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Reviews

Microbial energetics applied to waste repositories

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Summary. Through their catalytic abilities microbes can increase rates of chemical reactions which would take a very long time to reach equilibrium under abiotic conditions. Microbes also alter the concentration and composition of chemicals in the environment, thereby creating new conditions for further biological and chemical reactions. Rates of degradation and possible indirect consequences on leaching rates in waste repositories are a function of the presence or absence of microbes and of the conditions which allow them to become catalytically active.

Microbially mediated reactions are no exception to the rule that all chemical processes are basically governed by thermodynamic laws. Naturally occurring processes proceed in the direction that leads to the minimal potential energy level attained when equilibrium is reached. A continuous supply of energy to an ecosystem in the form of biochemically unstable compounds maintains non-equilibrium conditions, a prerequisite for all chemotrophic life. Energy is released as a chemical reaction progresses towards equilibrium. Microbes scavenge that portion of the free energy of reaction (ΔG_r) which can be converted into biochemically usable forms during the chemical oxidation processes. As 'electrontransfer catalysts', the microorganisms mediate reactions which are thermodynamically possible thereby stimulating reaction rates. Decomposition and mineralization in systems without a continuous supply of substrates and oxidants will lead to equilibria with minimal free energy levels at which point further microbial action would cease. The differences in the free energy levels of reactions (ΔG_r), represent the maximal energy which is available to microorganisms for maintenance and growth. How much of the released free energy will be conserved in energy-rich bonds, compounds (e.g. ATP), and chemical potentials (e.g. emf) useful for biosynthesis and biological work is characteristic for the microbes involved and the processes and metabolic routes employed.

Materials whose elements are not present in the most oxidized form attainable in the oxic environment of our planet are potentially reactive. Microbial activities are associated only with chemical reactions whose free energy changes are exergonic. This should be kept in mind for all investigations related to the role of microbes in repositories or in the layout of proper waste storage conditions. Rigorous application of thermodynamic concepts to environmental microbiology allows one to develop models and design experiments which are often difficult to conceive of in complex natural systems from physiological information alone. Thermodynamic considerations also aid in selecting proper deposition conditions and in carrying out thoughtful experiments in areas related to microbial ecology of waste repositories.

Key words. Microbial ecology; ecosystems; state parameters; microbial activity; thermochemical values; group increment method; Gibbs free energy of reaction; bitumen degradation; nuclear waste repositories.

Introduction

This presentation is an attempt to apply chemical thermodynamics to microbial ecology. I would like to illustrate, how simple concepts taken from the theory of chemical equilibrium thermodynamics might enable one to explain microbial action in natural and artificial ecosystems. Emphasis is placed on three aspects:

1) the microbial mediation and the consequences on habitat conditions of the degradation of organic substrates with the multitude of oxidants which are accessible to microbes; 2) the meaning of the basic laws of thermodynamics in ecophysiology and 3) evaluating and summarizing a consistent dataset of thermochemical values of inorganic and organic compounds involved in microbially mediated processes.

It seems appropriate to consider in this discussion the broad spectrum of enzymatic abilities present in the microbial communities of particular environments as a whole rather than looking at single physiological traits. This geo-microbiological approach can be employed to understand the multitude of microbially mediated oxidation-reduction reactions, their sequence under environmental conditions, their synergistic coupling and the consequences for dissolution and precipitation processes. Thus, chemical thermodynamics becomes a tool to make predictions about the behavior of microbial communities involved in biogeochemical processes in nature. It can also help to develop a unifying view about the role in geobiochemical processes of the great metabolic diversity of microbes.

The basic conclusions drawn from the 'eco-thermodynamic' thoughts might be helpful in designing material repositories in such a way that chemical reactivity and microbial action on the components are minimal or maximal. These conclusions might also be useful in predicting the long-term behavior of potentially reactive wastes stored under particular conditions. It should become clear that by understanding the few basic concepts to be developed here one can better evaluate microbially mediated processes thought to be relevant under conditions in waste repositories. The concepts can be a help in the development of appropriate models and permit one to define measures which would suppress or enhance microbial action.

Thermodynamic non-equilibrium conditions are a necessary prerequisite for chemical transformations to proceed but they are not a sufficient cause for microbial mediation. The mere presence of oxidizable materials in a microbially settled environment does not guarantee microbial action on the substrates per se. Unless the presence of usable oxidants, water activity (a_w), the nutrients necessary for growth and the prevailing activities of dissolved and solubilizable chemical species favor biochemical reactivity, the oxidizable material may escape microbial degradation. Eco-thermodynamic considerations are meaningful only when they are considered together with the environmental conditions which support microbial life and the physiological abilities of the indigenous microbes.

For natural cycles to function properly and to assure cycling of the elements through synthetic and degradative processes one would have to postulate that the cycles work for all components completely. This is not the case. Large amounts of ancient photosynthesis products stored in peats, coal, oil, etc., have been removed from continuous cycling. They represent sinks of organic matter which might still be mineralized under favorable oxidation conditions. Some were deposited in ancient anoxic ecosystems probably due to oxidant limitation. Either inorganic oxidants were depleted or it became thermodynamically impossible to couple prevailing oxidation reactions with available oxidants to give an exergonic reaction. The conditions might have been similar to those we observe today in sediments of eutrophic lakes and in certain ocean basins.

But even in the absence of inorganic oxidants, mineralization would be expected to proceed by fermentative processes coupled to methanogenesis as long as the overall-process remains exergonic. Observations in fossil carbon sinks and in modern sediments of eutrophic lakes demonstrate that microbially mediated mineralization can also be inadequate because microbes simply lack the necessary enzymes to break certain chemical bonds. Microbial inadequacy in anoxic degradation of lignins and certain man-made synthetic chemicals are modern examples which demonstrate that mineralization does not always take place rapidly in spite of an ample amount of oxidants and exergonic reaction conditions. The choice of a proper matrix material for waste containment might make use of this phenomenon of microbial inadequacy.

