If we consider, for example, acetate fermentation represented by

$$CH_3COO^- + H^+ \rightarrow CO_2(aq) + CH_4(aq) \tag{1A}$$

carried out, among others, by the thermophilic Archaeon *Methanosarcina thermophila* [6], we can write in the conventional form:

$$\Delta G^0_{1A} = -2.303\ RT\ \big(\log a_{CO_2(aq)} + \log a_{CH_4(aq)} - \log a_{CH_3COO^-} - \log a_{H^+}\big) \tag{2A}$$

However, this equation can also be written as:

$$\Delta G^0_{1A}{}' = -2.303\ RT\big(\log a_{CO_2(aq)} + \log a_{CH_4(aq)} - \log a_{CH_3COO^-}\big) \tag{3A}$$

where $\Delta G^0_{1A}{}'$ designates the standard Gibbs free energy of the reaction in the biological standard state, i.e., neutral pH (sometimes called the revised standard Gibbs free energy). Hence, because υ_{H^+} in Reaction 1A equals −1, Eq. 4 can be written as:

$$\Delta G^0_{1A}{}' = \Delta G^0_{1A} - G_n = \Delta G^0_{1A} + 2.303\ RT\ (\text{pH}) \tag{4A}$$

and at 55°C and 1 bar where *M. thermophila* grows optimally in the laboratory [128] and where neutral pH is 6.58:

$$\Delta G^0_{1A}{}' = \Delta G^0_{1A} + 41.30\ \text{kJ mol}^{-1} \tag{5A}$$

For comparison, at neutral pH, P_{SAT}, and 25 or 100°C, the conversions can be calculated with:

$$\Delta G^0_{1A}{}' = \Delta G^0_{1A} + 39.95\ \text{kJ mol}^{-1} \tag{6A}$$

and:

$$\Delta G^0_{1A}{}' = \Delta G^0_{1A} + 43.79\ \text{kJ mol}^{-1} \tag{7A}$$

respectively. Other values of neutral pH and interconver-

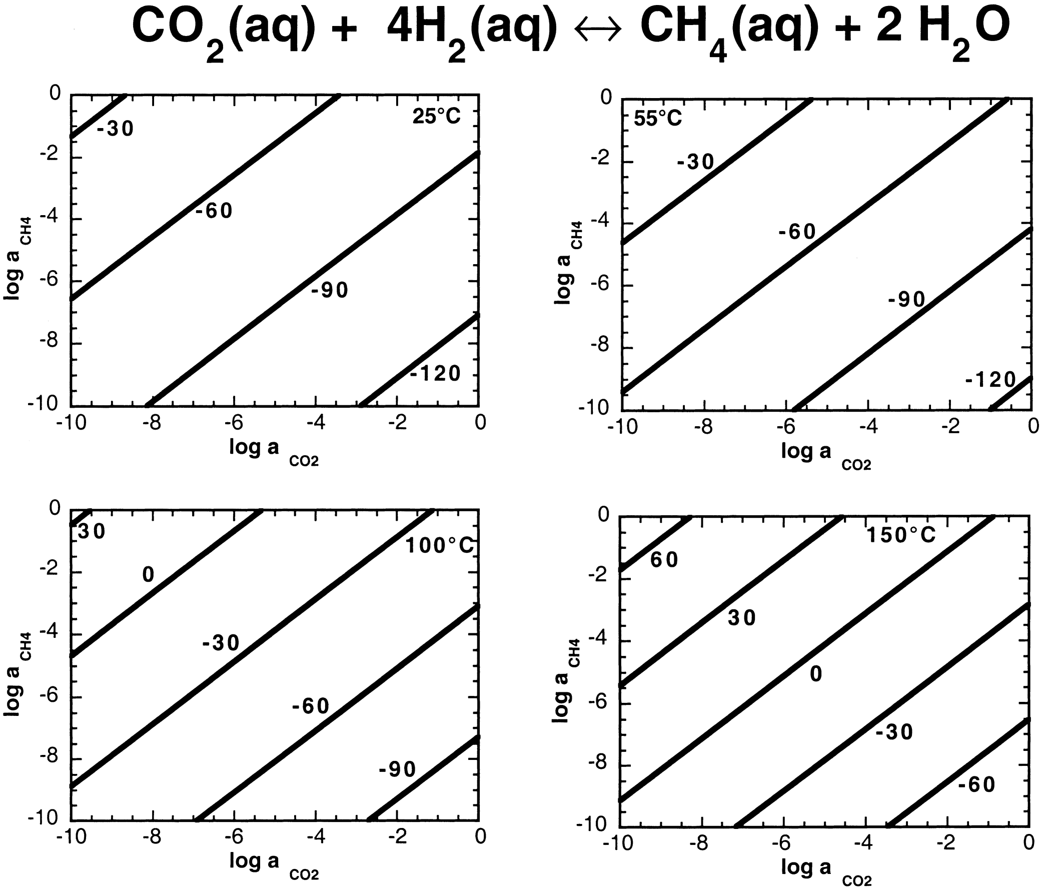

Fig. 14. Same as for Fig. 13, except that the activity of H_2(aq) is set at 10^{-5}.

sion of ΔG^0_{1A} and $\Delta G^0_{1A}{}'$ for water dissociation are given in Table 3.

A.2. Relationship between Gibbs free energies and electrode potentials

In this review, the energetics of all reactions are expressed in terms of their standard and overall Gibbs free energies, ΔG^0_r and ΔG_r, respectively. It is not uncommon, however, when describing redox reactions to express the energetics in terms of standard and overall electrode potentials represented as E^0_r and E_r, respectively. The relationship between ΔG^0_r and E^0_r is given by:

$$\Delta G^0_r = nFE^0_r \tag{8A}$$

and that between ΔG_r and E_r is given by:

$$\Delta G_r = nFE_r \tag{9A}$$

where n denotes the number of electrons transferred in the reaction, and F stands for the Faraday constant (96.48 kJ mol^{-1} V^{-1}). The relation between E_r and E^0_r is analogous to that between ΔG_r and ΔG^0_r. Here we consider, as an example, the reduction at 25°C and 1 bar of NO_3^- to NO_2^- (Reaction 11) which is the sum of two half reactions (Reactions 9 and 10) that explicitly include the transfer of two electrons. E^0_{11} can be calculated from Eq. 8A by rewriting it as:

$$E^0_r = \frac{\Delta G^0_r}{nF} \tag{10A}$$

At 25°C and 1 bar, ΔG^0_{11} equals −176.21 kJ mol^{-1}, and E^0_{11}, for n equals 2, is −0.91 V. Corresponding values of ΔG^0_{11} and E^0_{11} at 100°C and P_{SAT} are −174.44 kJ mol^{-1} and −0.90 V, respectively. As in the case of ΔG_r, the composition of the system can have a large effect on values of E_r relative to E^0_r. As an example, at 25°C, 1 bar, and equal activities of NO_3^- and NO_2^-, E_{11} varies between −0.62 and −0.82 V as the fugacity of H_2 changes from 10^{-10} to 10^{-3}.

A.3. Calculating activities from concentrations

Chemical information commonly required when evaluating metabolic reactions includes the concentration of individual compounds. However, to calculate values of ΔG_r, the activities of individual compounds, rather than their concentrations, need to be known. Here, we briefly review activity–concentration relations, focusing predom-

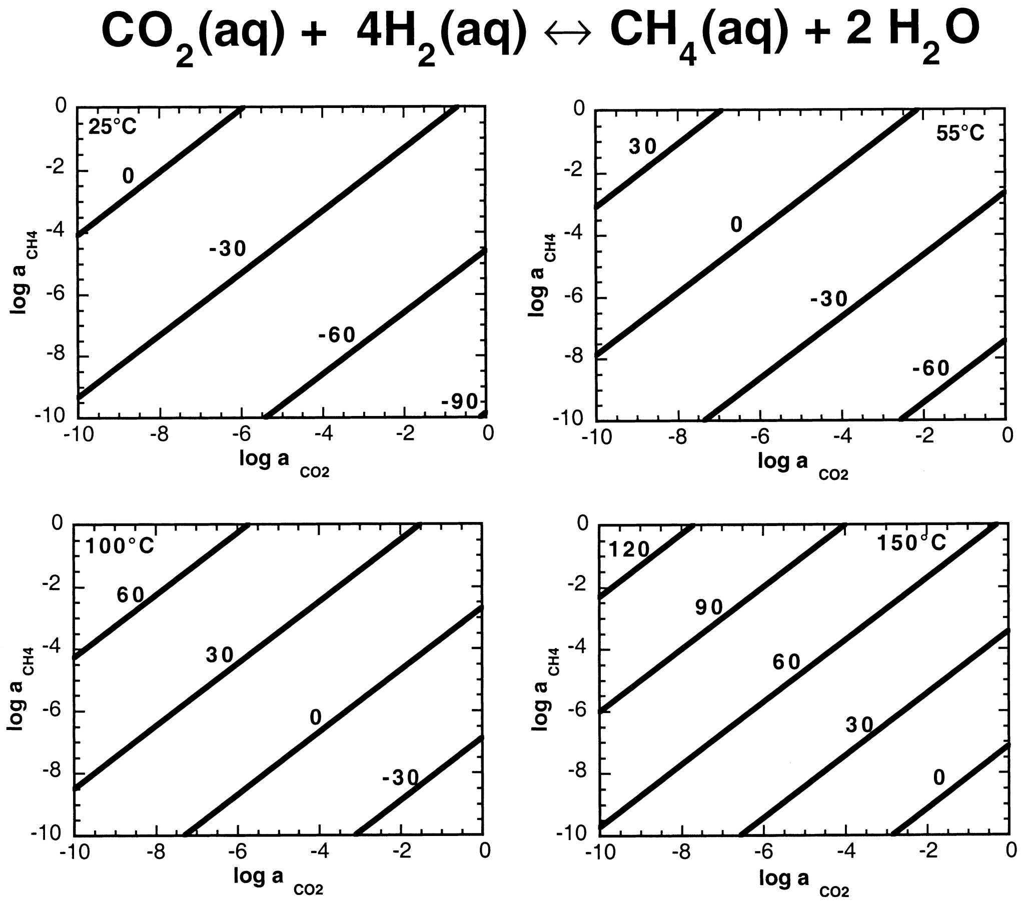

Fig. 15. Same as for Fig. 13, except that the activity of $H_2(aq)$ is set at 10^{-7}.

inantly on aqueous solutes. For more detailed discussions, textbooks in solution chemistry, thermodynamics, physical chemistry, or geochemistry [129–131] should be consulted.

The relationship between the concentration (commonly expressed in units of molality) and the activity of an individual aqueous electrolyte, nonelectrolyte, or ionic species can be given by:

$$a = \gamma m \tag{11A}$$

where a, γ, and m represent the activity, activity coefficient, and molality, respectively. Thus, to convert a concentration, which can be measured, into an activity, which is required for thermodynamic analysis of reaction energetics, the activity coefficient needs to be calculated. As an example, we discuss here the activity coefficients of electrolytes such as NaCl, K_2SO_4, and others. In an electrolyte solution, the solute is partially or completely dissociated into its ions. It has been shown that the activity coefficient of an electrolyte, commonly specified as $\gamma_\pm$, is a function of the ionic strength (I) of the aqueous solution which is defined as:

$$I = \tfrac{1}{2}\sum m_i z_i^2 \tag{12A}$$

where m_i and z_i stand for the molality and charge of the ith ion in the solution, respectively.

In Fig. A1 curves are shown of $\gamma_\pm$ versus ionic strength for several common electrolytes. The effect of valence of an electrolyte on the value of $\gamma_\pm$ can clearly be seen in this figure. As an example, NaCl, an electrolyte consisting of two univalent ions, has the largest value of $\gamma_\pm$ over the entire range of ionic strength; $CuSO_4$, composed of two divalent ions, exhibits the smallest value of $\gamma_\pm$. Fig. A1 further illustrates that values of $\gamma_\pm$ differ considerably from unity with increasing ionic strength, in some cases even at very modest values of I. For example, $\gamma_\pm$ for $CuSO_4$ equals ~0.65 at $I = 0.01$. A thorough analysis of activity coefficient relations in aqueous electrolyte solutions is given by Helgeson et al. (1981) [71].

Activity coefficients of individual ions are most commonly calculated with a form of the Debye–Hückel equation which takes account of long-range electrostatic forces of one ion upon another. Different Debye–Hückel expressions are appropriate for different ionic strengths, but each expression explicitly accounts for the charge of the ion and the value of I. At very low concentrations, below ~0.01 I, the Debye–Hückel limiting law is used, which is given by:

$$\log \gamma_i = -A z_i^2 \sqrt{I} \tag{13A}$$

where γ_i and z_i denote the activity coefficient and charge of the ith ion and A stands for a constant characteristic of the solvent. At higher concentrations, between approxi-

Table 8.1
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for aqueous and liquid organic compounds

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
Carboxylic acids												
Formate$^-$	−348.69	−350.24	−350.88	−351.95	−352.65	−353.51	−354.78	−356.03	−357.26	−358.48	−361.21	−364.79
Formic acid(aq)	−368.64	−371.17	−372.30	−374.28	−375.62	−377.33	−379.96	−382.66	−385.44	−388.29	−395.22	−405.78
Acetate$^-$	−367.36	−368.72	−369.33	−370.37	−371.07	−371.96	−373.31	−374.69	−376.08	−377.49	−380.79	−385.40
Acetic acid(aq)	−392.52	−395.25	−396.48	−398.66	−400.17	−402.09	−405.08	−408.18	−411.40	−414.72	−422.88	−435.44
Glycolate$^-$	−504.47	−506.21	−506.98	−508.30	−509.19	−510.32	−512.03	−513.75	−515.51	−517.27	−521.43	−527.28
Glycolic acid(aq)	−524.89	−527.61	−528.86	−531.07	−532.59	−534.55	−537.60	−540.77	−544.07	−547.48	−555.90	−568.93
Propanoate$^-$	−360.66	−362.33	−363.09	−364.46	−365.40	−366.63	−368.55	−370.56	−372.66	−374.85	−380.23	−388.35
Propanoic acid(aq)	−386.48	−389.58	−391.00	−393.54	−395.30	−397.58	−401.15	−404.89	−408.80	−412.87	−422.96	−438.69
Lactate$^-$	−509.69	−511.75	−512.67	−514.30	−515.41	−516.85	−519.06	−521.35	−523.72	−526.15	−532.04	−540.80
Lactic acid(aq)	−530.19	−533.29	−534.72	−537.29	−539.07	−541.38	−544.99	−548.78	−552.74	−556.87	−567.09	−583.05
Butanoic acid(aq)	−376.55	−380.02	−381.63	−384.53	−386.54	−389.16	−393.26	−397.57	−402.09	−406.79	−418.48	−436.74
Butanoate$^-$	−351.28	−353.27	−354.18	−355.82	−356.97	−358.45	−360.79	−363.26	−365.84	−368.54	−375.20	−385.41
Pentanoic acid(aq)	−367.75	−371.59	−373.39	−376.64	−378.92	−381.89	−386.57	−391.52	−396.71	−402.15	−415.71	−437.02
Pentanoate$^-$	−342.31	−344.64	−345.73	−347.72	−349.13	−350.97	−353.91	−357.05	−360.37	−363.86	−372.63	−386.39
Benzoate$^-$	−207.58	−209.84	−210.88	−212.75	−214.05	−215.75	−218.41	−221.22	−224.17	−227.25	−234.86	−246.58
Benzoic acid(aq)	−229.90	−233.27	−234.86	−237.71	−239.71	−242.31	−246.40	−250.73	−255.29	−260.04	−271.92	−290.58
Dicarboxylic acids												
Oxalate^{-2}	−672.66	−673.70	−674.05	−674.52	−674.76	−674.99	−675.18	−675.22	−675.09	−674.80	−673.49	−669.86
H–oxalate$^-$	−694.80	−697.28	−698.34	−700.13	−701.31	−702.78	−704.94	−707.08	−709.18	−711.26	−715.97	−722.25
Oxalic acid(aq)	−701.44	−704.31	−705.59	−707.83	−709.34	−711.26	−714.21	−717.23	−720.32	−723.48	−731.11	−742.65
Malonate^{-2}	−683.68	−684.78	−685.18	−685.75	−686.07	−686.39	−686.72	−686.87	−686.83	−686.62	−685.36	−681.53
H–malonate$^-$	−713.55	−716.43	−717.69	−719.83	−721.25	−723.02	−725.68	−728.32	−730.96	−733.59	−739.65	−748.04
Malonic acid(aq)	−728.75	−732.35	−733.97	−736.80	−738.73	−741.19	−744.98	−748.88	−752.88	−756.99	−766.94	−782.03
Succinate^{-2}	−685.69	−687.18	−687.77	−688.70	−689.27	−689.92	−690.78	−691.49	−692.07	−692.50	−692.89	−691.75
H–succinate$^-$	−715.58	−718.59	−719.91	−722.18	−723.71	−725.64	−728.56	−731.52	−734.51	−737.51	−744.61	−754.76
Succinic acid(aq)	−738.13	−742.12	−743.92	−747.10	−749.28	−752.07	−756.37	−760.82	−765.41	−770.13	−781.64	−799.16
Glutaric acid(aq)	−732.86	−737.53	−739.66	−743.40	−745.96	−749.23	−754.30	−759.53	−764.92	−770.47	−783.99	−804.54
H–glutarate$^-$	−709.86	−713.34	−714.89	−717.56	−719.37	−721.66	−725.14	−728.69	−732.30	−735.95	−744.66	−757.38
Glutarate^{-2}	−681.28	−683.18	−683.97	−685.24	−686.05	−687.02	−688.38	−689.63	−690.76	−691.77	−693.64	−694.82
Alcohols												
Methanol(aq)	−172.98	−175.01	−175.94	−177.59	−178.74	−180.22	−182.53	−184.95	−187.47	−190.10	−196.61	−206.76
Ethanol(aq)	−178.08	−180.27	−181.30	−183.16	−184.47	−186.18	−188.90	−191.78	−194.83	−198.04	−206.10	−218.94
Propanol(aq)	−171.70	−174.18	−175.36	−177.52	−179.05	−181.07	−184.28	−187.72	−191.38	−195.25	−205.05	−220.76
2-Propanol(aq)	−182.37	−184.52	−185.56	−187.48	−188.86	−190.68	−193.62	−196.80	−200.21	−203.85	−213.17	−228.39
Butanol(aq)	−158.41	−161.18	−162.51	−164.97	−166.72	−169.03	−172.74	−176.72	−180.96	−185.46	−196.90	−215.35
Pentanol(aq)	−156.32	−159.45	−160.97	−163.77	−165.78	−168.42	−172.68	−177.27	−182.18	−187.38	−200.64	−222.10
Alkanes												
Ethane(aq)	−14.01	−15.51	−16.26	−17.68	−18.70	−20.08	−22.32	−24.77	−27.42	−30.26	−37.58	−49.58
Propane(aq)	−5.38	−7.28	−8.22	−9.99	−11.27	−12.97	−15.75	−18.78	−22.04	−25.52	−34.46	−49.04
Butane(aq)	3.43	1.27	0.14	−2.00	−3.55	−5.64	−9.02	−12.69	−16.61	−20.80	−31.45	−48.67
Pentane(aq)	12.83	10.24	8.90	6.37	4.53	2.08	−1.90	−6.19	−10.79	−15.67	−28.08	−48.10
Octane(l)[a]	15.23	9.64	7.13	2.75	−0.24	−4.04	−9.89	−15.90	−22.09	−28.44	−43.88	−67.39
Nonane(l)[a]	21.22	15.16	12.43	7.64	4.38	0.21	−6.20	−12.82	−19.63	−26.63	−43.69	−69.72
Decane(l)[a]	27.22	20.66	17.71	12.53	8.99	4.48	−2.48	−9.66	−17.05	−24.65	−43.17	−71.45
Undecane(l)[a]	33.23	26.18	23.00	17.42	13.61	8.75	1.26	−6.48	−14.45	−22.65	−42.64	−73.17
Hexadecane(l)[a]	63.24	53.74	49.44	41.88	36.71	30.10	19.89	9.34	−1.54	−12.76	−40.15	−82.09
Amino acids												
Alanine(aq)	−367.97	−370.46	−371.59	−373.57	−374.93	−376.67	−379.38	−382.18	−385.08	−388.08	−395.45	−406.80
Arginine(aq)	−232.53	−237.68	−240.01	−244.09	−246.90	−250.49	−256.06	−261.84	−267.84	−274.04	−289.30	−312.88
Arginine$^+$	−284.86	−290.20	−292.60	−296.81	−299.69	−303.37	−309.06	−314.96	−321.07	−327.37	−342.81	−366.50
Asparagine(aq)	−519.57	−523.37	−525.06	−528.00	−530.00	−532.54	−536.47	−540.52	−544.71	−549.03	−559.59	−575.81
Aspartic acid(aq)	−716.56	−720.18	−721.79	−724.59	−726.51	−728.94	−732.70	−736.60	−740.62	−744.78	−754.97	−770.65
Aspartate$^-$	−695.24	−698.18	−699.44	−701.62	−703.09	−704.93	−707.74	−710.60	−713.51	−716.48	−723.57	−733.94
Cysteine(aq)	−331.80	−334.77	−336.11	−338.48	−340.11	−342.22	−345.50	−348.93	−352.51	−356.23	−365.44	−379.79
Glutamic acid(aq)	−718.30	−722.27	−724.05	−727.17	−729.30	−732.02	−736.23	−740.61	−745.13	−749.81	−761.29	−779.01
Glutamate$^-$	−695.38	−698.33	−699.62	−701.82	−703.31	−705.20	−708.08	−711.02	−714.03	−717.10	−724.48	−735.34
Glutamine(aq)	−522.50	−526.55	−528.36	−531.54	−533.72	−536.50	−540.81	−545.28	−549.92	−554.71	−566.48	−584.67
Glycine(aq)	−376.78	−379.39	−380.54	−382.52	−383.86	−385.54	−388.10	−390.71	−393.36	−396.05	−402.51	−412.17
Histidine(aq)	−196.45	−200.69	−202.60	−205.97	−208.29	−211.26	−215.87	−220.68	−225.68	−230.85	−243.61	−263.38
Histidine$^+$	−230.15	−234.67	−236.70	−240.26	−242.70	−245.81	−250.64	−255.65	−260.84	−266.21	−279.38	−299.64
Isoleucine(aq)	−338.63	−341.63	−343.05	−345.64	−347.46	−349.85	−353.62	−357.64	−361.89	−366.35	−377.57	−395.40

Table 8.1 (*continued*)

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
Leucine(aq)	−347.82	−350.86	−352.30	−354.93	−356.78	−359.20	−363.05	−367.15	−371.48	−376.05	−387.53	−405.81
Lysine(aq)	−332.23	−335.90	−337.58	−340.55	−342.60	−345.25	−349.39	−353.74	−358.27	−362.99	−374.70	−392.98
$Lysine^+$	−382.91	−386.87	−388.66	−391.83	−394.00	−396.80	−401.16	−405.71	−410.44	−415.35	−427.48	−446.28
Methionine(aq)	−496.85	−500.79	−502.59	−505.79	−508.00	−510.85	−515.29	−519.92	−524.75	−529.76	−542.10	−561.25
Phenylalanine(aq)	−201.72	−205.20	−206.83	−209.76	−211.82	−214.51	−218.76	−223.30	−228.09	−233.13	−245.85	−266.17
Proline(aq)	−303.13	−306.34	−307.78	−310.33	−312.07	−314.30	−317.75	−321.34	−325.04	−328.87	−338.26	−352.74
Serine(aq)	−514.03	−517.11	−518.49	−520.89	−522.53	−524.62	−527.84	−531.18	−534.63	−538.19	−546.91	−560.30
Threonine(aq)	−497.29	−500.10	−501.38	−503.65	−505.22	−507.26	−510.44	−513.79	−517.31	−520.97	−530.10	−544.42
Tryptophan(aq)	−106.79	−110.51	−112.23	−115.34	−117.54	−120.43	−125.05	−130.02	−135.34	−141.00	−155.48	−179.02
Tyrosine(aq)	−378.64	−382.39	−384.10	−387.16	−389.28	−392.01	−396.30	−400.81	−405.54	−410.46	−422.72	−441.93
Valine(aq)	−352.91	−355.72	−357.03	−359.39	−361.05	−363.20	−366.59	−370.18	−373.96	−377.91	−387.78	−403.37
Miscellaneous												
Methanamine(aq)	23.88	21.96	21.08	19.51	18.43	17.02	14.83	12.52	10.12	7.61	1.38	−8.34
Toluene(aq)	130.42	127.85	126.60	124.29	122.65	120.47	116.96	113.19	109.15	104.86	93.94	76.28
Toluene(l)	122.76	119.56	118.11	115.58	113.85	111.63	108.23	104.70	101.08	97.34	88.23	74.29
Ethylbenzene(aq)	140.05	137.13	135.72	133.10	131.23	128.76	124.80	120.53	115.98	111.16	98.92	79.24
Ethylbenzene(l)	125.55	121.61	119.83	116.72	114.60	111.89	107.72	103.42	98.99	94.43	83.33	66.39

[a] Thermodynamic data for liquid *n*-alkanes are taken from Helgeson et al. (1998) [74].

mately 0.01 and 0.1 I, the most common Debye–Hückel equation is:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+B\mathring{a}\sqrt{I}} \quad (14A)$$

where B denotes another constant of the solvent and $\mathring{a}$ stands for the distance of closest approach between oppositely charged ions. At concentrations $> \sim 0.1\ I$, a further extension of the Debye–Hückel limiting law is often used; a common one [71] is represented by:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+B\mathring{a}\sqrt{I}} + b_\gamma I \quad (15A)$$

where b_γ stands for an extended term parameter for computing the mean ionic activity coefficient. Regardless which of the numerous Debye–Hückel expressions is used, each accounts explicitly for the fact that values of γ_i for ions may differ considerably from unity, even at ionic strengths well below 0.1. This is particularly true for multivalent ions such as, for example, SO_4^{2-}, PO_4^{3-}, Fe^{2+}, and Fe^{3+}. The general trend is that values of γ_i for ions decrease from unity with increasing values of I, before increasing at high ionic strength [129,132].

Activity coefficients of neutral molecules in electrolyte solutions can also differ considerably from unity and thus need to be calculated explicitly. For example, gases dissolved in electrolyte solutions generally have activity coefficients greater than unity, as opposed to activity coefficients of ions and electrolytes discussed above. This is shown in Fig. A2 where activity coefficients, γ_m, for gaseous N_2, H_2, O_2, H_2S, and NH_3 dissolved in NaCl solutions at 25°C are plotted against ionic strength. It can be seen in this figure that values of the activity coefficients increase rapidly above 1.0 with increasing values of I. For example, $\gamma_{N_2(g)} > 1.5$ at $I = 1.0$.

A.4. Review of the revised HKF equations of state

The revised HKF equations of state can be used to calculate the standard state thermodynamic properties of organic and inorganic charged and neutral aqueous species at elevated temperatures and pressures. In order to calculate values of ΔG^0 for aqueous species in accord with Eq. 8 in the text, the standard partial molal heat capacity (C_p^0) and volume (V^0) as functions of temperature and pressure need to be integrated. The revised HKF equations of state for these properties are given, respectively, by:

$$C_p^0 = c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P \quad (16A)$$

Table 8.2
Metabolic reactions involving organic and inorganic carbon

E1	$4H_2$(aq)+$2CO_2$(aq) ↔ acetic acid(aq)+$2H_2O$(l)
E2	4formic acid(aq) ↔ CH_4(aq)+$3CO_2$(aq)+$2H_2O$(l)
E3	acetic acid(aq)+$2O_2$(aq) ↔ $2CO_2$(aq)+$2H_2O$(l)
E4	acetic acid(aq) ↔ CH_4(aq)+CO_2(aq)
E5	propanoic acid(aq)+$3.5O_2$(aq) ↔ $3CO_2$(aq)+$3H_2O$(l)
E6	2lactic acid(aq) ↔ 3acetic acid(aq)
E7	2succinic acid(aq)+$7O_2$(aq) ↔ $8CO_2$(aq)+$6H_2O$(l)
E8	methanol(aq)+H_2(aq) ↔ CH_4(aq)+H_2O(l)
E9	4methanol(aq) ↔ $3CH_4$(aq)+CO_2(aq)+$2H_2O$(l)
E10	2ethanol(aq)+$2CO_2$(aq) ↔ 3acetic acid(aq)
E11	2ethanol(aq)+CO_2(aq) ↔ 2acetic acid(aq)+CH_4(aq)
E12	4(2-)propanol(aq)+$3CO_2$(aq)+$2H_2O$(l) ↔ $3CH_4$(aq)+4lactic acid(aq)

Table 8.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 8.2

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
E1	−172.32	−170.74	−169.78	−167.82	−166.31	−164.23	−160.74	−156.84	−152.55	−147.91	−135.81	−115.71
E2	−179.98	−178.10	−177.54	−176.86	−176.59	−176.42	−176.47	−176.86	−177.54	−178.48	−181.56	−187.72
E3	−883.42	−883.07	−882.92	−882.66	−882.49	−882.27	−881.92	−881.57	−881.20	−880.81	−879.80	−878.03
E4	−23.70	−23.79	−23.95	−24.35	−24.70	−25.21	−26.13	−27.21	−28.43	−29.78	−33.41	−39.61
E5	−1536.84	−1536.54	−1536.37	−1536.03	−1535.78	−1535.43	−1534.83	−1534.14	−1533.37	−1532.52	−1530.19	−1525.93
E6	−117.19	−119.16	−120.00	−121.42	−122.36	−123.52	−125.26	−126.99	−128.71	−130.44	−134.46	−140.21
E7	−3137.41	−3138.35	−3138.85	−3139.84	−3140.57	−3141.56	−3143.18	−3144.95	−3146.84	−3148.85	−3153.85	−3161.34
E8	−114.26	−113.66	−113.42	−113.01	−112.74	−112.40	−111.89	−111.38	−110.86	−110.32	−109.04	−107.09
E9	−261.00	−260.12	−259.94	−259.86	−259.94	−260.15	−260.69	−261.47	−262.45	−263.60	−266.93	−273.03
E10	−54.38	−54.85	−54.89	−54.78	−54.59	−54.23	−53.47	−52.45	−51.21	−49.75	−45.59	−38.01
E11	−78.08	−78.64	−78.84	−79.13	−79.29	−79.45	−79.60	−79.66	−79.64	−79.53	−79.00	−77.62
E12	132.52	132.26	132.29	132.49	132.74	133.15	133.98	135.04	136.31	137.79	141.97	149.53

and

$$V^0 = a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T-\Theta}\right) - \omega Q + \left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial \omega}{\partial P}\right)_T \quad (17A)$$

where a_1, a_2, a_3, a_4, c_1, and c_2 stand for temperature/pressure independent parameters unique to each aqueous species; T, P, and P_r designate the temperature and pressure of interest and the reference pressure of 1 bar, respectively; ε corresponds to the dielectric constant for H_2O; Ψ and Θ refer to solvent parameters equal to 2600 bars and 228 K, respectively; Q, X, and Y represent Born functions given by:

$$Q \equiv \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial P}\right)_T \quad (18A)$$

$$X \equiv \frac{1}{\varepsilon}\left(\left(\frac{\partial^2 \ln \varepsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P^2\right) \quad (19A)$$

$$Y \equiv \frac{1}{\varepsilon}\left(\frac{\partial \ln \varepsilon}{\partial T}\right)_P \quad (20A)$$

and ω stands for the conventional Born coefficient of the species, which can be expressed as:

$$\omega \frac{694657 Z_e^2}{r_e} - 225392Z \quad (21A)$$

where Z_e and Z stand for the effective and formal charge (which are equivalent for charged species), respectively, and r_e denotes the effective electrostatic radius of the species, which for monoatomic ions is given by:

$$r_e = r_x + |Z|(k_Z + g) \quad (22A)$$

where r_x designates the crystal radius of the ion; $k_Z = 0.0$ for anions and 0.94 for cations; and g stands for a solvent function of density and temperature [51,72]. If the species

Table 8.4
Microorganisms that use the reactions specified in Table 8.2

Reaction	
E1	*Acetogenium kivui* [254], *Desulfotomaculum thermobenzoicum* [211], *D. thermoacetoxidans* [210]
E2	*M. halotolerans* [412], *Methanococcus* CS-1[165], *M. thermolithotrophicus* [302], *M. thermoflexum*, *M. defluvii* [298], *M. subterraneum* [43], *M. petrolearius* [413]
E3	*P. aerophilum* [345], *S. arcachonense* [380]
E4	*Methanothrix thermoacetophila* [414]
E5	*P. aerophilum* [345], *S. arcachonense* [380]
E6	*Natroniella acetigena* [415]
E7	*Bacillus stearothermophilus* [416], *S. arcachonense* [380]
E8	*Methanolobus siciliae* [417], *Methanohalophilus zhilinae* [418]
E9	*M. barkeri*, *Methanolobus tindarius* [419]
E10	*N. acetigena* [415]
E11	strain CV [420,421]
E12	*M. petrolearius* [413]

Table 8.5
Coupled metabolic reactions involving organic carbon and inorganic nitrogen

E13	formic acid(aq)+NO_3^- ↔ NO_2^-+H_2O(l)+CO_2(aq)
E14	4formic acid(aq)+NO_3^-+H^+ ↔ NH_3(aq)+4CO_2(aq)+3H_2O
E15	acetic acid(aq)+4NO_3^- ↔ 2CO_2(aq)+4NO_2^-+2H_2O(l)
E16	5acetic acid(aq)+8NO_3^-+8H^+ ↔ 4N_2(aq)+10CO_2(aq)+14H_2O(l)
E17	acetic acid(aq)+NO_3^-+H^+ ↔ 2CO_2(aq)+NH_3(aq)+H_2O(l)
E18	2.5propanoic acid(aq)+7NO_3^-+7H^+ ↔ 3.5N_2(aq)+7.5CO_2(aq)+11H_2O(l)
E19	lactic acid(aq)+6NO_3^- ↔ 6NO_2^-+3H_2O(l)+3CO_2(aq)
E20	lactic acid(aq)+2NO_3^- ↔ acetic acid(aq)+2NO_2^-+CO_2(aq)+H_2O(l)
E21	4lactic acid(aq)+2NO_3^-+2H^+ ↔ 4acetic acid(aq)+2NH_3(aq)+4CO_2(aq)+2H_2O(l)
E22	3lactic acid(aq)+2NO_2^-+2H^+ ↔ 3acetic acid(aq)+2NH_3(aq)+3CO_2(aq)+H_2O(l)
E23	2.5succinic acid(aq)+7NO_3^-+7H^+ ↔ 3.5N_2(aq)+10CO_2(aq)+11H_2O(l)
E24	benzoic acid(aq)+3.75NO_3^-+3.75H^++0.75H_2O(l) ↔ 3.75NH_3(aq)+7CO_2(aq)
E25	4methanamine(aq)+2H_2O(l) ↔ 3CH_4(aq)+CO_2(aq)+4NH_3(aq)
E26	ethylbenzene(aq)+8.4NO_3^-+8.4H^+ ↔ 8CO_2(aq)+4.2N_2(aq)+9.2H_2O(l)

Table 8.6
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 8.5

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
E13	−172.35	−172.18	−172.17	−172.22	−172.30	−172.44	−172.74	−173.12	−173.58	−174.11	−175.57	−178.11
E14	−683.27	−682.20	−682.04	−682.14	−682.42	−683.00	−684.28	−686.00	−688.12	−690.61	−697.73	−710.66
E15	−533.12	−534.41	−535.08	−536.37	−537.31	−538.57	−540.61	−542.83	−545.21	−547.73	−554.12	−564.32
E16	−4231.31	−4234.99	−4237.93	−4244.50	−4249.85	−4257.54	−4270.98	−4286.53	−4304.07	−4323.50	−4375.81	−4466.95
E17	−527.00	−527.89	−528.46	−529.63	−530.54	−531.79	−533.93	−536.35	−539.01	−541.92	−549.57	−562.55
E18	−3679.53	−3683.53	−3686.34	−3692.38	−3697.19	−3704.00	−3715.75	−3729.20	−3744.26	−3760.83	−3805.19	−3882.00
E19	−858.28	−861.19	−862.63	−865.26	−867.14	−869.62	−873.55	−877.74	−882.17	−886.82	−898.41	−916.58
E20	−325.16	−326.78	−327.54	−328.90	−329.83	−331.05	−332.94	−334.91	−336.96	−339.08	−344.29	−352.26
E21	−1288.37	−1294.10	−1296.91	−1302.09	−1305.78	−1310.63	−1318.39	−1326.67	−1335.44	−1344.70	−1368.06	−1405.51
E22	−963.22	−967.32	−969.37	−973.20	−975.95	−979.59	−985.45	−991.75	−998.49	−1005.62	−1023.77	−1053.25
E23	−3759.19	−3765.11	−3768.98	−3777.09	−3783.45	−3792.38	−3807.66	−3825.03	−3844.38	−3865.59	−3922.03	−4018.86
E24	−371.58	−371.71	−371.71	−372.36	−372.45	−373.02	−373.81	−375.54	−375.72	−378.17	−385.84	−401.48
E25	−203.07	−205.06	−206.14	−208.23	−209.75	−211.79	−215.10	−218.66	−222.45	−226.47	−236.57	−252.65
E26	−4388.83	−4394.12	−4397.62	−4404.99	−4410.78	−4418.92	−4432.87	−4448.76	−4466.49	−4485.96	−4537.93	−4627.75

under consideration has no formal charge, $(\partial\omega/\partial P)$, $(\partial\omega/\partial T)$, and $(\partial^2/\partial T^2)_P$ in Eqs. 16A and 17A are taken to be zero. In the absence of crystal radii and experimental data at high temperatures and pressures, values of a_1, a_2, a_3, a_4, c_1, c_2, and ω can be estimated for both charged and neutral species using correlation algorithms [49,50,57,61] or predicted using group additivity relations among organic compounds [63].

The revised HKF equations of state have been shown to be highly reliable in predicting the temperature and pressure dependencies of aqueous reactions. As examples, we include here plots of log K for the dissociation of acetic acid to acetate (Fig. A3) and HSO_4^- to SO_4^{2-} (Fig. A4) from 0 to 350°C at P_{SAT}. The symbols represent experimental data taken from the literature, but the curves were generated independently with the revised HKF equations. In other words, the curves shown in Figs. A3 and A4 do not represent the results of fitting curves to the data shown (which in the case of Fig. A4 should be obvious as the data post-date the prediction). Instead, they are constrained by C_p^0 and V^0 data for each species, values of log K at 25°C and 1 bar, and correlations among thermodynamic data and parameters in the revised HKF equations of state. It can be seen in these figures that predicted values of log K for these dissociation reactions are in very close agreement with the available experimental data over the entire temperature range investigated.

Table 8.7
Microorganisms that use the coupled carbon and nitrogen reactions specified in Table 8.5

Reaction	
E13	*B. infernus* [116]
E14	*A. degensii* [187], *T. thioparus* [277,278], *P. aerophilum* [345]
E15	*P. aerophilum* [345], *T. thioparus* [277,278]
E16	*P. aerophilum* [345]
E17	*Geobacter metallireducens* [422,423]
E18	*P. aerophilum* [345]
E19	*B. infernus* [116]
E20	*Sulfurospirillum barnesii* strain SES-3 [380,424], *Bacillus arsenicoselenatis*, *Bacillus selenitireducens* [425]
E21	*S. barnesii* strain SES-3 [380,424], *B. selenitireducens* [425]
E22	*B. selenitireducens* [425], *S. barnesii* strain SES-3 [380,424,426], *B. stearothermophilus* [381,416]
E23	*B. stearothermophilus* [416]
E24	*D. thermobenzoicum* [211]
E25	*M. barkeri* [427]
E26	strain EbN1, strain PbN1 [428]

In addition to equations of state for aqueous species, equations of state have also been generated for organic solids, liquids, and gases; inorganic gases; and rock-forming minerals. These equations are not documented explicitly here, because most of the compounds considered in this review are in the aqueous phase. For discussions of the equations for non-aqueous species see Helgeson et al. [74,76], Richard and Helgeson [75], and Sassani and Shock [56]. An example (Fig. A5 [50]) is included here to show how well the temperature dependencies of gas solubility reactions can be predicted. It can be seen in this figure that the calculated equilibrium constant for the solubility in water of CO_2(g) matches closely the experimental values as a function of temperature taken from the literature.

The revised HKF equations of state were used in this review to calculate values of ΔG^0 and ΔG_r^0 as functions of temperature and pressure for individual aqueous solutes and reactions in microbial metabolism. In Table A.1, we list sources of thermodynamic data for organic solutes that may serve as substrates in microbial metabolism, but for which we have not recovered direct, unequivocal evidence of microbial involvement. In each case, the sources of thermodynamic properties of aqueous solutes listed are consistent with the revised HKF equations of state. In the course of this study, we found it necessary to include thermodynamic data for a few additional compounds, which are listed in Table A.2.

Table 8.8
Coupled metabolic reactions involving organic carbon and inorganic sulfur

E27	CH_4(aq)+SO_4^{2-}+2H^+ ↔ H_2S(aq)+CO_2(aq)+2H_2O(l)
E28	4formic acid(aq)+SO_4^{2-}+2H^+ ↔ H_2S(aq)+4CO_2(aq)+4H_2O(l)
E29	3formic acid(aq)+SO_3^{2-}+2H^+ ↔ 3CO_2(aq)+H_2S(aq)+3H_2O(l)
E30	4formic acid(aq)+$S_2O_3^{2-}$+2H^+ ↔ 2H_2S(aq)+4CO_2(aq)+3H_2O(l)
E31	formic acid(aq)+S(s) ↔ CO_2(aq)+H_2S(aq)
E32	acetic acid(aq)+2H^++SO_4^{2-} ↔ 2CO_2(aq)+H_2S(aq)+2H_2O(l)
E33	3acetic acid(aq)+4SO_3^{2-}+8H^+ ↔ 6CO_2(aq)+4H_2S(aq)+6H_2O(l)
E34	acetic acid(aq)+$S_2O_3^{2-}$+2H^+ ↔ 2H_2S(aq)+2CO_2(aq)+H_2O(l)
E35	acetic acid(aq)+4S(s)+2H_2O(l) ↔ 2CO_2(aq)+4H_2S(aq)
E36	4propanoic acid(aq)+7SO_4^{2-}+14H^+ ↔ 7H_2S(aq)+12CO_2(aq)+12H_2O(l)
E37	4propanoic acid(aq)+3SO_4^{2-}+6H^+ ↔ 4acetic acid(aq)+4CO_2(aq)+3H_2S(aq)+4H_2O(l)
E38	3propanoic acid(aq)+7SO_3^{2-}+14H^+ ↔ 7H_2S(aq)+9CO_2(aq)+9H_2O(l)
E39	propanoic acid(aq)+SO_3^{2-}+2H^+ ↔ acetic acid(aq)+H_2S(aq)+CO_2(aq)+H_2O(l)
E40	4propanoic acid(aq)+7$S_2O_3^{2-}$+14H^+ ↔ 14H_2S(aq)+12CO_2(aq)+5H_2O(l)
E41	4propanoic acid(aq)+3$S_2O_3^{2-}$+6H^+ ↔ 4acetic acid(aq)+6H_2S(aq)+4CO_2(aq)+H_2O(l)
E42	propanoic acid(aq)+7S(s)+4H_2O(l) ↔ 3CO_2(aq)+7H_2S(aq)
E43	2lactic acid(aq)+3SO_4^{2-}+6H^+ ↔ 6CO_2(aq)+3H_2S(aq)+6H_2O(l)
E44	lactic acid(aq)+0.5SO_4^{2-}+H^+ ↔ acetic acid(aq)+0.5H_2S(aq)+CO_2(aq)+H_2O(l)
E45	lactic acid(aq)+2SO_3^{2-}+4H^+ ↔ 3CO_2(aq)+2H_2S(aq)+3H_2O(l)
E46	1.5lactic acid(aq)+SO_3^{2-}+2H^+ ↔ 1.5acetic acid(aq)+1.5CO_2(aq)+H_2S(aq)+1.5H_2O(l)
E47	2lactic acid(aq)+3$S_2O_3^{2-}$+6H^+ ↔ 6H_2S(aq)+6CO_2(aq)+3H_2O(l)
E48	2lactic acid(aq)+$S_2O_3^{2-}$+2H^+ ↔ 2H_2S(aq)+2acetic acid(aq)+2CO_2(aq)+H_2O(l)
E49	lactic acid(aq)+6S(s)+3H_2O(l) ↔ 3CO_2(aq)+6H_2S(aq)
E50	lactic acid(aq)+2S(s)+H_2O(l) ↔ 2H_2S(aq)+acetic acid(aq)+CO_2(aq)
E51	2butanoic acid(aq)+5SO_4^{2-}+10H^+ ↔ 5H_2S(aq)+8CO_2(aq)+8H_2O
E52	butanoic acid(aq)+1.5SO_4^{2-}+3H^+ ↔ acetic acid(aq)+2CO_2(aq)+1.5H_2S(aq)+2H_2O(l)
E53	1.5butanoic acid(aq)+5SO_3^{2-}+10H^+ ↔ 5H_2S(aq)+6CO_2(aq)+6H_2O
E54	butanoic acid(aq)+2SO_3^{2-}+4H^+ ↔ acetic acid(aq)+2CO_2(aq)+2H_2S(aq)+2H_2O(l)
E55	2butanoic acid(aq)+5$S_2O_3^{2-}$+10H^+ ↔ 10H_2S(aq)+8CO_2(aq)+3H_2O
E56	butanoic acid(aq)+1.5$S_2O_3^{2-}$+3H^+ ↔ acetic acid(aq)+2CO_2(aq)+3H_2S(aq)+0.5H_2O(l)
E57	4succinic acid(aq)+7SO_4^{2-}+14H^+ ↔ 16CO_2(aq)+7H_2S(aq)+12H_2O(l)
E58	3succinic acid(aq)+7SO_3^{2-}+14H^+ ↔ 7H_2S(aq)+12CO_2(aq)+9H_2O(l)
E59	4succinic acid(aq)+7$S_2O_3^{2-}$+14H^+ ↔ 14H_2S(aq)+16CO_2(aq)+5H_2O(l)
E60	benzoic acid(aq)+3.75SO_4^{2-}+7.5H^+ ↔ 3.75H_2S(aq)+7CO_2(aq)+3H_2O(l)
E61	benzoic acid(aq)+5SO_3^{2-}+10H^+ ↔ 5H_2S(aq)+7CO_2(aq)+3H_2O(l)
E62	benzoic acid(aq)+3.75$S_2O_3^{2-}$+7.5H^++0.75H_2O(l) ↔ 7.5H_2S(aq)+7CO_2(aq)
E63	4methanol(aq)+3SO_4^{2-}+6H^+ ↔ 3H_2S(aq)+4CO_2(aq)+8H_2O(l)
E64	methanol(aq)+SO_3^{2-}+2H^+ ↔ H_2S(aq)+CO_2(aq)+2H_2O(l)
E65	4methanol(aq)+3$S_2O_3^{2-}$+6H^+ ↔ 6H_2S(aq)+4CO_2(aq)+5H_2O(l)
E66	methanol(aq)+3S(s)+H_2O(l) ↔ CO_2(aq)+H_2S(aq)
E67	2ethanol(aq)+3SO_4^{2-}+6H^+ ↔ 4CO_2(aq)+3H_2S(aq)+6H_2O(l)
E68	2ethanol(aq)+SO_4^{2-}+2H^+ ↔ H_2S(aq)+2acetic acid(aq)+2H_2O
E69	ethanol(aq)+2SO_3^{2-}+4H^+ ↔ 2CO_2(aq)+2H_2S(aq)+3H_2O(l)
E70	1.5ethanol(aq)+SO_3^{2-}+2H^+ ↔ H_2S(aq)+1.5acetic acid(aq)+1.5H_2O
E71	2ethanol(aq)+3$S_2O_3^{2-}$+6H^+ ↔ 6H_2S(aq)+4CO_2(aq)+3H_2O(l)
E72	2ethanol(aq)+$S_2O_3^{2-}$+2H^+ ↔ 2H_2S(aq)+2acetic acid(aq)+H_2O
E73	ethanol(aq)+6S(s)+3H_2O(l) ↔ 2CO_2(aq)+6H_2S(aq)
E74	2propanol(aq)+4.5SO_4^{2-}+9H^+ ↔ 6CO_2(aq)+4.5H_2S(aq)+8H_2O(l)
E75	4propanol(aq)+5SO_4^{2-}+10H^+ ↔ 4acetic acid(aq)+4CO_2(aq)+5H_2S(aq)+8H_2O(l)
E76	2propanol(aq)+SO_4^{2-}+2H^+ ↔ 2propanoic acid(aq)+H_2S(aq)+2H_2O(l)
E77	propanol(aq)+3SO_3^{2-}+6H^+ ↔ 3H_2S(aq)+3CO_2(aq)+4H_2O(l)
E78	3propanol(aq)+5SO_3^{2-}+10H^+ ↔ 3acetic acid(aq)+5H_2S(aq)+3CO_2(aq)+6H_2O(l)
E79	2propanol(aq)+4.5$S_2O_3^{2-}$+9H^+ ↔ 9H_2S(aq)+6CO_2(aq)+3.5H_2O(l)
E80	4propanol(aq)+5$S_2O_3^{2-}$+10H^+ ↔ 4acetic acid(aq)+10H_2S(aq)+4CO_2(aq)+3H_2O(l)
E81	propanol(aq)+9S(s)+5H_2O(l) ↔ 3CO_2(aq)+9H_2S(aq)
E82	butanol(aq)+3SO_4^{2-}+6H^+ ↔ 4CO_2(aq)+3H_2S(aq)+5H_2O(l)
E83	butanol(aq)+SO_4^{2-}+2H^+ ↔ H_2S(aq)+2acetic acid(aq)+H_2O
E84	butanol(aq)+4SO_3^{2-}+8H^+ ↔ 4CO_2(aq)+4H_2S(aq)+5H_2O(l)
E85	3butanol(aq)+4SO_3^{2-}+8H^+ ↔ 4H_2S(aq)+6acetic acid(aq)+3H_2O
E86	butanol(aq)+3$S_2O_3^{2-}$+6H^+ ↔ 4CO_2(aq)+6H_2S(aq)+2H_2O(l)
E87	butanol(aq)+ $S_2O_3^{2-}$+2H^+ ↔ 2H_2S(aq)+2acetic acid(aq)
E88	4pentanol(aq)+15SO_4^{2-}+30H^+ ↔ 15H_2S(aq)+20CO_2(aq)+24H_2O
E89	pentanol(aq)+5SO_3^{2-}+10H^+ ↔ 5H_2S(aq)+5CO_2(aq)+6H_2O
E90	4pentanol(aq)+15$S_2O_3^{2-}$+30H^+ ↔ 30H_2S(aq)+20CO_2(aq)+9H_2O
E91	octane(l)+6.25SO_4^{2-}+12.5H^+ ↔ 8CO_2(aq)+6.25H_2S(aq)+9H_2O(l)
E92	nonane(l)+7SO_4^{2-}+14H^+ ↔ 9CO_2(aq)+7H_2S(aq) 10H_2O(l)
E93	decane(l)+7.75SO_4^{2-}+15.5H^+ ↔ 10CO_2(aq)+7.75H_2S(aq)+11H_2O(l)
E94	undecane(l)+8.5SO_4^{2-}+17H^+ ↔ 11CO_2(aq)+8.5H_2S(aq)+12H_2O(l)
E95	hexadecane(l)+12.25SO_4^{2-}+24.5H^+ ↔ 16CO_2(aq)+12.25H_2S(aq)+17H_2O(l)
E96	toluene(aq)+4.5SO_4^{2-}+9H^+ ↔ 7CO_2(aq)+4.5H_2S(aq)+4H_2O(l)

A.5. Gas solubility reactions

Reports in the literature may represent microbial metabolic processes that occur in the gas phase, the aqueous phase, or both. Furthermore, chemical analyses of reactants and products in natural and laboratory systems may be given either as concentrations for aqueous species or partial pressures for gases. Therefore, converting properties of gases to those of the corresponding aqueous solutes and vice versa in representations of chemical reactions may prove useful. To permit this conversion, we list 11 gas solubility reactions in Table A.3 with their corresponding values of ΔG_r^0 as a function of temperature in Table A.4. These can be combined as necessary with the appropriate reactions as described in the text (see Section 5.1).

A.6. Dissociation reactions

The metabolic reactions discussed in this review are catalyzed by a large number of microorganisms over a wide range of pH. It is evident from the illustrations in Figs. 3, 4, A3, and A4 that aqueous inorganic and organic species may occur in various protonated and deprotonated forms

Table 8.9
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 8.8

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
E27	−103.56	−107.47	−109.35	−112.80	−115.23	−118.41	−123.46	−128.82	−134.48	−140.44	−155.45	−179.71
E28	−283.54	−285.56	−286.89	−289.66	−291.82	−294.83	−299.93	−305.68	−312.02	−318.91	−337.02	−367.43
E29	−289.79	−292.39	−293.89	−296.90	−299.16	−302.26	−307.42	−313.13	−319.36	−326.07	−343.53	−372.59
E30	−296.06	−298.14	−299.50	−302.38	−304.63	−307.78	−313.12	−319.15	−325.81	−333.07	−352.17	−384.30
E31	−40.79	−41.28	−41.59	−42.25	−42.75	−43.45	−44.63	−45.95	−47.39	−48.93	−52.79	−59.05
E32	−127.26	−131.26	−133.30	−137.15	−139.93	−143.62	−149.59	−156.03	−162.91	−170.21	−188.86	−219.32
E33	−690.31	−706.64	−714.82	−730.06	−740.99	−755.45	−778.65	−803.57	−830.11	−858.20	−929.64	−1045.98
E34	−139.78	−143.83	−145.92	−149.87	−152.74	−156.57	−162.77	−169.50	−176.70	−184.38	−204.01	−236.18
E35	−6.90	−10.82	−12.79	−16.47	−19.11	−22.59	−28.18	−34.14	−40.44	−47.02	−63.02	−88.09
E36	−854.25	−883.47	−898.16	−925.55	−945.21	−971.20	−1012.95	−1057.76	−1105.46	−1155.94	−1284.20	−1492.70
E37	−345.20	−358.43	−364.95	−376.96	−385.50	−396.71	−414.60	−433.65	−453.83	−475.08	−528.76	−615.42
E38	−1180.61	−1210.10	−1224.71	−1251.74	−1271.02	−1296.42	−1337.02	−1380.43	−1426.52	−1475.18	−1598.50	−1798.57
E39	−163.43	−167.82	−169.96	−173.90	−176.68	−180.32	−186.12	−192.29	−198.80	−205.66	−222.95	−250.86
E40	−941.86	−971.46	−986.47	−1014.62	−1034.91	−1061.84	−1105.26	−1152.06	−1202.04	−1255.07	−1390.26	−1610.75
E41	−382.75	−396.15	−402.80	−415.13	−423.94	−435.56	−454.16	−474.07	−495.22	−517.56	−574.21	−666.02
E42	−2.92	−10.10	−13.65	−20.21	−24.87	−31.00	−40.76	−51.14	−62.04	−73.39	−100.83	−143.53
E43	−498.98	−512.94	−519.91	−532.86	−542.14	−554.39	−574.02	−595.07	−617.44	−641.08	−701.04	−798.16
E44	−122.23	−125.21	−126.65	−129.29	−131.14	−133.57	−137.42	−141.51	−145.81	−150.33	−161.66	−179.76
E45	−403.75	−412.90	−417.41	−425.74	−431.68	−439.48	−451.96	−465.28	−479.41	−494.32	−532.05	−593.09
E46	−260.47	−266.03	−268.70	−273.58	−277.01	−281.50	−288.61	−296.14	−304.06	−312.38	−333.26	−366.65
E47	−536.53	−550.65	−557.76	−571.04	−580.58	−593.23	−613.58	−635.48	−658.83	−683.57	−746.49	−848.75
E48	−256.97	−262.99	−265.92	−271.29	−275.10	−280.09	−288.03	−296.48	−305.42	−314.81	−338.47	−376.39
E49	−68.94	−75.81	−79.19	−85.42	−89.84	−95.65	−104.89	−114.70	−125.01	−135.75	−161.77	−202.24
E50	−62.04	−64.99	−66.40	−68.95	−70.73	−73.06	−76.72	−80.56	−84.58	−88.73	−98.74	−114.15
E51	−607.51	−628.74	−639.34	−659.04	−673.16	−691.80	−721.69	−753.76	−787.87	−823.95	−915.58	−1064.48
E52	−176.49	−183.11	−186.36	−192.37	−196.65	−202.28	−211.26	−220.85	−231.02	−241.76	−268.93	−312.93
E53	−841.29	−862.62	−873.14	−892.55	−906.38	−924.58	−953.63	−984.69	−1017.63	−1052.41	−1140.50	−1283.40
E54	−330.76	−339.54	−343.82	−351.68	−357.26	−364.57	−376.20	−388.60	−401.72	−415.53	−450.46	−506.94
E55	−670.09	−691.59	−702.41	−722.66	−737.23	−756.54	−787.63	−821.11	−856.85	−894.76	−991.33	−1148.81
E56	−195.27	−201.97	−205.29	−211.46	−215.87	−221.70	−231.04	−241.06	−251.72	−263.00	−291.65	−338.22
E57	−981.70	−1014.00	−1030.38	−1061.08	−1083.23	−1112.61	−1160.00	−1211.08	−1265.65	−1323.56	−1471.14	−1711.67
E58	−1276.20	−1308.01	−1323.88	−1353.39	−1374.54	−1402.47	−1447.31	−1495.43	−1546.66	−1600.89	−1738.71	−1962.79
E59	−1069.32	−1102.00	−1118.69	−1150.15	−1172.93	−1203.24	−1252.31	−1305.38	−1362.23	−1422.69	−1577.20	−1829.72
E60	−467.13	−483.38	−491.52	−506.69	−517.56	−531.94	−555.02	−579.79	−606.15	−634.05	−704.91	−820.03
E61	−852.79	−874.45	−885.15	−904.96	−919.07	−937.67	−967.38	−999.16	−1032.88	−1068.49	−1158.73	−1305.06
E62	−514.07	−530.51	−538.83	−554.40	−565.61	−580.49	−604.47	−630.31	−657.89	−687.16	−761.73	−883.27
E63	−571.68	−582.52	−588.00	−598.25	−605.62	−615.38	−631.06	−647.92	−665.88	−684.90	−733.29	−812.16
E64	−220.05	−223.84	−225.73	−229.22	−231.71	−234.99	−240.24	−245.86	−251.82	−258.12	−274.09	−300.05
E65	−609.23	−620.23	−625.85	−636.42	−644.06	−654.22	−670.63	−688.33	−707.27	−727.39	−778.74	−862.75
E66	−52.65	−55.30	−56.62	−59.06	−60.79	−63.07	−66.71	−70.57	−74.62	−78.83	−88.94	−104.62
E67	−436.16	−448.63	−454.80	−466.23	−474.37	−485.10	−502.23	−520.53	−539.93	−560.40	−612.18	−695.96
E68	−181.64	−186.10	−188.20	−191.93	−194.52	−197.86	−203.06	−208.48	−214.12	−219.97	−234.45	−257.33
E69	−372.34	−380.74	−384.85	−392.42	−397.79	−404.84	−416.06	−428.01	−440.66	−453.98	−487.62	−542.00
E70	−213.36	−217.79	−219.87	−223.60	−226.19	−229.54	−234.76	−240.23	−245.94	−251.86	−266.60	−290.00
E71	−473.71	−486.34	−492.65	−504.40	−512.82	−523.94	−541.79	−560.94	−581.32	−602.89	−657.63	−746.56
E72	−194.15	−198.68	−200.81	−204.66	−207.33	−210.80	−216.24	−221.95	−227.92	−234.13	−249.60	−274.19
E73	−37.53	−43.66	−46.64	−52.10	−55.96	−61.01	−68.99	−77.43	−86.26	−95.40	−117.33	−151.14
E74	−609.44	−628.69	−638.19	−655.75	−668.24	−684.68	−710.90	−738.89	−768.55	−799.81	−878.82	−1006.54
E75	−709.83	−732.35	−743.18	−762.90	−776.78	−794.87	−823.46	−853.68	−885.46	−918.75	−1002.21	−1135.80
E76	−182.32	−186.95	−189.12	−192.97	−195.64	−199.08	−204.43	−210.02	−215.81	−221.84	−236.73	−260.19
E77	−536.12	−548.99	−555.28	−566.84	−575.03	−585.78	−602.87	−621.07	−640.31	−660.57	−711.70	−794.29
E78	−918.04	−940.33	−951.02	−970.45	−984.09	−1001.88	−1029.96	−1059.63	−1090.83	−1123.50	−1205.47	−1336.88
E79	−665.77	−685.26	−694.97	−713.00	−725.91	−742.94	−770.25	−799.51	−830.63	−863.53	−947.00	−1082.43
E80	−772.42	−795.19	−806.26	−826.52	−840.85	−859.61	−889.40	−921.04	−954.45	−989.56	−1077.96	−1220.12
E81	−33.90	−43.36	−47.95	−56.35	−62.28	−70.03	−82.27	−95.20	−108.71	−122.71	−156.28	−208.01
E82	−398.27	−411.28	−417.70	−429.54	−437.96	−449.04	−466.72	−485.57	−505.55	−526.61	−579.82	−665.79
E83	−143.75	−148.77	−151.09	−155.24	−158.11	−161.80	−167.54	−173.52	−179.74	−186.18	−202.10	−227.15
E84	−706.80	−724.14	−732.61	−748.15	−759.17	−773.63	−796.61	−821.07	−846.93	−874.16	−942.88	−1053.82
E85	−739.77	−759.15	−768.19	−784.35	−795.54	−809.98	−832.52	−856.07	−880.59	−906.08	−969.35	−1069.49
E86	−435.82	−448.99	−455.55	−467.71	−476.41	−487.89	−506.28	−525.99	−546.94	−569.09	−625.27	−716.38
E87	−156.26	−161.34	−163.71	−167.97	−170.92	−174.75	−180.73	−187.00	−193.54	−200.34	−217.25	−244.02
E88	−1922.48	−1987.81	−2020.01	−2079.43	−2121.71	−2177.29	−2265.96	−2360.57	−2460.78	−2566.41	−2833.37	−3264.64

Table 8.9 (*continued*)

Reaction	T (°C) 2	18	25	37	45	55	70	85	100	115	150	200
E89	−866.28	−888.02	−898.64	−918.13	−931.94	−950.05	−978.86	−1009.51	−1041.92	−1076.05	−1162.16	−1301.19
E90	−2110.23	−2176.37	−2209.25	−2270.28	−2313.92	−2371.51	−2463.77	−2562.64	−2667.74	−2778.83	−3060.63	−3517.61
E91	−713.31	−738.55	−751.25	−774.94	−791.98	−814.53	−850.83	−889.89	−931.56	−975.74	−1088.29	−1271.94
E92	−793.56	−822.49	−837.00	−864.06	−883.49	−909.20	−950.55	−995.01	−1042.42	−1092.66	−1220.56	−1429.06
E93	−885.81	−917.45	−933.33	−962.96	−984.23	−1012.39	−1057.68	−1106.38	−1158.32	−1213.36	−1353.53	−1582.11
E94	−972.08	−1006.91	−1024.38	−1056.97	−1080.37	−1111.34	−1161.14	−1214.68	−1271.77	−1332.27	−1486.32	−1737.50
E95	−1403.39	−1454.17	−1479.61	−1527.02	−1561.04	−1606.05	−1678.38	−1756.12	−1838.97	−1926.74	−2150.12	−2514.15
E96	−524.20	−543.26	−552.75	−570.36	−582.95	−599.55	−626.12	−654.57	−684.79	−716.71	−797.61	−928.79

as a function of temperature and pH. In order to ensure that the appropriate aqueous species are used in representing metabolic processes, reactions from tables in the text can be combined with dissociation reactions listed in Table A.5. For example, at 100°C and pH = 8, the reduction of elemental sulfur to hydrogen sulfide (Reaction C19) should be combined with the dissociation reaction for H_2S (H8) in Table A.5 to yield:

$$S(s) + H_2(aq) \rightarrow HS^- + H^+ \tag{23A}$$

because HS^- is the dominant form of aqueous sulfide at this temperature and pH (see Fig. 3b). Values of ΔG_r^0 and pK_a as functions of temperature for reactions given in Table A.5 are listed in Tables A.6 and A.7, respectively.

A.7. Auxiliary redox, disproportionation, and hydrolysis reactions

In the tables in the text, we only list metabolic reactions known to be mediated by microorganisms. Our main criterion for including a reaction is a direct or inferred reference in the literature to that specific metabolic process. In this section, however, we include auxiliary aqueous redox and disproportionation reactions (Table A.8) which, to our knowledge, have not yet been documented as energy-yielding processes in microorganisms. Many of these proposed metabolic reactions involve the oxidation or reduction of trace aqueous species such as V, Cr, Mn, Co, As, Se, and Au. In addition, we list in Table A.8 one reaction denoting the hydrolysis of $Cr_2O_7^{2-}$ and several hydrolysis reactions in the H–O–P system. Values of ΔG_r^0 for reactions in Table A.8 as a function of temperature are listed in Table A.9. Reactions of the type given in Table A.8 may be essential in linking microbial metabolism to abiotic processes in both natural and artificial aqueous systems. As noted in Section 5.8 above, most of the P in metabolic processes does not undergo oxidation or reduction, remaining predominantly in the +5 oxidation state of phosphate. However, in Table A.10, we list several redox processes in the H–O–P system which involve species with P in the +3 and +1 oxidation state of phosphite and hypophosphite as well as the +5 oxidation state of phosphate. These redox reactions can now be combined with pyrophosphate hydrolysis (Table A.8) and/or phosphate or pyrophosphate dissociation (Table A.5) reactions to write the most appropriate and representative redox process in a system. Values of ΔG_r^0 for reactions in Table A.10 are listed in Table A.11.

A.8. Microbially mediated Cl redox reactions

It has long been known that microbes can reduce chlorate (ClO_3^-) or perchlorate (ClO_4^-) to chloride (Cl^-) and in some cases to chlorite (ClO_2^-) [133–138]. Many of these organisms were isolated from industrial or domestic sewage, including waste from paper mills, swine farm lagoons, and match and sugar factories, and others were cultured from natural systems, such as soil, sediments, and river water [139–143]. They include species of *Aerobacter*, *Micrococcus*, *Staphylococcus*, *Proteus*, *Acinetobacter*, *Ankistrodesmus*, *Ideonella*, *Wolinella*, *Chlorella*, *Aspergillus*, *Rhodobacter*, *Sarcina*, *Bacillus*, *Escherichia*, and members of the β subclass of the Proteobacteria [138–141,144–150].

In the laboratory, (per)chlorate reducers grow anaerobically on organic acids and other organic compounds as their carbon source. Among the organic acids metabolized, acetic acid is the most common, but propanoic, butanoic, lactic, succinic, fumaric, and maleic acids can also be oxidized. To date, there are no known thermophiles or hyperthermophiles that can mediate this mode of respiration (J.D. Coates, 1999, personal communication), although one species, *Acinetobacter thermotoleranticus*, is thermotolerant to 47°C [139]. Based on a thermodynamic analysis, neither thermophilic nor hyperthermophilic microbial chlorate and perchlorate reduction can be dismissed a priori as an energy-yielding process. Therefore, we calculated values of ΔG^0 as a function of temperature for Cl-species in different oxidation states (Table A.12). A subset of reactions known to be carried out by (per)chlorate reducers is listed in Table A.13, and values of ΔG_r^0 as a function of temperature for these reactions is given in Table A.14. We did not include every microbial Cl-redox reaction discussed in the literature as this would yield a table of unjustified length in a review on thermophilic and hyperthermophilic metabolism. However, the reader can readily combine reactions and solutes

Table 8.10
Microorganisms that use the coupled carbon and sulfur reactions specified in Table 8.8

Reaction	
E27	Cluster ANME-1 (suggested) [429]
E28	*D. putei* [175], *D. luciae* [175,208], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. geothermicum* [35], *D. hydrogenovorans* [395], *D. thermosapovorans* [212], *A. degensii* [187], *D. australicum* [178], *A. fulgidus* [328,329]
E29	*A. veneficus* [295], *D. putei* [175], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. geothermicum* [35], *D. hydrogenovorans* [395], *D. thermosapovorans* [212], *D. australicum* [178], *A. fulgidus* [328,329]
E30	*D. putei* [175], *D. luciae* [175,208], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermosapovorans* [212], *D. australicum* [178], *A. fulgidus* [328,329]
E31	*T. tenax* [377], *S. arcachonense* [380]
E32	*D. thermoacetoxidans* [210], *Thermodesulforhabdus norvegicus* [266], *D. kuznetsovii* [207], *D. australicum* [170]
E33	*A. veneficus* [295], *D. kuznetsovii* [207]
E34	*D. kuznetsovii* [207], *D. propionica* [214]
E35	*Desulfuromonas palmitatis* [430], *Desulfuromonas acetoxidans* [431], *Geobacter sulfurreducens* [432], *D. kamchatkensis*, *D. propionica* [214], *Desulfurella acetivorans* [213]
E36	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E37	*Desulforhopalus vacuolatus* [433], *D. geothermicum* [35], *D. rhabdoformis* [237]
E38	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E39	*D. rhabdoformis* [237], *D. vacuolatus* [433], *D. geothermicum* [35]
E40	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. propionica* [214], *D. thermocisternum* [180]
E41	*D. rhabdoformis* [237], *D. vacuolatus* [433]
E42	*D. propionica* [214]
E43	*A. fulgidus* [328–330], *D. thermoacetoxidans* [210], *Desulfotomaculum nigrificans* ssp. *salinus* [209], *T. mobile* [264,265], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermosapovorans* [212], *D. australicum* [170]
E44	*D. auripigmentum* [393], *D. vacuolatus* [433], *T. commune* [263], *D. putei* [175], *D. luciae* [175,208], *T. yellowstonii* [267], *D. geothermicum* [35], *D. thermocisternum* [180], *D. australicum* [178], *D. rhabdoformis* [396]
E45	*D. nigrificans* ssp. *salinus* [209], *T. mobile* [264,265], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermosapovorans* [212], *A. fulgidus* [328–330]
E46	*D. australicum* [178], *D. rhabdoformis* [396], *D. vacuolatus* [433], *D. geothermicum* [35], *D. putei* [175], *D. thermocisternum* [180]
E47	*D. nigrificans* ssp. *salinus* [209], *T. mobile* [264,265], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. propionica* [214], *D. thermosapovorans* [212], *A. fulgidus* [328–330]
E48	*S. barnesii* strain SES-3 ([380,426], *T. commune* [263], *D. putei* [175], *D. luciae* [175,208], *D. australicum* [178], *D. rhabdoformis* [396], *D. thermocisternum* [180], *Thermoanaerobacter sulfurophilus* [256]
E49	*D. kamchatkensis*, *D. propionica* [214]
E50	*S. barnesii* strain SES-3 [380,426], *S. arcachonense* [380], *T. sulfurophilus* [256]
E51	*D. thermocisternum* [180][a]
E52	*D. thermobenzoicum* [211], *Desulfobacula toluolica* [434], *D. auripigmentum* [435], *D. kuznetsovii* [207], *D. geothermicum* [35], *D. thermosapovorans* [212][b]
E53	*D. thermocisternum* [180][a]
E54	*D. thermobenzoicum* [211], *D. kuznetsovii* [207], *D. geothermicum* [35], *D. thermosapovorans* [212][b]
E55	*D. thermocisternum* [180][a]
E56	*D. thermobenzoicum* [211], *D. kuznetsovii* [207], *D. thermosapovorans* [212][b]
E57	*D. toluolica* [434], *D. kuznetsovii* [207]
E58	*D. kuznetsovii* [207]
E59	*D. kuznetsovii* [207]
E60	*D. thermobenzoicum* [211], *D. toluolica* [434], *D. australicum* [170]
E61	*D. thermobenzoicum* [211]
E62	*D. thermobenzoicum* [211]
E63	*D. putei* [175], *D. kuznetsovii* [207], *D. thermosapovorans* [212]
E64	*D. kuznetsovii* [207], *D. thermosapovorans* [212]
E65	*D. kuznetsovii* [207], *D. thermosapovorans* [212]
E66	*T. tenax* [377]
E67	*D. nigrificans* ssp. *salinus* [209], *D. putei* [175], *D. luciae* [175,208], *D. toluolica* [434], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. geothermicum* [35], *D. thermocisternum* [180], *D. australicum* [170]
E68	*D. thermosapovorans* [212], *D. australicum* [178], *D. rhabdoformis* [396]
E69	*A. veneficus* [295], *D. putei* [175], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. geothermicum* [35], *D. thermocisternum* [180]
E70	*D. thermosapovorans* [212], *D. australicum* [178], *D. rhabdoformis* [396]
E71	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E72	*D. thermosapovorans* [212], *D. australicum* [178], *D. rhabdoformis* [396]
E73	*D. acetoxidans* [431], *T. tenax* [377]
E74	*D. toluolica* [434], *D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E75	*D. rhabdoformis* [396]
E76	*D. thermosapovorans* [212]
E77	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E78	*D. rhabdoformis* [396]
E79	*D. kuznetsovii* [207], *D. thermobenzoicum* [211], *D. thermocisternum* [180]
E80	*D. rhabdoformis* [396]
E81	*D. acetoxidans* [431]
E82	*D. thermobenzoicum* [211], *D. toluolica* [434], *D. kuznetsovii* [207], *D. thermocisternum* [180]
E83	*D. thermosapovorans* [212], *D. australicum* [178]
E84	*D. thermobenzoicum* [211], *D. kuznetsovii* [207], *D. thermocisternum* [180]
E85	*D. thermosapovorans* [212], *D. australicum* [178]
E86	*D. thermobenzoicum* [211], *D. kuznetsovii* [207], *D. thermocisternum* [180]
E87	*D. thermosapovorans* [212], *D. australicum* [178]
E88	*D. thermosapovorans* [212]
E89	*D. thermosapovorans* [212]
E90	*D. thermosapovorans* [212]
E91	strain TD3[436]
E92	strain TD3[436]
E93	strain TD3[436]
E94	strain TD3[436]
E95	strain Hxd3[437]
E96	*D. toluolica* [434]

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[a] *D. thermocisternum* can also utilize long chain fatty acids C_5–C_{10} and C_{14}–C_{17} with sulfate, sulfite and thiosulfate for growth [180].

[b] *D. thermosapovorans* can also utilize long chain fatty acids C_5–C_{10}, C_{12}, C_{16}, C_{18}, C_{20}, and C_{22} with sulfate, sulfite and thiosulfate for growth [212].