With respect to waste repositories we may conclude

- Separating reactive materials or maintaining environmental conditions unfavorable to microbial activity can prevent transformations. Continuously providing oxidizable materials with potential oxidants and mixing them appropriately, on the other hand, can lead to vigorous microbial action.
- Microbes can only thrive on and catalyze reactions as long as the reactions are exergonic. Energetic synergism between microbes is no contradiction to this rule. An oxidation reaction which is basically endergonic will proceed if it can be coupled to a second reaction which is strongly exergonic. The overall-reaction might be catalyzed by microbes acting synergistically, gaining energy for growth from coupled, exergonic overall-reactions.
- Though in any ecosystem one can exclude from consideration any reactions which are thermodynamically unfavorable, it does not necessarily follow that all thermodynamically favorable reactions will proceed at measurable rates. The capacity of the environment to accommodate these reactions must also be met.
- Information needed to predict microbial activities includes the qualitative and quantitative composition of the waste and its containments, temperature, pressure and water activity at the site, accessibility by external sources of oxidants and nutrients, and escape routes of possible degradation products.

One might conclude that precisely defining the micro-environmental factors in a repository and evaluating their role on microbial behavior should be the primary tasks of 'repository geo-microbiologists'.

1. The potential of thermodynamics in microbial ecology

It is appropriate to describe microbial ecosystems in terms of habitats, conditions, organisms and reactions. The prevailing conditions determine the chemical reactions which are thermodynamically possible. They also select for the microorganisms with the enzymatic capacity to catalytically mediate the reactions. Microbial life can only be supported in a habitat as long as thermodynamic non-equilibrium conditions are maintained. If natural ecosystems were isolated thermodynamic systems they would rapidly head towards equilibrium, i.e., a state of maximum entropy (S) and minimal free energy (G). Through the continuous exchange of enthalpy (H) and entropy – associated with the flow of matter across the boundary of the ecosystem – the free energy content is maintained above equilibrium conditions. In contained waste repositories these prerequisites are not necessarily fulfilled.

Renewing biomass through biochemical synthesis is one of the main tasks of microorganisms in evolution and ecology. Since biosyntheses are basically endergonic processes, the microorganisms need to couple them, under chemotrophic conditions, with exergonic dissimilation reactions and, under phototrophic conditions, with radiation conversion processes. The Gibbs free energy made available while dissimilation reactions shift toward equilibrium ($\Delta G_r < 0$) is employed to drive assimilation reactions ($\Delta G_r > 0$), i.e., the free energy released by the dissimilatory reaction system is partially used to increase the enthalpy and reduce the entropy of the organismic system (e.g., for the formation of new biomass). The mechanism and the efficiency by which microorganisms transfer energy into enthalpy increase and entropy decrease under natural conditions is the fundamental content of ecological bioenergetics.

The *extent* of the non-equilibrium state determines the bioenergetic capacity of an ecosystem. Non-equilibrium is maintained by a steady supply of oxidizable substrates and the removal of reaction products; it is quantitatively described by their concentrations. The larger the differences of free energy of reaction are between actual environmental state and equilibrium ($\Delta G_r \ll 0$) the more readily microbially mediated reactions might proceed. While a positive value of ΔG_r is a clear indication that the particular reaction is not feasible, a large negative ΔG_r is not a sufficient indication that a reaction will occur measurably in a microbial ecosystem. The reaction rate might be too slow, the enzymatic pathways necessary for substrate conversion might be absent or inhibited, or alternative reactions might compete with the biochemical ones.

In the following paragraphs I will summarize some rules of thermodynamics and illustrate their application in microbial ecology.

1.1 The redox-concept in microbiology

The oxidation of organic molecules with inorganic oxidants can be conceptually combined. By assigning formal oxidation states to the redox-labile elements in organic compounds one can stoichiometrically balance chemical equations for microbially mediated reactions involving organic and inorganic substrates and products. Assigning oxidation states to single atoms in organic molecules is artificial because it formally assigns shared electrons in bonding orbitals between atoms of different electronegativity fully to the more electronegative atom of a covalent bond. But by doing this we can count the number of electrons belonging to each atom, as one frequently does for inorganic ions, and thus balance microbially mediated electron transfer.

Some of the most common elements in biological systems (H, C, N, O, S, Mn and Fe) exhibit multiple oxidation states. Phosphorus which is also essential for all living organisms is a redox-conservative element. In biological compounds it is present in the oxidation state V + , in inorganic ions as well as covalently bound in organic compounds.

The oxidation state is determined by the number of exchangeable electrons present in the outer orbitals. The elemental configuration is assigned the oxidation state zero. Addition of electrons to the orbitals makes the oxidation state more negative, removal of electrons makes it more positive.

Mean oxidation states and the corresponding electron donating capacities are related as depicted in figure 1.1 for carbon, nitrogen and sulfur in several organic compounds. The carbon atom tetravalently bound to other carbons (R_4C) is assigned the oxidation state 0 (fig. 1.1 a). The carbon is reduced if R is replaced by hydrogen or phosphorus, and oxidized through bonds with oxygen, nitrogen or other more electronegative elements like halogens. It does not change through bonds to sulfur, which has the same electronegativity as carbon, or to other carbon atoms. The rules can be applied similarly to organically bound nitrogen and sulfur (figs 1.1 b and 1.1 c). So, for any atom the oxidation state may be computed by adding + 1 for each bond to a less electro-