Table 8.11
Metabolic reactions involving amino acids

E97[a]	3acetic acid(aq)+NH_3(aq)+1.5O_2(aq) $\leftrightarrow$ glutamic acid(aq)+CO_2(aq)+3H_2O(l)
E98[b]	3ethanol(aq)+NH_3(aq)+4.5O_2(aq) $\leftrightarrow$ glutamic acid(aq)+CO_2(aq)+6H_2O(l)
E99[b]	2lactic acid(aq)+NH_3(aq)+1.5O_2(aq) $\leftrightarrow$ glutamic acid(aq)+CO_2(aq)+3H_2O(l)
E100	serine(aq)+H_2O(l) $\leftrightarrow$ acetic acid(aq)+formic acid(aq)+NH_3(aq)
E101	threonine(aq)+H_2O(l) $\leftrightarrow$ propanoic acid(aq)+formic acid(aq)+NH_3(aq)
E102[c]	serine(aq)+0.5H_2O(l) $\leftrightarrow$ 1.25acetic acid(aq)+0.5CO_2(aq)+NH_3(aq)
E103[c]	alanine(aq)+0.5H_2O(l)+0.5$S_2O_3^{2-}$+H^+ $\leftrightarrow$ acetic acid(aq)+CO_2(aq)+H_2S(aq)+NH_3(aq)
E104[c]	asparagine(aq)+1.5H_2O(l)+0.5$S_2O_3^{2-}$+H^+ $\leftrightarrow$ acetic acid(aq)+2CO_2(aq)+H_2S(aq)+2NH_3(aq)
E105[c]	methionine(aq)+H_2O(l)+$S_2O_3^{2-}$+2H^+ $\leftrightarrow$ propanoic acid(aq)+2CO_2(aq)+3H_2S(aq)+NH_3(aq)
E106[d]	methionine(aq)+threonine(aq)+5H_2O(l) $\leftrightarrow$ 2propanoic acid(aq)+3formic acid(aq)+2NH_3(aq)+H_2S(aq)+2H_2(aq)
E107[e]	glutamic acid(aq)+H_2(aq) $\leftrightarrow$ alanine(aq)+acetic acid(aq)
E108[e]	glutamic acid(aq)+2H_2O(l) $\leftrightarrow$ 2acetic acid(aq)+formic acid(aq)+NH_3(aq)
E109[e]	glutamic acid(aq)+2H_2O(l) $\leftrightarrow$ 2acetic acid(aq)+CO_2(aq)+NH_3(aq)+H_2(aq)
E110	alanine(aq)+2glycine(aq)+2H_2O(l) $\leftrightarrow$ 3acetic acid(aq)+CO_2(aq)+3NH_3(aq)

[a] Reaction taken from Yamada et al. (1972) [438].

[b] Reaction inferred from Yamada et al. (1972) [438].

[c] Reaction inferred from Magot et al. (1997) [439].

[d] Reaction inferred from Tarlera et al. (1997) [200].

[e] Reaction inferred from Tarlera et al. (1997) [200] who state that 'the fermentation products from glutamate (10 mM) included acetate (15.9 mM), formate (2.7), alanine (1.9 mM), bicarbonate (5.2 mM) (which was not measured but calculated by subtracting the amount of formate from half of the amount of acetate), and hydrogen (2.2 mmol per liter)'. Mass balance determined for the overall reaction matches the sum of these reactions using stoichiometry imposed from the concentrations of the measured products alanine, formate, and acetate.

in Tables A.12 and A.13 with reactions and chemical species given in tables throughout the text and appendix to generate a wide array of known and hypothesized Cl-redox reactions.

Microbial redox reactions involving other halogens, such as Br and I, for example, have not received comparable attention. Tsunogai and Sase (1969) [151] indicate that in near-surface seawater, marine microorganisms use the enzyme nitrate reductase to catalyze the reduction of iodate (IO_3^-) to iodide (I^-). The ability of chlorate reducers to make use of bromate (BrO_3^-) or iodate as an electron acceptor is only now starting to be investigated in detail (J.D. Coates, 1999, personal communication). In anticipation of the discovery of a wide variety of halate reducers, we included in Table A.12 values of ΔG^0 as a function of temperature for Br and I compounds in various oxidation states ranging from +7 for perbromate (BrO_4^-) and periodate (IO_4^-) to −1 for bromide (Br^-) and iodide. To ensure that the appropriate protonated or deprotonated forms of Cl-, Br-, and I-species are used in writing reactions, we included several dissociation reactions for the halogen-containing compounds in Table A.5 and their values of ΔG_r^0 as function of temperature in Table A.6.

A.9. Mineral redox and hydrolysis and cation hydrolysis reactions

As noted in the text (see Section 5.7), numerous mineral oxidation or reduction reactions are known to be microbially mediated, energy-yielding processes. Perhaps the most well-known of these redox processes involve iron sulfide minerals such as pyrite (FeS_2) or pyrrhotite (FeS). Here, we include mineral redox reactions (Table A.15) which, to our knowledge, have not been documented in the literature as being microbially mediated, but may well be. Values of ΔG_r^0 as a function of temperature for these reactions are listed in Table A.16. Regardless of whether these reactions are biotically or abiotically catalyzed, they can be coupled to known microbial metabolic processes in order to describe accurately many net

Table 8.12
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 8.11

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
E97	−635.10	−631.78	−630.24	−627.48	−625.58	−623.12	−619.30	−615.32	−611.18	−606.90	−596.37	−580.06
E98	−2219.88	−2218.93	−2218.25	−2216.81	−2215.67	−2214.06	−2211.29	−2208.14	−2204.62	−2200.78	−2190.56	−2173.06
E99	−752.29	−750.94	−750.23	−748.90	−747.94	−746.64	−744.56	−742.30	−739.89	−737.33	−730.83	−720.27
E100	−35.79	−38.56	−39.82	−42.04	−43.55	−45.48	−48.45	−51.50	−54.63	−57.84	−65.61	−77.40
E101	−46.48	−49.91	−51.45	−54.16	−55.99	−58.33	−61.92	−65.59	−69.35	−73.20	−82.50	−96.54
E102	−74.86	−77.14	−78.22	−80.17	−81.52	−83.28	−86.03	−88.91	−91.91	−95.01	−102.65	−114.43
E103	−79.35	−83.58	−85.62	−89.35	−91.97	−95.42	−100.88	−106.67	−112.78	−119.20	−135.29	−160.93
E104	−99.92	−105.11	−107.65	−112.34	−115.68	−120.05	−127.01	−134.42	−142.23	−150.43	−170.99	−203.60
E105	−0.15	−7.48	−11.08	−17.70	−22.41	−28.61	−38.50	−49.06	−60.25	−72.04	−101.79	−149.54
E106	257.45	248.96	245.07	238.18	233.43	227.35	217.90	208.09	197.93	187.44	161.71	122.02
E107	−61.09	−61.55	−61.74	−62.06	−62.26	−62.50	−62.84	−63.15	−63.43	−63.68	−64.14	−64.55
E108	11.60	8.05	6.44	3.61	1.69	−0.77	−4.56	−8.45	−12.44	−16.54	−26.44	−41.43
E109	15.61	12.16	10.49	7.44	5.29	2.49	−1.96	−6.65	−11.58	−16.73	−29.53	−49.53
E110	−41.14	−46.15	−48.51	−52.81	−55.82	−59.75	−65.95	−72.50	−79.39	−86.58	−104.50	−132.52

Table 8.13
Microorganisms that use the amino acid reactions specified in Table 8.11

Reaction	
E97	*Brevibacterium flavum*, *Corynebacterium acetoacidophilum*, *Corynebacterium acetoglutamicum*, *Corynebacterium acetophilum* [438]
E98	*Brevibacterium* [438]
E99	*Brevibacterium glutaricum* [438]
E100	*E. coli* [440]
E101	*E. coli* [440]
E102	*Dethiosulfovibrio peptidovorans* [439]
E103	*D. peptidovorans* [439]
E104	*D. peptidovorans* [439]
E105	*D. peptidovorans* [439]
E106	*Caloramator proteoclasticus* [200]
E107	*C. proteoclasticus* [200]
E108	*C. proteoclasticus* [200]
E109	*C. proteoclasticus* [200]
E110	*Clostridium sporogenes* [441]

biogeochemical processes including mineral dissolution and precipitation. In this vein, mineral and cation hydrolysis reactions (Tables A.15 and A17, respectively) may also prove helpful to best characterize the chemical processes in biogeochemical systems. Values of ΔG_r^0 as a function of temperature for reactions given in Tables A.15 and A17 are in Tables A.16 and A18, respectively. Chemical formulas for minerals mentioned in Tables 9.1, 9.2, 9.5 and A15 are listed in Table A.19.

References

[1] Woese, C.R., Kandler, O. and Wheelis, M.L. (1990) Towards a natural system of organisms: Proposal for the domains Archaea, Bacteria, and Eucarya. Proc. Natl. Acad. Sci. USA 87, 4576–4579.

[2] Olsen, G.J. and Woese, C.R. (1997) Archaeal genomics: an overview. Cell 89, 991–994.

[3] Pennisi, E. (1998) Genome data shake the tree of life. Science 280, 672–674.

[4] Woese, C. (1998) The universal ancestor. Proc. Natl. Acad. Sci. USA 95, 6854–6859.

[5] Pace, N.R. (1997) A molecular view of microbial diversity and the biosphere. Science 276, 734–740.

[6] Thauer, R.K., Jungermann, K. and Decker, K. (1977) Energy conservation in chemotrophic anaerobic bacteria. Bacteriol. Rev. 41, 100–180.

[7] Madigan, M.T., Martinko, J.M. and Parker, J. (2000) Brock Biology of Microorganisms, edn. 9, Prentice Hall, Upper Saddle River, NJ.

[8] Kelly, R.M. and Adams, M.W.W. (1994) Metabolism in hyperthermophilic microorganisms. Antonie Van Leeuwenhoek 66, 247–270.

[9] Blöchl, E., Rachel, R., Burggraf, S., Hafenbradl, D., Jannasch, H.W. and Stetter, K.O. (1997) *Pyrolobus fumarii*, gen. and sp. nov., represents a novel group of archaea, extending the upper temperature limit for life to 113°C. Extremophiles 1, 14–21.

[10] Daniel, R.M. (1992) Modern life at high temperatures. Orig. Life Evol. Biosph. 22, 33–42.

[11] Segerer, A.H., Burggraf, S., Fiala, G., Huber, G., Huber, R., Pley, U. and Stetter, K.O. (1993) Life in hot springs and hydrothermal vents. Orig. Life Evol. Biosph. 23, 77–90.

[12] Baross, J.A. and Deming, J.W. (1983) Growth of 'black smoker' bacteria at temperatures of at least 250°C. Nature 303, 423–426.

[13] Straube, W.L., Deming, J.W., Somerville, C.C., Colwell, R.R. and Baross, J.A. (1990) Particulate DNA in smoker fluids: evidence for existence of microbial populations in hot hydrothermal systems. Appl. Environ. Microbiol. 56, 1440–1447.

[14] Deming, J.W. and Baross, J.A. (1993) Deep-sea smokers: Windows to a subsurface biosphere. Geochim. Cosmochim. Acta 57, 3219–3230.

[15] Cragg, B.A. and Parkes, R.J. (1994) Bacterial profiles in hydrothermally active deep sediment layers from Middle Valley (N.E. Pacific), sites 857 and 858. Proc. Ocean Drill. Prog. Sci. Res. 139.

[16] Bargar, K.E., Fournier, R.O. and Theodore, T.G. (1985) Particles in fluid inclusions from Yellowstone National Park – Bacteria? Geology 13, 483–486.

[17] White, R.H. (1984) Hydrolytic stability of biomolecules at high temperatures and its implication for life at 250°C. Nature 310, 430–432.

Table 8.14
Standard and overall Gibbs free energies of heterotrophic reactions in which organic compounds are oxidized to CO_2 coupled to the reduction of sulfate to sulfide

Reaction	ΔG_r^0 (kJ mol^{-1})	ΔG_r (per mol of organic C species)	ΔG_r (per mol of SO_4^{2-})
E27	−134.48	−63.05	−63.05
E28	−312.02	−60.15	−240.59
E32	−162.91	−120.06	−120.06
E36	−1105.46	−208.50	−119.14
E43	−617.44	−258.72	−172.48
E51	−787.87	−301.07	−120.43
E57	−1265.65	−277.12	−158.36
E60	−606.15	−509.71	−135.92
E63	−665.88	−112.89	−150.53
E67	−539.93	−191.39	−127.59
E74	−768.55	−280.69	−124.75
E82	−505.55	−376.97	−125.66
E88	−2460.78	−461.61	−123.10
E91	−931.56	−685.11	−109.62
E92	−1042.42	−770.97	−110.14
E93	−1158.32	−861.87	−111.21
E94	−1271.77	−950.31	−111.80
E95	−1838.97	−1392.50	−113.67
E96	−684.79	−534.78	−118.84

Table 9.1
Values of ΔG^0 (in kJ mol^{-1}) at P_{SAT} as a function of temperature for minerals and aqueous compounds containing metals[a]

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
Mg^{2+}	−457.12	−454.95	−453.98	−452.32	−451.21	−449.82	−447.73	−445.65	−443.55	−441.45	−436.47	−429.13
$MgOH^+$	−626.45	−625.05	−624.48	−623.55	−622.97	−622.27	−621.27	−620.35	−619.49	−618.68	−616.98	−614.86
$MgHCO_3^+$	−1046.70	−1046.70	−1046.80	−1046.80	−1047.00	−1047.00	−1047.40	−1047.40	−1047.80	−1048.40	−1050.10	−1053.30
$MgCO_3(aq)$	−1001.20	−999.66	−998.97	−997.74	−996.89	−995.81	−994.15	−992.44	−990.69	−988.91	−984.63	−978.30
Magnesite	−1026.40	−1027.40	−1027.80	−1028.60	−1029.20	−1029.90	−1031.10	−1032.20	−1033.50	−1034.80	−1037.90	−1043.00
Ca^{2+}	−554.05	−553.18	−552.79	−552.10	−551.64	−551.05	−550.16	−549.24	−548.31	−547.35	−545.00	−541.28
$CaOH^+$	−716.07	−716.52	−716.72	−717.06	−717.29	−717.58	−718.02	−718.47	−718.94	−719.41	−720.54	−722.15
$CaHCO_3^+$	−1144.40	−1145.30	−1145.70	−1146.60	−1147.20	−1148.00	−1149.40	−1150.90	−1152.50	−1154.20	−1158.60	−1165.60
$CaCO_3(aq)$	−1099.40	−1099.70	−1099.80	−1099.90	−1099.90	−1099.90	−1099.90	−1099.80	−1099.70	−1099.60	−1099.10	−1098.20
Calcite	−1127.10	−1128.50	−1129.20	−1130.30	−1131.10	−1132.10	−1133.60	−1135.20	−1136.90	−1138.60	−1142.80	−1149.30
Dolomite	−2162.90	−2165.20	−2166.30	−2168.20	−2169.50	−2171.20	−2173.80	−2176.60	−2179.40	−2182.40	−2189.60	−2201.00
VO_4^{3-}	−902.69	−900.18	−899.14	−897.41	−896.29	−894.94	−892.96	−891.04	−889.15	−887.28	−882.82	−875.66
HVO_4^{2-}	−974.86	−974.79	−974.87	−975.16	−975.43	−975.86	−976.68	−977.65	−978.77	−980.02	−983.28	−988.36
$H_2VO_4^-$	−1018.21	−1020.02	−1020.86	−1022.35	−1023.38	−1024.70	−1026.76	−1028.90	−1031.10	−1033.35	−1038.80	−1046.82
$H_3VO_4(aq)$	−1039.16	−1041.58	−1042.66	−1044.54	−1045.81	−1047.43	−1049.90	−1052.41	−1054.97	−1057.59	−1063.85	−1073.21
VO_2^+	−587.92	−587.31	−587.02	−586.50	−586.14	−585.68	−584.97	−584.24	−583.49	−582.72	−580.83	−577.89
$VOOH^+$	−653.27	−651.98	−651.44	−650.59	−650.04	−649.39	−648.48	−647.63	−646.85	−646.11	−644.57	−642.69
VO^{2+}	−449.64	−447.38	−446.43	−444.86	−443.83	−442.60	−440.80	−439.06	−437.38	−435.76	−432.09	−427.03
VO^+	−443.16	−443.75	−443.92	−444.10	−444.16	−444.17	−444.07	−443.84	−443.50	−443.05	−441.60	−438.68
VOH^{2+}	−467.42	−466.82	−466.52	−465.96	−465.57	−465.05	−464.24	−463.37	−462.47	−461.51	−459.09	−455.14
V^{3+}	−247.50	−243.86	−242.25	−239.48	−237.63	−235.30	−231.81	−228.28	−224.74	−221.16	−212.65	−199.93
VOH^+	−419.25	−418.05	−417.56	−416.76	−416.26	−415.66	−414.82	−414.04	−413.32	−412.65	−411.25	−409.56
V^{2+}	−220.50	−218.47	−217.56	−216.00	−214.94	−213.62	−211.61	−209.59	−207.54	−205.46	−200.51	−193.05
$Cr_2O_7^{2-}$	−1302.41	−1307.35	−1309.47	−1313.06	−1315.42	−1318.35	−1322.69	−1326.97	−1331.18	−1335.33	−1344.71	−1357.19
CrO_4^{2-}	−729.76	−730.94	−731.36	−732.00	−732.36	−732.75	−733.22	−733.56	−733.76	−733.82	−733.43	−731.32
$HCrO_4^-$	−764.12	−767.24	−768.60	−770.95	−772.51	−774.47	−777.41	−780.37	−783.32	−786.28	−793.17	−802.86
CrO_2^-	−524.80	−524.44	−524.26	−523.90	−523.64	−523.31	−522.76	−522.17	−521.54	−520.87	−519.10	−515.95
$HCrO_2(aq)$	−577.07	−577.62	−577.81	−578.08	−578.22	−578.36	−578.51	−578.60	−578.63	−578.61	−578.36	−577.64
CrO^+	−390.66	−389.03	−388.27	−386.92	−385.99	−384.81	−382.97	−381.08	−379.13	−377.13	−372.27	−364.82
$CrOH^{2+}$	−424.99	−421.84	−420.49	−418.19	−416.67	−414.79	−412.01	−409.25	−406.52	−403.81	−397.51	−388.43
Cr^{3+}	−213.57	−208.51	−206.27	−202.38	−199.77	−196.48	−191.51	−186.48	−181.40	−176.26	−163.98	−145.64
MnO_4^-	−445.71	−448.84	−450.20	−452.54	−454.09	−456.04	−458.95	−461.87	−464.79	−467.70	−474.47	−483.93
MnO_4^{2-}	−501.98	−503.28	−503.75	−504.47	−504.88	−505.34	−505.89	−506.29	−506.57	−506.69	−506.42	−504.44
Mn^{3+}	−91.94	−87.09	−84.93	−81.19	−78.68	−75.50	−70.70	−65.84	−60.92	−55.94	−44.02	−26.15
Mn^{2+}	−232.07	−231.01	−230.54	−229.72	−229.17	−228.49	−227.45	−226.41	−225.37	−224.31	−221.76	−217.86
$MnOH^+$	−407.10	−407.09	−407.10	−407.12	−407.15	−407.20	−407.28	−407.40	−407.53	−407.69	−408.12	−408.83
$MnO(aq)$	−338.09	−339.03	−339.65	−339.91	−340.16	−340.40	−340.62	−340.76	−340.86	−341.00	−341.06	−341.18
MnO_2^{2-}	−430.43	−429.70	−429.28	−428.45	−427.82	−426.97	−425.57	−424.00	−422.28	−420.41	−415.42	−406.54
$HMnO_2^-$	−507.12	−506.53	−506.26	−505.80	−505.49	−505.11	−504.52	−503.93	−503.33	−502.72	−501.18	−498.59
Alabandite	−216.51	−217.76	−218.31	−219.29	−219.95	−220.80	−222.09	−223.42	−224.78	−226.16	−229.51	−234.53
Rhodochrosite	−813.84	−815.38	−816.07	−817.29	−818.13	−819.19	−820.84	−822.55	−824.31	−826.13	−830.58	−837.41
Fe^{3+}	−23.53	−19.17	−17.23	−13.89	−11.64	−8.82	−4.54	−0.22	4.14	8.56	19.09	34.87
$FeOH^{2+}$	−244.24	−242.57	−241.83	−240.55	−239.69	−238.61	−236.97	−235.32	−233.65	−231.96	−227.93	−221.84
FeO^+	−223.02	−222.48	−222.17	−221.56	−221.12	−220.51	−219.52	−218.44	−217.28	−216.03	−212.84	−207.61
$HFeO_2(aq)$	−420.54	−422.32	−423.00	−424.05	−424.67	−425.38	−426.32	−427.11	−427.77	−428.32	−429.19	−429.56
FeO_2^-	−366.92	−367.86	−368.19	−368.67	−368.94	−369.22	−369.53	−369.73	−369.83	−369.82	−369.41	−367.77
Hematite	−743.48	−744.80	−745.40	−746.48	−747.22	−748.19	−749.69	−751.27	−752.92	−754.64	−758.91	−765.62
Magnetite	−1011.72	−1013.93	−1014.93	−1016.72	−1017.95	−1019.53	−1021.99	−1024.56	−1027.23	−1029.99	−1036.82	−1047.44
Fe^{2+}	−93.90	−92.24	−91.50	−90.22	−89.37	−88.29	−86.66	−85.02	−83.36	−81.68	−77.67	−71.62
$FeOH^+$	−276.53	−275.81	−275.52	−275.03	−274.72	−274.35	−273.83	−273.35	−272.90	−272.48	−271.60	−270.48
$FeO(aq)$	−213.17	−212.51	−212.21	−211.71	−211.38	−210.97	−210.35	−209.75	−209.16	−208.59	−207.30	−205.58
$HFeO_2^-$	−400.68	−399.60	−399.15	−398.42	−397.96	−397.40	−396.61	−395.85	−395.14	−394.45	−392.91	−390.62
Pyrrhotite	−99.43	−100.35	−100.77	−101.50	−102.01	−102.66	−103.66	−104.71	−105.79	−106.91	−109.73	−114.30
Siderite	−677.20	−678.82	−679.54	−680.82	−681.70	−682.82	−684.54	−686.32	−688.16	−690.05	−694.66	−701.71
Pyrite	−159.06	−159.85	−160.22	−160.87	−161.32	−161.90	−162.81	−163.76	−164.75	−165.78	−168.33	−172.32
Co^{3+}	126.98	131.76	133.89	137.58	140.06	143.19	147.92	152.71	157.56	162.47	174.21	191.81
$CoOH^{2+}$	−98.88	−97.04	−96.23	−94.83	−93.89	−92.72	−90.94	−89.17	−87.37	−85.57	−81.27	−74.83
Co^{2+}	−56.95	−55.18	−54.39	−53.03	−52.11	−50.97	−49.23	−47.48	−45.71	−43.93	−39.67	−33.25
$CoOH^+$	−235.47	−234.71	−234.41	−233.93	−233.63	−233.29	−232.83	−232.43	−232.07	−231.76	−231.18	−230.63
$CoO(aq)$	−185.82	−184.61	−184.09	−183.20	−182.62	−181.90	−180.82	−179.77	−178.74	−177.74	−175.47	−172.43
$HCoO_2^-$	−351.54	−349.70	−348.95	−347.70	−346.90	−345.94	−344.56	−343.26	−342.00	−340.80	−338.10	−334.31
CoO_2^{2-}	−267.43	−265.37	−264.42	−262.76	−261.61	−260.15	−257.89	−255.56	−253.15	−250.66	−244.42	−234.25

Table 9.1 (*continued*)

Compound	*T* (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
Ni^{2+}	−48.51	−46.50	−45.60	−44.04	−43.00	−41.68	−39.68	−37.66	−35.61	−33.55	−28.59	−21.13
NiOH^{+}	−222.98	−221.66	−221.12	−220.25	−219.70	−219.04	−218.12	−217.27	−216.48	−215.75	−214.22	−212.38
NiO(aq)	−162.23	−163.87	−164.59	−165.86	−166.72	−167.80	−169.45	−171.13	−172.84	−174.58	−178.76	−184.99
HNiO$_2^-$	−346.67	−344.08	−343.00	−341.24	−340.11	−338.76	−336.81	−334.96	−333.18	−331.49	−327.71	−322.53
NiO$_2^{2-}$	−272.27	−269.74	−268.61	−266.64	−265.31	−263.63	−261.08	−258.48	−255.82	−253.10	−246.43	−235.80
Cu^{2+}	63.37	64.91	65.59	66.75	67.53	68.50	69.96	71.41	72.87	74.34	77.80	82.98
CuOH^{+}	−127.01	−126.54	−126.36	−126.06	−125.89	−125.69	−125.42	−125.19	−125.00	−124.83	−124.56	−124.35
CuO(aq)	−88.21	−87.39	−87.03	−86.40	−85.99	−85.47	−84.69	−83.92	−83.15	−82.39	−80.58	−77.89
HCuO$_2^-$	−251.32	−251.44	−251.46	−251.45	−251.42	−251.37	−251.24	−251.07	−250.86	−250.62	−249.91	−248.52
CuO$_2^{2-}$	−174.37	−173.04	−172.38	−171.17	−170.31	−169.18	−167.39	−165.48	−163.45	−161.30	−155.75	−146.28
Chalcopyrite	−184.95	−186.96	−187.87	−189.45	−190.54	−191.92	−194.05	−196.24	−198.50	−200.82	−206.46	−215.01
Covellite	−51.28	−52.31	−52.77	−53.58	−54.13	−54.84	−55.92	−57.03	−58.17	−59.35	−62.19	−66.48
Cu^{+}	50.88	50.28	50.00	49.50	49.15	48.70	47.99	47.24	46.46	45.65	43.66	40.61
Chalcocite	−83.59	−85.46	−86.30	−87.77	−88.77	−90.04	−91.99	−94.00	−96.05	−98.28	−103.77	−112.09
Cuprite	−145.98	−147.41	−148.05	−149.17	−149.94	−150.91	−152.41	−153.95	−155.53	−157.15	−161.08	−167.00
Bornite	−353.45	−359.89	−362.78	−367.82	−371.25	−375.60	−382.28	−389.11	−396.11	−403.26	−420.51	−446.42
Copper	0.74	0.23	0	−0.41	−0.68	−1.03	−1.57	−2.13	−2.70	−3.29	−4.72	−6.87
Zn^{2+}	−149.76	−148.04	−147.27	−145.95	−145.07	−143.96	−142.30	−140.63	−138.95	−137.26	−133.26	−127.29
ZnOH^{+}	−338.29	−339.26	−339.70	−340.46	−340.98	−341.64	−342.67	−343.71	−344.79	−345.89	−348.54	−352.50
ZnO(aq)	−282.23	−282.14	−282.08	−281.97	−281.89	−281.78	−281.61	−281.43	−281.24	−281.05	−280.59	−279.93
ZnO$_2^{2-}$	−394.10	−391.49	−390.32	−388.30	−386.94	−385.22	−382.61	−379.97	−377.26	−374.50	−367.75	−357.05
HZnO$_2^-$	−464.87	−463.73	−463.25	−462.47	−461.97	−461.36	−460.49	−459.66	−458.86	−458.09	−456.33	−453.70
Sphalerite	−199.30	−200.20	−200.61	−201.33	−201.82	−202.44	−203.40	−204.39	−205.41	−206.46	−209.02	−212.89
AsO$_4^{3-}$	−651.63	−649.49	−648.39	−646.33	−644.84	−642.86	−639.68	−636.23	−632.52	−628.57	−618.30	−600.79
HAsO$_4^{2-}$	−714.41	−714.58	−714.59	−714.52	−714.43	−714.28	−713.95	−713.51	−712.98	−712.33	−710.34	−706.11
H$_2$AsO$_4^-$	−750.46	−752.35	−753.17	−754.57	−755.51	−756.68	−758.45	−760.21	−761.97	−763.73	−767.79	−773.33
H$_3$AsO$_4$(aq)	−761.96	−764.81	−766.09	−768.33	−769.85	−771.77	−774.71	−777.72	−780.79	−783.91	−791.43	−802.69
AsO$_2^-$	−348.93	−349.70	−349.99	−350.45	−350.74	−351.06	−351.50	−351.88	−352.21	−352.49	−352.90	−352.82
HAsO$_2$(aq)	−399.78	−401.79	−402.67	−404.19	−405.20	−406.47	−408.40	−410.34	−412.30	−414.27	−418.95	−425.79
SeO$_4^{2-}$	−439.93	−441.01	−441.41	−442.01	−442.35	−442.73	−443.19	−443.52	−443.73	−443.83	−443.54	−441.67
HSeO$_4^-$	−448.91	−451.25	−452.29	−454.10	−455.32	−456.85	−459.18	−461.53	−463.91	−466.31	−471.94	−479.93
SeO$_3^{2-}$	−369.30	−369.75	−369.87	−369.96	−369.97	−369.92	−369.72	−369.39	−368.93	−368.34	−366.40	−362.07
HSeO$_3^-$	−408.37	−410.51	−411.46	−413.09	−414.18	−415.55	−417.63	−419.73	−421.84	−423.95	−428.89	−435.81
H$_2$SeO$_3$(aq)	−421.50	−424.70	−426.14	−428.68	−430.40	−432.59	−435.95	−439.39	−442.92	−446.52	−455.20	−468.28
Selenium[b]	0.95	0.29	0	−0.51	−0.86	−1.31	−1.98	−2.68	−3.39	−4.12	−5.87	−8.50
HSe$^-$	45.85	44.49	43.93	42.99	42.39	41.65	40.57	39.53	38.53	37.58	35.51	33.08
MoO$_4^{2-}$	−837.40	−838.20	−838.48	−838.88	−839.11	−839.34	−839.61	−839.77	−839.82	−839.76	−839.17	−836.96
HMoO$_4^-$	−860.57	−862.64	−863.58	−865.24	−866.38	−867.83	−870.06	−872.35	−874.70	−877.09	−882.81	−891.13
Molybdenite[b]	−261.58	−262.53	−262.96	−263.73	−264.25	−264.93	−265.99	−267.08	−268.22	−269.40	−272.29	−276.76
Ag^{+}	78.76	77.61	77.10	76.21	75.61	74.84	73.68	72.49	71.27	70.04	67.07	62.66
Silver	0.95	0.29	0	−0.52	−0.87	−1.31	−2.00	−2.70	−3.41	−4.15	−5.91	−8.54
WO$_4^{2-}$	−913.08	−913.91	−914.21	−914.65	−914.91	−915.18	−915.51	−915.74	−915.86	−915.89	−915.50	−913.61
HWO$_4^-$	−931.83	−933.81	−934.71	−936.30	−937.40	−938.80	−940.96	−943.19	−945.48	−947.81	−953.41	−961.57
Au^{3+}	428.23	431.86	433.47	436.22	438.07	440.38	443.87	447.38	450.91	454.47	462.95	475.61
Au^{+}	165.65	163.92	163.18	161.89	161.03	159.95	158.34	156.71	155.07	153.42	149.55	143.96
Gold	1.07	0.33	0	−0.58	−0.97	−1.46	−2.22	−2.99	−3.78	−4.58	−6.51	−9.39
Hg^{2+}	163.85	164.43	164.68	165.12	165.40	165.75	166.28	166.79	167.29	167.80	168.99	170.82
HgOH^{+}	−51.72	−52.66	−53.14	−54.02	−54.66	−55.50	−56.86	−58.32	−59.88	−61.53	−65.68	−72.26
HgO(aq)	−36.33	−36.99	−37.24	−37.63	−37.86	−38.14	−38.51	−38.84	−39.14	−39.41	−39.93	−40.48
HHgO$_2^-$	−188.77	−189.04	−189.12	−189.20	−189.24	−189.25	−189.22	−189.13	−188.97	−188.77	−188.04	−186.30
Quicksilver	1.72	0.53	0	−0.92	−1.54	−2.32	−3.51	−4.72	−5.95	−7.18	−10.14	−14.49
Pb^{2+}	−23.42	−23.76	−23.89	−24.09	−24.21	−24.35	−24.55	−24.72	−24.87	−25.00	−25.19	−25.16
PbOH^{+}	−226.60	−226.01	−225.73	−225.21	−224.84	−224.37	−223.63	−222.85	−222.04	−221.20	−219.11	−215.81
PbO(aq)	−162.34	−163.98	−164.64	−165.71	−166.38	−167.18	−168.31	−169.36	−170.35	−171.28	−173.23	−175.58
Galena	−94.66	−96.08	−96.72	−97.82	−98.57	−99.52	−100.98	−102.47	−103.99	−105.54	−109.26	−114.80
Anglesite	−809.86	−812.15	−813.18	−814.98	−816.22	−817.79	−820.20	−822.68	−825.23	−827.84	−834.17	−843.72
HPbO$_2^-$	−336.87	−338.35	−338.90	−339.74	−340.23	−340.78	−341.47	−342.03	−342.45	−342.74	−342.95	−342.05
UO$_2^{2+}$	−954.91	−953.30	−952.61	−951.44	−950.67	−949.71	−948.30	−946.90	−945.50	−944.11	−940.85	−936.02
UO$_2$OH^{+}	−1159.63	−1159.90	−1160.01	−1160.23	−1160.37	−1160.56	−1160.86	−1161.17	−1161.50	−1161.84	−1162.68	−1163.90
UO$_3$(aq)	−1132.17	−1131.32	−1130.94	−1130.29	−1129.86	−1129.32	−1128.52	−1127.73	−1126.95	−1126.18	−1124.43	−1122.02
HUO$_4^-$	−1319.16	−1317.73	−1317.12	−1316.13	−1315.49	−1314.72	−1313.60	−1312.52	−1311.48	−1310.46	−1308.14	−1304.70
UO$_4^{2-}$	−1240.88	−1239.24	−1238.46	−1237.06	−1236.08	−1234.82	−1232.84	−1230.75	−1228.56	−1226.26	−1220.41	−1210.61
UO$_2^+$	−961.50	−961.19	−961.02	−960.70	−960.47	−960.16	−959.65	−959.11	−958.53	−957.91	−956.35	−953.77

Table 9.1 (*continued*)

Compound	*T* (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
$UO_2OH(aq)$	−1095.97	−1094.95	−1094.53	−1093.86	−1093.44	−1092.94	−1092.24	−1091.60	−1091.02	−1090.50	−1089.47	−1088.44
UO_3^-	−991.83	−990.51	−989.93	−988.96	−988.32	−987.53	−986.36	−985.19	−984.04	−982.88	−980.14	−975.91
U^{4+}	−539.48	−532.82	−529.90	−524.90	−521.56	−517.40	−511.15	−504.89	−498.61	−492.30	−477.37	−455.34
UOH^{3+}	−768.66	−765.40	−764.00	−761.61	−760.04	−758.10	−755.22	−752.36	−749.53	−746.71	−740.14	−730.53
UO^{2+}	−758.74	−756.60	−755.63	−753.93	−752.78	−751.32	−749.09	−746.81	−744.48	−742.12	−736.39	−727.66
HUO_2^+	−976.81	−976.04	−975.71	−975.14	−974.76	−974.30	−973.61	−972.93	−972.25	−971.59	−970.04	−967.79
$UO_2(aq)$	−980.80	−978.99	−978.22	−976.93	−976.09	−975.07	−973.57	−972.13	−970.73	−969.38	−966.39	−962.49
Uraninite	−1030.10	−1031.28	−1031.82	−1032.76	−1033.40	−1034.22	−1035.49	−1036.81	−1038.16	−1039.56	−1042.97	−1048.19
HUO_3^-	−1151.10	−1148.07	−1146.83	−1144.83	−1143.56	−1142.05	−1139.91	−1137.91	−1136.03	−1134.26	−1130.44	−1125.46

[a] See text for discussion of nonconventional hydroxide species and Table A.19 in the Appendix for chemical formulas of the minerals.

[b] See Table A.2 in the Appendix for the thermodynamic properties and equation of state parameters used to calculate these values of ΔG^0.

[18] Yanagawa, H. and Kojima, K. (1985) Thermophilic microspheres of peptide-like polymers and silicates formed at 250°C. J. Biochem. 97, 1521–1524.

[19] Hennet, R.J.-C., Holm, N.G. and Engel, M.H. (1992) Abiotic synthesis of amino acids under hydrothermal conditions and the origin of life: a perpetual phenomenon? Naturwissenschaften 79, 361–365.

[20] Helgeson, H.C. and Amend, J.P. (1994) Relative stabilities of biomolecules at high temperatures and pressures. Thermochim. Acta 245, 89–119.

[21] Pace, N.R. (1991) Origin of life: Facing up to the physical setting. Cell 65, 531–533.

[22] Russell, M.J. and Hall, A.J. (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. J. Geol. Soc. Lond. 154, 377–402.

[23] Galtier, N., Tourasse, N. and Gouy, M. (1999) A nonhyperthermophilic common ancestor to extant life forms. Science 283, 220–221.

[24] Brock, T.D. (1971) Bimodal distribution of pH values of thermal springs of the world. Geol. Soc. Am. Bull. 82, 1393–1394.

[25] Holden, J.F. and Baross, J.A. (1995) Enhanced thermotolerance by hydrostatic pressure in the deep-sea hyperthermophile *Pyrococcus* strain ES4. FEMS Microbiol. Ecol. 18, 27–34.

[26] Miller, J.F., Shah, N.N., Nelson, C.M., Ludlow, J.M. and Clark, D.S. (1988) Pressure and temperature effects on growth and methane production of the extreme thermophile *Methanococcus jannaschii*. Appl. Environ. Microbiol. 54, 3039–3042.

[27] Whitman, W.B., Coleman, D.C. and Wiebe, W.J. (1998) Prokaryotes: the unseen majority. Proc. Natl. Acad. Sci. USA 95, 6578–6583.

[28] Parkes, R.J., Cragg, B.A., Bale, S.J., Getliff, J.M., Goodman, K., Rochelle, P.A., Fry, J.C., Weightman, A.J. and Harvey, S.M. (1994) Deep bacterial biosphere in Pacific Ocean sediments. Nature 371, 410–413.

[29] Stevens, T.O., McKinley, J.P., Boone, D.R., Griffin, W.T., Russell, B.F., Colwell, F.S., Phelps, T.J. and Balkwill, D.L. (1993) Detection of anaerobic bacteria in 2800-m-deep samples from the terrestrial subsurface (Abstract). Am. Soc. Microbiol., 16–20.

[30] Stevens, T.O. and McKinley, J.P. (1995) Lithoautotrophic microbial ecosystems in deep basalt aquifers. Science 270, 450–454.

[31] Onstott, T.C., Tobin, K., Dong, H., DeFlaun, M.F., Frederickson, J.K., Bailey, T., Brockman, F., Kieft, T., Peacock, A., White, D.C., Balkwill, D., Phelps, T.J. and Boone, D.R. (1997) The deep gold mines of South Africa: Windows into the subsurface biosphere. Proc. SPIE-Int. Soc. Opt. Eng. 3111, 344–357.