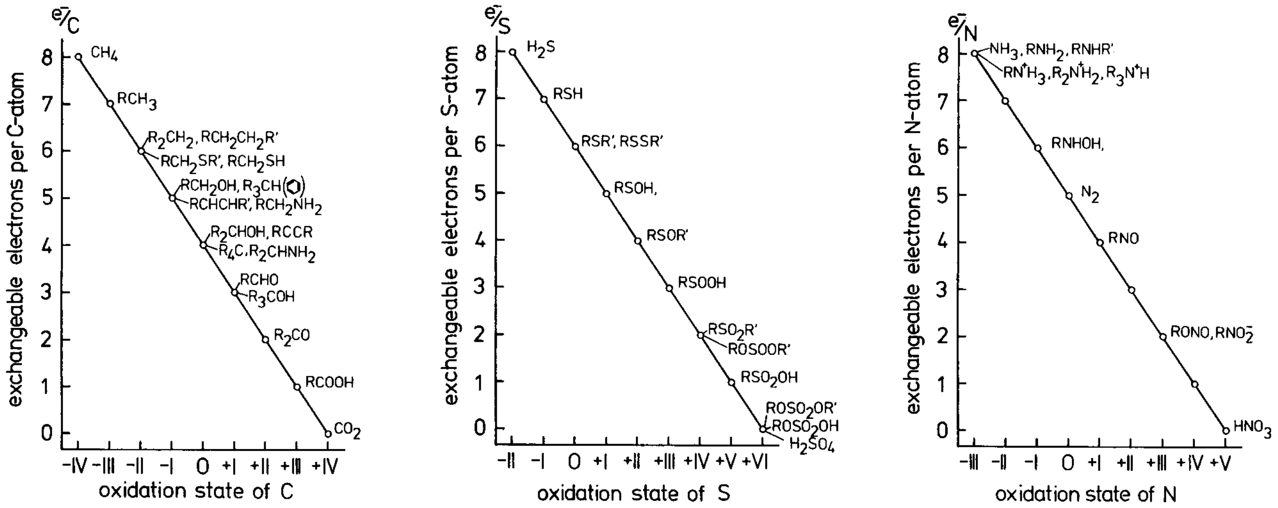


Figure 1.1. Oxidation states for carbon, sulfur and nitrogen in organic and inorganic compounds. *a*) Oxidation of the carbon atom in a compound occurs if hydrogen or phosphorus are removed or if oxygen, nitrogen, or halogens are added as bonding atoms. Hydrolysis of a carbon-carbon bond reduces one carbon by adding hydrogen but it oxidizes the other through the addition of a hydroxyl oxygen. *b*) Oxidation of the sulfur atom occurs if hydrogens are removed or if oxygen, halogens or nitrogen are added as bonding atoms. R symbolizes a carbon containing residue. The C–S bond does not change the oxidation state of either atom since both have the same electronegativity. *c*) Oxidation of the nitrogen atom occurs if hydrogen, carbon or sulfur atoms are removed or if oxygen or halogen atoms are added as bonding partners.

negative atom. Whereas a bond to a negatively *charged* atom diminishes the oxidation state by -1, a bond to a positively charged atom increases the oxidation state by $+1$. A bond to an identical atom or to one with the same electronegativity does not lead to a change in the oxidation state of the two bonding atoms. Thus, sulfur is assigned the oxidation state 0 in organic sulfides and disulfides if the bond partners are C or S or $-$I if one bond partner is H. The oxidation state of C or S will decrease when bonded to hydrogen or phosphorus atoms and increase when bonded to nitrogen and oxygen. Bonds of nitrogen with hydrogen, carbon, sulfur and phosphorus will decrease the oxidation state of the nitrogen atom while bonds to oxygen and halogens will increase it. The range for oxidation states in nitrogen containing compounds is therefore from $-$III as in amines and ammonia to $+$V as in the nitrate ion. By assigning these 'artificial' oxidation states one can link reduction and oxidation of organic molecules to biological reactions and describe them in terms of electron flow via microbial electron transport enzymes to either inorganic or organic electron acceptors. The ability of microbes to transfer electrons between particular reductants and oxidants is one of the most important features of their involvement in chemical reactions.

1.2 Stoichiometry of mineralization

In this section mineralization of organic matter is treated as a redox process under a variety of oxidation conditions. Oxygen trapped in the air at the time the waste is packaged will probably be used up rapidly and will not be resupplied. Anaerobic processes will then dominate inside the well-sealed containment and at least originally, the degradation products will be retained.

The amount, availability and accessibility of biochemically usable oxidants will further regulate the kind of microbial processes taking place under anoxic conditions. Some of the formal stoichiometries for degradation which have been used for model calculations are summarized in table 1.1. Degradation, associated with H_2-production will serve to outline the stoichiometries.

Organic waste is assumed to contain molecules predominantly made up of the elements C, H, O, N, P and S. These are present in the stoichiometric ratio a:b:c:d:e:f. Inorganic components of the degradable waste and halogens are omitted from the examples given in table 1.1. I assign a negative surplus charge h to the organic matter unit molecule

$$\langle C^{U}_{a} H_b O_c N_d P_e S_f M^{R+}_{g} \rangle^{h-}.$$

M symbolizes elements which are not considered in detail; R and U are the average oxidation state numbers of M and carbon respectively. Redox states of the other covalently bound elements are I+ for H, II- for O, III- for N, V+ for P and I- or 0 for S. During complete aerobic degradation redox states of N, S and C will change to V+, VI+ and IV+ respectively. Under anoxic conditions CO_2, NH_4^+, HS^-, H_2, CH_4 and other products still containing reduced C are formed. The number of electrons which can be transferred from the organic carbon is $n = 4 - U$ where U is calculated by applying the rules developed in section 1.1.:

$$U = -\tfrac{1}{a}(b - 2c - 3d + 5e - f + gR + h).$$

Fermentative breakdown of organic matter associated with hydrogen gas production, for example, is described by the stoichiometry:

$$\boxed{\begin{array}{c} \langle C^{U}_{a}H_bO_cN_dP_eS^{I-}_{f}M^{R+}_{g}\rangle^{h-} + zH_2O \\ \downarrow \\ aCO_2 + yH^+ + xH^0_2 + dNH^+_4 + eHPO^{2-}_4 + fHS^- \\ + gM^{R+} \end{array}}$$

Expressions for the 4 unknowns z, y, x and U are obtained from balance equations for oxygen, charges, hydrogen and electrons:

$$x = \tfrac{1}{2}(4a + b - 2c - 3d + 5e - 2f + gR + h)$$

$$y = -d + 2e + f - gR - h$$

$$z = 2a - c + 4e$$

U = as outlined above

The coefficients will be different, if other oxidation states are assigned to N and/or S.

Nutrients released during mineralization serve to support growth. Gaseous and ionic products might influence pH, buffering capacity, solubility, ionic strength and redox conditions of the habitat. By changing concentrations and activities of solutes, microbes thus contribute through mineralization (and biosynthesis) to the regulation of thermodynamically governed reactions.