[32] Kieft, T.L., Fredrickson, J.K., Onstott, T.C., Gorby, Y.A., Kostandarithes, H.M., Bailey, T.J., Kennedy, D.W., Li, S.W., Plymale, A.E., Spadoni, C.M. and Gray, M.S. (1999) Dissimilatory reduction of Fe(III) and other electron acceptors by a *Thermus* isolate. Appl. Environ. Microbiol. 65, 1214–1221.

[33] Szewzyk, U., Szewzyk, R. and Stenstrom, T. (1994) Thermophilic, anaerobic bacteria isolated from a granite in Sweden. Proc. Natl. Acad. Sci. USA 91, 1810–1813.

[34] Szewzyk, U., Szewzyk, R. and Stenstrom, T. (1997) Thermophilic fermentative bacteria from a deep borehole in granitic rock in Sweden. Proc. SPIE-Int. Soc. Opt. Eng. 3111, 330–334.

[35] Daumas, S., Cord-Ruwisch, R. and Garcia, J.L. (1988) *Desulfotomaculum geothermicum* sp. nov., a thermophilic, fatty acid-degrading, sulfate reducing bacterium isolated with H_2 from geothermal ground water. Antonie Van Leeuwenhoek 54, 165–178.

[36] Rosnes, J.T., Torsvik, T. and Lien, T. (1991) Spore-forming thermophilic sulfate-reducing bacteria isolated from North Sea oil field waters. Appl. Environ. Microbiol. 57, 2302–2307.

[37] Stetter, K.O., Huber, R., Blöchl, E., Kurr, M., Eden, R.D., Fielder, M., Cash, H. and Vances, I. (1993) Hyperthermophilic archaea are thriving in deep North Sea and Alaskan oil reservoirs. Nature 365, 743–745.

[38] L'Haridon, S., Reysenbach, A.-L., Glenat, P., Prieur, D. and Jeanthon, C. (1995) Hot subterranean biosphere in a continental oil reservoir. Nature 377, 223–224.

[39] Zobell, C.E. and Morita, R.Y. (1957) Barophilic bacteria in some deep sea sediments. J. Bacteriol. 73, 563–568.

[40] Pedersen, K. and Ekendahl, S. (1990) Distribution and activity of bacteria in deep granitic groundwaters of southeastern Sweden. Microb. Ecol. 20, 37–52.

[41] Pedersen, K. (1997) Microbial life in deep granitic rock. FEMS Microbiol. Rev. 20, 399–414.

[42] Motamedi, M. and Pedersen, K. (1998) *Desulfovibrio aespoeensis* sp. nov., a mesophilic sulfate-reducing bacterium from deep groundwater at Äspö hard rock laboratory, Sweden. Int. J. Syst. Bacteriol. 48, 311–315.

Table 9.2

Coupled metabolic reactions involving inorganic aqueous compounds and/or minerals

F1	$S_4O_6^{2-}+10H_2O(l)+14Fe^{3+} \leftrightarrow 4SO_4^{2-}+20H^++14Fe^{2+}$
F2	$S(s)+6Fe^{3+}+4H_2O(l) \leftrightarrow HSO_4^-+6Fe^{2+}+7H^+$
F3	$H_2(aq)+2Fe^{3+} \leftrightarrow 2Fe^{2+}+2H^+$
F4	$2Fe^{2+}+0.5O_2(aq)+2H^+ \leftrightarrow 2Fe^{3+}+H_2O(l)$
F5	$2pyrite(s)+7.5O_2(aq)+H_2O(l) \leftrightarrow 2Fe^{3+}+4SO_4^{2-}+2H^+$
F6	$pyrite(s)+3.5O_2(aq)+H_2O(l) \leftrightarrow Fe^{2+}+2SO_4^{2-}+2H^+$
F7	$pyrrhotite(s)+2O_2(aq) \leftrightarrow Fe^{2+}+SO_4^{2-}$
F8	$2chalcopyrite(s)+8.5O_2(aq)+2H^+ \leftrightarrow 2Cu^{2+}+2Fe^{3+}+4SO_4^{2-}+H_2O(l)$
F9	$covellite(s)+2O_2(aq) \leftrightarrow Cu^{2+}+SO_4^{2-}$
F10	$sphalerite(s)+2O_2(aq) \leftrightarrow Zn^{2+}+SO_4^{2-}$
F11	$galena(s)+2O_2(aq) \leftrightarrow Pb^{2+}+SO_4^{2-}$
F12	$H_2(aq)+UO_2^{2+} \leftrightarrow Uraninite(s)+2H^+$
F13	$uraninite(s)+0.5O_2(aq)+2H^+ \leftrightarrow UO_2^{2+}+H_2O(l)$

Table 9.3
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 9.2

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
F1	−569.15	−594.45	−605.19	−623.18	−634.91	−649.31	−670.38	−690.90	−710.90	−730.44	−774.47	−834.00
F2	−233.23	−246.73	−252.63	−262.74	−269.47	−277.86	−290.42	−302.94	−315.45	−327.96	−357.12	−399.30
F3	−159.62	−164.25	−166.26	−169.66	−171.91	−174.71	−178.86	−182.98	−187.08	−191.15	−200.64	−214.30
F4	−104.32	−99.20	−96.92	−92.96	−90.29	−86.92	−81.80	−76.62	−71.36	−66.03	−53.26	−34.13
F5	−2609.37	−2588.78	−2578.74	−2560.34	−2547.33	−2530.29	−2503.23	−2474.47	−2444.08	−2412.10	−2331.30	−2200.16
F6	−1252.53	−1244.79	−1240.91	−1233.69	−1228.52	−1221.69	−1210.71	−1198.93	−1186.36	−1173.04	−1139.01	−1083.01
F7	−775.83	−770.76	−768.27	−763.70	−760.46	−756.21	−749.45	−742.25	−734.63	−726.59	−706.17	−672.72
F8	−2920.94	−2895.43	−2883.18	−2860.94	−2845.31	−2824.98	−2792.92	−2759.09	−2723.56	−2686.36	−2593.04	−2443.04
F9	−666.72	−661.65	−659.19	−654.65	−651.44	−647.24	−640.57	−633.49	−626.01	−618.14	−598.25	−565.95
F10	−731.83	−726.71	−724.20	−719.61	−716.36	−712.11	−705.35	−698.18	−690.59	−682.62	−662.49	−629.82
F11	−710.13	−706.55	−704.72	−701.25	−698.74	−695.41	−690.02	−684.18	−677.94	−671.28	−654.17	−625.76
F12	−94.08	−96.09	−96.93	−98.30	−99.19	−100.27	−101.81	−103.30	−104.73	−106.12	−109.24	−113.51
F13	−169.86	−167.36	−166.25	−164.31	−163.01	−161.36	−158.85	−156.30	−153.70	−151.05	−144.67	−134.93

[43] Kotelnikova, S., Macario, A.J.L. and Pedersen, K. (1998) *Methanobacterium subterraneum* sp. nov., a new alkaliphilic, eurythermic and halotolerant methanogen isolated from deep granitc groundwater. Int. J. Syst. Bacteriol. 48, 357–367.

[44] Stevens, T. (1997) Lithoautotrophy in the subsurface. FEMS Microbiol. Rev. 20, 327–337.

[45] Anderson, R.T., Chapelle, F.H. and Lovley, D.R. (1998) Evidence against hydrogen-based microbial ecosystems in basalt aquifers. Science 281, 976–977.

[46] Amend, J.P., Amend, A.C. and Valenza, M. (1998) Determination of volatile fatty acids in the hot springs of Vulcano, Aeolian Islands, Italy. Org. Geochem. 28, 699–705.

[47] Stetter, K.O. (1982) Ultrathin mycelia-forming organisms from submarine volcanic areas having an optimum growth temperature of 105°C. Nature 300, 258–260.

[48] Amend, J.P. (2001) Calculation of metabolic energy from sulfur reduction by hyperthermophiles in Vulcano hot springs. Extremophiles, in preparation.

[49] Shock, E.L. and Helgeson, H.C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. Geochim. Cosmochim. Acta 52, 2009–2036.

[50] Shock, E.L., Helgeson, H.C. and Sverjensky, D.A. (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. Geochim. Cosmochim. Acta 53, 2157–2183.

[51] Shock, E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A. and Helgeson, H.C. (1992) Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000°C and 5 kbar. J. Chem. Soc. Faraday Trans. 88, 803–826.

[52] Shock, E.L., Sassani, D.C., Willis, M. and Sverjensky, D.A. (1997) Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. Geochim. Cosmochim. Acta 61, 907–950.

[53] Shock, E.L., Sassani, D.C. and Betz, H. (1997) Uranium in geologic fluids: estimates of standard partial molal properties, oxidation potential, and hydrolysis constants at high temperatures and pressures. Geochim. Cosmochim. Acta 61, 4245–4266.

[54] Haas, J.R., Shock, E.L. and Sassani, D.C. (1995) Rare earth elements in hydrothermal systems: Estimates of standard partial molal thermodynamic properties of aqueous complexes of the REE at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 4329–4350.

[55] Sverjensky, D.A., Shock, E.L. and Helgeson, H.C. (1997) Prediction of the thermodynamic and transport properties of aqueous metal complexes to 1000°C and 5 kb. Geochim. Cosmochim. Acta 61, 1359–1412.

[56] Sassani, D.C. and Shock, E.L. (1998) Solubility and transport of platinum-group elements in supercritical fluids: Summary and estimates of thermodynamic properties for Ru, Rh, Pd, and Pt solids, aqueous ions and aqueous complexes. Geochim. Cosmochim. Acta 62, 2643–2671.

Table 9.4
Microorganisms that use the metal reactions specified in Table 9.2

Reaction	
F1	**As written:** *S. acidophilus*, *S. thermosulfidooxidans* [183]
F2	**As written:** *S. acidocaldarius*, *T. thiooxidans*, *T. ferrooxidans* [442]
F3	**As written:** *G. sulfurreducens* [432], *Thermoterrabacterium ferrireducens* [275]
F4	**As written:** *S. thermosulfidooxidans* [246,443], *A. brierleyi* [292,294], *T. prosperus* [406], *S. acidophilus* [245], *Acidimicrobium ferrooxidans* [182], *S. yellowstonii* [322]
F5	**As written:** *S. thermosulfidooxidans* [246,443], *T. ferrooxidans* [387], *S. yellowstonii* [322], *T. prosperus* [406] **Inferred:** *A. brierleyi* [292,297,444],
F6	**As written:** *S. thermosulfidooxidans* [246,443], *M. sedula* [297], *S. metallicus* [317], *M. prunae* [296], *T. prosperus* [406], *S. yellowstonii* [322] **Inferred:** *A. brierleyi* [292,297,444]
F7	**As written:** *S. hakonensis* [316]
F8	**As written:** *S. thermosulfidooxidans* [246,443], *M. sedula* [297], *S. metallicus* [317], *M. prunae* [296], *T. prosperus* [406], *S. yellowstonii* [322] **Inferred:** *A. brierleyi* [297]
F9	**As written:** *S. thermosulfidooxidans* [246]
F10	**As written:** *S. yellowstonii* [322], *T. prosperus* [406], *S. metallicus* [317], *S. thermosulfidooxidans* [246,443], *M. sedula* [297], *M. prunae* [296] **Inferred:** *A. brierleyi* [297]
F11	**As written:** *S. thermosulfidooxidans* [246], *T. prosperus* [406]
F12	**As written:** *Shewanella putrefaciens* [114,115], *D. desulfuricans* [114]
F13	**Inferred:** *T. prosperus* [406], *S. metallicus* [317], *M. sedula* [297], *M. prunae* [296]

Table 9.5
Coupled metabolic reactions involving organic compounds and inorganic aqueous compounds or minerals

F14	formic acid(aq)+$2Fe^{3+}$+H_2O(l)$\leftrightarrow$siderite(s)+Fe^{2+}+$4H^+$
F15	acetic acid(aq)+$8Fe^{3+}$+$2H_2O$(l)$\leftrightarrow$$8Fe^{2+}$+$2CO_2$(aq)+$8H^+$
F16	acetic acid(aq)+$8Co^{3+}$+$2H_2O$(l)$\leftrightarrow$$2CO_2$(aq)+$8Co^{2+}$+$8H^+$
F17	3acetic acid(aq)+$4SeO_4^{2-}$+$8H^+$$\leftrightarrow$ 4selenium(s)+$6CO_2$(aq)+$10H_2O$(l)
F18	acetic acid(aq)+$2H_2O$(l)+$4UO_2^{2+}$$\leftrightarrow$4uraninite(s)+$2CO_2$(aq)+$8H^+$
F19	lactic acid(aq)+$12Fe^{3+}$+$3H_2O$(l)$\leftrightarrow$$3CO_2$(aq)+$12Fe^{2+}$+$12H^+$
F20	lactic acid(aq)+$12Fe^{3+}$+$6H_2O$(l)$\leftrightarrow$3siderite(s)+$9Fe^{2+}$+$18H^+$
F21	lactic acid(aq)+$4Fe^{3+}$+H_2O(l)$\leftrightarrow$ $4Fe^{2+}$+acetic acid(aq)+CO_2(aq)+$4H^+$
F22	lactic acid(aq)+$2HAsO_4^{2-}$+$4H^+$$\leftrightarrow$ acetic acid(aq)+$2HAsO_2$(aq)+CO_2(aq)+$3H_2O$(l)
F23	lactic acid(aq)+$2HAsO_4^{2-}$+$2H^+$$\leftrightarrow$ acetic acid(aq)+$2AsO_2^-$+CO_2(aq)+$3H_2O$(l)
F24	lactic acid(aq)+$2SeO_4^{2-}$$\leftrightarrow$ acetic acid(aq)+$2SeO_3^{2-}$+CO_2(aq)+H_2O(l)
F25	3lactic acid(aq)+$2SeO_4^{2-}$+$4H^+$$\leftrightarrow$ 3acetic acid(aq)+2selenium(s)+$3CO_2$(aq)+$5H_2O$(l)
F26	lactic acid(aq)+SeO_3^{2-}+$2H^+$$\leftrightarrow$ acetic acid(aq)+selenium+CO_2(aq)+$2H_2O$(l)
F27	lactic acid(aq)+$3H_2O$(l)+$6UO_2^{2+}$$\leftrightarrow$ 6uraninite(s)+$3CO_2$(aq)+$12H^+$
F28	butanoic acid(aq)+$6HAsO_4^{2-}$+$12H^+$$\leftrightarrow$ acetic acid(aq)+$2CO_2$(aq)+$6HAsO_2$(aq)+$8H_2O$(l)
F29	succinic acid(aq)+$14Fe^{3+}$+$4H_2O$(l)$\leftrightarrow$$4CO_2$(aq)+$14Fe^{2+}$+$14H^+$

[57] Shock, E.L. and Helgeson, H.C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. Geochim. Cosmochim. Acta 54, 915–945.

[58] Helgeson, H.C. (1992) Calculation of the thermodynamic properties and relative stabilities of aqueous acetic and chloroacetic acids, acetate and chloroacetates, and acetyl and chloroacetyl chlorides at high and low temperatures and pressures. Appl. Geochem. 7, 291–308.

[59] Shock, E.L. (1992) Chemical environments of submarine hydrothermal systems. Orig. Life Evol. Biosph. 22, 67–107.

[60] Shock, E.L. (1993) Hydrothermal dehydration of aqueous organic compounds. Geochim. Cosmochim. Acta 57, 3341–3349.

[61] Shock, E.L. (1995) Organic acids in hydrothermal solution: Standard molal thermodynamic properties of carboxylic acids and estimates of dissociation constants at high temperatures and pressures. Am. J. Sci. 295, 496–580.

[62] Schulte, M.D. and Shock, E.L. (1993) Aldehydes in hydrothermal solution: Standard partial molal thermodynamic properties and relative stabilities at high temperatures and pressures. Geochim. Cosmochim. Acta 57, 3835–3846.

[63] Amend, J.P. and Helgeson, H.C. (1997) Group additivity equations of state for calculating the standard molal thermodynamic properties of aqueous organic species at elevated temperatures and pressures. Geochim. Cosmochim. Acta 61, 11–46.

[64] Amend, J.P. and Helgeson, H.C. (1997) Calculation of the standard molal thermodynamic properties of aqueous biomolecules at elevated temperatures and pressures. Part 1. L-α-Amino acids. J. Chem. Soc. Faraday Trans. 93, 1927–1941.

[65] Dale, J.D., Shock, E.L., MacLeod, G., Aplin, A.C. and Larter, S.R. (1997) Standard partial molal properties of aqueous alkylphenols at high pressures and temperatures. Geochim. Cosmochim. Acta 61, 4017–4024.

[66] Haas, J.R. and Shock, E.L. (1999) Halocarbons in the environment: Estimates of thermodynamic properties for aqueous chloroethylene species and their stabilities in natural settings. Geochim. Cosmochim. Acta 63, 3429–3441.

[67] Plyasunov, A.V. and Shock, E.L. (2000) Thermodynamic functions of hydration of hydrocarbons at 298.15 K and 0.1 MPa. Geochim. Cosmochim. Acta 64, 439–468.

[68] Shock, E.L. and Koretsky, C.M. (1993) Metal–organic complexes in geochemical processes: Calculation of standard partial molal thermodynamic properties of aqueous acetate complexes at high pressures and temperatures. Geochim. Cosmochim. Acta 57, 4899–4922.

[69] Shock, E.L. and Koretsky, C.M. (1995) Metal–organic complexes in geochemical processes: Estimation of standard partial molal thermodynamic properties of aqueous complexes between metal cations and monovalent organic acid ligands at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 1497–1532.

[70] Prapaipong, P., Shock, E.L. and Koretsky, C.M. (1999) Metal–organic complexes in geochemical processes: Temperature dependence of the standard thermodynamic properties of aqueous complexes between metal cations and dicarboxylate ligands. Geochim. Cosmochim. Acta 63, 2547–2577.

[71] Helgeson, H.C., Kirkham, D.H. and Flowers, G.C. (1981) Theoretical prediction of the thermodynamic behavior of aqueous electro-

Table 9.6
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for reactions given in Table 9.5

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
F14	−119.75	−124.84	−127.09	−130.95	−133.53	−136.75	−141.59	−146.42	−151.27	−156.14	−167.63	−184.59
F15	−466.16	−486.27	−495.25	−510.83	−521.34	−534.60	−554.71	−575.10	−595.76	−616.70	−666.75	−741.49
F16	−1374.63	−1397.23	−1407.36	−1425.00	−1436.93	−1452.01	−1474.95	−1498.27	−1521.96	−1546.03	−1603.69	−1690.09
F17	−1716.45	−1727.08	−1732.60	−1743.09	−1750.74	−1760.97	−1777.61	−1795.72	−1815.22	−1836.07	−1889.84	−1979.19
F18	−204.00	−213.63	−217.93	−225.40	−230.45	−236.83	−246.52	−256.37	−266.39	−276.59	−301.12	−338.32
F19	−757.84	−788.98	−802.87	−826.96	−843.19	−863.66	−894.70	−926.15	−957.99	−990.26	−1067.35	−1182.34
F20	−650.28	−683.08	−697.51	−722.30	−738.85	−759.55	−790.66	−821.85	−853.16	−884.64	−959.06	−1068.91
F21	−291.68	−302.71	−307.62	−316.13	−321.85	−329.06	−339.99	−351.05	−362.24	−373.57	−400.60	−440.85
F22	76.27	70.14	67.22	61.91	58.20	53.35	45.71	37.61	29.09	20.14	−2.46	−39.23
F23	−221.81	−227.47	−230.10	−234.81	−238.07	−242.29	−248.89	−255.81	−263.04	−270.57	−289.32	−319.08
F24	−340.23	−341.31	−341.82	−342.77	−343.44	−344.32	−345.72	−347.21	−348.79	−350.45	−354.59	−361.10
F25	−1034.01	−1042.28	−1046.30	−1053.67	−1058.90	−1065.77	−1076.69	−1088.34	−1100.68	−1113.69	−1146.61	−1199.90
F26	−346.89	−350.49	−352.24	−355.45	−357.73	−360.72	−365.48	−370.56	−375.94	−381.62	−396.01	−419.40
F27	−364.59	−380.02	−386.89	−398.81	−406.85	−417.00	−432.41	−448.06	−463.95	−480.10	−518.92	−577.58
F28	−780.34	−802.43	−812.78	−831.33	−844.23	−860.92	−887.06	−914.50	−943.20	−973.18	−1048.19	−1168.72
F29	−838.49	−874.77	−891.00	−919.22	−938.28	−962.36	−998.97	−1036.16	−1073.90	−1112.24	−1204.08	−1341.73

Table 9.7
Microorganisms that use the coupled metal and organic carbon reactions specified in Table 9.5

Reaction	
F14	*B. infernus* [116]
F15	*G. metallireducens* [422,423], *D. palmitatis* [430], *G. sulfurreducens* [432]
F16	*G. sulfurreducens* [432]
F17	strain SES [445]
F18	*G. metallireducens* [114,115]
F19	*D. palmitatis* [430]
F20	*B. infernus* [116]
F21	*S. barnesii* strain SES-3 [380,426], *B. arsenicoselenatis*, *B. selenitireducens* [425]
F22	*D. auripigmentum* [393], *B. arsenicoselenatis*, *B. selenitireducens* [425]
F23	*S. barnesii* strain SES-3 [380,426], *B. arsenicoselenatis*, *B. selenitireducens* [425]
F24	*S. barnesii* strain SES-3 [380,424], *B. arsenicoselenatis*, *B. selenitireducens* [425]
F25	*S. barnesii* strain SES-3 [380,424], *B. arsenicoselenatis*, *B. selenitireducens* [425]
F26	*B. arsenicoselenatis*, *B. selenitireducens* [425]
F27	*S. putrefaciens* [114,115], *D. desulfuricans* [114], *G. metallireducens* [114,115]
F28	*D. auripigmentum* [393]
F29	*D. palmitatis* [430]

lytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb. Am. J. Sci. 281, 1249–1516.

[72] Tanger, J.C. and Helgeson, H.C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes. Am. J. Sci. 288, 19–98.

[73] Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992) SUPCRT92: A software package for calculating the standard molal properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. Comput. Geosci. 18, 899–947.

[74] Helgeson, H.C., Owens, C.E., Knox, A.M. and Richard, L. (1998) Calculation of the standard molal thermodynamic properties of crystalline, liquid, and gas organic molecules at high temperatures and pressures. Geochim. Cosmochim. Acta 62, 985–1081.

[75] Richard, L. and Helgeson, H.C. (1998) Calculation of the thermodynamic properties at elevated temperatures and pressures of saturated and aromatic high molecular weight solid and liquid hydrocarbons in kerogen, bitumen, petroleum, and other organic matter of biogeochemical interest. Geochim. Cosmochim. Acta 62, 3591–3636.

[76] Helgeson, H.C., Delany, J.M., Nesbitt, W.H. and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. Am. J. Sci. 278A, 1–229.

[77] Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Cherney, K.L. and Nuttall, R.L. (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units. J. Phys. Chem. Ref. Data 11, 392.

[78] Chan, G.W. and Shock, E.L. (2001) Geochemical bioenergetics in the hydrothermal habitat of the pink filament community of Octopus Spring, Yellowstone National Park. Appl. Environ. Microbiol., in preparation.

[79] Alberty, R.A. and Goldberg, R.N. (1992) Standard thermodynamic formation properties for the adenosine 5′-triphosphate series. Biochemistry 31, 10610–10615.

[80] Alberty, R.A. (1998) Calculation of standard transformed Gibbs energies and standard transformed enthalpies of biochemical reactants. Arch. Biochem. Biophys. 353, 116–130.

[81] Gurrieri, S., Helgeson, H.C., Amend, J.P. and Danti, K. (2000) Biogeochemistry of the geothermal system in the Aeolian Islands: Authigenic phase relations in the hot springs of Vulcano. Chem. Geol., in preparation.

[82] Huber, R., Wilharm, T., Huber, D., Trincone, A., Burggraf, S., König, H., Rachel, R., Rockinger, I., Fricke, H. and Stetter, K.O. (1992) *Aquifex pyrophilus* gen. nov. sp. nov., represents a novel group of marine hyperthermophilic hydrogen oxidizing bacteria. Syst. Appl. Microbiol. 15, 340–351.

[83] Deckert, G., Warren, P.V., Gaasterland, T., Young, W.G., Lenox, A.L., Graham, D.E., Overbeek, R., Snead, M.A., Keller, M., Aujay, M., Huber, R., Feldman, R.A., Short, J.M., Olsen, G.J. and Swanson, R.V. (1998) The complete genome of the hyperthermophilic bacterium *Aquifex aeolicus*. Nature 392, 353–358.

[84] Hafenbradl, D., Keller, M., Dirmeier, R., Rachel, R., Rossnagel, P., Burggraf, S., Huber, H. and Stetter, K.O. (1996) *Ferroglobus placidus* gen. nov., sp. nov., a novel hyperthermophilic archaeum that oxidizes Fe^{2+} at neutral pH under anoxic conditions. Arch. Microbiol. 166, 308–314.

[85] Broda, E. (1977) Two kinds of lithotrophs missing in nature. Z. Allg. Mikrobiol. 17, 491–493.

Table 9.8
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for inorganic aqueous compounds in the system H–O–P

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
H_3PO_4(aq)	−1139.09	−1141.55	−1142.65	−1144.59	−1145.90	−1147.56	−1150.11	−1152.73	−1155.39	−1158.11	−1164.66	−1174.47
$H_2PO_4^-$	−1128.15	−1129.63	−1130.27	−1131.35	−1132.06	−1132.95	−1134.27	−1135.58	−1136.87	−1138.15	−1141.04	−1144.80
HPO_4^{2-}	−1089.65	−1089.35	−1089.14	−1088.68	−1088.32	−1087.81	−1086.94	−1085.94	−1084.81	−1083.55	−1080.07	−1073.54
PO_4^{3-}	−1023.36	−1020.31	−1018.80	−1016.02	−1014.05	−1011.46	−1007.33	−1002.92	−998.24	−993.29	−980.65	−959.59
$H_4P_2O_7$(aq)	−2026.26	−2030.32	−2032.17	−2035.44	−2037.68	−2040.55	−2044.95	−2049.49	−2054.16	−2058.95	−2070.57	−2088.19
$H_3P_2O_7^-$	−2018.63	−2021.91	−2023.39	−2025.98	−2027.75	−2030.01	−2033.45	−2036.98	−2040.59	−2044.26	−2053.02	−2065.87
$H_2P_2O_7^{2-}$	−2006.32	−2008.86	−2010.00	−2011.97	−2013.31	−2015.00	−2017.56	−2020.15	−2022.76	−2025.38	−2031.46	−2039.74
$HP_2O_7^{3-}$	−1971.15	−1972.01	−1972.34	−1972.86	−1973.19	−1973.56	−1974.07	−1974.49	−1974.83	−1975.07	−1975.18	−1973.79
$P_2O_7^{4-}$	−1921.30	−1919.97	−1919.20	−1917.67	−1916.50	−1914.91	−1912.25	−1909.28	−1905.99	−1902.39	−1892.71	−1875.29
H_3PO_2(aq)	−519.92	−522.35	−523.42	−525.29	−526.55	−528.14	−530.56	−533.02	−535.53	−538.06	−544.13	−553.14
$H_2PO_2^-$	−509.77	−511.41	−512.13	−513.33	−514.13	−515.12	−516.59	−518.06	−519.51	−520.95	−524.21	−528.53
H_3PO_3(aq)	−852.79	−855.62	−856.88	−859.10	−860.60	−862.51	−865.42	−868.40	−871.43	−874.53	−881.97	−893.13
$H_2PO_3^-$	−843.60	−845.71	−846.63	−848.23	−849.30	−850.65	−852.69	−854.73	−856.80	−858.86	−863.68	−870.42
HPO_3^{2-}	−811.13	−811.57	−811.70	−811.86	−811.93	−811.98	−811.98	−811.88	−811.70	−811.41	−810.33	−807.51

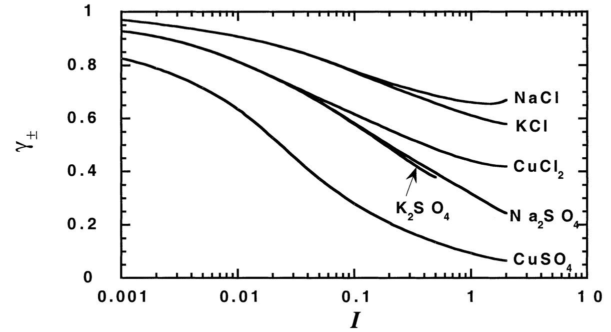

Fig. A1. Activity coefficients of electrolytes ($\gamma_{\pm}$) plotted against ionic strength (redrawn from data given by Garrels and Christ (1965) [129]).

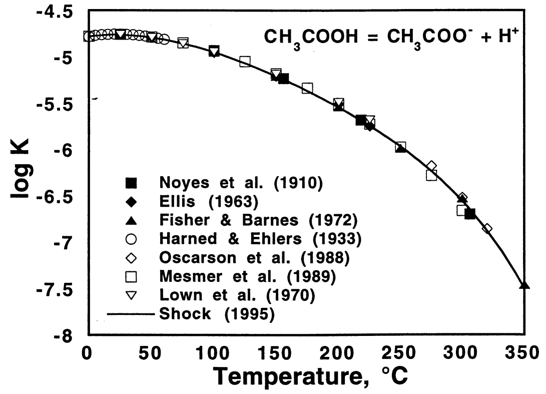

Fig. A3. Log K (= -pK_a) plotted against temperature at P_{SAT} for the dissociation of acetic acid. Symbols represent experimental data from the literature [152–158], but the curve is an independent prediction with the revised HKF equation of state [61].

[86] Strous, M., Fuerst, J.A., Kramer, E.H.M., Logemann, S., Muyzer, G., Van De-Pas-Schoonen, K.T., Webb, R., Kuenen, J.G. and Jetten, M.S.M. (1999) Missing lithotroph identified as new planctomycete. Nature 400, 446–449.

[87] Kelly, D.P. (1999) Thermodynamic aspects of energy conservation by chemolithotrophic sulfur bacteria in relation to sulfur oxidation pathways. Arch. Microbiol. 171, 219–229.

[88] Balch, W.E., Fox, G.E., Magrum, L.J., Woese, C.R. and Wolfe, R.S. (1979) Methanogens: Reevaluation of a unique biological group. Microbiol. Rev. 43, 260–296.

[89] Daniels, L., Sparling, R. and Sprott, G.D. (1984) The bioenergetics of methanogens. Biochim. Biophys. Acta 768, 113–163.

[90] Thauer, R.K., Möller-Zinkhan, D. and Spormann, A.M. (1989) Biochemistry of acetate catabolism in anaerobic chemotrophic bacteria. Annu. Rev. Microbiol. 43, 43–67.

[91] Sprott, G.D., Ekiel, I. and Patel, G.B. (1993) Metabolic pathways in *Methanococcus jannaschii* and other methanogenic bacteria. Appl. Environ. Microbiol. 59, 1092–1098.

[92] Blaut, M. (1994) Metabolism of methanogens. Antonie Van Leeuwenhoek 66, 187–208.

[93] Stams, A.J.M. (1994) Metabolic interactions between anaerobic bacteria in methanogenic environments. Antonie Van Leeuwenhoek 66, 271–294.

[94] Kurr, M., Huber, R., König, H., Jannasch, H.W., Fricke, H., Trincone, A., Kristjansson, J.K. and Stetter, K.O. (1991) *Methanopyrus kandleri*, gen. and sp. nov. represents a novel group of hyperthermophilic methanoges, growing at 110°C. Arch. Microbiol. 156, 239–247.

[95] Casagrande, D.J. (1984) in: The Okefenokee Swamp (Cohen, A.D., Casagrande, D.J., Andrejko, M.J., Best, G.R., Eds.), Los Alamos, NM: Wetland surveys, pp. 391–408.

[96] Fisher, J.B. (1987) Distribution and occurrence of aliphatic acid anions in deep subsurface waters. Geochim. Cosmochim. Acta 51, 2459–2468.

[97] Cody, J.D., Hutcheon, I.E. and Krouse, H.R. (1999) Fluid flow, mixing and the origin of CO_2 and H_2S by bacterial sulphate reduction in the Mannville Group, southern Alberta, Canada. Mar. Pet. Geol. 16, 495–510.

[98] Nordstrom, D.K. and Southam, G. (1997) in: Geomicrobiology: Interactions between Microbes and Minerals, vol. 35 (Banfield, J.F., Nealson, K.H., Eds.), pp. 361–390. Mineralogical Society of America, Washington DC.

[99] Edwards, K.J., Schrenk, M.O., Hamers, R. and Banfield, J.F. (1998) Microbial oxidation of pyrite: experiments using microorganisms from an extreme acidic environment. Am. Mineral. 83, 1444–1453.

[100] Edwards, K.J., Goebel, B.M., Rodgers, T.M., Schrenk, M.O., Gihring, T.M., Cardona, M.M., Hu, B., McGuire, M.M., Hamers, R.J., Pace, N.R. and Banfield, J.F. (1999) Geomicrobiology of pyrite

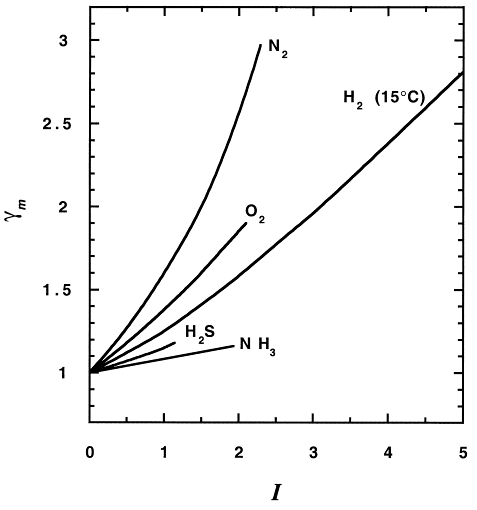

Fig. A2. Activity coefficients of gases (γ_m) dissolved in NaCl solutions at 25°C plotted against ionic strength (redrawn from data given by Garrels and Christ (1965) [129]).

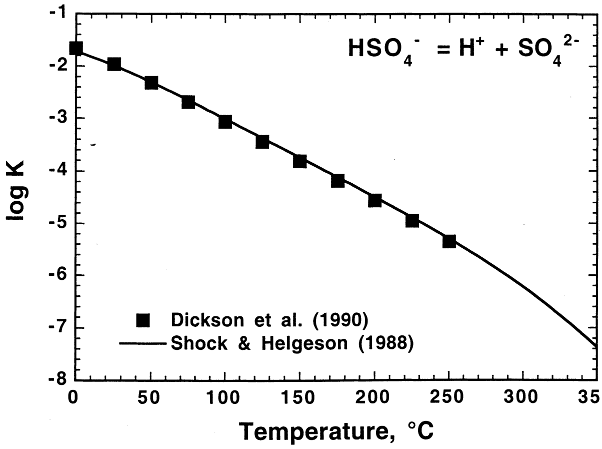

Fig. A4. Log K against temperature at P_{SAT} for the dissociation of HSO_4^-. The curve depicts values calculated with data and parameters from Shock and Helgeson (1988) [49], and the symbols represent subsequent experimental data [159] confirming the accuracy of the predicted values.

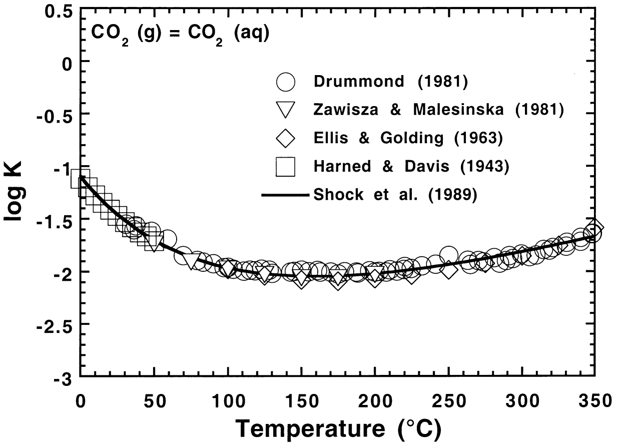

Fig. A5. Log K plotted against temperature at P_{SAT} for the solubility in water of gaseous CO_2. Symbols represent experimental data from the literature [154,160–162], but the curve is an independent prediction generated with the revised HKF equation of state [50].

(FeS$_2$) dissolution: case study at Iron Mountain, California. Geomicrobiol. J. 16, 155–179.

[101] Schrenk, M.O., Edwards, K.J., Goodman, R.M., Hamers, R.J. and Banfield, J.F. (1998) Distribution of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*: implications for generation of acid mine drainage. Science 279, 1519–1522.

[102] Edwards, K.J., Bond, P.L., Gihring, T.M. and Banfield, J.F. (2000) An archaeal iron-oxidizing extreme acidophile important in acid mine drainage. Science 287, 1796–1799.

[103] White, R.H. (1999) Morenci: making the most of world class resources, in: Copper Leaching, Solvent Extraction, Electrowinning Technology (Jergensen, G.V., II., Ed.), Society for Mining, Metallurgy, and Exploration, Littleton, CO.

[104] Krebs, W., Brombacher, C., Bosshard, P.P., Bachofen, R. and Brandl, H. (1997) Microbial recovery of metals from solids. FEMS Microbiol. Rev. 20, 605–617.

[105] Stolz, J.F. and Oremland, R.S. (1999) Bacterial respiration of arsenic and selenium. FEMS Microbiol. Rev. 23, 615–627.

[106] Newman, D.K., Ahmann, D. and Morel, F.M.M. (1998) A brief review of microbial arsenate respiration. Geomicrobiol. J. 15, 255–268.

[107] Lloyd, J.R., Yong, P. and Macaskie, L.E. (1998) Enzymatic recovery of elemental palladium by using sulfate-reducing bacteria. Appl. Environ. Microbiol. 64, 4607–4609.

[108] Lloyd, J.R., Nolting, H.-F., Sole, V.A., Bosecker, K. and Macaskie, L.E. (1998) Technetium reduction and precipitation by sulfate-reducing bacteria. Geomicrobiol. J. 15, 45–58.

[109] Smith, T., Pitts, K., McGarvey, J.A. and Summers, A.O. (1998) Bacterial oxidation of mercury metal vapor, Hg(0). Appl. Environ. Microbiol. 64, 1328–1332.