Example: Applying the degradation scheme outlined above to the fermentative, hydrogenic breakdown of 'resin', whose composition is given in table 2.1., the amount of hydrogen gas produced per mol-equivalent of resin degraded can be determined from

$$\boxed{\begin{array}{c} \langle C^{U}_{19}H_{20}O_4N^{III-}_{1}S^{V+}_{1}\rangle^{+} + zH_2O \\ \downarrow \\ 19\,CO_2 + yH^+ + xH_2 + 1\,NH^+_4 + 1\,HS^- \end{array}}$$

with $h = -(-1) \quad (= y)$

and $U = \dfrac{+20 - 8 - 3 + 5 - 1}{-19} = -0.6842.$

Oxidation states of N, present in quaternary ammonium groups, and of S, present in sulfonate groups, are III- and

Table 1.1. Degradation of organic matter of composition $\langle C_aH_bO_cN_dP_eS_f\rangle^{h-}$ (modeling stoichiometries for dissimilation processes)

Degradation process	Reactants: Oxidant	H^+	HPO_4^{2-}	NO_3^-, NH_4^+	SO_4^{2-}, HS^-	$CH_4, CH_3COO^-, H_2, Fe^{2+}$	CO_2	H_2O
Aerobic respiration	O_2: $-\frac{1}{4}(4a+b-2c+5d+5e+6f+h)$	$d+2e+2f-h$	e	NO_3^-: d	SO_4^{2-}: f	–	a	$\frac{1}{2}(b-d-3e-2f+h)$
Sulfidogeneses from sulfate (complete)	SO_4^{2-}: $-\frac{1}{8}(4a+b-2c-3d+5e-2f+h)$	$-\frac{1}{8}(4a+b-2c+5d-11e-10f+9h)$	e	NH_4^+: d	HS^-: $\frac{1}{8}(4a+b-2c-3d+5e+6f+h)$	–	a	$\frac{1}{2}(b-3d-3e-2f+h)$
Sulfidogeneses from sulfate (incomplete)	SO_4^{2-}: $-\frac{1}{8}(2a+b-2c-3d+5e+2f+h)$	$-\frac{1}{8}(b-2c+5d-11e-10f+9h)$	e	NH_4^+: d	HS^-: $\frac{1}{8}(2a+b-2c-3d+5e+6f+h)$	CH_3COO^-: $(C_2H_3O_2^-)$ $\frac{1}{4}a$	$\frac{1}{2}a$	$-\frac{1}{2}(a-b+3d+3e+2f-h)$
Sulfidogeneses from sulfur	$S^0_{(s)}$: $-\frac{1}{2}(4a+b-2c-3d+5e-2f+h)$	$\frac{1}{2}(4a+b-2c-5d+9e-h)$	e	NH_4^+: d	HS^-: $\frac{1}{2}(4a+b-2c-3d+5e+h)$	–	a	$-(2a-c+4e)$
Methanogeneses	–	$-(d-2e-f+h)$	e	NH_4^+: d	HS^-: f	CH_4: $\frac{1}{8}(4a+b-2c-3d+5e-2f+h)$	$\frac{1}{8}(4a-b+2c+3d-5e+2f-h)$	$-\frac{1}{4}(4a-b-2c+3d+11e+2f-h)$
Acetogeneses	–	$\frac{1}{8}(4a+b-2c-11d+21e+6f-7h)$	e	NH_4^+: d	HS^-: f	CH_3COO^-: $(C_2H_3O_2^-)$ $\frac{1}{8}(4a+b-2c-3d+5e-2f+h)$	$\frac{1}{4}(-b+2c+3d-5e+2f-h)$	$-\frac{1}{4}(4a-b-2c+3d+11e+2f-h)$
Hydrogeneses	–	$-(d-2e-f+h)$	e	NH_4^+: d	HS^-: f	H_2: $\frac{1}{2}(4a+b-2c-3d+5e-2f+h)$	a	$-(2a-c+4e)$
Ferric iron reduction	$FeO(OH)_{(s)}$ $-(4a+b-2c-3d+5e-2f+h)$	$-(8a+2b-4c-5d+8e-5f+3h)$	e	NH_4^+: d	HS^-: f	Fe^{2+}: $(4a+b-2c-3d+5e-2f+h)$	a	$(6a+2b-3c-6d+6e-4f+2h)$

The – sign indicates consumption of the particular reactant.

V+ respectively. The values for $y = 1$ and $z = 34$ follow from charge and oxygen balances respectively, for x from the electron balance equation

$$2x + 8 + 8 = 18(4 - U) + 8 + 1$$

which yields $x = 41$ moles (equivalent to 0.919 Nm^3) of hydrogen gas per mol (= 358 g) of resin degraded.

1.3 Application of thermodynamic laws to environmental processes

The laws of equilibrium thermodynamics are applicable to closed systems with constant pressure and temperature. Quantitative thermochemical values are most frequently listed for standard conditions of pressure ($p^0 = 1.01325 \cdot 10^5$ Pa $\triangleq$ 1 atm or 1 bar $\triangleq 10^5$ Pa) and temperature (298.15 K) (tables A.1 and A.2). Applying thermodynamics to natural ecosystems requires due appreciation of these restrictions and proper corrections for deviations from standard conditions.

The meaning of ΔH_r^0, ΔS_r^0, ΔG_r^0 and ΔG_r will be discussed for a few examples and the influence of microbial activity on certain state parameters (Q, IAP, K_s, pH, E and pe) and the corrections which need to be considered most often will be outlined in this section. Most of the reactions illustrating the discussion points are summarized in tables 1.3 and 1.4.

1.3.1 Direction and likelihood of reactions. A reaction is termed exothermic if *enthalpy* escapes from the reaction system ($\Delta H_r < 0$); it is endothermic if enthalpy needs to be supplied ($\Delta H_r > 0$). Exothermic reactions are more probable since they tend to transfer enthalpy which is stored in the system to its surroundings. Endothermic reactions, on the other hand, increase enthalpy within the system, mostly as heat. Thus the formation of certain pure solid phases and molecular complexes increase the enthalpy of the system in which the reactions take place. The degradation of biomass and the decay of minerals can lead to an increase or a decrease in *entropy* (ΔS_r = molecular disorder). Mineralization of certain organic molecules and the formation of stable aquo-complexes from a few pure solid phases, are reactions which decrease ΔS_r *and* ΔH_r of the system. Entropy changes associated with biomass formation depend on the kind of substrates used for biomass synthesis.