[110] Southam, G. and Beveridge, T.J. (1994) The in vitro formation of placer gold by bacteria. Geochim. Cosmochim. Acta 58, 4527–4530.

[111] Watterson, J.R. (1991) Preliminary evidence for the involvement of budding bacteria in the origin of Alaskan placer gold. Geology 20, 315–318.

[112] Sillitoe, R.H., Folk, R.L. and Saric, N. (1996) Bacteria as mediators

Table A.1
References for thermodynamic properties and equation of state parameters of additional organic compounds

Species	References
C_5–C_{12} aqueous monocarboxylic acids	Shock (1995)[a] [61]
C_5–C_{20} aqueous monocarboxylic acids	Amend and Helgeson (1997) [63]
C_5–C_{12} monocarboxylate anions	Shock (1995)[a] [61]
C_5–C_{10} aqueous dicarboxylic acids	Shock (1995)[a] [61]
C_5–C_{10} dicarboxylate monovalent anions	Shock (1995)[a] [61]
C_5–C_{10} dicarboxylate divalent anions	Shock (1995)[a] [61]
C_6–C_8 aqueous alkanes	Shock and Helgeson (1990) [57]
C_6–C_{20} aqueous alkanes	Amend and Helgeson (1997) [63]
C_6–C_8 aqueous alcohols	Shock and Helgeson (1990) [57]
C_6–C_{20} aqueous alcohols	Amend and Helgeson (1997) [63]
C_1–C_{50}, C_{60}, C_{70}, C_{80}, C_{90}, and C_{100} liquid, solid, and gas alkanes	Helgeson et al. (1998) [74]
C_1–C_{20} liquid and gas alcohols	Helgeson et al. (1998) [74]
C_2–C_{20} liquid monocarboxylic acids	Helgeson et al. (1998) [74]
C_2–C_{20} aqueous amides	Amend and Helgeson (1997) [63]
C_1–C_{20} aqueous amines	Amend and Helgeson (1997) [63]
C_3–C_8 aqueous alkenes	Shock and Helgeson (1990) [57]
C_3–C_8 aqueous alkynes	Shock and Helgeson (1990) [57]
C_3–C_8 aqueous ketones	Shock and Helgeson, 1990) [57]
C_1–C_{10} aqueous aldehydes	Schulte and Shock (1993) [62]
Metal–acetate complexes	Shock and Koretsky (1993) [68]
Metal–monocarboxylate complexes	Shock and Koretsky (1995) [68]
Metal–dicarboxylate complexes	Prapaipong et al. (1999) [70]
Chlorinated ethenes	Haas and Shock (1999) [66]
Aromatic compounds	
C_6–C_{14} aqueous alkylbenzenes	Shock and Helgeson (1990) [57]
Benzene(l)	Helgeson et al. (1998) [74]
C_6–C_{20} aqueous alkylbenzenes	Amend and Helgeson (1997) [63]
Phenol(aq)	Dale et al. (1997) [65]
m-o-p-Cresol(aq)	Dale et al. (1997) [65]
Aqueous *m-o-p*-toluic acid	Shock (1995)[a] [61]
Aqueous dimethylphenols	Dale et al. (1997) [65]

[a] See also Shock (2001) [446] for minor corrections to enthalpies of formation.

Table A.2
Summary of thermodynamic properties and equation of state parameters for updated and new species

Species	ΔG_f^0 (J mol^{-1})	ΔH_f^0 (J mol^{-1})	S^0 (J mol^{-1} K^{-1})	V^0 (cm^3 mol^{-1})	C_p^0 (J mol^{-1} K^{-1})	Maier–Kelley coefficients			T (K) limit
						a (J mol^{-1} K^{-1})	b ($\times 10^3$ J mol^{-1} K^{-2})	c ($\times 10^{-5}$ J K mol^{-1})	
NO(g)	86567[a]	90249[a]	210.761[a]	–	29.79[j]	26.3400[i]	7.6827[i]	1.04090[i]	1000[k]
N_2O(g)	104198[a]	82048[a]	219.848[a]	–	38.49[j]	41.1429[i]	14.6955[i]	−6.2409[i]	1000[k]
Selenium[b]	0.0	0.0	42.271	16.42	25.058	25.4446	5.1940	−1.73326	494
		6160[g]	12.460[h]			18.8799	13.380	25.7634	957
Molybdenite	−262956[f]	−271800[d]	62.59[c]	32.02[e]	63.55[c]	71.6958[c]	7.448[c]	−9.2107[c]	1200[e]

[a] Taken from Wagman et al. (1982) [77].

[b] All Selenium data taken or calculated from Robie and Hemingway (1995) [447].

[c] Fredrickson and Chasanov (1971) [448].

[d] O'Hare et al. (1988) [449].

[e] Robie and Hemingway (1995) [447].

[f] ΔG_f^0 calculated using ΔH_f^0 from O'Hare et al. (1988) [449] and S_f^0 calculated using S^0 for Mo from Wagman et al. (1982) [77], S^0 for S from McCollom and Shock (1997) [450], and S^0 for MoS_2 from Fredrickson and Chasanov (1971) [448].

[g] ΔH^0 of fusion.

[h] ΔS^0 of fusion.

[i] Maier–Kelley Coefficients calculated from fitting a curve of the Maier–Kelley equation to the C_p^0 data from Stull et al. (1969) [451].

[j] Calculated from the Maier–Kelley equation at 298.15 K.

[k] Stull et al. (1969) [451].

of copper sulfide enrichment during weathering. Science 272, 1153–1155.

[113] Gorby, Y.A. and Lovely, D.R. (1992) Enzymic uranium precipitation. Environ. Sci. Technol. 26, 205–207.

[114] Lovley, D.R. and Phillips, E.J.P. (1992) Reduction of uranium by *Desulfovibrio desulfuricans*. Appl. Environ. Microbiol. 58, 850–856.

[115] Lovley, D.R., Phillips, E.J.P., Gorby, Y.A. and Landa, E.R. (1991) Microbial reduction of uranium. Nature 350, 413–416.

[116] Boone, D.R., Liu, Y., Zhao, Z.-J., Balkwill, D., Drake, G.R., Stevens, T.O. and Aldrich, H. (1995) *Bacillus infernus* sp. nov., an Fe(III)- and Mn(IV)-reducing anaerobe from the deep terrestrial subsurface. Int. J. Syst. Bacteriol. 45, 441–448.

[117] Wilke, J.A. and Hering, J.G. (1998) Rapid oxidation of geothermal arsenic(III) in streamwaters of the eastern Sierra Nevada. Environ. Sci. Technol. 32, 657–662.

[118] Kirkland, D.W., Denison, R.E. and Rooney, M.A. (1995) Diagenetic alteration of Permian strata at oil fields of south central Oklahoma, USA. Mar. Pet. Geol. 12, 629–644.

[119] Kontak, D.J. and Kerrick, R. (1997) An isotopic (C, O, Sr) study of vein gold deposits in the Meguma terrane, Nova Scotia: Implication for source reservoirs. Econ. Geol. 92, 161–180.

[120] MacAulay, C.I., Fallick, A.E., McLaughlin, O.M., Haszeldine, R.S. and Pearson, M.J. (1998) The significance of $\delta^{13}C$ of carbonate cements in reservoir sandstones: a regional perspective from the Jurassic of the northern North Sea. Int. Assoc. Sediment, Spec. Publ. 26, 395–408.

[121] Stakes, D.S., Orange, D., Paduan, J.F., Salamy, K.A. and Maher, N. (1999) Cold-seeps and authigenic carbonate formation in Monterey Bay, California. Mar. Geol. 159, 93–109.

[122] Criss, R.E., Cooke, G.A. and Day, S.D. (1988) An organic origin for the carbonate concretions of the Ohio Shale. US Geol. Surv. Bull. 1836, 1–21.

[123] Danson, M.J. (1993) in: The Biochemistry of the Archaea (Archaebacteria) (Kates, M. Ed.), p. 582. Elsevier Science, Amsterdam.

[124] Schröder, C., Selig, M. and Schönheit, P. (1994) Glucose fermentation to acetate, CO_2 and H_2 in the anaerobic hyperthermophilic eubacterium *Thermotoga maritima*: involvement of the Embden–Meyerhof pathway. Arch. Microbiol. 161, 460–470.

[125] Andreesen, J.R. (1994) Glycine metabolism in anaerobes. Antonie Van Leeuwenhoek 66, 223–237.

[126] Jones, W.J., Leigh, J.A., Mayer, F., Woese, C.R. and Wolfe, R.S. (1983) *Methanococcus jannaschii* sp. nov., an extremely thermophilic methanogen from a submarine hydrothermal vent. Arch. Microbiol. 136, 254–261.

[127] Bult, C.J., White, O., Olsen, G.J., Zhou, L., Fleischmann, R.D., Sutton, G.G., Blake, J.A., FitzGerald, L.M., Clayton, R.A., Gocayne, J.D., Kerlavage, A.R., Dougherty, B.A., Tomb, J.-F., Adams, M.D., Reich, C.I., Overbeek, R., Kirkness, E.F., Weinstock, K.G., Merrick, J.M., Glodek, A., Scott, J.L., Geoghagen, N.S.M., Weidman, J.F., Fuhrmann, J.L., Nguyen, D., Utterback, T.R., Kelley, J.M., Peterson, J.D., Sadow, P.W., Hanna, M.C., Cotton, M.D., Roberts, K.M., Hurst, M.A., Kaine, B.P., Borodovsky, M., Klenk, H.-P., Fraser, C.M., Smith, H.O., Woese, C.R. and Venter, J.C. (1996) Complete genome sequence of the methanogenic Archaeon, *Methanococcus jannaschii*. Science 273, 1058–1073.

[128] Zinder, S.H., Sowers, K.R. and Ferry, J.G. (1985) *Methanosarcina thermophila* sp. nov., a thermophilic, acetotrophic, methane-producing bacterium. Int. J. Syst. Bacteriol. 35, 522–523.

[129] Garrels, R.M. and Christ, C.L. (1965) Solutions, Minerals, and Equilibria, Freeman, Cooper and Company, San Francisco, CA.

[130] Stumm, W. and Morgan, J.J. (1996) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, edn. 3, John Wiley and Sons, New York.

[131] Anderson, G.M. (1996) Thermodynamics of Natural Systems, John Wiley and Sons, New York.

[132] Langmuir, D. (1997) Aqueous Environmental Geochemistry, Prentice Hall, Upper Saddle River, NJ.

Table A.3
Gas solubility reactions

G1	$H_2(g) \leftrightarrow H_2(aq)$
G2	$O_2(g) \leftrightarrow O_2(aq)$
G3	$NO(g) \leftrightarrow NO(aq)$
G4	$N_2O(g) \leftrightarrow N_2O(aq)$
G5	$N_2(g) \leftrightarrow N_2(aq)$
G6	$NH_3(g) \leftrightarrow NH_3(aq)$
G7	$SO_2(g) \leftrightarrow SO_2(aq)$
G8	$H_2S(g) \leftrightarrow H_2S(aq)$
G9	$CO_2(g) \leftrightarrow CO_2(aq)$
G10	$CH_4(g) \leftrightarrow CH_4(aq)$
G11	$CO(g) \leftrightarrow CO(aq)$

Table A.4
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.3

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
G1	15.91	17.20	17.72	18.56	19.09	19.72	20.59	21.40	22.13	22.79	24.11	25.46
G2	14.12	15.85	16.54	17.65	18.34	19.15	20.27	21.28	22.20	23.02	24.59	26.04
G3[a]	13.18	14.83	15.49	16.54	17.20	17.96	18.99	19.92	20.75	21.49	22.93	24.39
G4[a]	6.62	8.45	9.18	10.35	11.08	11.93	13.09	14.13	15.05	15.87	17.42	18.90
G5	15.77	17.50	18.18	19.29	19.97	20.78	21.89	22.90	23.82	24.63	26.19	27.63
G6	−12.24	−10.85	−10.26	−9.25	−8.59	−7.78	−6.59	−5.43	−4.30	−3.19	−0.72	2.59
G7	−3.12	−1.59	−0.97	0.03	0.66	1.41	2.46	3.44	4.34	5.18	6.88	8.76
G8	3.65	5.06	5.64	6.56	7.15	7.85	8.82	9.71	10.54	11.29	12.80	14.42
G9	5.96	7.69	8.38	9.49	10.18	10.99	12.12	13.14	14.07	14.91	16.57	18.29
G10	13.76	15.56	16.27	17.39	18.08	18.89	20.00	20.98	21.85	22.61	24.02	25.18
G11	14.73	16.47	17.16	18.25	18.91	19.69	20.74	21.67	22.48	23.19	24.45	25.34

[a] Values from Plyasunov et al. (2001) [452]

[133] Quastel, J.H., Stephenson, M. and Whetham, M.D. (1925) Some reactions of resting bacteria in relation to anaerobic growth. Biochem. J. 19, 304–317.

[134] Aslander, A. (1928) Experiments on the eradication of Canada Thistle, *Cirsium arvense*, with chlorates and other herbicides. J. Agric. Res. 36, 915–934.

[135] Bryan, E.H. and Rohlich, G.A. (1954) Biological reduction of sodium chlorate as applied to measurement of sewage B.O.D. Sewage and Industrial Wastes, 1315–1324.

[136] Hackenthal, E. (1965) Die Reduktion von Perchlorat durch Bakterien-II. Biochem. Pharmacol. 14, 1313–1324.

[137] Malmqvist, A., Welander, T. and Gunnarsson, L. (1991) Anaerobic growth of microorganisms with chlorate as an electron acceptor. Appl. Environ. Microbiol. 57, 2229–2232.

[138] Wallace, W., Ward, T., Breen, A. and Attaway, H. (1996) Identification of an anaerobic bacterium which reduces perchlorate and chlorate as *Wolinella succinogenes*. J. Ind. Microbiol. 16, 68–72.

[139] Stepanyuk, V.V., Smirnova, G.F., Klyushnikova, T.M., Kanyuk, N.I., Panchenko, L.P., Nogina, T.M. and Prima, V.I. (1992) New species of the *Acinetobacter* genus – *Acinetobacter thermotoleranticus* sp. nov. Mikrobiologiya (in Russian) 61, 490–500.

[140] van Ginkel, C.G., Plugge, C.M. and Stroo, C.A. (1995) Reduction of chlorate with various energy subsrates and inocula under anaerobic conditions. Chemosphere 31, 4057–4066.

[141] Bruce, R.A., Achenbach, L.A. and Coates, J.D. (1999) Reduction of (per)chlorate by a novel organism isolated from paper mill waste. Environ. Microbiol. 1, 319–329.

Table A.5
Dissociation reactions

H1	$H_2O_2(aq) \leftrightarrow H^+ + HO_2^-$
H2	$NH_4^+ \leftrightarrow NH_3(aq) + H^+$
H3	$HNO_3(aq) \leftrightarrow H^+ + NO_3^-$
H4	$HNO_2(aq) \leftrightarrow H^+ + NO_2^-$
H5	$SO_2(aq) + H_2O \leftrightarrow HSO_3^- + H^+$
H6	$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$
H7	$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$
H8	$H_2S(aq) \leftrightarrow HS^- + H^+$
H9	$CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+$
H10	$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$
H11	formic acid(aq) $\leftrightarrow$ formate$^-$+H$^+$
H12	acetic acid(aq) $\leftrightarrow$ acetate$^-$+H$^+$
H13	glycolic acid(aq) $\leftrightarrow$ glycolate$^-$+H$^+$
H14	propanoic acid(aq) $\leftrightarrow$ propanoate$^-$+H$^+$
H15	lactic acid(aq) $\leftrightarrow$ lactate$^-$+H$^+$
H16	butanoic acid(aq) $\leftrightarrow$ butanoate$^-$+H$^+$
H17	pentanoic acid(aq) $\leftrightarrow$ pentanoate$^-$+H$^+$
H18	benzoic acid(aq) $\leftrightarrow$ benzoate$^-$+H+
H19	oxalic acid(aq) $\leftrightarrow$ H–oxalate$^-$+H$^+$
H20	H–oxalate$^-$ $\leftrightarrow$ oxalate^{-2}+H$^+$
H21	malonic acid(aq) $\leftrightarrow$ H–malonate$^-$+H$^+$
H22	H–malonate$^-$ $\leftrightarrow$ malonate^{-2}+H$^+$
H23	succinic acid(aq) $\leftrightarrow$ H–succinate$^-$+H$^+$
H24	H–succinate$^-$ $\leftrightarrow$ succinate^{-2}+H$^+$
H25	glutaric acid(aq) $\leftrightarrow$ H–glutarate$^-$+H$^+$
H26	H–glutarate$^-$ $\leftrightarrow$ glutarate^{-2}+H$^+$
H27	arginine$^+$ $\leftrightarrow$ arginine(aq)+H$^+$
H28	aspartic acid(aq) $\leftrightarrow$ aspartate$^-$+H$^+$
H29	glutamic acid(aq) $\leftrightarrow$ glutamate$^-$+H$^+$
H30	histidine$^+$ $\leftrightarrow$ histidine(aq)+H$^+$
H31	lysine$^+$ $\leftrightarrow$ lysine(aq)+H$^+$
H32	$VO_2^+ + 2H_2O(l) \leftrightarrow H_3VO_4(aq) + H^+$
H33	$H_3VO_4(aq) \leftrightarrow H_2VO_4^- + H^+$
H34	$H_2VO_4^- \leftrightarrow HVO_4^{2-} + H^+$
H35	$HVO_4^{2-} \leftrightarrow VO_4^{3-} + H^+$
H36	$H_3AsO_4(aq) \leftrightarrow H_2AsO_4^- + H^+$
H37	$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$
H38	$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+$
H39	$HAsO_2(aq) \leftrightarrow AsO_2^- + H^+$
H40	$HSeO_4^- \leftrightarrow SeO_4^{2-} + H^+$
H41	$H_2SeO_3(aq) \leftrightarrow HSeO_3^- + H^+$
H42	$HSeO_3^- \leftrightarrow SeO_3^{2-} + H^+$
H43	$HMoO_4^- \leftrightarrow MoO_4^{2-} + H^+$
H44	$HWO_4^- \leftrightarrow WO_4^{2-} + H^+$
H45	$H_3PO_4(aq) \leftrightarrow H_2PO_4^- + H^+$
H46	$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$
H47	$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$
H48	$H_4P_2O_7(aq) \leftrightarrow H_3P_2O_7^- + H^+$
H49	$H_3P_2O_7^- \leftrightarrow H_2P_2O_7^{2-} + H^+$
H50	$H_2P_2O_7^{2-} \leftrightarrow HP_2O_7^{3-} + H^+$
H51	$HP_2O_7^{3-} \leftrightarrow P_2O_7^{4-} + H^+$
H52	$HCl(aq) \leftrightarrow H^+ + Cl^-$
H53	$HClO(aq) \leftrightarrow H^+ + ClO^-$
H54	$HBrO(aq) \leftrightarrow H^+ + BrO^-$
H55	$HIO_3(aq) \leftrightarrow H^+ + IO_3^-$
H56	$HIO(aq) \leftrightarrow H^+ + IO^-$

Table A.6
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.5

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
H1	64.14	65.87	66.70	68.18	69.22	70.56	72.68	74.89	77.21	79.63	85.70	95.43
H2	52.66	52.72	52.75	52.79	52.81	52.83	52.86	52.87	52.87	52.86	52.78	52.53
H3	−8.02	−7.64	−7.43	−7.02	−6.71	−6.29	−5.59	−4.82	−3.97	−3.05	−0.60	3.73
H4	18.25	18.33	18.41	18.59	18.74	18.95	19.34	19.79	20.32	20.91	22.56	25.69
H5	8.77	10.00	10.62	11.79	12.64	13.76	15.59	17.57	19.70	21.98	27.84	37.62
H6	37.53	39.97	41.13	43.22	44.69	46.57	49.54	52.66	55.91	59.30	67.78	81.32
H7	9.15	10.58	11.30	12.64	13.61	14.88	16.92	19.11	21.43	23.89	30.16	40.48
H8	38.84	39.51	39.89	40.64	41.20	41.98	43.28	44.72	46.31	48.04	52.63	60.54
H9	34.52	35.63	36.22	37.37	38.22	39.37	41.27	43.36	45.63	48.09	54.47	65.19
H10	55.81	57.94	58.96	60.80	62.09	63.76	66.38	69.14	72.04	75.06	82.63	94.79
H11	19.95	20.93	21.42	22.33	22.97	23.82	25.18	26.64	28.18	29.82	34.01	40.99
H12	25.16	26.52	27.15	28.30	29.10	30.13	31.77	33.50	35.32	37.23	42.09	50.04
H13	20.41	21.40	21.88	22.77	23.40	24.23	25.57	27.02	28.56	30.21	34.47	41.66
H14	25.82	27.25	27.91	29.09	29.90	30.96	32.60	34.33	36.13	38.02	42.73	50.34
H15	20.49	21.54	22.05	22.99	23.66	24.53	25.93	27.43	29.02	30.71	35.05	42.25
H16	25.26	26.75	27.45	28.70	29.58	30.70	32.47	34.32	36.25	38.26	43.28	51.33
H17	25.44	26.95	27.66	28.92	29.79	30.91	32.66	34.47	36.35	38.29	43.08	50.63
H18	22.32	23.43	23.97	24.96	25.65	26.56	27.99	29.51	31.11	32.80	37.05	44.00
H19	6.64	7.03	7.25	7.69	8.02	8.49	9.26	10.15	11.13	12.21	15.15	20.39
H20	22.14	23.59	24.30	25.61	26.56	27.79	29.76	31.86	34.10	36.46	42.48	52.40
H21	15.20	15.91	16.28	16.97	17.48	18.17	19.30	20.55	21.92	23.40	27.29	34.00
H22	29.86	31.66	32.51	34.07	35.18	36.63	38.96	41.46	44.13	46.97	54.30	66.50
H23	22.55	23.53	24.02	24.92	25.56	26.42	27.81	29.30	30.90	32.62	37.03	44.40
H24	29.89	31.40	32.13	33.48	34.45	35.73	37.79	40.02	42.43	45.01	51.71	63.02
H25	23.00	24.19	24.77	25.83	26.59	27.58	29.15	30.84	32.63	34.52	39.33	47.17
H26	28.58	30.16	30.92	32.32	33.32	34.64	36.76	39.06	41.53	44.18	51.02	62.55
H27	52.32	52.52	52.59	52.71	52.79	52.88	53.00	53.12	53.23	53.33	53.51	53.61
H28	21.32	22.01	22.34	22.97	23.42	24.01	24.97	26.00	27.11	28.30	31.40	36.71
H29	22.92	23.94	24.43	25.34	25.98	26.82	28.16	29.59	31.10	32.71	36.82	43.66
H30	33.70	33.98	34.10	34.29	34.41	34.56	34.77	34.97	35.17	35.36	35.77	36.25
H31	50.68	50.97	51.09	51.28	51.40	51.55	51.76	51.97	52.17	52.36	52.79	53.30
H32	20.05	19.13	18.73	18.04	17.59	17.03	16.22	15.44	14.68	13.95	12.31	10.06
H33	20.95	21.56	21.80	22.19	22.43	22.72	23.13	23.51	23.88	24.23	25.05	26.39
H34	43.36	45.23	45.98	47.19	47.94	48.84	50.09	51.25	52.32	53.33	55.52	58.45
H35	72.17	74.60	75.73	77.75	79.14	80.93	83.71	86.61	89.62	92.74	100.47	112.70
H36	11.50	12.47	12.93	13.76	14.34	15.09	16.27	17.51	18.81	20.18	23.64	29.36
H37	36.05	37.76	38.58	40.05	41.07	42.41	44.50	46.69	49.00	51.40	57.45	67.22
H38	62.78	65.09	66.20	68.19	69.59	71.41	74.27	77.29	80.45	83.76	92.04	105.32
H39	50.85	52.09	52.68	53.73	54.47	55.41	56.90	58.45	60.08	61.78	66.05	72.97
H40	8.97	10.24	10.88	12.09	12.96	14.12	15.99	18.01	20.18	22.48	28.40	38.26
H41	13.13	14.19	14.69	15.59	16.22	17.03	18.31	19.66	21.08	22.56	26.31	32.48
H42	39.07	40.76	41.59	43.12	44.21	45.64	47.91	50.34	52.90	55.61	62.49	73.73
H43	23.17	24.44	25.10	26.36	27.27	28.48	30.45	32.58	34.88	37.33	43.64	54.17
H44	18.75	19.90	20.50	21.65	22.49	23.62	25.46	27.46	29.62	31.93	37.91	47.95
H45	10.94	11.92	12.38	13.24	13.84	14.62	15.85	17.15	18.52	19.97	23.63	29.67
H46	38.50	40.28	41.13	42.67	43.74	45.13	47.33	49.64	52.06	54.60	60.97	71.26
H47	66.29	69.04	70.34	72.66	74.27	76.36	79.61	83.02	86.57	90.26	99.42	113.95
H48	7.63	8.41	8.79	9.46	9.93	10.54	11.50	12.51	13.57	14.69	17.54	22.32
H49	12.32	13.05	13.39	14.01	14.44	15.01	15.90	16.83	17.82	18.87	21.56	26.14
H50	35.16	36.85	37.66	39.11	40.12	41.43	43.49	45.66	47.93	50.31	56.28	65.94
H51	49.86	52.04	53.14	55.20	56.68	58.65	61.81	65.21	68.84	72.68	82.48	98.51
H52	−2.82	−3.73	−4.05	−4.52	−4.77	−5.02	−5.27	−5.38	−5.34	−5.17	−4.19	−1.29
H53	40.96	42.41	43.10	44.33	45.19	46.30	48.05	49.87	51.79	53.78	58.77	66.81
H54	46.79	48.26	48.96	50.20	51.07	52.19	53.94	55.79	57.71	59.71	64.74	72.84
H55	3.64	4.28	4.60	5.22	5.67	6.26	7.22	8.26	9.37	10.57	13.68	18.99
H56	58.45	59.97	60.67	61.91	62.76	63.85	65.54	67.29	69.10	70.97	75.62	83.01

[142] Coates, J.D., Michaelidou, U., Bruce, R.A., O'Connor, S.M. and Crespi, J.N. (1999) Ubiquity and diversity of dissimilatory (per)-chlorate-reducing bacteria. Appl. Environ. Microbiol. 65, 5234–5241.

[143] Michaelidou, U., Coates, J.D. and Achenbach, L.A. (1999) Isolation and characterization of two novel (per)chlorate-reducing bacteria from swine waste lagoons. Book of Abstracts, 218th ACS National Meeting.

Table A.7
Values of pK_a at P_{SAT} as a function of temperature for the reactions given in Table A.5

Reaction	*T* (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
H1	12.18	11.82	11.69	11.48	11.36	11.23	11.06	10.92	10.81	10.72	10.58	10.54
H2	10.00	9.46	9.24	8.89	8.67	8.41	8.05	7.71	7.40	7.11	6.52	5.80
H3	−1.52	−1.37	−1.30	−1.18	−1.10	−1.00	−0.85	−0.70	−0.56	−0.41	−0.07	0.41
H4	3.46	3.29	3.23	3.13	3.08	3.02	2.94	2.89	2.84	2.81	2.79	2.84
H5	1.67	1.79	1.86	1.99	2.07	2.19	2.37	2.56	2.76	2.96	3.44	4.15
H6	7.12	7.17	7.21	7.28	7.34	7.41	7.54	7.68	7.83	7.98	8.37	8.98
H7	1.74	1.90	1.98	2.13	2.23	2.37	2.58	2.79	3.00	3.22	3.72	4.47
H8	7.37	7.09	6.99	6.84	6.77	6.68	6.59	6.52	6.48	6.47	6.50	6.68
H9	6.55	6.39	6.35	6.29	6.28	6.27	6.28	6.32	6.39	6.47	6.72	7.20
H10	10.59	10.40	10.33	10.24	10.19	10.15	10.10	10.08	10.08	10.10	10.20	10.47
H11	3.79	3.76	3.75	3.76	3.77	3.79	3.83	3.88	3.95	4.01	4.20	4.53
H12	4.78	4.76	4.76	4.77	4.78	4.80	4.84	4.89	4.94	5.01	5.20	5.52
H13	3.88	3.84	3.83	3.84	3.84	3.86	3.89	3.94	4.00	4.07	4.26	4.60
H14	4.90	4.89	4.89	4.90	4.91	4.93	4.96	5.01	5.06	5.12	5.28	5.56
H15	3.89	3.87	3.86	3.87	3.88	3.91	3.95	4.00	4.06	4.13	4.33	4.66
H16	4.80	4.80	4.81	4.83	4.86	4.89	4.94	5.01	5.07	5.15	5.34	5.67
H17	4.83	4.84	4.85	4.87	4.89	4.92	4.97	5.03	5.09	5.15	5.32	5.59
H18	4.24	4.20	4.20	4.20	4.21	4.23	4.26	4.30	4.36	4.41	4.57	4.86
H19	1.26	1.26	1.27	1.30	1.32	1.35	1.41	1.48	1.56	1.64	1.87	2.25
H20	4.20	4.23	4.26	4.31	4.36	4.42	4.53	4.65	4.77	4.91	5.24	5.78
H21	2.89	2.86	2.85	2.86	2.87	2.89	2.94	3.00	3.07	3.15	3.37	3.75
H22	5.67	5.68	5.70	5.74	5.78	5.83	5.93	6.05	6.18	6.32	6.70	7.34
H23	4.28	4.22	4.21	4.20	4.20	4.21	4.23	4.27	4.33	4.39	4.57	4.90
H24	5.67	5.63	5.63	5.64	5.66	5.69	5.75	5.84	5.94	6.06	6.38	6.96
H25	4.37	4.34	4.34	4.35	4.37	4.39	4.44	4.50	4.57	4.65	4.85	5.21
H26	5.43	5.41	5.42	5.44	5.47	5.51	5.60	5.70	5.81	5.95	6.30	6.91
H27	9.93	9.42	9.21	8.88	8.67	8.42	8.07	7.75	7.45	7.18	6.61	5.92
H28	4.05	3.95	3.91	3.87	3.85	3.82	3.80	3.79	3.80	3.81	3.88	4.05
H29	4.35	4.30	4.28	4.27	4.27	4.27	4.29	4.32	4.35	4.40	4.55	4.82
H30	6.40	6.10	5.97	5.78	5.65	5.50	5.29	5.10	4.92	4.76	4.42	4.00
H31	9.62	9.14	8.95	8.64	8.44	8.21	7.88	7.58	7.30	7.05	6.52	5.88
H32	3.81	3.43	3.28	3.04	2.89	2.71	2.47	2.25	2.06	1.88	1.52	1.11
H33	3.98	3.87	3.82	3.74	3.68	3.62	3.52	3.43	3.34	3.26	3.09	2.91
H34	8.23	8.12	8.06	7.95	7.87	7.77	7.62	7.47	7.32	7.18	6.85	6.45
H35	13.70	13.38	13.27	13.09	12.99	12.88	12.74	12.63	12.55	12.48	12.40	12.44
H36	2.18	2.24	2.27	2.32	2.35	2.40	2.48	2.55	2.63	2.72	2.92	3.24
H37	6.84	6.78	6.76	6.75	6.74	6.75	6.77	6.81	6.86	6.92	7.09	7.42
H38	11.92	11.68	11.60	11.49	11.43	11.37	11.31	11.27	11.26	11.27	11.36	11.63
H39	9.65	9.35	9.23	9.05	8.94	8.82	8.66	8.53	8.41	8.31	8.15	8.06
H40	1.70	1.84	1.91	2.04	2.13	2.25	2.43	2.63	2.82	3.03	3.51	4.22
H41	2.49	2.55	2.57	2.63	2.66	2.71	2.79	2.87	2.95	3.04	3.25	3.59
H42	7.42	7.31	7.29	7.26	7.26	7.26	7.29	7.34	7.41	7.48	7.71	8.14
H43	4.40	4.39	4.40	4.44	4.48	4.53	4.64	4.75	4.88	5.02	5.39	5.98
H44	3.56	3.57	3.59	3.65	3.69	3.76	3.88	4.01	4.15	4.30	4.68	5.29
H45	2.08	2.14	2.17	2.23	2.27	2.33	2.41	2.50	2.59	2.69	2.92	3.28
H46	7.31	7.23	7.21	7.19	7.18	7.18	7.20	7.24	7.29	7.35	7.53	7.87
H47	12.58	12.39	12.32	12.24	12.19	12.15	12.12	12.11	12.12	12.15	12.27	12.58
H48	1.45	1.51	1.54	1.59	1.63	1.68	1.75	1.83	1.90	1.98	2.17	2.46
H49	2.34	2.34	2.35	2.36	2.37	2.39	2.42	2.46	2.50	2.54	2.66	2.89
H50	6.68	6.61	6.60	6.59	6.59	6.60	6.62	6.66	6.71	6.77	6.95	7.28
H51	9.47	9.34	9.31	9.30	9.31	9.34	9.41	9.51	9.64	9.78	10.18	10.88
H52	−0.54	−0.67	−0.71	−0.76	−0.78	−0.80	−0.80	−0.78	−0.75	−0.70	−0.52	−0.14
H53	7.78	7.61	7.55	7.47	7.42	7.37	7.31	7.27	7.25	7.24	7.25	7.38
H54	8.88	8.66	8.58	8.46	8.38	8.31	8.21	8.14	8.08	8.04	7.99	8.04
H55	0.69	0.77	0.81	0.88	0.93	1.00	1.10	1.20	1.31	1.42	1.69	2.10
H56	11.10	10.76	10.63	10.43	10.30	10.16	9.98	9.81	9.67	9.55	9.33	9.16

[144] Hackenthal, E., Mannheim, W., Hackenthal, R. and Becher, R. (1964) Die Reduktion von Perchlorat durch Bakterien. I. Untersuchungen an intakten Zellen. Biochem. Pharm. 13, 195–206.

[145] Stouthamer, A.H. (1967) Nitrate reduction in *Aerobacter aerogenes*. Arch. Mikrobiol. 56, 68–75.

[146] De Groot, G.N. and Stouthamer, A.H. (1969) Regulation of reductase formation in *Proteus mirabilis* 1. Formation of reductases and enzymes of the formic hydrogen–lyase complex in the wild type and in chlorate-resistant mutants. Arch. Microbiol. 66, 220–233.

[147] Romanenko, V.I., Koren'kov, V.N. and Kuznetsov, S.I. (1976) Bacterial decomposition of ammonium perchlorate. Mikrobiologiya (in Russian) 45, 204–209.

Table A.8
Auxiliary redox, disproportionation, and hydrolysis reactions

J1	$2H_2O_2(aq) \leftrightarrow 2H_2O(l)+O_2(aq)$
J2	$VO_2^+ +H^+ +0.5H_2(aq) \leftrightarrow VO^{2+}+H_2O(l)$
J3	$VO^{2+}+H^+ +0.5H_2(aq) \leftrightarrow V^{3+}+H_2O(l)$
J4	$V^{3+}+0.5H_2(aq) \leftrightarrow V^{2+}+H^+$
J5	$Cr_2O_7^{2-}+H_2O(l) \leftrightarrow 2CrO_4^{2-}+2H^+$
J6	$CrO_4^{2-}+5H^+ +1.5H_2(aq) \leftrightarrow Cr^{3+}+4H_2O(l)$
J7	$MnO_4^- +0.5H_2(aq) \leftrightarrow MnO_4^{2-}+H^+$
J8	$MnO_4^{2-}+5H^+ +1.5H_2(aq) \leftrightarrow Mn^{3+}+4H_2O(l)$
J9	$Mn^{3+}+0.5H_2(aq) \leftrightarrow Mn^{2+}+H^+$
J10	$Co^{3+}+0.5H_2(aq) \leftrightarrow Co^{2+}+H^+$
J11	$Cu^{2+}+0.5H_2(aq) \leftrightarrow Cu^{2+}+H^+$
J12	$HAsO_2(aq)+2H_2O(l) \leftrightarrow HAsO_4^{2-}+2H^+ +H_2(aq)$
J13	$SeO_3^{2-}+H_2O(l) \leftrightarrow SeO_4^{2-}+H_2(aq)$
J14	$HSe^- +3H_2O(l) \leftrightarrow SeO_3^{2-}+3H_2(aq)+H^+$
J15	$Au^{3+}+H_2(aq) \leftrightarrow Au^+ +2H^+$
J16	$P_2O_7^{4-}+H_2O(l) \leftrightarrow 2HPO_4^{2-}$
J17	$H_2P_2O_7^{2-}+H_2O(l) \leftrightarrow 2H_2PO_4^-$
J18	$HP_2O_7^{3-}+H_2O(l) \leftrightarrow 2HPO_4^{2-}+H^+$

[148] Malmqvist, A., Welander, T., Moore, E., Ternstrom, A., Molin, G. and Stenstrom, I.-M. (1994) *Ideonella dechloratans* gen. nov., sp. nov., a new bacterium capable of growing anaerobically with chlorate as an electron acceptor. Syst. Appl. Microbiol. 17, 58–64.

[149] Roldan, M.D., Reyes, F., Moreno-Vivian, C. and Castillo, F. (1994) Chlorate and nitrate reduction in the phototrophic bacteria *Rhodobacter capsulatus* and *Rhodobacter sphaeroides*. Curr. Microbiol. 29, 241–245.

[150] Rikken, G.B., Kroon, A.G.M. and van Ginkel, C.G. (1996) Transformation of (per)chlorate into chloride by a newly isolated bacterium: reduction and dismutation. Appl. Microbiol. Biotechnol. 45, 420–426.

[151] Tsunogai, S. and Sase, T. (1969) Formation of iodide–iodine in the ocean. Deep-Sea Res. 16, 489–496.

[152] Noyes, A.A., Kato, Y. and Sosman, R.B. (1910) The hydrolysis of ammonium acetate and the ionization of water at high temperatures. J. Am. Chem. Soc. 32, 159–178.

[153] Harned, H.S. and Ehlers, R.W. (1933) The dissociation constant of acetic acid from 0 to 60° centigrade. J. Am. Chem. Soc. 55, 652–656.

[154] Ellis, A.J. (1963) The ionization of acetic, propionic, *n*-butyric and benzoic acid in water, from conductance measurements up to 225°. J. Chem. Soc. 1963, 2299–2310.

[155] Lown, D.A., Thirsk, H.R. and Wynne-Jones, L. (1970) Temperature and pressure dependence of the volume of ionization of acetic acid in water from 25 to 225°C and 1–3000 bar. Trans. Faraday Soc. 66, 51–73.

[156] Fisher, J.R. and Barnes, H.L. (1972) The ion-product constant of water to 350°C. J. Phys. Chem. 76, 90–99.

[157] Oscarson, J.L., Gillespie, S.E., Christensen, J.J., Izatt, R.M. and Brown, P.R. (1988) Thermodynamic quantities for the interaction of H^+ and Na^+ with $C_2H_3O_2^-$ and Cl^- in aqueous solution from 275 to 320°C. J. Sol. Chem. 17, 865–885.

[158] Mesmer, R.E., Patterson, C.S., Busey, R.H. and Holmes, H.F. (1989) Ionization of acetic acid in NaCl(aq) media: A potentiometric study to 573 K and 130 bar. J. Phys. Chem. 93, 7483–7490.

[159] Dickson, A.G., Wesolowski, D.J., Palmer, D.A. and Mesmer, R.E. (1990) Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250°C. J. Phys. Chem. 94, 7978–7985.

[160] Harned, H.S. and Davis Jr., R. (1943) The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°. J. Am. Chem. Soc. 65, 2030–2037.

[161] Drummond, S.E. (1981) Ph.D. thesis, Pennsylvania State University, PA.

[162] Zawisza, A. and Malesinska, B. (1981) Solubility of carbon dioxide in liquid water and water in gaseous carbon dioxide in the range 0.2–5 MPa and at temperatures up to 473 K. J. Chem. Eng. Data 26, 388–391.

[163] Krumholz, L.R., McKinley, J.P., Ulrich, G.A. and Suflita, J.M. (1997) Confined subsurface microbial communities in Cretaceous rock. Nature 386, 64–66.

[164] Phelps, T.J., Raione, E.G., White, D.C. and Fliermans, C.B. (1989) Microbial activities in deep subsurface environments. Geomicrobiol. J. 7, 79–92.

[165] Jones, W.J., Stugard, C.E. and Jannasch, H.W. (1989) Comparison of thermophilic methanogens from submarine hydrothermal vents. Arch. Microbiol. 151, 314–318.

[166] Haldeman, D.L., Amy, P.S., Ringelberg, D. and White, D.C. (1993) Characterization of the microbiology within a 21 m^3 section of rock from the deep subsurface. Microb. Ecol. 26, 145–159.

[167] Russell, C.E., Jacobson, R., Haldeman, D.L. and Amy, P.S. (1994)

Table A.9
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.8

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
J1	−190.99	−190.09	−189.79	−189.39	−189.20	−189.03	−188.93	−188.99	−189.19	−189.54	−190.88	−193.93
J2	−106.80	−105.83	−105.46	−104.89	−104.56	−104.19	−103.71	−103.32	−103.02	−102.78	−102.48	−102.50
J3	−42.95	−42.23	−41.87	−41.16	−40.66	−39.98	−38.89	−37.72	−36.48	−35.15	−31.78	−26.26
J4	17.56	16.33	15.82	14.99	14.45	13.81	12.88	12.00	11.16	10.36	8.59	6.22
J5	78.53	82.18	83.93	87.10	89.34	92.24	96.82	101.66	106.75	112.09	125.51	147.24
J6	−454.71	−451.54	−450.22	−448.03	−446.62	−444.93	−442.51	−440.23	−438.09	−436.08	−431.88	−427.07
J7	−65.70	−63.49	−62.41	−60.43	−59.02	−57.18	−54.25	−51.12	−47.81	−44.33	−35.51	−21.18
J8	−560.87	−557.78	−556.49	−554.37	−553.01	−551.37	−549.04	−546.85	−544.80	−542.89	−538.92	−534.46
J9	−149.58	−152.98	−154.46	−157.02	−158.73	−160.86	−164.06	−167.27	−170.49	−173.71	−181.30	−192.37
J10	−193.37	−196.00	−197.14	−199.10	−200.41	−202.03	−204.46	−206.89	−209.31	−211.74	−217.44	−225.73
J11	−21.93	−23.69	−24.45	−25.75	−26.61	−27.68	−29.28	−30.87	−32.45	−34.02	−37.70	−43.03
J12	175.54	178.72	180.17	182.73	184.49	186.74	190.22	193.82	197.56	201.43	211.05	226.39
J13	183.90	183.55	183.36	182.98	182.71	182.34	181.73	181.07	180.36	179.59	177.63	174.42
J14	348.44	350.18	350.92	352.13	352.92	353.88	355.29	356.67	358.01	359.34	362.42	366.91
J15	−281.47	−286.05	−288.01	−291.32	−293.50	−296.19	−300.16	−304.06	−307.92	−311.72	−320.51	−332.98
J16	−22.36	−22.03	−21.89	−21.66	−21.51	−21.32	−21.05	−20.79	−20.54	−20.30	−19.77	−19.10
J17	−14.35	−13.71	−13.36	−12.68	−12.18	−11.51	−10.40	−9.20	−7.90	−6.50	−2.95	2.83
J18	27.49	30.01	31.25	33.54	35.18	37.33	40.76	44.42	48.30	52.38	62.71	79.41

Table A.10
Redox reactions in the system H–O–P

K1	$H_3PO_4(aq) \leftrightarrow H_3PO_3(aq)+0.5O_2(aq)$
K2	$H_4P_2O_7(aq)+H_2O(l) \leftrightarrow 2H_3PO_3(aq)+O_2(aq)$
K3	$H_3PO_4(aq) \leftrightarrow H_3PO_2(aq)+O_2(aq)$
K4	$H_4P_2O_7(aq)+H_2O(l) \leftrightarrow 2H_3PO_2(aq)+2O_2(aq)$
K5	$H_3PO_3(aq) \leftrightarrow H_3PO_2(aq)+0.5O_2(aq)$

Heterogeneity of deep subsurface microorganisms and correlations to hydrogeological and geochemical parameters. Geomicrobiol. J. 12, 37–51.

[168] Brown, D.A., Kamineni, D.C., Sawicki, J.A. and Beveridge, T.J. (1994) Minerals associated with biofilms occurring on exposed rock in a granitic underground research laboratory. Appl. Environ. Microbiol. 60, 3182–3191.

[169] Brown, D.A. and Sherriff, B.L. (1997) Active ultramicrobacterial alteration of iron in granite. Proc. SPIE-Int. Soc. Opt. Eng. 3111, 510–518.

[170] Love, C.A., Patel, B.K.C., Nichols, P.D. and Stackebrandt, E. (1993) *Desulfotomaculum australicum*, sp. nov., a thermophilic sulfate-reducing bacterium isolated from the Great Artesian basin of Australia. Syst. Appl. Microbiol. 16, 244–251.

[171] Wynter, C., Patel, B.K.C., Bain, P., Jersey, J.d., Hamilton, S. and Inkerman, P.A. (1996) A novel thermostable dextranase from a *Thermoanaerobacter* species cultured from the geothermal waters of the Great Artesian Basin of Australia. FEMS Microbiol. Lett. 140, 271–276.

[172] Byers, H.K., Stackebrandt, E., Hayward, C. and Balckall, L.L. (1998) Molecular investigation of a microbial mat associated with the Great Artesian Basin. FEMS Microb. Ecol. 25, 391–403.

[173] Ekendahl, S. and Pedersen, K. (1994) Carbon transformation by attached bacterial populations in granitic groundwater from deep crystalline bed-rock of the Stripa research mine. Microbiology 140, 1565–1573.

[174] Olson, G.J., Dockins, W.S., McFeters, G.A. and Iverson, W.P. (1981) Sulfate-reducing and methanogenic bacteria from deep aquifers in Montana. Geomicrobiol. J. 2, 327–340.

[175] Liu, Y., Karnauchow, T.M., Jarrell, K.F., Balkwill, D.L., Drake, G.R., Ringelberg, D., Clarno, R. and Boone, D.R. (1997) Description of two new thermophilic *Desulfotomaculum* spp., *Desulfotomaculum putei* sp. nov., from a deep terrestrial subsurface, and *Desulfotomaculum luciae* sp. nov., from a hot spring. Int. J. Syst. Bacteriol. 47, 615–621.

[176] Grossman, D. and Schulman, S. (1995) The biosphere below, Earth, June 4, 35–40.

[177] Daumas, S., Lombart, R. and Bianchi, A. (1986) A Bacteriological study of geothermal spring waters dating from the Dogger and Trias Period in the Paris Basin. Geomicrobiol. J. 4, 423–433.

[178] Tardy-Jacquenod, C., Magot, M., Patel, B.K.C., Matheron, R. and Caumette, P. (1998) *Desulfotomaculum halophilum* sp. nov., a halophilic sulfate-reducing bacterium isolated from oil production facilities. Int. J. Syst. Bacteriol. 48, 333–338.

[179] Onstott, T.C., Phelps, T.J., Colwell, F.S., Ringelberg, D., White, D.C. and Boone, D.R. (1998) Observations pertaining to the origin and ecology of microorganisms recoverd from the deep subsurface of Taylorsville Basin, Virginia. Geomicrobiol. J. 15, 353–385.

[180] Nilsen, R.K., Torsvik, T. and Lien, T. (1996) *Desulfotomaculum thermocisternum* sp. nov., a sulfate reducer isolated from a hot North Sea oil reservoir. Int. J. Syst. Bacteriol. 46, 397–402.

[181] Greene, A.C., Patel, B.K.C. and Sheehy, A.J. (1997) *Deferribacter thermophilus* gen. nov. sp. nov., a novel thermophilic manganese- and iron-reducing bacterium isolated from a petroleum reservoir. Int. J. Syst. Bacteriol. 47, 505–509.

[182] Clark, D.A. and Norris, P.R. (1996) *Acidimicrobium ferrooxidans* gen. nov., sp. nov. mixed-culture ferrous iron oxidation with *Sulfobacillus* species. Microbiology 142, 785–790.

[183] Bridge, T.A.M. and Johnson, B. (1998) Reduction of soluble iron and reductive dissolution of ferric iron-containing minerals by moderately thermophilic iron oxidizing bacteria. Appl. Environ. Microbiol. 64, 2181–2186.

[184] Wisotzkey, J.D., Jurtshuk Jr., P., Fox, G.E., Deinhard, G. and Poralla, K. (1992) Comparitive sequence analyses on the 16S rRNA (rDNA) of *Bacillus acidocaldarius, Bacillus acidoterrestris*, and *Bacillus cycloheptanicus* and proposal for creation of a new genus, *Alicyclobacillus* gen. nov. Int. J. Syst. Bacteriol. 42, 263–269.

[185] Darland, G. and Brock, T.D. (1971) *Bacillus acidocaldarius* sp. nov., an acidophilic thermophilic spore-forming bacterium. J. Gen. Microbiol. 67, 9–15.

[186] Nicolaus, B., Improta, R., Manca, M.C., Lama, L., Esposito, E. and Gambacorta, A. (1998) *Alicyclobacilli* from an unexplored geothermal soil in Antarctica: Mount Rittmann. Polar Biol. 19, 131–141.

[187] Huber, R., Rossnagel, P., Woese, C.R., Rachel, R., Langworthy, T.A. and Stetter, K.O. (1996) Formation of ammonium from nitrate during chemolithoautotrophic growth of the extremely thermophilic bacterium *Ammonifex degensii* gen. nov. sp. nov. Syst. Appl. Microbiol. 19, 40–49.

[188] Engle, M., Li, Y., Woese, C. and Wiegel, J. (1995) Isolation and characterization of a novel alkalitolerant thermophile, *Anaerobranca horikoshii* gen. nov., sp. nov. Int. J. Syst. Bacteriol. 45, 454–461.

[189] Schenk, A. and Aragno, M. (1979) *Bacillus schlegelii*, a new species of thermophilic, facultatively chemolithoautotrophic bacterium oxidizing molecular hydrogen. J. Gen. Microbiol. 115, 333–341.

[190] Nicolaus, B., Lama, L., Esposito, E., Manca, M.C., Di Prisco, G. and Gambacorta, A. (1996) *Bacillus thermoantarcticus* sp. nov., from Mount Melbourne, Antarctica a novel thermophilic species. Polar Biol. 16, 101–104.

[191] Nicolaus, B., Marsiglia, F., Esposito, E., Trincone, A., Lama, L., Sharp, R., Di Prisco, G. and Gambacorta, A. (1991) Isolation of five strains of thermophilic eubacteria in Antarctica. Polar Biol. 11, 425–429.

[192] Sunna, A., Tokajian, S., Burghardt, J., Rainey, F., Antranikian, G. and Hashwa, F. (1997) Identification of *Bacillus kaustophilus, Bacillus thermocatenulatus* and *Bacillus* strain HSR as members of *Bacillus thermoleovorans*. Syst. Appl. Microbiol. 20, 232–237.

[193] Anderson, M., Laukkanen, M., Nurmiaho-Lassila, E.-L., Rainey, F.A., Niemela, S.I. and Salkinoja-Salonen, M. (1995) *Bacillus ther-*

Table A.11
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.10

Reaction	*T* (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
K1	295.71	294.57	294.04	293.08	292.40	291.53	290.17	288.73	287.24	285.68	281.82	275.75
K2	575.14	573.07	572.13	570.47	569.33	567.87	565.63	563.32	560.94	558.49	552.54	543.45
K3	637.98	636.49	635.78	634.48	633.57	632.37	630.50	628.51	626.42	624.24	618.79	610.17
K4	1259.69	1256.89	1255.59	1253.27	1251.65	1249.56	1246.29	1242.87	1239.31	1235.61	1226.48	1212.27
K5	342.27	341.91	341.73	341.40	341.16	340.84	340.33	339.77	339.18	338.56	336.97	334.41

Table A.12
Values of ΔG^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for compounds in the system H–O–halogen

Compound	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
HCl(aq)	−127.04	−127.15	−127.24	−127.42	−127.58	−127.81	−128.21	−128.69	−129.24	−129.86	−131.59	−134.75
Cl^-	−129.86	−130.88	−131.29	−131.94	−132.35	−132.83	−133.48	−134.07	−134.58	−135.03	−135.78	−136.04
ClO^-	−35.73	−36.52	−36.82	−37.30	−37.58	−37.92	−38.38	−38.79	−39.14	−39.44	−39.90	−39.91
HClO(aq)	−76.69	−78.93	−79.92	−81.63	−82.78	−84.23	−86.43	−88.66	−90.93	−93.22	−98.67	−106.72
ClO_2^-	19.57	17.87	17.15	15.95	15.18	14.22	12.81	11.44	10.11	8.82	5.96	2.38
$HClO_2$(aq)	10.08	7.16	5.85	3.57	2.01	0.04	−2.97	−6.06	−9.20	−12.42	−20.14	−31.73
ClO_3^-	−4.16	−6.81	−7.95	−9.89	−11.17	−12.76	−15.13	−17.47	−19.80	−22.10	−27.36	−34.51
ClO_4^-	−4.32	−7.26	−8.54	−10.72	−12.17	−13.98	−16.69	−19.41	−22.13	−24.84	−31.15	−39.97
Br^-	−102.02	−103.47	−104.06	−105.02	−105.64	−106.37	−107.42	−108.39	−109.31	−110.15	−111.83	−113.47
BrO^-	−32.41	−33.18	−33.47	−33.93	−34.21	−34.54	−34.98	−35.36	−35.69	−35.97	−36.38	−36.31
HBrO(aq)	−79.21	−81.44	−82.43	−84.13	−85.28	−86.73	−88.92	−91.15	−93.40	−95.68	−101.12	−109.14
BrO_3^-	22.43	19.76	18.61	16.69	15.43	13.87	11.57	9.30	7.07	4.88	−0.08	−6.68
BrO_4^-	122.60	119.38	117.98	115.60	114.01	112.03	109.07	106.11	103.16	100.22	93.41	83.93
I^-	−49.35	−51.17	−51.93	−53.18	−53.99	−54.97	−56.38	−57.72	−58.99	−60.20	−62.72	−65.55
IO^-	−38.47	−38.52	−38.49	−38.39	−38.29	−38.13	−37.83	−37.46	−37.02	−36.52	−35.06	−32.20
HIO(aq)	−96.92	−98.49	−99.16	−100.30	−101.05	−101.98	−103.37	−104.75	−106.12	−107.49	−110.68	−115.20
IO_3^-	−125.24	−127.20	−128.03	−129.44	−130.36	−131.50	−133.19	−134.84	−136.46	−138.05	−141.62	−146.27
HIO_3(aq)	−128.87	−131.47	−132.64	−134.66	−136.03	−137.76	−140.40	−143.09	−145.83	−148.62	−155.30	−165.26
IO_4^-	−53.47	−57.03	−58.58	−61.24	−63.02	−65.23	−68.55	−71.88	−75.20	−78.53	−86.24	−97.09

Table A.13
Metabolic reactions involving Cl

L1	ClO_4^-+acetic acid(aq)$\leftrightarrow Cl^-+2CO_2(aq)+2H_2O$(l)
L2	$2ClO_4^-$+acetic acid(aq)$\leftrightarrow 2ClO_2^-+2CO_2(aq)+2H_2O$(l)
L3	$ClO_4^- \leftrightarrow Cl^-+2O_2$(aq)
L4	$4ClO_3^-$+3acetic acid(aq)$\leftrightarrow 4Cl^-+6CO_2(aq)+6H_2O$(l)
L5	$4ClO_3^-$+acetic acid(aq)$\leftrightarrow 4ClO_2^-+2CO_2(aq)+2H_2O$(l)
L6	$ClO_3^- \leftrightarrow Cl^-+1.5O_2$(aq)
L7	$ClO_3^-+3H_2$(aq)$\leftrightarrow Cl^-+3H_2O$(l)
L8	$ClO_3^-+3H_2S$(aq)$\leftrightarrow Cl^-+3S$(s)$+3H_2O$(l)
L9	$ClO_2^- \leftrightarrow Cl^-+O_2$(aq)

mosphaericus sp. nov. a new thermophilic ureolytic *Bacillus* isolated from air. Syst. Appl. Microbiol. 18, 203–220.

[194] Bonjour, F. and Aragno, M. (1984) *Bacillus tusciae*, a new species of thermoacidophilic, facultatively chemolithoautotrophic, hydrogen oxidizing sporeformer from a geothermal area. Arch. Microbiol. 139, 397–401.

[195] Kryukov, V.R., Savel'eva, N.D. and Pusheva, M.A. (1983) *Calderobacterium hydrogenophilum* gen. et. sp. nov., an extremely thermophilic hydrogen bacterium and its hydrogenase activity. Mikrobiologiya (in Russian) 52, 781–788.

[196] Mladenovska, Z., Mathrani, I.M. and Ahring, B. (1995) Isolation and characterization of *Caldicellulosiruptor lactoaceticus* sp. nov., an extremely thermophilic, cellulolytic, anaerobic bacterium. Arch. Microbiol. 163, 223–230.

[197] Huang, C.-Y., Patel, B., Mah, R. and Baresi, L. (1998) *Caldicellulosiruptor owensensis* sp. nov., an anaerobic, extremely thermophilic, xylanolytic bacterium. Int. J. Syst. Bacteriol. 48, 91–97.

[198] Rainey, F.A., Donnison, A.M., Janssen, P.H., Saul, D., Rodrigo, A., Bergquist, P.L., Daniel, R.M., Stackebrandt, E. and Morgan, H.W. (1994) Description of *Caldicellulosiruptor saccharolyticus* gen. nov., sp. nov.: An obligately anaerobic, extremely thermophilic, cellulolytic bacterium. FEMS Microbiol. Let. 120, 263–266.

[199] Chrisostomos, S., Patel, B.K.C., Dwivedi, P.P. and Denman, S.E. (1996) *Caloramator indicus* sp. nov., a new thermophilic anaerobic bacterium isolated from the deep-seated nonvolcanically heated waters of an Indian artesian aquifer. Int. J. Syst. Bacteriol. 46, 497–501.

[200] Tarlera, S., Muxi, L., Soubes, M. and Stams, A.J.M. (1997) *Caloramator proteoclasticus* sp. nov., a new moderately thermophilic anaerobic proteolytic bacterium. Int. J. Syst. Bacteriol. 47, 651–656.

[201] Pierson, B.K. and Castenholz, R.W. (1974) A phototrophic gliding filamentous bacterium of hot springs, *Chloroflexus aurantiacus*, gen. and sp. nov. Arch. Microbiol. 100, 5–24.

[202] Li, Y., Mandelco, L. and Wiegel, J. (1993) Isolation and characterization of a moderately thermophilic anaerobic alkaliphile, *Clostridium paradoxum* sp. nov. Int. J. Syst. Bacteriol. 43, 450–460.

Table A.14
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.13

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
L1	−971.34	−972.13	−972.59	−973.53	−974.24	−975.21	−976.83	−978.61	−980.54	−982.62	−987.92	−996.45
L2	−798.02	−798.24	−798.46	−798.96	−799.37	−799.97	−801.03	−802.24	−803.61	−805.11	−809.09	−815.68
L3	−87.92	−89.05	−89.67	−90.87	−91.75	−92.94	−94.90	−97.04	−99.34	−101.81	−108.12	−118.42
L4	−3040.19	−3041.80	−3042.87	−3045.13	−3046.89	−3049.35	−3053.53	−3058.23	−3063.40	−3069.00	−3083.53	−3107.25
L5	−750.87	−749.79	−749.42	−748.92	−748.68	−748.45	−748.28	−748.29	−748.45	−748.77	−750.02	−752.81
L6	−97.48	−98.15	−98.53	−99.29	−99.86	−100.64	−101.94	−103.38	−104.95	−106.65	−111.03	−118.29
L7	−889.29	−888.51	−888.05	−887.14	−886.46	−885.51	−883.94	−882.18	−880.26	−878.18	−872.74	−863.59
L8	−754.87	−752.33	−751.12	−748.93	−747.39	−745.39	−742.25	−738.95	−735.52	−731.99	−723.61	−710.74
L9	−130.62	−131.47	−131.90	−132.72	−133.31	−134.09	−135.35	−136.70	−138.13	−139.65	−143.48	−149.59

Table A.15
Mineral hydrolysis and redox reactions

M1	$\text{magnesite(s)}+H^+ \leftrightarrow Mg^{2+}+HCO_3^-$
M2	$\text{calcite(s)}+H^+ \leftrightarrow Ca^{2+}+HCO_3^-$
M3	$\text{dolomite(s)}+2H^+ \leftrightarrow Ca^{2+}+Mg^{2+}+2HCO_3^-$
M4	$\text{alabandite(s)}+2H^+ \leftrightarrow Mn^{2+}+H_2S(aq)$
M5	$\text{rhodochrosite(s)}+H^+ \leftrightarrow Mn^{2+}+HCO_3^-$
M6	$\text{hematite(s)}+6H^+ \leftrightarrow 2Fe^{3+}+3H_2O$
M7	$\text{hematite(s)}+4H^++H_2(aq) \leftrightarrow 2Fe^{2+}+3H_2O(l)$
M8	$\text{magnetite(s)}+6H^++H_2(aq) \leftrightarrow 3Fe^{2+}+4H_2O$
M9	$\text{pyrrhotite(s)}+2H^+ \leftrightarrow Fe^{2+}+H_2S(aq)$
M10	$\text{siderite(s)}+H^+ \leftrightarrow Fe^{2+}+HCO_3^-$
M11	$\text{pyrite(s)}+2H^++H_2(aq) \leftrightarrow Fe^{2+}+2H_2S(aq)$
M12	$\text{chalcopyrite(s)}+4H^+ \leftrightarrow Cu^{2+}+Fe^{2+}+2H_2S(aq)$
M13	$\text{covellite(s)}+2H^+ \leftrightarrow Cu^{2+}+H_2S(aq)$
M14	$\text{chalcocite(s)}+2H^+ \leftrightarrow 2Cu^++H_2S(aq)$
M15	$\text{cuprite(s)}+2H^+ \leftrightarrow 2Cu^++H_2O(l)$
M16	$\text{bornite(s)}+8H^+ \leftrightarrow 5Cu^++Fe^{3+}+4H_2S(aq)$
M17	$\text{bornite(s)}+5H^++9.25O_2(aq) \leftrightarrow 5Cu^{2+}+Fe^{3+}+4SO_4^{2-}+2.5H_2O(l)$
M18	$\text{sphalerite(s)}+2H^+ \leftrightarrow Zn^{2+}+H_2S(aq)$
M19	$\text{selenium(s)}+H_2(aq) \leftrightarrow HSe^-+H^+$
M20	$\text{selenium(s)}+H_2O(l)+1O_2(aq) \leftrightarrow HSeO_3^-+H^+$
M21	$\text{molybdenite(s)}+4H_2O(l) \leftrightarrow MoO_4^{2-}+2H_2S(aq)+2H^++H_2(aq)$
M22	$\text{silver(s)}+H^+ \leftrightarrow Ag^++0.5H_2(aq)$
M23	$\text{gold(s)}+H^+ \leftrightarrow Au^++0.5H_2(aq)$
M24	$\text{quicksilver(s)}+2H^+ \leftrightarrow Hg^{2+}+H_2(aq)$
M25	$\text{galena(s)}+2H^+ \leftrightarrow Pb^{2+}+H_2S(aq)$
M26	$\text{anglesite(s)} \leftrightarrow Pb^{2+}+SO_4^{2-}$
M27	$\text{uraninite(s)}+2H^+ \leftrightarrow UO_2^{2+}+H_2(aq)$
M28	$\text{uraninite(s)} \leftrightarrow UO_2(aq)$

[203] Drent, W.J., Lahpor, G.A., Wiegant, W.M. and Gottschal, J.C. (1991) Fermentation of inulin by *Clostridium thermosuccinogenes* sp. nov., a thermophilic anaerobic bacterium isolated from various habitats. Appl. Environ. Microbiol. 57, 455–462.

[204] Rainey, F.A. and Stackebrandt, E. (1993) Transfer of the type species of the genus *Thermobacteroides* to the genus *Thermoanaerobacter* as *Thermoanaerobacter acetoethylicus* (Ben-Bassat and Zeikus 1981) comb. nov., Description of *Coprothermobacter* gen. nov., and reclassification of *Thermobacteroides proteolyticus* as *Coprothermobacter proteolyticus* (Ollivier et al., 1985) comb. nov. Int. J. Syst. Bacteriol. 43, 857–859.

[205] Ferreira, A.C., Nobre, M.F., Rainey, F.A., Silva, M.T., Wait, R., Burghardt, J., Ching, A.P. and Da Costa, M.S. (1997) *Deinococcus geothermalis* sp. nov. and *Deinococcus murrayi* sp. nov., two extremely radiation-resistant and slightly thermophilic species from hot springs. Int. J. Bacteriol. 47, 939–947.

[206] Rees, G.N., Grassia, G.S., Sheehy, A.J., Dwivedi, P.P. and Patel, B.K.C. (1995) *Desulfacinum infernum* gen. nov., sp. nov., a thermophilic sulfate-reducing bacterium from a petroleum reservoir. Int. J. Syst. Bacteriol. 45, 85–89.

[207] Nazina, T.N., Ivanova, A.E., Kanchaveli, L.P. and Rozanova, E.P. (1988) A new sporeforming thermophilic methylotrophic sulfate-reducing bacterium, *Desulfotomaculum kuznetsovii* sp. nov. Mikrobiologiya (in Russian) 57, 823–827.

[208] Karnauchow, T.M., Koval, S.F. and Jarrell, K.F. (1992) Isolation and characterization of three thermophilic anaerobes from a St. Lucia hot spring. Syst. Appl. Microbiol. 15, 296–310.

[209] Nazina, T.N. and Rozanova, E.P. (1978) Thermophilic sulfate-reducing bacteria from oil strata. Mikrobiologiya (in Russian) 47, 142–148.

[210] Min, H. and Zinder, S.H. (1990) Isolation and characterization of a thermophilic sulfate-reducing bacterium *Desulfotomaculum thermoacetoxidans* sp. nov. Arch. Microbiol. 153, 399–404.

Table A.16
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.15

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
M1	−15.37	−13.82	−13.09	−11.79	−10.90	−9.76	−7.98	−6.13	−4.20	−2.19	2.85	11.12
M2	−11.56	−10.89	−10.55	−9.91	−9.44	−8.82	−7.82	−6.72	−5.53	−4.24	−0.81	5.29
M3	−17.56	−15.39	−14.34	−12.44	−11.11	−9.38	−6.64	−3.74	−0.67	2.57	10.93	25.13
M4	−40.77	−40.31	−40.15	−39.90	−39.76	−39.63	−39.48	−39.39	−39.35	−39.37	−39.55	−40.02
M5	−2.86	−1.88	−1.41	−0.54	0.06	0.85	2.10	3.43	4.84	6.34	10.20	16.84
M6	−10.51	−3.64	−0.62	4.58	8.05	12.39	18.89	25.41	31.95	38.53	54.11	77.28
M7	−170.13	−167.89	−166.87	−165.08	−163.86	−162.32	−159.97	−157.57	−155.12	−152.62	−146.53	−137.02
M8	−231.43	−227.71	−226.02	−223.10	−221.14	−218.66	−214.90	−211.11	−207.26	−203.36	−193.96	−179.51
M9	−19.67	−18.95	−18.66	−18.19	−17.90	−17.57	−17.11	−16.70	−16.33	−16.00	−15.23	−14.01
M10	−1.33	0.33	1.10	2.48	3.44	4.67	6.59	8.60	10.69	12.88	18.37	27.38
M11	−4.14	−4.61	−4.85	−5.28	−5.60	−6.02	−6.70	−7.44	−8.22	−9.03	−11.05	−14.02
M12	104.01	105.51	106.10	107.04	107.60	108.26	109.11	109.86	110.48	111.02	111.98	112.98
M13	89.45	90.16	90.43	90.86	91.11	91.40	91.76	92.06	92.28	92.46	92.69	92.76
M14	160.14	158.96	158.38	157.30	156.52	155.50	153.85	152.09	150.21	148.36	143.79	136.62
M15	12.10	11.26	10.87	10.13	9.61	8.92	7.81	6.63	5.37	4.05	0.72	−4.47
M16	483.48	483.88	483.85	483.54	483.17	482.53	481.22	479.53	477.50	475.17	468.70	457.57
M17	−3091.33	−3063.58	−3050.32	−3026.31	−3009.51	−2987.69	−2953.39	−2917.31	−2879.52	−2840.04	−2741.31	−2583.23
M18	24.33	25.11	25.41	25.90	26.20	26.53	26.99	27.37	27.69	27.97	28.45	28.90
M19	26.02	26.09	26.21	26.52	26.79	27.20	27.94	28.82	29.85	31.02	34.27	40.25
M20	−192.49	−191.39	−190.81	−189.71	−188.90	−187.81	−186.02	−184.05	−181.92	−179.61	−173.61	−163.45
M21	335.21	335.12	335.09	335.05	335.03	335.03	335.06	335.14	335.28	335.49	336.30	338.51
M22	87.25	86.37	85.96	85.22	84.71	84.04	82.99	81.88	80.73	79.52	76.53	71.87
M23	174.03	172.65	172.04	170.96	170.23	169.29	167.86	166.39	164.88	163.34	159.62	154.02
M24	181.01	182.01	182.41	183.02	183.40	183.84	184.41	184.90	185.31	185.66	186.24	186.64
M25	46.03	45.26	44.90	44.26	43.81	43.23	42.32	41.36	40.35	39.31	36.77	32.95
M26	42.69	44.08	44.83	46.27	47.33	48.76	51.09	53.64	56.42	59.40	67.25	80.82
M27	94.08	96.09	96.93	98.30	99.19	100.27	101.81	103.30	104.73	106.12	109.24	113.51
M28	49.31	52.30	53.60	55.82	57.30	59.15	61.91	64.67	67.43	70.18	76.58	85.70

Table A.17
Cation hydrolysis reactions

N1	$Mg^{2+}+H_2O(l)\leftrightarrow MgOH^{+}+H^{+}$
N2	$Ca^{2+}+H_2O(l)\leftrightarrow CaOH^{+}+H^{+}$
N3	$VO^{2+}+H_2O(l)\leftrightarrow VOOH^{+}+H^{+}$
N4	$VOH^{2+}\leftrightarrow VO^{+}+H^{+}$
N5	$V^{3+}+H_2O(l)\leftrightarrow VOH^{2+}+H^{+}$
N6	$V^{2+}+H_2O(l)\leftrightarrow VOH^{+}+H^{+}$
N7	$Cr^{3+}+2H_2O(l)\leftrightarrow CrO_2^{-}+4H^{+}$
N8	$Cr^{3+}+2H_2O(l)\leftrightarrow HCrO_2(aq)+3H^{+}$
N9	$Cr^{3+}+H_2O(l)\leftrightarrow CrO^{+}+2H^{+}$
N10	$Cr^{3+}+H_2O(l)\leftrightarrow CrOH^{2+}+H^{+}$
N11	$Mn^{2+}+H_2O(l)\leftrightarrow MnOH^{+}+H^{+}$
N12	$Mn^{2+}+H_2O(l)\leftrightarrow MnO(aq)+2H^{+}$
N13	$Mn^{2+}+2H_2O(l)\leftrightarrow HMnO_2^{-}+3H^{+}$
N14	$Mn^{2+}+2H_2O(l)\leftrightarrow MnO_2^{2-}+4H^{+}$
N15	$Fe^{3+}+H_2O(l)\leftrightarrow FeOH^{2+}+H^{+}$
N16	$Fe^{3+}+H_2O(l)\leftrightarrow FeO^{+}+2H^{+}$
N17	$Fe^{3+}+2H_2O(l)\leftrightarrow HFeO_2(aq)+3H^{+}$
N18	$Fe^{3+}+2H_2O(l)\leftrightarrow FeO_2^{-}+4H^{+}$
N19	$Fe^{2+}+H_2O(l)\leftrightarrow FeOH^{+}+H^{+}$
N20	$Fe^{2+}+H_2O(l)\leftrightarrow FeO(aq)+2H^{+}$
N21	$Fe^{2+}+2H_2O(l)\leftrightarrow HFeO_2^{-}+3H^{+}$
N22	$Co^{3+}+H_2O(l)\leftrightarrow CoOH^{2+}+H^{+}$
N23	$Co^{2+}+H_2O(l)\leftrightarrow CoOH^{+}+H^{+}$
N24	$Co^{2+}+H_2O(l)\leftrightarrow CoO(aq)+2H^{+}$
N25	$Co^{2+}+2H_2O(l)\leftrightarrow HCoO_2^{-}+3H^{+}$
N26	$Co^{2+}+2H_2O(l)\leftrightarrow CoO_2^{2-}+4H^{+}$
N27	$Ni^{2+}+H_2O(l)\leftrightarrow NiOH^{+}+H^{+}$
N28	$Ni^{2+}+H_2O(l)\leftrightarrow NiO(aq)+2H^{+}$
N29	$Ni^{2+}+2H_2O(l)\leftrightarrow HNiO_2^{-}+3H^{+}$
N30	$Ni^{2+}+2H_2O(l)\leftrightarrow NiO_2^{2-}+4H^{+}$
N31	$Cu^{2+}+H_2O(l)\leftrightarrow CuOH^{+}+H^{+}$
N32	$Cu^{2+}+H_2O(l)\leftrightarrow CuO(aq)+2H^{+}$
N33	$Cu^{2+}+2H_2O(l)\leftrightarrow HCuO_2^{-}+3H^{+}$
N34	$Cu^{2+}+2H_2O(l)\leftrightarrow CuO_2^{2-}+4H^{+}$
N35	$Zn^{2+}+H_2O(l)\leftrightarrow ZnOH^{+}+H^{+}$
N36	$Zn^{2+}+H_2O(l)\leftrightarrow ZnO(aq)+2H^{+}$
N37	$Zn^{2+}+2H_2O(l)\leftrightarrow HZnO_2^{-}+3H^{+}$
N38	$Zn^{2+}+2H_2O(l)\leftrightarrow ZnO_2^{2-}+4H^{+}$
N39	$Hg^{2+}+H_2O(l)\leftrightarrow HgOH^{+}+H^{+}$
N40	$Hg^{2+}+H_2O(l)\leftrightarrow HgO(aq)+2H^{+}$
N41	$Hg^{2+}+2H_2O(l)\leftrightarrow HHgO_2^{-}+3H^{+}$
N42	$Hg^{2+}+2H_2O(l)\leftrightarrow HgO_2^{-2}+4H^{+}$
N43	$Pb^{2+}+H_2O(l)\leftrightarrow PbOH^{+}+H^{+}$
N44	$Pb^{2+}+H_2O(l)\leftrightarrow PbO(aq)+2H^{+}$
N45	$Pb^{2+}+2H_2O(l)\leftrightarrow HPbO_2^{-}+3H^{+}$
N46	$UO_2^{2+}+H_2O(l)\leftrightarrow UO_2OH^{+}+H^{+}$
N47	$UO_2^{2+}+H_2O(l)\leftrightarrow UO_3(aq)+2H^{+}$
N48	$UO_2^{2+}+2H_2O(l)\leftrightarrow HUO_4^{-}+3H^{+}$
N49	$UO_2^{2+}+2H_2O(l)\leftrightarrow UO_4^{2-}+4H^{+}$
N50	$UO_2^{+}+H_2O(l)\leftrightarrow UO_2OH(aq)+H^{+}$
N51	$UO_2^{+}+H_2O(l)\leftrightarrow UO_3^{-}+2H^{+}$
N52	$U^{4+}+3H_2O(l)\leftrightarrow HUO_3^{-}+5H^{+}$
N53	$U^{4+}+H_2O(l)\leftrightarrow UO^{2+}+2H^{+}$
N54	$U^{4+}+2H_2O(l)\leftrightarrow HUO_2^{+}+3H^{+}$
N55	$U^{4+}+2H_2O(l)\leftrightarrow UO_2(aq)+4H^{+}$

[211] Tasaki, M., Kamagata, Y., Nakamura, K. and Mikami, E. (1991) Isolation and characterization of a thermophilic benzoate-degrading, sulfate-reducing bacterium, *Desulfotomaculum thermobenzoicum* sp. nov. Arch. Microbiol. 155, 348–352.