The *free energy difference* (ΔG_r) which describes in a single term the effects of enthalpy and entropy changes of a system is expressed by the free energy equation:

$$\Delta G_r = \Delta H_r^0 - T \cdot \Delta S_r^0 + R \cdot T \cdot \ln Q.$$

The equation states that an increase in molecular disorder of a reaction system is proportional to an augmentation in Gibbs free energy. Free energy of a system (ΔG_r^0) is minimal, entropy is maximal and ΔG_r is zero once the system has attained equilibrium. In the free energy equation above $\Delta G_r^0 = \Delta H_r^0 - T \cdot \Delta S_r^0$ is formulated for standard conditions. Superscript and subscript indicate: ^{0} = reactants and products are in their pure state, present at a pressure of 1 atm if the reactants are gases or 1-molal concentrations if the reactants are solutes; r stands for *r*eaction; it serves to distinguish ΔG_r^0 from ΔGf^0 which applies to the formation reaction from the elements in their stable state and to the combustion reaction with oxygen.

A positive value for ΔG_r^0 (endergonic) indicates that the reaction is improbable under standard state conditions in the stoichiometric direction for which ΔG_r^0 has been calculated. The reverse reaction ($\Delta G_r^0 < 0$; exergonic) would then be the favored one. Reactions are exergonic or endergonic depending on the magnitude and the sign of ΔH_r^0 and ΔS_r^0. Exothermic reactions always lead to exergonic ones if the system entropy increases (case A, table 1.2.). Exothermic reactions associated with an entropy decrease, however, can become exergonic or endergonic (cases B and C, table 1.2) depending on the magnitude of the associated entropy changes. Dissolution reactions (table 1.3, reactions 32–35) are examples illustrating case C.

Entropy also increases if certain pure solid phases or complexes are formed from thermodynamically more stable dissolved species (the order of the system decreases in these cases). Examples listed in table 1.3. are the formation of carbonate minerals (reactions 11, 22–25 and 28) and of pyrrhotite (reaction 20) from aquo-complexes, and certain complex-forming reactions for Ca^{2+} (reac-

Table 1.2. Probabilities of reactions to occur. The influence of the sign of ΔH_r^0 and ΔS_r^0 on ΔG_r^0.

Case		if ΔH_r^0 (3)	and ΔS_r^0 (4)	then ΔG_r^0 (1), (5)	Conditions	Overall reaction according to ΔG_r^0	Examples (2)
A	exothermic	−	+	−	always	exergonic	6, 7, 8, 10, 11, 12, 20 etc.
B	exothermic	−	−	−	$\lvert T \cdot \Delta S_r^0 \rvert < \lvert \Delta H_r^0 \rvert$	exergonic	2, 3, 9, 13, 17–19 etc.
C	exothermic	−	−	+	$\lvert T \cdot \Delta S_r^0 \rvert > \lvert \Delta H_r^0 \rvert$	endergonic	1, 5, 32–35
D	endothermic	+	+	+	$\lvert T \cdot \Delta S_r^0 \rvert < \lvert \Delta H_r^0 \rvert$	endergonic	14–16, 37
E	endothermic	+	+	−	$\lvert T \cdot \Delta S_r^0 \rvert > \lvert \Delta H_r^0 \rvert$	exergonic	22–25, 29
F	endothermic	+	−	+	always	endergonic	4, 30, 31, 38

(1) $\Delta G_r^0 = \Delta H_r^0 - T \cdot \Delta S_r^0$
(2) reference to reactions of table 1.3.
(3) + : system requires enthalpy; − : system releases enthalpy.
(4) + : system entropy increases; − : system entropy decreases.
(5) + : system requires energy; − : system releases free energy.

Table 1.3. Thermodynamic coupling of selected redox-reactions (commented on in the text)

Nr.	Stoichiometric reaction equation	ΔH_r^0 [kJ/mol]	ΔS_r^0 [J/K · mol]	$T \cdot \Delta S_r^0$ [kJ/mol]	ΔG_r^0 [kJ/mol]
1	$C_7H_{8(g)} + 8\,FeO(OH)_{(s)} + 4\frac{1}{2}\,H^+_{(aq)} \longrightarrow 3\frac{1}{2}\,CH_3COO^-_{(aq)} + 8\,Fe(OH)^+_{(aq)} + H_2O_{(l)}$	− 169.39	− 717.9	−214.04	+ 51.65
2	$C_7H_{8(g)} + 36\,FeO(OH)_{(s)} + 36\,H^+_{(aq)} \longrightarrow 7\,CO_{2(aq)} + 36\,Fe(OH)^+_{(aq)} + 22\,H_2O_{(l)}$	− 799.39	−1429.1	−426.09	− 373.3
3	$C_7H_{8(g)} + 9\,O_{2(aq)} \longrightarrow 7\,CO_{2(aq)} + 4\,H_2O_{(l)}$	−3984.49	− 215.0	− 64.10	−3920.39
4	$C_7H_{8(g)} + 2\,CO_{2(aq)} + 5\,H_2O_{(l)} \longrightarrow 4\frac{1}{2}\,CH_3COO^-_{(aq)} + 4\frac{1}{2}\,H^+_{(aq)}$	+ 19.61	− 514.7	−153.46	+ 173.1
5	$C_7H_{8(g)} + 1\,SO^{2-}_{4(aq)} + 3\,H_2O_{(l)} \longrightarrow 3\frac{1}{2}\,CH_3COO^-_{(aq)} + 1\,HS^-_{(aq)} + 2\frac{1}{2}\,H^+_{(aq)}$	− 1.59	− 182.3	− 54.35	+ 52.76
6	$CH_3COO^-_{(aq)} + 1\,SO^{2-}_{4(aq)} + 2\,H^+_{(aq)} \longrightarrow 2\,CO_{2(aq)} + 1\,HS^-_{(aq)} + 2\,H_2O_{(l)}$	− 21.2	+ 332.4	+ 99.11	− 120.30
7	$C_7H_{8(g)} + 4\frac{1}{2}\,SO^{2-}_{4(aq)} + 4\frac{1}{2}\,H^+_{(aq)} \longrightarrow 7\,CO_{2(aq)} + 4\frac{1}{2}\,HS^-_{(aq)} + 4\,H_2O_{(l)}$	− 75.79	+ 981.1	+ 292.51	− 368.3
8	$2\,HS^-_{(aq)} + 2\,FeO(OH)_{(s)} + 3\,H^+_{(aq)} \longrightarrow FeS_{(s)} + Fe(OH)^+_{(aq)} + S^0_{(s)} + 3\,H_2O_{(l)}$	− 129.0	+ 13.2	+ 3.94	− 132.94
9	(Reaction 5) + $\frac{1}{2}$ · (Reaction 8)	− 66.09	− 175.7	− 52.38	− 13.70
10	(Reaction 7) + $2\frac{1}{4}$ · (Reaction 8)	− 366.04	+1010.8	+301.37	− 667.41
11	$Fe(OH)^+_{(aq)} + 1\,HCO^-_{3(aq)} \longrightarrow FeCO_{3(s)} + H_2O_{(l)}$	− 9.7	+ 100.6	+ 29.99	− 39.7
12	(Reaction 7) + $2\frac{1}{4}$ · (Reaction 8) + $2\frac{1}{4}$ · (Reaction 11)	− 387.86	+1237.15	+368.86	− 756.72
13	(Reaction 5) + $\frac{1}{2}$ · (Reaction 8) + $\frac{1}{2}$ · (Reaction 11)	− 70.94	− 125.4	− 37.39	− 33.55
14	$C_7H_{8(g)} + 7\,H_2O_{(l)} \longrightarrow 3\frac{1}{2}\,CH_3COO^-_{(aq)} + 8\,e^-_{(g)} + 11\frac{1}{2}\,H^+_{(aq)}$	+ 249.61	+ 15.7	+ 4.68	+ 244.93
15	$C_7H_{8(g)} + 14\,H_2O_{(l)} \longrightarrow 7\,CO_{2(aq)} + 36\,e^-_{(g)} + 36\,H^+_{(aq)}$	+1054.61	+1872.1	+558.2	+ 496.4
16	$CH_3COO^-_{(aq)} + 2\,H_2O_{(l)} \longrightarrow 2\,CO_{2(aq)} + 8\,e^-_{(g)} + 7\,H^+_{(aq)}$	+ 230.0	+ 530.4	+158.14	+ 71.86
17	$FeO(OH)_{(s)} + 1\,e^-_{(g)} + 2\,H^+_{(aq)} \longrightarrow Fe(OH)^+_{(aq)} + H_2O_{(l)}$	− 75.7	− 167.4	− 49.9	− 25.8
18	$SO^{2-}_{4(aq)} + 8\,e^-_{(g)} + 9\,H^+_{(aq)} \longrightarrow HS^-_{(aq)} + 4\,H_2O_{(l)}$	− 251.2	− 198.0	− 59.03	− 192.2
19	$O_{2(g)} + 4\,e^-_{(g)} + 4\,H^+_{(aq)} \longrightarrow 2\,H_2O_{(l)}$	− 571.6	− 326.0	− 97.20	− 474.4
20	$HS^-_{(aq)} + Fe(OH)^+_{(aq)} \longrightarrow FeS_{(s)} + H_2O_{(l)}$	− 43.9	+ 96.4	+ 28.74	− 72.64
21	$HCO^-_{3(aq)} \longrightarrow CO^{2-}_{3(aq)} + H^+_{(aq)}$	+ 14.9	− 148.1	− 44.15	+ 59.05
22	$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow CaCO_{3(s)}$ (Calcite)	+ 13.0	+ 202.9	+ 60.49	− 47.49
23	$Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow MgCO_{3(s)}$ (Magnesite)	+ 48.1	+ 260.7	+ 77.73	− 29.63
24	$Fe^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow FeCO_{3(s)}$ (Siderite)	+ 25.6	+ 286.8	+ 85.51	− 59.91
25	$Mn^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow MnCO_{3(s)}$ (Rhodochrosite)	+ 3.7	+ 216.3	+ 64.49	− 60.79
26	$Ca(HCO_3)^+_{(aq)} \longrightarrow CaCO_{3(s)} + H^+_{(aq)}$				+ 16.2
27	$Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \longrightarrow Ca(HCO_3)^+_{(aq)}$				− 4.5
28	$Ca(OH)^+_{(aq)} + HCO^-_{3(aq)} \longrightarrow CaCO_{3(s)} + H_2O_{(l)}$	− 36.4	+ 86.2	+ 25.7	− 62.1
29	$Ca^{2+}_{(aq)} + OH^-_{(aq)} \longrightarrow Ca(OH)^+_{(aq)}$	+ 8.5	+ 49.2	+ 14.67	− 6.17
30	$Ca^{2+}_{(aq)} + H_2O_{(l)} \longrightarrow Ca(OH)^+_{(aq)} + H^+_{(aq)}$	+ 64.3	− 31.4	− 9.36	+ 73.66
31	$H_2O_{(l)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)}$	+ 55.8	− 80.6	− 24.03	+ 79.83
32	$CaSO_{4(s)}$ (Anhydrite) $\longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$	− 18.3	− 141.0	− 42.04	+ 23.74
33	$CaSO_4 \cdot 2\,H_2O_{(s)}$ (Gypsum) $\longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)} + 2\,H_2O_{(l)}$	− 1.4	− 88.6	− 26.42	+ 25.02
34	$CaMg(CO_3)_{2(s)}$ (Dolomite) $\longrightarrow Ca^{2+}_{(aq)} + Mg^{2+}_{(aq)} + 2\,CO^{2-}_{3(aq)}$	− 37.5	− 460.2	−137.21	+ 99.71
35	$CaCO_{3(s)}$ (Aragonite) $\longrightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$	− 12.8	− 198.7	− 59.24	+ 46.44
36	$4\,CO_{2(aq)} + 17\,e^-_{(g)} + 17\,H^+_{(aq)} \longrightarrow \langle C_4H_7O_3\rangle_{(g)} + 5\,H_2O_{(l)}$	− 293.56	− 893.65	−266.44	− 27.12
37	$2\frac{1}{8} \cdot CH_3COO^-_{(aq)} + 2\frac{1}{8}\,H^+_{(aq)} \longrightarrow \langle C_4H_7O_3\rangle_{(g)} + \frac{1}{4}\,CO_{2(aq)} + \frac{3}{4}\,H_2O_{(l)}$ ≙ (Reaction 36) + $2\frac{1}{8}$ · (Reaction 16)	+ 195.19	+ 233.45	+ 69.60	+ 125.59
38	$\frac{17}{36}\,C_7H_{8(g)} + \frac{25}{36}\,CO_{2(aq)} + 1\frac{11}{18}\,H_2O_{(l)} \longrightarrow \langle C_4H_7O_3\rangle_{(g)}$ ≙ (Reaction 36) + $\frac{17}{36}$ · (Reaction 15)	+ 204.45	− 9.6	− 2.86	+ 207.31
39	(Reaction 38) + 0.56273 · (Reaction 7)	+ 161.8	+ 542.5	+161.8	0
40	0.56273 · (Reaction 7)	− 42.6	+ 552.1	+164.7	− 207.31