[212] Fardeau, M.-L., Ollivier, B., Patel, B.K.C., Dwivedi, P., Ragot, M. and Garcia, J.-L. (1995) Isolation and characterization of a thermophilic sulfate-reducing bacterium, *Desulfotomaculum thermosapovorans* sp. nov. Int. J. Syst. Bacteriol. 45, 218–221.

[213] Bonch-Osmolovskaya, E.A., Sokolova, T.G., Kostrikina, N.A. and Zavarzin, G.A. (1990) *Desulfurella acetivorans* gen. nov. and sp. nov. – a new thermophilic sulfur reducing eubacterium. Arch. Microbiol. 153, 151–155.

[214] Miroshnichenko, M.L., Rainey, F.A., Hippe, H., Chernyh, N.A., Kostrikina, N.A. and Bonch-Osmolovskaya, E.A. (1998) *Desulfurella kamchatkensis* sp. nov. and *Desulfurella propionica* sp. nov., new sulfur-respiring thermophilic bacteria from Kamchatka thermal environments. Int. J. Syst. Bacteriol. 48, 475–479.

[215] Miroshnichenko, M.L., Gongadze, G.A., Lysenko, A.M. and Bonch-Osmolovskaya, E.A. (1994) *Desulfurella multipotens* sp. nov., a new sulfur-respiring thermophilic eubacterium from Raoul Island (Kermadec archipelago, New Zealand). Arch. Microbiol. 161, 88–93.

[216] L'Haridon, S., Cilia, V., Messner, P., Raguenes, G., Gambacorta, A., Sleytr, U.B., Prieur, D. and Jeanthon, C. (1998) *Desulfurobacterium thermolithotrophum* gen. nov. sp. nov., a novel autotrophic sulphur-reducing bacterium isolated from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 48, 701–711.

[217] Svetlichnii, V.A. and Svetlichnaya, T.P. (1988) *Dictyoglomus turgidus* sp. nov., a new extreme thermophilic eubacterium isolated from hot springs in the Uzon volcano crater. Mikrobiologiya (in Russian) 57, 435–441.

[218] Huber, R., Woese, C.R., Langworthy, T.A., Kristjansson, J. and Stetter, K.O. (1990) *Fervidobacterium islandicum* sp. nov., a new extremely thermophilic eubacterium belonging to the '*Thermotogales*'. Arch. Microbiol. 154, 105–111.

[219] Patel, B.K.C., Morgan, H.W. and Daniel, R.M. (1985) *Fervidobacterium nodosum* gen. nov. and spec. nov., a new chemoorganotrophic, caldoactive, anaerobic bacterium. Arch. Microbiol. 141, 63–69.

[220] Friedrich, A.B. and Antranikian, G. (1996) Keratin degradation by *Fervidobacterium pennavorans*, a novel thermophilic anaerobic species of the order *Thermotogales*. Appl. Environ. Microbiol. 62, 2875–2882.

[221] Fiala, G., Woese, C.R., Langworthy, T.A. and Stetter, K.O. (1990) *Flexistipes sinusarabici*, a novel genus and species of eubacteria occurring in the Atlantis II Deep brines of the Red Sea. Arch. Microbiol. 154, 120–126.

[222] Davey, M.E., Wood, W.A., Key, R., Nakamura, K. and Stahl, D.A. (1993) Isolation of three species of *Geotoga* and *Petrotoga*: two new genera, representing a new lineage in the bacterial line of descent distantly related to the '*Thermotogales*'. Syst. Appl. Microbiol. 16, 191–200.

[223] Cayol, J.-L., Ollivier, B., Patel, B.K.C., Prensier, G., Guezennec, J. and Garcia, J.-L. (1994) Isolation and characterization of *Halothermothrix orenii* gen. nov., sp. nov., a halophilic, thermophilic, fermentative, strictly anaerobic bacterium. Int. J. Syst. Bacteriol. 44, 534–540.

[224] Shima, S. and Suzuki, K.-I. (1993) *Hydrogenobacter acidophilus* sp. nov., a thermoacidophilic, aerobic, hydrogen-oxidizing bacterium requiring elemental sulfur for growth. Int. J. Syst. Bacteriol. 43, 703–708.

[225] Nishihara, H., Igarashi, Y. and Kodama, T. (1990) A new isolate of *Hydrogenobacter*, an obligately chemolithoautotrophic, thermophilic, halophilic and aerobic hydrogen-oxidizing bacterium from seaside saline hot spring. Arch. Microbiol. 153, 294–298.

[226] Kawasumi, T., Igarashi, Y., Kodama, T. and Minoda, Y. (1984) *Hydrogenobacter thermophilus* gen. nov., sp. nov., an extremely ther-

Table A.18
Values of ΔG_r^0 (kJ mol^{-1}) at P_{SAT} as a function of temperature for the reactions given in Table A.17

Reaction	T (°C)											
	2	18	25	37	45	55	70	85	100	115	150	200
N1	66.32	66.59	66.68	66.81	66.88	66.95	67.04	67.10	67.14	67.17	67.16	66.96
N2	73.62	73.36	73.25	73.09	72.99	72.87	72.71	72.58	72.45	72.35	72.13	71.82
N3	32.01	32.10	32.17	32.31	32.42	32.59	32.89	33.23	33.62	34.05	35.18	37.03
N4	17.78	19.44	20.08	21.10	21.73	22.46	23.44	24.31	25.08	25.76	27.01	28.11
N5	15.72	13.74	12.92	11.56	10.69	9.64	8.14	6.72	5.36	4.06	1.22	−2.51
N6	36.89	37.12	37.19	37.28	37.31	37.35	37.36	37.35	37.30	37.22	36.92	36.18
N7	160.05	157.47	156.38	154.56	153.39	151.96	149.89	147.91	146.02	144.20	140.21	135.07
N8	107.80	104.29	102.82	100.38	98.81	96.90	94.14	91.49	88.94	86.47	80.95	73.38
N9	58.55	56.18	55.18	53.50	52.40	51.06	49.11	47.20	45.35	43.53	39.38	33.51
N10	24.23	23.37	22.96	22.23	21.73	21.07	20.07	19.03	17.96	16.85	14.14	9.90
N11	60.61	60.61	60.62	60.63	60.65	60.68	60.74	60.82	60.92	61.03	61.31	61.72
N12	126.54	126.65	126.72	126.90	127.05	127.26	127.63	128.06	128.54	129.06	130.40	132.46
N13	196.24	197.88	198.64	200.00	200.94	202.16	204.07	206.09	208.20	210.41	215.91	224.65
N14	272.93	274.71	275.63	277.35	278.61	280.29	283.04	286.02	289.25	292.71	301.67	316.70
N15	14.94	13.30	12.59	11.38	10.58	9.60	8.14	6.71	5.29	3.89	0.64	−4.02
N16	36.15	33.40	32.25	30.36	29.15	27.69	25.59	23.59	21.66	19.82	15.73	10.21
N17	74.27	70.25	68.60	65.92	64.23	62.21	59.37	56.72	54.25	51.94	47.04	40.95
N18	127.89	124.71	123.41	121.30	119.97	118.38	116.16	114.10	112.19	110.44	106.83	102.74
N19	53.01	53.13	53.17	53.24	53.28	53.33	53.40	53.47	53.54	53.61	53.74	53.82
N20	116.37	116.44	116.47	116.55	116.62	116.72	116.88	117.07	117.28	117.50	118.04	118.73
N21	164.50	166.04	166.72	167.88	168.67	169.67	171.20	172.77	174.38	176.04	180.10	186.38
N22	9.79	7.90	7.06	5.63	4.68	3.49	1.71	−0.08	−1.85	−3.63	−7.82	−13.95
N23	57.12	57.17	57.17	57.14	57.11	57.06	56.97	56.86	56.73	56.58	56.16	55.32
N24	106.77	107.26	107.48	107.86	108.12	108.46	108.98	109.51	110.05	110.60	111.86	113.51
N25	176.70	178.87	179.81	181.41	182.48	183.81	185.81	187.84	189.88	191.95	196.90	204.32
N26	260.80	263.20	264.33	266.35	267.76	269.60	272.48	275.52	278.73	282.09	290.58	304.38
N27	61.17	61.54	61.66	61.84	61.93	62.02	62.13	62.19	62.22	62.20	62.04	61.44
N28	121.93	119.33	118.19	116.22	114.91	113.27	110.80	108.34	105.86	103.37	97.50	88.83
N29	173.13	175.83	176.97	178.89	180.15	181.70	184.02	186.31	188.60	190.88	196.21	203.99
N30	247.53	250.16	251.36	253.48	254.95	256.83	259.75	262.79	265.96	269.26	277.50	290.71
N31	45.27	45.25	45.24	45.22	45.21	45.20	45.20	45.20	45.22	45.24	45.30	45.37
N32	84.06	84.40	84.57	84.88	85.12	85.42	85.92	86.47	87.06	87.68	89.28	91.82
N33	156.60	157.05	157.32	157.88	158.31	158.91	159.95	161.12	162.43	163.86	167.62	173.89
N34	233.55	235.45	236.40	238.16	239.42	241.09	243.79	246.71	249.84	253.18	261.78	276.12
N35	47.12	45.48	44.76	43.53	42.72	41.71	40.21	38.72	37.25	35.79	32.38	27.48
N36	103.18	102.6	102.37	102.02	101.81	101.57	101.26	101.01	100.8	100.63	100.34	100.05
N37	156.18	157.71	158.39	159.57	160.37	161.39	162.95	164.58	166.26	167.99	172.27	178.97
N38	226.95	229.95	231.32	233.73	235.40	237.53	240.83	244.27	247.86	251.58	260.84	275.63
N39	20.07	19.61	19.36	18.90	18.57	18.14	17.44	16.70	15.91	15.09	13.00	9.61
N40	35.46	35.28	35.26	35.30	35.37	35.50	35.79	36.17	36.65	37.20	38.74	41.39
N41	118.68	119.93	120.57	121.76	122.62	123.78	125.66	127.70	129.90	132.25	138.30	148.26
N42	118.68	119.93	120.57	121.76	122.62	123.78	125.66	127.70	129.90	132.25	138.30	148.26
N43	32.47	34.45	35.35	36.92	38.00	39.38	41.49	43.68	45.92	48.20	53.74	62.04
N44	96.73	96.48	96.43	96.42	96.47	96.57	96.81	97.17	97.60	98.13	99.63	102.27
N45	157.85	158.81	159.35	160.43	161.24	162.35	164.22	166.30	168.59	171.07	177.57	188.49
N46	30.92	30.11	29.78	29.25	28.93	28.54	28.01	27.53	27.08	26.68	25.84	24.81
N47	58.39	58.69	58.86	59.20	59.45	59.79	60.35	60.97	61.63	62.34	64.09	66.68
N48	107.04	108.98	109.86	111.39	112.44	113.78	115.85	117.98	120.19	122.47	128.04	136.70
N49	185.32	187.46	188.51	190.46	191.85	193.68	196.61	199.76	203.11	206.67	215.77	230.79
N50	101.17	102.94	103.67	104.88	105.66	106.61	107.98	109.31	110.59	111.83	114.55	118.02
N51	205.31	207.38	208.27	209.78	210.78	212.02	213.87	215.72	217.57	219.44	223.88	230.56
N52	95.31	94.85	94.61	94.19	93.90	93.52	92.96	92.40	91.83	91.27	89.93	87.95
N53	16.38	12.92	11.45	9.01	7.42	5.48	2.64	−0.11	−2.79	−5.41	−11.36	−19.63
N54	33.96	30.17	28.56	25.84	24.07	21.89	18.69	15.57	12.52	9.52	2.66	−7.07
N55	29.97	27.23	26.05	24.05	22.73	21.11	18.72	16.37	14.04	11.73	6.31	−1.77

mophilic, aerobic, hydrogen-oxidizing bacterium. Int. J. Syst. Bacteriol. 34, 5–10.

[227] Kristjansson, J.K., Ingason, A. and Alfredsson, G.A. (1985) Isolation of thermophilic obligately autotrophic hydrogen-oxidizing bacteria, similar to *Hydrogenobacter thermophilus*, from Icelandic hot springs. Arch. Microbiol. 140, 321–325.

[228] Hayashi, N.R., ishida, T., Yokota, A., Kodama, T. and Igarashi, Y. (1999) *Hydrogenophilus thermoluteolus* gen. nov. sp. nov. a thermo-

Table A.19
Chemical formulas for the minerals mentioned in Tables 9.1, 9.2, 9.5 and A.11

Mineral	Formula
Magnesite	$MgCO_3$
Calcite	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Alabandite	MnS
Rhodochrosite	$MnCO_3$
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Pyrrhotite	FeS
Siderite	$FeCO_3$
Pyrite	FeS_2
Chalcopyrite	$CuFeS_2$
Covellite	CuS
Chalcocite	Cu_2S
Cuprite	Cu_2O
Bornite	Cu_5FeS_4
Sphalerite	ZnS
Molybdenite	MoS_2
Quicksilver	Hg
Galena	PbS
Anglesite	$PbSO_4$
Uraninite	UO_2

philic, facultatively chemolithoautotrophic, hydrogen-oxidizing bacterium. Int. J. Syst. Bacteriol. 49, 783–786.

[229] Goto, E., Kodama, T. and Minoda, Y. (1978) Growth and taxonomy of thermophilic hydrogen bacteria. Agric. Biol. Chem. 42, 1305–1308.

[230] Giovannoni, S.J., Schabtach, E. and Castenholz, R.W. (1987) *Isosphaera pallida*, gen. and comb. nov., a gliding, budding eubacterium from hot springs. Arch. Microbiol. 147, 276–284.

[231] Chung, A.P., Rainey, F., Nobre, M.F., Burghardt, J. and Da Costa, M.S. (1997) *Miothermus cerbereus* sp. nov., a new slightly thermophilic species with high levels of 3-hydroxy fatty acids. Int. J. Syst. Bacteriol. 47, 1225–1230.

[232] Nobre, M.F., Truper, H.G. and Da Costa, M.S. (1996) Transfer of *Thermus ruber* (Loginova et al., 1984), *Thermus silvanus* (Tenreiro et al., 1995), and *Thermus chliarophilus* (Tenreiro et al., 1995) to *Miothermus* gen. nov. as *Miothermus ruber* comb. nov., *Miothermus silvanus* comb. nov. and *Miothermus chliarophilus* com. nov., respectively and emendation of the genus *Thermus*. Int. J. Syst. Bacteriol. 46, 604–606.

[233] Malashenko, Y.R., Romanovskaya, V.A., Bogachenko, V.N. and Shved, A.D. (1975) Thermophilic and thermotolerant methane-assimilating bacteria. Mikrobiolgiya (in Russian) 44, 855–862.

[234] Slobodkin, A., Reysenbach, A.-L., Mayer, F. and Wiegel, J. (1997) Isolation and characterization of the homoacetogenic thermophilic bacterium *Moorella glycerini* sp. nov. Int. J. Syst. Bacteriol. 47, 969–974.

[235] Fontaine, F.E., Peterson, W.H., McCoy, E., Johnson, M.J. and Ritter, G.J. (1942) A new type of glucose fermentation by *Clostridium thermoaceticum* nov. sp. J. Bacteriol. 43, 701–715.

[236] Collins, M.D., Lawson, P.A., Willems, A., Cordoba, J.J., Fernandez-Garayzabal, J., Garcia, P., Cai, J., Hippe, H. and Farrow, J.A.E. (1994) The phylogeny of the genus *Clostridium*: Proposal of five new genera and eleven new species combinations. Int. J. Syst. Bacteriol. 44, 812–826.

[237] Lien, T., Madsen, M., Rainey, F.A. and Birkeland, N.-K. (1998) *Petrotoga mobilis* sp. nov., from a North Sea oil-production well. Int. J. Syst. Bacteriol. 48, 1007–1013.

[238] Alfredsson, G.A., Kristjansson, J.K., Hjörleifsdottir, S. and Stetter, K.O. (1988) *Rhodothermus marinus*, gen. nov., sp. nov., a thermophilic, halophilic bacterium from submarine hot springs in Iceland. J. Gen. Microbiol., 299–306.

[239] Sako, Y., Takai, K., Ishida, Y., Uchida, A. and Katayama, Y. (1996) *Rhodothermus obamensis* sp. nov., a modern lineage of extremely thermophilic marine bacteria. Int. J. Syst. Bacteriol. 46, 1099–1104.

[240] Carreto, L., Moore, E., Nobre, M.F., Wait, R., Riley, P.W., Sharp, R.J. and Da Costa, M.S. (1996) *Rubrobacter xylanophilus* sp. nov., a new thermophilic species isolated from a thermally polluted effluent. Int. J. Syst. Bacteriol. 46, 460–465.

[241] Suzuki, K., Collins, M.D., Iijima, E. and Komagata, K. (1988) Chemotaxonomic characterization of a radiotolerant bacterium, *Arthrobacter radiotolerans*: Description of *Rubrobacter radiotolerans* gen. nov., comb. nov. FEMS Microbiol. Let. 52, 33–40.

[242] Demharter, W., Hensel, R., Smida, J. and Stackebrandt, E. (1989) *Sphaerobacter thermophilus* gen. nov., sp. nov. A deeply rooting member of the actinomycetes subdivision isolated from thermophilically treated sewage sludge. Syst. Appl. Microbiol. 11, 261–266.

[243] Pohlschroeder, M., Leschine, S.B. and Canale-Parola, E. (1994) *Spirochaeta caldaria* sp. nov., a thermophilic bacterium that enhances cellulose degradation by *Clostridium thermocellum*. Arch. Microbiol. 161, 17–24.

[244] Aksenova, H.Y., Rainey, F.A., Janssen, P.H. and Zavarzin, G.A. (1992) *Spriochaeta thermophila* sp. nov., an obligately anaerobic, polysaccharolytic, extremely thermophilic bacterium. Int. J. Syst. Bacteriol. 42, 175–177.

[245] Norris, P.R., Clark, D.A., Owen, J.P. and Waterhouse, S. (1996) Characteristics of *Sulfobacillus acidophilus* sp. nov. and other moderately thermophilic mineral-sulphide-oxidizing bacteria. Microbiology 142, 775–783.

[246] Golovacheva, R.S. and Karavaiko, G.I. (1978) A new genus of thermophilic spore-forming bacteria, *Sulfobacillus*. Mikrobiologiya (in Russian) 47, 815–822.

[247] Golovacheva, R.S. (1979) Attachment of *Sulfobacillus thermosulfidooxidans* cells to the surface of sulfide minerals. Mikrobiologiya (in Russian) 48, 528–533.

[248] Takai, K., Inoue, A. and Hirokoshi, K. (1999) *Thermaerobacter marianensis* gen. nov., sp. nov., an aerobic extremely thermophilic marine bacterium from the 11 000 m deep Mariana trench. Int. J. Syst. Bacteriol. 49, 619–628.

[249] Ben-Bassat, A. and Zeikus, J.G. (1981) *Thermobacteroides acetoethylicus* gen. nov. and spec. nov., a new chemoorganotrophic, anaerobic, thermophilic bacterium. Arch. Microbiol. 128, 365–370.

[250] Cayol, J.-L., Ollivier, B., Patel, B.K.C., Ravot, G., Magot, M., Ageron, E., Grimont, P.A.D. and Garcia, J.-L. (1995) Description of *Thermoanaerobacter brockii* subsp. *lactiethylicus* subsp. nov., isolated from a deep subsurface French oil well, a proposal to reclassify *Thermoanaerobacter finnii* as *Thermoanaerobacter brockii* subsp. *finnii* comb. nov., and an emended description of *Thermoanaerobacter brockii*. Int. J. Syst. Bacteriol. 45, 783–789.

[251] Zeikus, J.G., Hegge, P.W. and Anderson, M.A. (1979) *Thermoanaerobium brockii* gen. nov. and sp. nov., a new chemoorganotrophic, caldoactive anaerobic bacterium. Arch. Microbiol. 122, 41–48.

[252] Lee, Y.-E., Jain, M.K., Lee, C., Lowe, S.E. and Zeikus, G. (1993) Taxonomic distinction of saccharolytic thermophilic anaerobes: description of *Thermoanaerobacterium xylanolyticum* gen. nov., sp. nov., and *Thermoanaerobacterium saccharolyticum* gen. nov., sp. nov.; reclassification of *Thermoanaerobium brockii, Clostridium thermosulfurogenes*, and *Clostridium thermohydrosulfuricum* E100-69 as *Thermoanaerobacter brockii* comb. nov., *Thermoanaerobacterium thermosulfurigenes* com. nov., and *Thermoanaerobacter thermohydrosulfuricus* comb. nov., respectively; and transfer of *Clostridium thermohydrosulfuricum* 39E to *Thermoanaerobacter ethanolicus*. Int. J. Syst. Bacteriol. 43, 41–51.

[253] Wiegel, J. and Ljungdahl, L.G. (1981) *Thermoanaerobacter ethanolicus* gen. nov., spec. nov., a new, extreme thermophilic, anaerobic bacterium. Arch. Microbiol. 128, 343–348.

[254] Leigh, J.A., Mayer, F. and Wolfe, R.S. (1981) *Acetogenium kivui*, a new thermophilic hydrogen-oxidizing, acetogenic bacterium. Arch. Microbiol. 129, 275–280.

[255] Larsen, L., Nielsen, P. and Ahring, B.K. (1997) *Thermoanaerobacter mathranii* sp. nov., an ethanol-producing, extremely thermophilic anaerobic bacterium from a hot spring in Iceland. Arch. Microbiol. 168, 114–119.

[256] Bonch-Osmolovskaya, E.A., Miroshnichenko, M.L., Chernykh, N.A., Kostrikina, N.A., Pikuta, E.V. and Rainey, F.A. (1997) Reduction of elemental sulfur by moderately thermophilic organotrophic bacteria and the description of *Thermoanaerobacter sulfurophilus* sp. nov. Microbiology 66, 483–489.

[257] Cook, G.M., Rainey, F.A., Patel, B.K.C. and Morgan, H.W. (1996) Characterization of a new obligately anaerobic thermophile, *Thermoanaerobacter wiegelii* sp. nov. Int. J. Syst. Bacteriol. 46, 123–127.

[258] Liu, S.-Y., Rainey, F.A., Morgan, H.W., Mayer, F. and Wiegel, J. (1996) *Thermoanaerobacterium aotearoense* sp. nov., a slightly acidophilic, anaerobic thermophile isoltaed from various hot springs in New Zealand and emendation of the genus *Thermoanerobacterium*. Int. J. Syst. Bacteriol. 46, 388–396.

[259] Itoh, T., Suzuki, K.-i. and Nakase, T. (1998) *Thermocladium modestius* gen. nov., sp. nov., a new genus of the rod-shaped, extremely thermophilic *Crenarchaeote*. Int. J. Syst. Bacteriol. 48, 879–887.

[260] Engle, M., Li, Y., Rainey, F., DeBlois, S., Mai, V., Reichert, A., Mayer, F., Messner, P. and Wiegel, J. (1996) *Thermobrachium celere* gen. nov. sp. nov., a rapidly growing thermophilic, alkalitolerant, and proteolytic obligate anaerobe. Int. J. Syst. Bacteriol. 46, 1025–1033.

[261] Huber, R., Dyba, D., Huber, H., Burggraf, S. and Rachel, R. (1998) Sulfur-inhibited *Thermosphaera aggregans* sp. nov., a new genus of hyperthermophilic archaea isolated after its prediction from environmentally derived 16S rRNA sequences. Int. J. Syst. Bacteriol. 48, 31–38.

[262] Korn-Wendisch, F., Rainey, F., Kroppenstedt, R.M., Kempf, A., Majazza, A., Kutzner, H.J. and Stackebrandt, E. (1995) *Thermocrispum* gen. nov., a new genus of the order *Actinomycetales*, and description of *Thermocrispum municipale* sp. nov. and *Thermocrispum agreste* sp. nov. Int. J. Syst. Bacteriol. 45, 67–77.

[263] Zeikus, J.G., Dawson, M.A., Thompson, T.E., Ingvorsen, K. and Hatchikian, E.C. (1983) Microbial ecology of volcanic sulphidogenesis: isolation and characterization of *Thermodesulfobacterium commune* gen. nov. and sp. nov. J. Gen. Microbiol. 129, 1159–1169.

[264] Rozanova, E.P. and Khudyakova, A.I. (1974) A new nonspore-forming thermophilic sulfate-reducing organism, *Desulfovibrio thermophilus* nov. sp. Mikrobiologiya (in Russian) 43, 1069–1075.

[265] Rozanova, E.P. and Pivovarova, T.A. (1988) Reclassification of *Desulfovibrio thermophilus* (Rozanova, Khudyakova, 1974). Mikrobiologiya (in Russian) 57, 102–106.

[266] Beeder, J., Torsvik, T. and Lien, T. (1995) *Thermodesulforhabdus norvegicus* gen. nov., sp. nov., a novel thermophilic sulfate-reducing bacterium from oil field water. Arch. Microbiol. 164, 331–336.

[267] Henry, E.A., Devereux, R., Maki, J.S., Gilmour, C.C., Woese, C.R., Mandelco, L., Schauder, R., Ramsen, C.C. and Mitchell, R. (1994) Characterization of a new thermophilic sulfate-reducing bacterium *Thermodesulfovibrio yellowstonii*, gen. nov. and sp. nov. its phylogenetic relationship to *Thermodesulfobacterium commune* and their origins deep within the bacterial domain. Arch. Microbiol. 161, 62–69.

[268] Cayol, J.-L., Ducerf, S., Garcia, J.-L. and Patel, B.K.C. (1998) *Thermohalobacter berrensis* gen. nov., sp. nov., a novel thermophilic strictly halophilic bacterium from a solar saltern. Int. Conf. Thermophiles '98 Prog. Abstr. B-P2.

[269] Zacharova, E.V., Mitrofanova, T.I., Krasilnikova, E.N. and Kondratieva, E.N. (1993) *Thermohydrogenium kirishiense* gen. nov. and sp. nov., a new anaerobic thermophilic bacterium. Arch. Microbiol. 160, 492–497.

[270] Zarilla, K.A. and Perry, J.J. (1984) *Thermophilum album* gen. nov. and sp. nov., a bacterium obligate for thermophily and *n*-alkane substrates. Arch. Microbiol. 137, 286–290.

[271] Jackson, T.J., Ramaley, R.F. and Meinschein, W.G. (1973) *Thermomicrobium* a new genus of extremely thermophilic bacteria. Int. J. Syst. Bacteriol. 23, 28–36.

[272] Tenreiro, S., Nobre, M.F., Rainey, F.A., Miguel, C. and Da Costa, M.S. (1997) *Thermonema rossianum* sp. nov., a new thermophilic and slightly halophilic species from saline hot springs in Naples, Italy. Int. J. Syst. Bacteriol. 47, 122–126.

[273] Huber, R., Woese, C.R., Langworthy, T.A., Fricke, H. and Stetter, K.O. (1989) *Thermosipho africanus* gen. nov., represents a new genus of thermophilic eubacteria within the '*Thermotogales*'. Syst. Appl. Microbiol. 12, 32–37.

[274] Svetlitshnyi, V., Rainey, F. and Wiegel, J. (1996) *Thermosyntropha lipolytica* gen. nov., sp. nov., a lipolytic, anaerobic, alkalitolerant, thermophilic bacterium utilizing short- and long-chain fatty acids in syntrophic coculture with a methanogenic archaeum. Int. J. Syst. Bacteriol. 46, 1131–1137.

[275] Slobodkin, A., Reysenbach, A.-L., Strutz, N., Dreier, M. and Wiegel, J. (1997) *Thermoterrabacterium ferrireducens* gen. nov., sp. nov., a thermophilic anaerobic dissimilatory Fe(III)-reducing bacterium from a continental hot spring. Int. J. Syst. Bacteriol. 47, 541–547.

[276] Odinstova, E.V., Jannasch, H.W., Mamone, J.A. and Langworthy, T.A. (1996) *Thermothrix azorensis* sp. nov., an obligately chemolithoautotrophic, sulfur-oxidizing, thermophilic bacterium. Int. J. Syst. Bacteriol. 46, 422–428.

[277] Caldwell, D.E., Caldwell, S.J. and Laycock, J.P. (1976) *Thermothrix thioparus* gen. et sp. nov. a facultatively anaerobic facultative chemolithotroph living at neutral pH and high temperature. Can. J. Microbiol. 22, 1509–1517.

[278] Brannan, D.K. and Caldwell, D.E. (1980) *Thermothrix thiopara*: growth and metabolism of a newly isolated thermophile capable of oxidizing sulfur and sulfur compounds. Appl. Environ. Microbiol. 40, 211–216.

[279] Ravot, G., Magot, M., Fardeau, M.-L., Patel, B.K.C., Prensier, G., Egan, A., Garcia, J.-L. and Ollivier, B. (1995) *Thermotoga elfii* sp. nov., a novel thermophilic bacterium from an African oil-producing well. Int. J. Syst. Bacteriol. 45, 308–314.

[280] Fardeau, M.-L., Ollivier, B., Patel, B.K.C., Magot, M., Thomas, P., Rimbault, A., Rocchiccioli, F. and Garcia, J.-L. (1997) *Thermotoga hypogea* sp. nov., a xylanolytic, thermophilic bacterium from an oil-producing well. Int. J. Syst. Bacteriol. 47, 1013–1019.

[281] Jeanthon, C., Reysenbach, A.-L., L'Haridon, S., Gambacorta, A., Pace, N.R., Glenat, P. and Prieur, D. (1995) *Thermotoga subterranea* sp. nov., a new thermophilic bacterium isolated from a continental oil reservoir. Arch. Microbiol. 64, 91–97.

[282] Windberger, E., Huber, R., Trincone, A., Fricke, H. and Stetter, K.O. (1989) *Thermotoga thermarum* sp. nov. and *Thermotoga neapolitana* occurring in African continental solfataric springs. Arch. Microbiol. 151, 506–512.

[283] Brock, T.D. and Freeze, H. (1969) *Thermus aquaticus* gen. nov. and sp. nov., a non-sporulating extreme thermophile. J. Bacteriol. 98, 289–297.

[284] Williams, R.A.D., Smith, K.E., Welch, S.G. and Micallef, J. (1996) *Thermus oshimai* sp. nov., isolated from hot springs in Portugal, Iceland, and the Azores, and comment on the concept of a limited geopgraphical distribution of *Thermus* species. Int. J. Syst. Bacteriol. 46, 403–408.

[285] Oshima, T. and Imahori, K. (1974) Description of *Thermus thermophilus* (Yoshida and Oshima) comb. nov., a nonsporulating thermophilic bacterium from a Japanese thermal spa. Int. J. Syst. Bacteriol. 24, 102–112.

[286] Egorova, A.A. and Deryugina, Z.P. (1963) The spore-forming thermophilic thiobacterium. Mikrobiologiya (in Russian) 32, 439–446.

[287] Huber, R., Langworthy, T.A., König, H., Thomm, M., Woese, C.R., Sleytr, U.B. and Stetter, K.O. (1986) *Thermotoga maritima*

sp. nov. represents a new genus of unique extremely thermophilic eubacteria growing up to 90°C. Arch. Microbiol. 144, 324–333.

[288] Jannasch, H.W., Huber, R., Belkin, S. and Stetter, K.O. (1988) *Thermotoga neapolitana* sp. nov. of the extremely thermophilic, eubacterial genus *Thermotoga*. Arch. Microbiol. 150, 103–104.

[289] Fuchs, T., Huber, H., Burggraf, S. and Stetter, K.O. (1996) 16S rDNA-based phylogeny of the Archaeal order *Sulfolobales* and reclassification of *Desulfurolobus ambivalens* as *Acidianus ambivalens* comb. nov. Syst. Appl. Microbiol. 19, 56–60.

[290] Zillig, W., Yeats, S., Holz, I., Bock, A., Gropp, F., Rettenberger, M. and Lutz, S. (1985) Plasmid-related anaerobic autotrophy of the novel archaebacterium *Sulfolobus ambivalens*. Nature 313, 789–791.

[291] Zillig, W., Yeats, S., Holz, I., Bock, A., Rettenberger, M., Gropp, F. and Simon, G. (1986) *Desulfurolobus ambivalens*, gen. nov., sp. nov., an autotrophic archaebacterium facultatively oxidizing or reducing sulfur. Syst. Appl. Microbiol. 8, 197–203.

[292] Segerer, A., Neuner, A., Kristjansson, J. and Stetter, K.O. (1986) *Acidianus infernus* gen. nov., sp. nov., and *Acidianus brierleyi* comb. nov. facultatively aerobic, extremely acidophilic thermophilic sulfur-metabolizing archaebacteria. Int. J. Syst. Bacteriol. 36, 559–564.

[293] Huber, G., Drobner, E., Huber, H. and Stetter, K.O. (1992) Growth by aerobic oxidation of molecular hydrogen in Archaea – a metabolic property so far unknown for this domain. Syst. Appl. Microbiol. 15, 502–504.

[294] Brierley, C.L. and Brierley, J.A. (1973) A chemoautotrophic and thermophilic microorganism isolated from an acid hot spring. Can. J. Microbiol. 19, 183–188.

[295] Huber, H., Jannasch, H., Rachel, R., Fuchs, T. and Stetter, K.O. (1997) *Archaeoglobus veneficus* sp. nov., a novel facultative chemolithoautotrophic hyperthermophilic sulfite reducer, isolated from abyssal black smokers. Syst. Appl. Microbiol. 20, 374–380.

[296] Fuchs, T., Huber, H., Teiner, K., Burggraf, S. and Stetter, K.O. (1995) *Metallosphaera prunae*, sp. nov., a novel metal-mobilizing, thermoacidophilic archaeum, isolated from a uranium mine in Germany. Syst. Appl. Microbiol. 18, 560–566.

[297] Huber, G., Spinnler, C., Gambacorta, A. and Stetter, K.O. (1989) *Metallosphaera sedula* gen. and sp. nov. represents a new genus of aerobic, metal-mobilizing, thermoacidophilic archaebacteria. Syst. Appl. Microbiol. 12, 38–47.

[298] Kotelnikova, S.V., Obraztsova, A.Y., Gongadze, G.M. and Laurinavichius, K.S. (1993) *Methanobacterium thermoflexum* sp. nov. and *Methanobacterium defluvii* sp. nov., thermophilic rod-shaped methanogens isolated from anaerobic digestor sludge. Syst. Appl. Microbiol. 16, 427–435.

[299] Blotevogel, K.-H. and Fischer, U. (1985) Isolation and characterization of a new thermophilic and autotrophic methane producing bacterium: *Methanobacterium thermoaggregans* spec. nov. Arch. Microbiol. 142, 218–222.

[300] Blotevogel, K.-H., Fischer, U., Mocha, M. and Jannsen, S. (1985) *Methanobacterium thermoalcaliphilum* spec. nov., a new moderately alkaliphilic and thermophilic autotrophic methanogen. Arch. Microbiol. 142, 211–217.

[301] Laurinavichyus, K.S., Kotel'nikova, S.V. and Obraztsova, A.Y. (1988) New species of thermophilic methane-producing bacteria. Mikrobiologiya (in Russian) 57, 1035–1041.

[302] Huber, H., Thomm, M., König, H., Thies, G. and Stetter, K.O. (1982) *Methanococcus thermolithotrophicus*, a novel thermophilic lithotrophic methanogen. Arch. Microbiol. 132, 47–50.

[303] Jeanthon, C., L'Haridon, S., Reysenbach, A.L., Corre, E., Vernet, M., Messner, P., Sleytr, U.B. and Prieur, D. (1999) *Methanococcus vulcanius* sp. nov., a novel hyperthermophilic methanogen isolated from East Pacific Rise, and identification of *Methanococcus* sp. DSM 4213^T as *Methanococcus fervens* sp. nov. Int. J. Syst. Bacteriol. 49, 583–589.

[304] Boone, D.R., Whitman, W.B. and Rouviere, P., (1993) in: Methanogenesis – Ecology, Physiology, Biochemistry and Genetics (Ferry, J.G., Ed.), pp. 35–80. Chapman and Hall, New York.

[305] Zhulina, T.N. and Zavarzin, G.A. (1987) *Methanohalobium evestigatus* nov. gen., nov. sp., an extreme halophilic methane-forming archaebacterium. Doklady Akad. Nauk SSSR (in Russian) 293, 464–468.

[306] Zeikus, J.G. and Wolfe, R.S. (1972) *Methanobacterium thermoautotrophicus* sp. nov., an anaerobic, autotrophic, extreme thermophile. J. Bacteriol. 109, 707–713.

[307] Winter, J., Lerp, C., Zabel, H.-P., Wildenauer, F.X., König, H. and Schindler, F. (1984) *Methanobacterium wolfei*, sp. nov., a new tungsten-requiring, thermophilic, autotrophic methanogen. Syst. Appl. Microbiol. 5, 457–466.

[308] Kamagata, Y., Kawasaki, H., Oyzizu, H., Nakamura, K., Mikami, E., Endo, G., Koga, Y. and Yamasato, K. (1992) Characterization of three thermophilic strains of *Methanothrix* ('*Methanosaeta*') *thermophila* sp. nov. and rejection of *Methanothrix* ('*Methanosaeta*') *thermoacetophila*. Int. J. Syst. Bacteriol. 42, 463–468.

[309] Takai, K., Sugai, A., Itoh, T. and Horikoshi, K. (2000) *Palaeococcus ferrophilus* gen. nov., sp. nov., a barophilic, hyperthermophilic archaeon from a deep-sea hydrothermal vent chimney. Int. J. Syst. Evol. Microbiol. 50, 489–500.

[310] Schleper, C., Puehler, G., Holz, I., Gambacorta, A., Janekovic, D., Santarius, U., Klenk, H.-P. and Zillig, W. (1995) *Picrophilus* gen. nov., fam. nov. a novel aerobic, heterotrophic, thermoacidophilic genus and family comprising archaea capable of growth around pH 0. J. Bacteriol. 177, 7050–7059.