Standard conditions: $T = 298.15\,K$, $p = 1\,atm$, concentration = 1 − molal, $pH = 0$, $I = 0$

tion 29). The carbonate precipitation reactions lose enthalpy ($\Delta H_r > 0$) *and* are associated with an increase in the systems entropy ($\Delta S_r > 0$) which amounts to a decrease in molecular order. At first this might be surprising, since crystals are highly ordered structures. But the dissolved aquo-complexes are even more highly ordered molecular entities than the corresponding solid carbonates. The formation of aquo-complexes of Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and CO_3^{2-} from the elements in their stable standard states is associated with an entropy decrease ($Sf^0 < 0$, table A.1) while the formation from the elements of the corresponding mineral phases leads to an entropy increase ($Sf^0 > 0$). The formation of the solid mineral phases from the aquo-complexes (reactions 22–25, table 1.3) are thus associated with an entropy increase ($\Delta S_r^0 > 0$). Larger values of ΔS_r^0 subtracted from ΔH_r^0 lead to more negative values for ΔG_r^0. The precipitation reactions are exergonic and remain so as long as $|T \cdot \Delta S_r| > |\Delta H_r|$ (case E, table 1.2).

The endothermic dissociation reactions of other complexes (reaction 30) and of water (reaction 31) (case F, table 1.2) and the exothermic dissolution of sulfate and carbonate components of the solid habitat matrix (reactions 32–35, table 1.3., case C, table 1.2) lead to a decrease in entropy and, for all cases mentioned, to endergonic reactions.

The extent of degradation and the oxidant employed determine the likelihood of reactions to occur and the free energy gain for standard conditions. Reactions 1–7 (table 1.3) illustrate these points. Incomplete degradation of toluene with various oxidants under anoxic conditions is endergonic (reactions 1, 4, 5). Complete anaerobic degradation (reactions 2, 6, 7) is exergonic. Employing oxygen as the electron acceptor (reaction 3) leads to a greater than tenfold increase in ΔG_r^0. If endergonic reaction 5 is coupled to exergonic reaction 8, which describes the sulfidation of ferric(hydr)oxide, the incomplete degradation reaction can become exergonic (reaction 9). Coupling two or more exergonic reactions makes ΔG_r^0 of the overall reaction more negative. The conversion described by the coupled reactions becomes more favorable; reaction 10 is given as an example.

In a closed system, endergonic reactions 32–35 could proceed in the dissolution direction only if coupling them to mineral-consuming degradation reactions (e.g., sulfate consumption for the cases of gypsum or anhydrite dissolution) would make exergonic overall reactions. ΔG_r^0 for toluene degradation by sulfate reducing bacteria (reaction 7) can be more than doubled (reaction 12) under conditions which lead to the concomittant precipitation of pyrrhotite (reaction 8) and siderite (reaction 11). Incomplete degradation of toluene (reaction 5) will become exergonic when coupled under similar conditions (reaction 13).

If dissolution processes occur uncoupled from biological reactions (e.g., acid catalyzed dissolution of carbonates) they might put a halt on microbial activity by making environmental conditions thermodynamically unfavorable and physiologically inhibitory. Precipitation, dissolution and complex-formation coupled with degradation can thus increase or decrease the probability for biological degradation reactions to occur.

Overall reactions can be dissected into electrochemical half-reactions. Oxidation half-reactions listed (14–16 table 1.3) are formally endergonic, reduction half-reactions (17–19) are exergonic at standard conditions. The formalism of half-reactions is helpful for thermodynamic evaluations involving several reaction combination possibilities. I have also applied the formalism of half-reactions to describe redox-potentials (E) and electron-activity (pe) as environmental state parameters (see 1.3.7).

Thermodynamic analyses of individual reactions and half-reactions may be coupled in various ways allowing one to design scenarios and make predictions about the kind of reactions that can take place, the direction in which they will proceed, the likelihood of their occurrence and possible alterations of environmental conditions. Some of these points will be discussed in the following paragraphs.

1.3.2 Microbial alteration of ΔG_r. The *free energy of reaction* (ΔG_r) is contained in its reactants. Quantitatively it is the difference between the free energy of formation (Gf^0) of the products (P) and of the substrates (S) under non-equilibrium concentration conditions (neq) diminished by the free energy of formation contained in the reactants under equilibrium concentration conditions (eq):

$$\Delta G_r = (\Delta Gf^0)_{neq} - (\Delta Gf^0)_{eq}$$

with ΔGf^0 being defined as:

$$\Delta Gf^0 = \sum_j v_j Gf^0_{P_j} - \sum_i v_i Gf^0_{S_i}$$

The differences of the free energy of formation (ΔGf^0) are proportional to the activity ratios of the reactants:

$$(\Delta Gf^0)_{neq} = R \cdot T \cdot \ln \frac{\prod_j \{P_{j\,neq}\}^{v_j}}{\prod_i \{S_{i\,neq}\}^{v_i}} = R \cdot T \cdot \ln Q$$

$$(\Delta Gf^0)_{eq} = R \cdot T \cdot \ln \frac{\prod_j \{P_{j\,eq}\}^{v_j}}{\prod_i \{S_{i\,eq}\}^{v_i}} = R \cdot T \cdot \ln Keq$$

($v_{j,i}$ are stoichiometric coefficients, P and S designate products and substrates respectively and $Keq \equiv K^0$). ΔG_r thus becomes:

$$\Delta G_r = R \cdot T \cdot \ln Q - R \cdot T \cdot \ln K^0 \qquad (1)$$

$$\Delta G_r = R \cdot T \cdot \ln \frac{Q}{K^0} \qquad (2)$$

The reaction is exergonic as long as $\Delta G_r < 0$, which is fulfilled for $Q/K^0 < 1$. Equilibrium is characterized by $\Delta G_r = 0$ or $Q = K^0$. For $Q/K^0 > 1$, the reaction becomes endergonic ($\Delta G_r > 0$). Equation (1) is stated more frequently in the form

$$\Delta G_r = \Delta G_r^0 + R \cdot T \cdot \ln Q \qquad (3)$$

This implies that a reaction system which is not in the equilibrium state will release energy until equilibrium is attained ($\Delta G_r = 0$, $\Delta G_r^0 = -R \cdot T \cdot \ln K^0$). Microorganisms harvest portions of the free energy of reactions for biosynthesis and cellular work. By changing concentrations of reactants as a consequence of metabolic conversions, microbes influence Q and thus the direction of reactions. An example is acetogenesis from propionate:

$$CH_3CH_2COO^-_{(aq)} + 3\,H_2O_{(l)} \longrightarrow CH_3COO^-_{(aq)} + HCO^-_{3(aq)} + 3\,H_{2(aq)} + H^+_{(aq)}$$