[311] Schleper, C., Puhler, G., Klenk, H.-P. and Zillig, W. (1996) *Picrophilus oshimae* and *Picrophilus torridus* fam. nov., gen. nov., sp. nov., two species of hyperacidophilic, thermophilic, heterotrophic, aerobic archaea. Int. J. Syst. Bacteriol. 46, 814–816.

[312] Segerer, A.H., Trincone, A., Gahrtz, M. and Stetter, K.O. (1991) *Stygiolobus azoricus* gen. nov., sp. nov. represents a novel genus of anaerobic, extremely thermoacidophilic archaebacteria of the order *Sulfolobales*. Int. J. Syst. Bacteriol. 41, 495–501.

[313] Brock, T.D., Brock, K.M., Belly, R.T. and Weiss, R.L. (1972) *Sulfolobus*: a new genus of sulfur-oxidizing bacteria living at low pH and high temperature. Arch. Microbiol. 84, 54–68.

[314] Segerer, A., Stetter, K.O. and Klink, F. (1985) Two contrary modes of chemolithotrophy in the same archaebacterium. Nature 313, 787–789.

[315] Brock, T.D., Cook, S., Petersen, S. and Mosser, J.L. (1976) Biogeochemistry and bacteriology of ferrous iron oxidation in geothermal habitats. Geochim. Cosmochim. Acta 40, 493–500.

[316] Takayanagi, S., Kawasaki, H., Sugimori, K., Yamada, T., Sugai, A., Ito, T., Yamasato, K. and Shioda, M. (1996) *Sulfolobus hakonensis* sp. nov., a novel species of acidothermophilic archaeon. Int. J. Syst. Bacteriol. 46, 377–382.

[317] Huber, G. and Stetter, K.O. (1991) *Sulfolobus metallicus*, sp. nov., a novel strictly chemolithoautotroph thermophilic archaeal species of metal-mobilizers. Syst. Appl. Microbiol. 14, 372–378.

[318] Grogan, D., Palm, P. and Zillig, W. (1990) Isolate B12, which harbors a virus-like element, represents a new species of the archaebacterial genus *Sulfolobus*, *Sulfolobus shibatae*, sp. nov. Arch. Microbiol. 154, 594–599.

[319] Grogan, D.W. (1989) Phenotypic characterization of the archaebacterial genus *Sulfolobus*: comparison of five wild-type strains. J. Bacteriol. 171, 6710–6719.

[320] Zillig, W., Stetter, K.O., Wunderl, S., Schulz, W., Priess, H. and Scholz, I. (1980) The *Sulfolobus* – 'Caldariella' group: taxonomy on the basis of the structure of DNA-dependent RNA polymerases. Arch. Microbiol. 125, 259–269.

[321] Golovacheva, R.S., Val'ekho-Roman, K.M. and Troitskii, A.V. (1987) *Sulfurococcus mirabilis* gen. nov., sp. nov., a new thermophilic archaebacterium with the ability to oxidize sulfur. Mikrobiologiya (in Russian) 56, 100–107.

[322] Karavaiko, G.I., Golyshina, O.V., Troitskii, A.V., Valieho-Roman, K.M., Golovacheva, R.S. and Pivovarova, T.A. (1994) *Sulfurococcus yellowstonii* sp. nov., a new species of iron and sulfur oxidizing

thermoacidophilic archaebacteria. Mikrobiologiya (in Russian) 63, 668–682.

[323] Ronimus, R.S., Reysenbach, A.-L., Musgrave, D.R. and Morgan, H.W. (1997) The phylogenetic position of the *Thermococcus* isolate AN1 based on 16S rRNA gene sequence analysis: a proposal that AN1 represents a new species, *Thermococcus zilligii* sp. nov. Arch. Microbiol. 168, 245–248.

[324] Klages, K.U. and Morgan, H.W. (1994) Characterization of an extremely thermophilic sulphur-metabolizing archaebacterium belonging to the Thermococcales. Arch. Microbiol. 162, 261–266.

[325] Segerer, A., Langworthy, T.A. and Stetter, K.O. (1988) *Thermoplasma acidophilum* and *Thermoplasma volcanium* sp. nov. from solfatara fields. Syst. Appl. Microbiol. 10, 161–171.

[326] Darland, G., Brock, T.D., Samsonoff, W. and Conti, S.F. (1970) A thermophilic, acidophilic, mycoplasma isolated from a coal refuse pile. Science 170, 1416–1418.

[327] Sako, Y., Nomura, N., Uchida, A., Ishida, Y., Morii, H., Koga, Y., Hoaki, T. and Maruyama, T. (1996) *Aeropyrum pernix* gen. nov., sp. nov., a novel aerobic hyperthermophilic archaeon growing at temperatures up to 100°C. Int. J. Syst. Bacteriol. 46, 1070–1077.

[328] Stetter, K.O., Lauerer, G., Thomm, M. and Neuner, A. (1987) Isolation of extremely thermophilic sulfate reducers: evidence for a novel branch of archaebacteria. Science 236, 822–824.

[329] Stetter, K.O. (1988) *Archaeoglobus fulgidus* gen. nov., sp. nov. a new taxon of extremely thermophilic archaebacteria. Syst. Appl. Microbiol. 10, 172–173.

[330] Beeder, J., Nilsen, R.K., Rosnes, J.T., Torsvik, T. and Lien, T. (1994) *Archaeoglobus fulgidus* isolated from hot North Sea oil field waters. Appl. Environ. Microbiol. 60, 1227–1231.

[331] Burggraf, S., Jannasch, H.W., Nicolaus, B. and Stetter, K.O. (1990) *Archaeoglobus profundus* sp. nov., represents a new species within the sulfate-reducing archaebacteria. Syst. Appl. Microbiol. 13, 24–28.

[332] Itoh, T., Suzuki, K.-I., Sanchez, P.C. and Nakase, T. (1999) *Caldivirga maquilingensis* gen. nov., sp. nov., a new genus of rod-shaped crenarchaeote isolated from a hot spring in the Philippines. Int. J. Syst. Bacteriol. 49, 1157–1163.

[333] Svetlitshnyi, V.A., Slesarev, A.I., Svetlichnaya, T.P. and Zavarzin, G.A. (1987) *Caldococcus litoralis* gen. nov. sp. nov., a new marine extremely thermophilic archaebacterium reducing elemental sulfur. Mikrobiologiya (in Russian) 56, 831–838.

[334] Aoshima, M., Yamagishi, A. and Oshima, T. (1996) Eubacteria-type isocitrate dehydrogenase from an archaeon: cloning, sequencing, and expression of a gene encoding isocitrate dehyrogenase from a hyperthermophilic archaebacterium, *Caldococcus noboribetus*. Arch. Biochem. Biophys. 336, 77–85.

[335] Aoshima, M. and Oshima, T. (1997) Purification and characterization of isocitrate dehydrogenase from a hyperthermophilic archaebacterium, *Caldococcus noboribetus*. Biochim. Biophys. Acta 1340, 227–234.

[336] Bonch-Osmolovskaya, E.A., Slesarev, A.I., Miroshnichenko, M.L., Svetlichnaya, T.P. and Alekseev, V.A. (1988) Characteristics of *Desulfurococcus amylolyticus* nov. sp. – a new extremely thermophilic archaebacterium isolated from thermal springs of Kamchatka and Kunashir Island. Mikrobiologiya (in Russian) 57, 94–101.

[337] Zillig, W., Stetter, K.O., Prangishvilli, D., Schäfer, W., Wunderl, S., Janekovic, D., Holz, I. and Palm, P. (1982) *Desulfurococcaceae*, the second family of extremely thermophilic, anaerobic, sulfur-respiring *Thermoproteales*. Zentralblatt Bakteriol. Mikrobiol. Hyg. 1 Abt. Originale C 3, 304–317.

[338] Zillig, W., Holz, I., Janekovic, D., Klenk, H.-P., Imsel, E., Trent, J., Wunderl, S., Forjaz, V.H., Coutinho, R. and Ferreira, T. (1990) *Hyperthermus butylicus*, a hyperthermophilic sulfur-reducing archaebacterium that ferments peptides. J. Bacteriol. 172, 3959–3965.

[339] Zhao, H., Wood, A.G., Widdel, F. and Bryant, M.P. (1988) An extremely thermophilic *Methanococcus* from a deep sea hydrothermal vent and its plasmid. Arch. Microbiol. 150, 178–183.

[340] Burggraf, S., Fricke, H., Neuner, A., Kristjansson, J., Rouvier, P., Mandelco, L., Woese, C.R. and Stetter, K.O. (1990) *Methanococcus igneus* sp. nov., a novel hyperthermophilic methanogen from a shallow submarine hydrothermal vent. Syst. Appl. Microbiol. 13, 263–269.

[341] Jeanthon, C., L'Haridon, S., Reysenbach, A.L., Vernet, M., Messner, P., Sleytr, U.B. and Prieur, D. (1998) *Methanococcus infernus* sp. nov., a novel hyperthermophilic lithotrophic methanogen isolated from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 48, 913–918.

[342] Huber, R., Kurr, M., Jannasch, H.W. and Stetter, K.O. (1989) A novel group of abyssal methanogenic archaebacteria (*Methanopyrus*) growing at 110°C. Nature 342, 833–834.

[343] Stetter, K.O., Thomm, M., Winter, J., Wildgruber, G., Huber, H., Zillig, W., Janecovic, D., König, H., Palm, P. and Wunderl, S. (1981) *Methanothermus fervidus*, sp. nov., a novel extremely thermophilic methanogen isolated from an Icelandic hot spring. Zent.bl. Bakteriol. Mikrobiol. Hyg. 1 Abt. Originale C 2, 166–178.

[344] Lauerer, G., Kristjansson, J.K., Langworthy, T.A., König, H. and Stetter, K.O. (1986) *Methanothermus sociabilis* sp. nov., a second species within the *Methanothermaceae* growing at 97°C. Syst. Appl. Microbiol. 8, 100–105.

[345] Völkl, P., Huber, R., Drobner, E., Rachel, R., Burggraf, S., Trincone, A. and Stetter, K.O. (1993) *Pyrobaculum aerophilum* sp. nov., a novel nitrate-reducing hyperthermophilic archaeum. Appl. Environ. Microbiol. 1993, 2918–2926.

[346] Huber, R., Kristjansson, J.K. and Stetter, K.O. (1987) *Pyrobaculum* gen. nov., a new genus of neutrophilic rod-shaped archaebacteria from continental solfataras growing optimally at 100°C. Arch. Microbiol. 149, 95–101.

[347] Erauso, G., Reysenbach, A.-L., Godfroy, A., Muenier, J.-R., Crump, B., Partensky, F., Baross, J.A., Marteinsson, V., Barbier, G., Pace, N.R. and Prieur, D. (1993) *Pyrococcus abyssi* sp. nov., a new hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent. Arch. Microbiol. 160, 338–349.

[348] Pledger, R.J. and Baross, J.A. (1991) Preliminary description and nutritional characterization of a chemoorganotrophic archaeobacterium growing at temperatures of up to 100°C isolated from a submarine hydrothermal vent environment. J. Gen. Microbiol. 137, 203–211.

[349] Fiala, G. and Stetter, K.O. (1986) *Pyrococcus furiosus* sp. nov. represents a novel genus of marine heterotrophic archaebacteria growing optimally at 100°C. Arch. Microbiol. 145, 56–61.

[350] Gonzalez, J.M., Masuchi, Y., Robb, F.T., Ammerman, J.W., Maeder, D.L., Yanagibayashi, M., Tamaoka, J. and Kato, C. (1998) *Pyrococcus horikoshii* sp. nov., a hyperthermophilic archaeon isolated from a hydrothermal vent at the Okinawa Trough. Extremophiles 2, 123–130.

[351] Zillig, W., Holz, I., Klenk, H.-P., Trent, J., Wunderl, S., Janekovic, D., Imsel, E. and Haas, B. (1987) *Pyrococcus woesei*, sp. nov., an ultra-thermophilic marine archaebacterium, representing a novel order, *Thermococcales*. Syst. Appl. Microbiol. 9, 62–70.

[352] Pley, U., Schipka, J., Gambacorta, A., Jannasch, H.W., Fricke, H., Rachel, R. and Stetter, K.O. (1991) *Pyrodictum abyssi* sp. nov. represents a novel heterotrophic marine archaeal hyperthermophile growing at 110°C. Syst. Appl. Microbiol. 14, 245–253.

[353] Stetter, K.O., König, H. and Stackebrandt, E. (1983) *Pyrodictium* gen. nov., a new genus of submarine disc-shaped sulphur reducing archaebacteria growing optimally at 105°C. Syst. Appl. Microbiol. 4, 535–551.

[354] Fiala, G., Stetter, K.O., Jannasch, H.W., Langworthy, T.A. and Madon, J. (1986) *Staphylothermus marinus* sp. nov. represents a novel genus of extremely thermophilic submarine heterotrophic archaebacteria growing up to 98°C. Syst. Appl. Microbiol. 8, 106–113.

[355] Jochimsen, B., Peinemann-Simon, S., Volker, H., Stuben, D., Botz, R., Stoffers, P., Dando, P.R. and Thomm, M. (1997) *Stetteria hy-*

drogenophila, gen. nov. and sp. nov., a novel mixotrophic sulfur-dependent *crenarchaeote* isolated from Milos, Greece. Extremophiles 1, 67–73.

[356] Hensel, R., Matussek, K., Michalke, K., Tacke, L., Tindall, B.J., Kohlhoff, M., Siebers, B. and Dielenschneider, J. (1997) *Sulfophobococcus zilligii* gen. nov., spec. nov. a novel hyperthermophilic Archaeum isolated from hot alkaline springs of Iceland. Syst. Appl. Microbiol. 20, 102–110.

[357] Kurosawa, N., Itoh, Y.H., Iwai, T., Sugai, A., Uda, I., Kimura, N., Horiuchi, T. and Itoh, T. (1998) *Sulfurisphaera ohwakuensis* gen. nov., sp. nov., a novel extremely thermophilic acidophile of the order *Sulfolobales*. Int. J. Syst. Bacteriol. 48, 451–456.

[358] Dirmeier, R., Keller, M., Hafenbradl, D., Braun, F.-J., Rachel, R., Burggraf, S. and Stetter, K.O. (1998) *Thermococcus acidaminovorans* sp. nov., a new hyperthermophilic alkalophilic archaeon growing on amino acids. Extremophiles 2, 109–114.

[359] Canganella, F., Jones, W.J., Gambacorta, A. and Antranikian, G. (1998) *Thermococcus guaymasensis* sp. nov. and *Thermococcus aggregans* sp. nov., two novel thermophilic archaea isolated from Guaymas Basin hydrothermal vent site. Int. J. Syst. Bacteriol. 48, 1181–1185.

[360] Keller, M., Braun, F.-J., Dirmeier, R., Hafenbradl, D., Burggraf, S., Rachel, R. and Stetter, K.O. (1995) *Thermococcus alcaliphilus* sp. nov., a new hyperthermophilic archaeum growing on polysulfide at alkaline pH. Arch. Microbiol. 164, 390–395.

[361] Marteinsson, V.T., Birrien, J.-L., Reysenbach, A.-L., Vernet, M., Marie, D., Gambacorta, A., Messner, P., Sleytr, U.B. and Prieur, D. (1999) *Thermococcus barophilus* sp. nov., a new barophilic and hyperthermophilic archaeon isolated under high hydrostatic pressure from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 49, 351–359.

[362] Duffaud, G.D., D'Hennezel, O.B., Peek, A.S., Reysenbach, A.-L. and Kelly, R.M. (1998) Isolation and characterization of *Thermococcus barossii*, sp. nov., a hyperthermophilic archaeon isolated from a hydrothermal vent flange formation. Syst. Appl. Microbiol. 21, 40–49.

[363] Zillig, W., Holz, I., Janekovic, D., Schafer, W. and Reiter, W.D. (1983) The archaebacterium *Thermococcus celer* represents a novel genus within the thermophilic branch of the archaebacteria. Syst. Appl. Microbiol. 4, 88–94.

[364] Huber, R., Stohr, J., Hohenhaus, S., Rachel, R., Burggraf, S., Jannasch, H.W. and Stetter, K.O. (1995) *Thermococcus chitonophagus* sp. nov., a novel, chitin-degrading, hyperthermophilic archaeum from a deep-sea hydrothermal vent environment. Arch. Microbiol. 164, 255–264.

[365] Godfroy, A., Meunier, J.-R., Guezennec, J., Lesongeur, F., Raguenes, G., Rimbault, A. and Barbier, G. (1996) *Thermococcus fumicolans* sp. nov., a new hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent in the North Fiji Basin. Int. J. Syst. Bacteriol. 46, 1113–1119.

[366] Miroshnichenko, M.L., Gongadze, G.M., Rainey, F.A., Kostyukova, A.S., Lysenko, A.M., Chernyh, N.A. and Bonch-Osmolovskaya, E.A. (1998) *Thermococcus gorgonarius* sp. nov. and *Thermococcus pacificus* sp. nov. heterotrophic extremely thermophilic archaea from New Zealand submarine hot vents. Int. J. Syst. Bacteriol. 48, 23–29.

[367] Godfroy, A., Lesongeur, F., Raguenes, G., Querellou, J., Antoine, E., Meunier, J.-R., Guezennec, J. and Barbier, G. (1997) *Thermococcus hydrothermalis* sp. nov., a new hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 47, 622–626.

[368] Neuner, A., Jannasch, H.W., Belkin, S. and Stetter, K.O. (1990) *Thermococcus litoralis* sp. nov. a new species of extremely thermophilic marine archaebacteria. Arch. Microbiol. 153, 205–207.

[369] Belkin, S. and Jannasch, H.W. (1985) A new extremely thermophilic, sulfur-reducing heterotrophic, marine bacterium. Arch. Microbiol. 141, 181–186.

[370] Gonzalez, J.M., Kato, C. and Horikoshi, K. (1995) *Thermococcus peptonophilus* sp. nov., a fast-growing, extremely thermophilic archaebacterium isolated from deep-sea hydrothermal vents. Arch. Microbiol. 164, 159–164.

[371] Kobayashi, T., Kwak, Y.S., Akiba, T., Kudo, T. and Horikoshi, K. (1994) *Thermococcus profundus* sp. nov., a new hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent. Syst. Appl. Microbiol. 17, 232–236.

[372] Grote, R., Li, L., Tamaoka, J., Kato, C., Horikoshi, K. and Antranikian, G. (1999) *Thermococcus siculi* sp. nov., a novel hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent at the Mid-Okinawa trough. Extremophiles 3, 55–62.

[373] Miroshnichenko, M.L., Bonch-Osmolovskaya, E.A., Neuner, A., Kostrikina, N.A., Chernych, N.A. and Alekseev, V.A. (1989) *Thermococcus stetteri* sp. nov., a new extremely thermophilic marine sulfur-metabolizing archaebacterium. Syst. Appl. Microbiol. 12, 257–262.

[374] Stetter, K.O., Fiala, G., Huber, G., Huber, R. and Segerer, A. (1990) Hyperthermophilic microorganisms. FEMS Microbiol. Rev. 75, 117–124.

[375] Fischer, F., Zillig, W., Stetter, K.O. and Schreiber, G. (1983) Chemolithoautotrophic metabolism of anaerobic extremely thermophilic archaebacteria. Nature 301, 511–513.

[376] Zillig, W., Gierl, A., Schreiber, G., Wunderl, S., Janekovic, D., Stetter, K.O. and Klenk, H.P. (1983) The archaebacterium *Thermofilum pendens* represents a novel genus of thermophilic, anaerobic sulfur respiring *Thermoproteales*. Syst. Appl. Microbiol. 4, 79–87.

[377] Zillig, W., Stetter, K.O., Schäfer, W., Janekovic, D., Wunderl, S., Holz, I. and Palm, P. (1981) *Thermoproteales*: a novel type of extremely thermoacidophilic anaerobic archaebacteria isolated from Icelandic solfataras. Zent.bl. Bakteriol. Mikrobiol. Hyg. 1. Abt. Originale C 2, 205–227.

[378] Bonch-Osmolovskaya, E.A., Miroshnichenko, M.L., Kostrikina, N.A., Chernych, N.A. and Zavarzin, G.A. (1990) *Thermoproteus uzoniensis* sp. nov., a new extremely thermophilic archaebacterium from Kamchatka continental hot springs. Arch. Microbiol. 154, 556–559.

[379] The Prokaryotes: A Handbook on the Biology of Bacteria: Ecophysiology, Isolation, Identification, Applications, vol. 1 (Balows A., Truper, H.G., Dworkin, M., Harder, W. and Schleifer, K.-H., Eds.), Springer-Verlag, (1992) New York.

[380] Finster, K., Liesack, W. and Tindall, B.J. (1997) *Sulfurospirillum arachanense* sp. nov., a new microaerophilic sulfur reducing bacterium. Int. J. Syst. Bacteriol. 47, 1212–1217.

[381] Doelle, H.W. (1969) Bacterial Metabolism, Academic Press, New York.

[382] Plyasunov, A.V., O'Connell, J.P., Wood, R.H. and Shock, E.L. (2000) Infinite dilution partial molar properties of aqueous solutions on nonelectrolytes. II. Equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures. Geochim. Cosmochim. Acta 64, 2779–2795.

[383] Drozd, J.W. (1976) Energy coupling and respiration in *Nitrosomonas europea*. Arch. Microbiol. 110, 257–262.

[384] Suzuki, I., Dular, U. and Kwok, S.C. (1974) Ammonia or ammonium ion as substrate for oxidation by *Nitrosomonas europaea* cells and extracts. J. Bacteriol. 120, 556–558.

[385] Tamegai, H., Li, L., Masui, N. and Kato, C. (1997) A denitrifying bacterium from the deep sea at 11000 m depth. Extremophiles 1, 207–211.

[386] Petursdottir, S.K. and Kristjansson, J.K. (1997) *Silicibacter lacuscaerulensis* gen. nov., sp. nov., a mesophilic moderately halophilic bacterium characteristic of the Blue Lagoon geothermal lake in Iceland. Extremophiles 1, 94–99.

[387] Gottschalk, G. (1986) Bacterial Metabolism, 2nd edn., Springer-Verlag, New York.

[388] Murray, P.A. and Zinder, S.H. (1984) Nitrogen fixation by a methanogenic archaebacterium. Nature 312, 284–286.

[389] Postgate, J.R. and Kent, H.M. (1985) Diazotrophy within *Desulfovibrio*. J. Gen. Microbiol. 131, 2119–2122.

[390] Nazina, T.N., Rozanova, E.P. and Kalininskaya, T.A. (1979) Fixation of molecular nitrogen by sulfate-reducing bacteria from oil strata. Mikrobiologiya (in Russian) 48, 133–136.

[391] Bergey's Manual of Systematic Bacteriology, vol. 3 (Holt, J.G., Staley, J.T., Bryant, M.P. and Pfennig, N., Eds.), Williams and Wilkins, (1989) Baltimore, MD.

[392] Olsen, G. (1999) What's eating the free lunch? Nature 400, 403–405.

[393] Newman, D.K., Kennedy, E.K., Coates, J.D., Ahmann, D., Ellis, D.J., Lovley, D.R. and Morel, F.M.M. (1997) Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. Arch. Microbiol. 168, 380–388.

[394] Pikuta, E.V., Zhilina, T.N., Zavarzin, G.A., Kostrikina, N.A., Osipov, G.A. and Rainey, F.A. (1998) *Desulfonatronum lacustre* gen. nov., sp. nov. a new alkaliphilic sulfate-reducing bacterium utilizing ethanol. Mikrobiologiya (in Russian) 67, 123–131.

[395] Zhilina, T.N., Zavarzin, G.A., Rainey, F.A., Pikuta, E.N., Osipov, G.A. and Kostrikina, N.A. (1997) *Desulfonatronovibrio hydrogenovorans* gen. nov., sp. nov., an alkaliphilic, sulfate-reducing bacterium. Int. J. Syst. Bacteriol. 47, 144–149.

[396] Lien, T., Madsen, M., Steen, I.H. and Gjerdevik, K. (1998) *Desulfobulbus rhabdoformis* sp. nov., a sulfate reducer from a water–oil separation system. Int. J. Syst. Bacteriol. 48, 469–474.

[397] Bak, F. and Cypionka, H. (1987) A novel type of energy metabolism involving fermentation of inorganic sulphur compounds. Nature 326, 891–892.

[398] Bak, F. and Pfennig, N. (1987) Chemolithotrophic growth of *Desulfovibrio sulfodismutans* sp. nov. by disproportionation of inorganic sulfur compounds. Arch. Microbiol. 147, 184–189.

[399] Finster, K., Liesack, W. and Thamdrup, B. (1998) Elemental sulfur and thiosulfate disproportionation by *Desulfocapsa sulfoexigens* sp. nov., a new anaerobic bacterium isolated from marine surface sediment. Appl. Environ. Microbiol. 64, 119–125.

[400] Janssen, P.H., Schuhmann, A., Bak, F. and Liesack, W. (1996) Disproportionation of inorganic sulfur compounds by sulfate-reducing bacterium *Desulfocapsa thiozymogenes* gen. nov., sp. nov. Arch. Microbiol. 166, 184–192.

[401] Durand, P., Reysenbach, A.-L., Prieur, D. and Pace, N. (1993) Isolation and characterization of *Thiobacillus hydrothermalis* sp. nov., a mesophilic obligately chemolithotrophic bacterium isolated from a deep-sea hydrothermal vent in Fiji Basin. Arch. Microbiol. 159, 39–44.

[402] Jannasch, H.W., Wirsen, C.O., Nelson, D.C. and Robertson, L.A. (1985) *Thiomicrospira crunogena* sp. nov., a colorless, sulfur-oxidizing bacterium from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 35, 422–424.

[403] Brinkhoff, T., Muyzer, G., Wirsen, C. and Kuever, J. (1999) *Thiomicrospira chilensis* sp. nov., a mesophilic obligately chemolithoautotrophic sulfur-oxidizing bacterium isolated from a *Thioploca* mat. Int. J. Syst. Bacteriol. 49, 875–879.

[404] Ehrlich, H.L. (1996) Geomicrobiology, 3rd edn., Marcel Dekker, New York.

[405] Pollock, M.R. and Knox, R. (1943) Bacterial reduction of tetrathionate. Biochem. J. 37, 476–481.

[406] Huber, H. and Stetter, K.O. (1989) *Thiobacillus prosperus* sp. nov., represents a new group of halotolerant metal-mobilizing bacteria isolated from a marine geothermal field. Arch. Microbiol. 151, 479–485.

[407] The Prokaryotes: A Handbook on Habitats, Isolation and Identification of Bacteria, vol. 1 (Starr, M.P., Stolp, H., Truper, H.G., Belows, A. and Schlegel, H.G., Eds.), Springer-Verlag, (1981) New York.

[408] Gundersen, J.K., Jorgensen, B.B., Larsen, E. and Jannasch, H.W. (1992) Mats of giant sulphur bacteria on deep-sea sediments due to fluctuating hydrothermal flow. Nature 360, 454–456.

[409] Jorgensen, B.B. and Revsbech, N.P. (1983) Colorless sulfur bacteria, *Beggiotoa* spp. and *Thiovulum* spp., in O_2 and H_2S microgradients. Appl. Environ. Microbiol. 45, 1261–1270.

[410] van den Ende, F.P. and van Gemerden, H. (1993) Sulfide oxidation under oxygen limitation by a *Thiobacillus thioparus* isolated from a marine microbial mat. FEMS Microbiol. Ecol. 13, 69–78.

[411] Fossing, H., Gallardo, V.A., Jorgensen, B.B., Huttel, M., Nielsen, L.P., Schulz, H., Canfield, D.E., Forster, S., Glud, R.N., Gundersen, J.K., Kuver, J., Ramsing, N.B., Teske, A., Thamdrup, B. and Ulloa, O. (1995) Concentration and transport of nitrate by the mat forming sulphur bacterium *Thioploca*. Nature 374, 713–715.

[412] Ollivier, B., Fardeau, M.-L., Cayol, J.-L., Magot, M., Patel, B.K.C., Prensier, G. and Garcia, J.-L. (1998) *Methanocalculus halotolerans* gen. nov., sp. nov., isolated from an oil-producing well. Int. J. Syst. Bacteriol. 48, 821–828.

[413] Ollivier, B., Cayol, J.-L., Patel, B.K.C., Magot, M., Fardeau, M.-L. and Garcia, J.-L. (1997) *Methanoplanus petrolearius* sp. nov., a novel methanogenic bacterium from an oil producing well. FEMS Microbiol. Lett. 147, 51–56.

[414] Nozhevnikova, A.N. and Chudina, V.I. (1984) Morphology of the thermophilic acetate methane bacterium *Methanothrix thermoacetophila* sp. nov. Mikrobiologiya (in Russian) 53, 756–760.

[415] Zhilina, T.N., Zavarzin, G.A., Detkova, E.N. and Rainey, F.A. (1996) *Natroniella acetigena* gen. nov. sp. nov., an extremely haloalkaliphilic, homoacetic bacterium: a new member of *Haloanerobiales*. Curr. Microbiol. 32, 320–326.

[416] Downey, R.J. (1966) Nitrate reductase and respiratory adaptation in *Bacillus stearothermophilus*. J. Bacteriol. 91, 634–641.

[417] Ni, S. and Boone, D.R. (1991) Isolation and characterization of a dimethyl sulfide-degrading methanogen, *Methanolobus siciliae* HI350, from an oil well, characterization of *M. siliae* T4/M^T, and emendation of *M. siciliae*. Int. J. Syst. Bacteriol. 41, 410–416.

[418] Mathrani, I.M., Boone, D.R., Mah, R.A., Fox, G.E. and Lau, P.P. (1988) *Methanohalophilus zhilinae* sp. nov., an alkaliphilic, halophilic, methylotrophic methanogen. Int. J. Syst. Bacteriol. 38, 139–142.

[419] Zinder, S.H. (1993) in: Methanogenesis – Ecology, Physiology, Biochemistry, and Genetics (Ferry, J. Ed.), Chapman and Hall, New York.

[420] Widdel, F. (1986) Growth of methanogenic bacteria in pure culture with 2-propanol and other alcohols as hydrogen donors. Appl. Environ. Microbiol. 51, 1056–1062.

[421] Zellner, G. and Winter, J. (1987) Secondary alcohols as hydrogen donors for CO_2-reduction by methanogenesis. FEMS Microbiol. Lett. 44, 323–328.

[422] Lovley, D.R. and Phillips, E.J.P. (1988) Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Appl. Environ. Microbiol. 54, 1472–1480.

[423] Lovley, D.R., Giovannoni, S.J., White, D.C., Champine, J.E., Phillips, E.J.P., Gorby, Y.A. and Goodwin, S. (1993) *Geobacter metallireducens* gen. nov. sp. nov., a microorganism capable of coupling the complete oxidation of organic compounds to the reduction of iron and other metals. Arch. Microbiol. 159, 336–344.

[424] Oremland, R.S., Blum, J.S., Culbertson, C.W., Visscher, P.T., Miller, L.G., Dowdle, P. and Strohmaier, F.E. (1994) Isolation, growth and metabolism of an obligately anaerobic selenate-respiring bacterium, strain SES-3. Appl. Environ. Microbiol. 60, 3011–3019.

[425] Blum, J.S., Bindi, A.B., Buzzelli, J., Stolz, J.F. and Oremland, R.S. (1998) *Bacillus arsenicoselenatis*, sp. nov., and *Bacillus selenitireducens*, sp. nov. two haloalkaliphiles from Mono Lake, California that respire oxyanions of selenium and arsenic. Arch. Microbiol. 171, 19–30.

[426] Laverman, A., Blum, J.S., Shaefer, J.K., Phillips, E.J.P., Lovley, D.R. and Oremland, R.S. (1995) Growth of strain SES-3 with arsenate and other diverse electron acceptors. Appl. Environ. Microbiol. 61, 3556–3561.

[427] Hippe, H., Caspari, D., Fiebig, K. and Gottschalk, G. (1979) Utilization of trimethylamine and other *N*-methyl compounds for growth and methane formation by *Methanosarcina barkeri*. Proc. Natl. Acad. Sci. USA 76, 494–498.

[428] Rabus, R. and Widdel, F. (1995) Anaerobic degradation of ethylbenzene and other aromatic hydrocarbons by new denitrifying bacteria. Arch. Microbiol. 163, 96–103.

[429] Hinrichs, K.-U., Hayes, J.M., Sylva, S.P., Brewer, P.G. and DeLong, E.F. (1999) Methane-consuming archaebacteria in marine sediments. Nature 398, 802–805.

[430] Coates, J.D., Lonergan, D.J., Philips, E.J.P., Jenter, H. and Lovely, D.R. (1995) *Desulfuromonas palmitatis* sp. nov., a marine dissimilatory Fe(III) reducer that can oxidize long-chain fatty acids. Arch. Microbiol. 164, 406–413.

[431] Pfennig, N. and Biebl, H. (1976) *Desulfuromonas acetoxidans* gen. nov. and sp. nov., a new anaerobic, sulfur-reducing, acetate-oxidizing bacterium. Arch. Microbiol. 110, 3–12.

[432] Caccavo Jr., F., Lonergan, D.J., Lovley, D.R., Davis, M., Stolz, J. and McInerney, M.J. (1994) *Geobacter sulfurreducens* sp. nov., a hydrogen- and acetate-oxidizing dissimilatory metal-reducing microorganism. Appl. Environ. Microbiol. 60, 3752–3759.

[433] Isaksen, M.F. and Teske, A. (1996) *Desulforhopalus vacuolatus* gen. nov., sp. nov., a new moderately psychrophilic sulfate-reducing bacterium with gas vacuoles isolated from a temperate estuary. Arch. Microbiol. 166, 160–168.

[434] Rabus, R., Nordhaus, R., Ludwig, W. and Widdel, F. (1993) Complete oxidation of toluene under strictly anoxic conditions by a new sulfate redcuing bacterium. Appl. Environ. Microbiol. 59, 1444–1451.

[435] Newman, D.K., Beveridge, T.J. and Morel, F.M.M. (1997) Precipitation of arsenic trisulfide by *Desulfotomaculum auripigmentum*. Appl. Environ. Microbiol. 63, 2022–2028.

[436] Rueter, P., Rabus, R., Wilkes, H., Aeckersberg, F., Rainey, F.A., Jannasch, H.W. and Widdel, F. (1994) Anaerobic oxidation of hydrocarbons in crude oil by new types of sulphate-reducing bacteria. Nature 372, 455–458.

[437] Aeckersberg, F., Bak, F. and Widdel, F. (1991) Anaerobic oxidation of saturated hydrocarbons to CO_2 by a new type of sulfate-reducing bacterium. Arch. Microbiol. 156, 5–14.

[438] Yamada, K., Kinoshita, S., Tsunoda, T. and Aida, K. (1972) The Microbial Production of Amino Acids, Halsted Press, New York.

[439] Magot, M., Ravot, G., Campaignolle, X., Ollivier, B., Patel, B.K.C., Fardeau, M.L., Thomas, P., Crolet, J.L. and Garcia, J.L. (1997) *Dethiosulfovibrio peptidovorans* gen. nov., sp. nov., a new anaerobic, slightly halophilic, thiosulfate-reducing bacterium from corroding offshore oil wells. Int. J. Syst. Bacteriol. 47, 818–824.

[440] Sawers, G. (1998) The anaerobic degredation of L-serine and L-threonine in enterobacteria: networks of pathways and regulatory signals. Arch. Microbiol. 171, 1–5.

[441] Madigan, M.T., Martinko, J.M. and Parker, J. (1997) Brock Biology of Microorganisms, edn. 8, Prentice Hall, Upper Saddle River, NJ.

[442] Brock, T.D. and Gustafson, J. (1976) Ferric iron reduction by sulfur-and iron-oxidizing bacteria. Appl. Environ. Microbiol. 32, 567–571.

[443] Thermophiles: General, Molecular and Applied Microbiology (Brock, T.D., Ed.), John Wiley and Sons, (1986) New York.

[444] Extremophiles: Microbial Life in Extreme Environments (Horikoshi, K. and Grant, W.D. Eds.), Wiley-Liss, (1998) New York.

[445] Oremland, R.S., Hollibaugh, J.T., Maest, A.S., Presser, T.S., Miller, L.G. and Culbertson, C.W. (1989) Selenate reduction to elemental selenium by anaerobic bacteria in sediments and culture: biogeochemical significance of a novel sulfate-independent respiration. Appl. Environ. Microbiol. 55, 2333–2343.

[446] Shock, E.L. (2001) Corrections to standard partial molal enthalpies of formation of aqueous species. Geochim. Cosmochim. Acta, in preparation.

[447] Robie, R.A. and Hemingway, B.S. (1995) Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pa) Pressure and at Higher Temperatures, US Geological Survey Bulletin, vol. 2131, United States Government Printing Office, Washington, DC.

[448] Fredrickson, D.R. and Chasanov, M.G. (1971) The enthalpy of molybdenum disulfide to 1200 K by drop calorimetry. J. Chem. Thermo. 3, 693–696.

[449] O'Hare, P.A.G., Lewis, B.M. and Parkinson, B.A. (1988) Standard molar enthalpy of formation by flourine-combustion calorimetry of tungsten diselenide (WSe_2). Thermodynamics of high-temperature vaporization of WSe_2. Revised value of the standard molar enthalpy of formation of molybdenite (MoS_2). J. Chem. Thermo. 20, 681–691.

[450] McCollom, T.M. and Shock, E.L. (1997) Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal systems. Geochim. Cosmochim. Acta 61, 4375–4391.

[451] Stull, D.R., Westrum, E.F., Jr. and Sinke, G.C. (1969) The Chemical Thermodynamics of Organic Compounds, John Wiley and Sons, New York.

[452] Plyasunov, A.V., O'Connell, J.P., Wood, R.H. and Shock, E.L. (2001) Infinite dilution partial molar properties of aqueous nonelectrolytes. III. Prediction algorithm and parameters for some inorganic solutes. Geochim. Cosmochim. Acta, in preparation.