The reaction is endergonic under standard conditions ($\Delta G_r^0 = +169.2$ [kJ/mol], $K^0 = 2.2791 \cdot 10^{-30}$). For the boundary conditions: pH = 7.5, $[HCO_3{}^-{}_{(aq)}] = 2 \cdot 10^{-2}$ [mol/l] remaining constant, initial acetate concentration = 10^{-6} [mol/l] and initial propionate concentration = 10^{-3} [mol/l] (neglecting activity corrections) applied in conjunction with equation (2) the reaction becomes exergonic if $[H_{2(aq)}] < 1.533 \cdot 10^{-6}$ [mol/l] which corresponds to $p_{H_2} = 1.857 \cdot 10^{-3}$ [atm]. Since other microorganisms scavenge H_2 thus maintaining its concentration below the thermodynamic threshold value of $1.533 \cdot 10^{-6}$ [mol/l] propionate degradation is more favored. If $[H_{2(aq)}]$ is kept at 10^{-7} [mol/l] by sulfate reducing bacteria living in close association with the propionate oxidizers, ΔG_r becomes -20.302 [kJ/mol]. At 10^{-9} and 10^{-12} [mol/l] H_2, ΔG_r is -54.550 and -105.922 [kJ/mol] respectively. At pH = 12 and 10^{-9} [mol/l] H_2, ΔG_r of the proton producing reaction above decreases to -80.236 [kJ/mol].

All reactions discussed in this review are assumed to take place in dilute aqueous solutions. The concentration of water is 55.51 [mol/l]. It remains unaltered even under conditions where H_2O is a substrate or a product of the reaction. The activity of water is 1 and can be included in the operational equilibrium constant. K^0 calculated from ΔG_r^0 is thus defined for ionic strength $I = 0$. Deviations from this convention (i.e., elevated solute concentrations = lowered water availability) require that the equilibrium constant be corrected by the terms discussed in the section on solubility products (see 1.3.5).

1.3.3 Effect of temperature on ΔG_r. The Gibbs free energy change of a reaction taking place at an actual *temperature* (T_{act}) which is different from the standard reference temperature (T_{ref}) can be calculated with the solution to the Gibbs-Helmholtz equation

$$\Delta G^0_{r,T_{act}} = \Delta G^0_{r,T_{ref}} \cdot \frac{T_{act}}{T_{ref}} + \Delta H^0_{r,T_{ref}} \cdot \frac{T_{ref} - T_{act}}{T_{ref}} \qquad (4)$$

The corresponding equilibrium constant at T_{act} is derived from

$$\Delta G^0_{r,T_{act}} = -2.3026 \cdot R \cdot T_{act} \cdot \log K^0_{act}$$

which gives

$$pK^0_{act} = pK^0_{ref} + \frac{\Delta H^0_{r,T_{ref}}}{2.3026 \cdot R} \cdot \frac{T_{ref} - T_{act}}{T_{ref} \cdot T_{act}} \qquad (5)$$

The solutions assume that temperature changes within the physiological temperature span do not influence ΔH_r^0 markedly.

Example: With the values for ΔG_r^0 and ΔH_r^0 for the dissociation of water at 298.15 K (reaction 31, table 1.3) one calculates $pK_W^0 = +13.9855$. ΔG_r^0 and pK_W^0 for T = 5 °C are calculated with equations (4) and (5) respectively:

$$\Delta G^0_{278} = +78.218 \text{ [kJ/mol]}$$

$$pK^0_{W/278} = 14.688$$

The example illustrates that the water dissociation reaction becomes less endergonic at lower temperatures. Similarly, a temperature decrease from 25 °C to 5 °C makes the dissociation reaction of bicarbonate (reaction 21, table 1.3) less endergonic (+ 59.05 vs + 56.09 [kJ/mol]). In turn the value for the second dissociation constant increases from $pK^0_{298} = 10.345$ to $pK^0_{278} = 10.533$.

The thermodynamic solubility product for calcite at 5 °C calculated from the values of reaction 22 (table 1.3) increases by 46% from $K^0_{s/298} = 4.788 \cdot 10^{-9}$ to $K^0_{s/278} = 6.982 \cdot 10^{-9}$ which indicates that calcite is slightly more soluble in low temperature environments.

1.3.4 Effect of pH on ΔG_r. Under certain circumstances it is more appropriate to define reference conditions for proton producing and consuming reactions for a pH-value different from 0.

The Gibbs free energy change of a reaction with all reaction partners, except protons, kept at their equilibrium conditions is labelled $\Delta G_r^{0\prime}$. It is calculated for a proton producing reaction

$$SH_q \Leftrightarrow S^{q-} + q \cdot H^+$$

from

$$\Delta G_r^{0\prime} = \Delta G_r^0 + R \cdot T \cdot \ln \frac{\{S^{q-}\} \cdot \{H^+\}^q_{act}}{\{SH_q\}} \qquad (6)$$

Since $\{S^{q-}\}$ and $\{SH_q\}$ do not change at standard state conditions, equation (6) reduces to

$$\Delta G_r^{0\prime} = \Delta G_r^0 + R \cdot T \cdot \ln \{H^+\}^q_{act}$$

which is

$$\Delta G_r^{0\prime} = \Delta G_r^0 - 2.3026 \cdot R \cdot T \cdot q \cdot pH_{act} \qquad (7)$$

(q always stands for the number of H^+ exchanged; it is + if protons are produced and − if protons are consumed).

For reactions under alkaline conditions, which might be created by the cement of the nuclear waste solidification matrix, it is more appropriate to evaluate the processes with standard free energy changes defined for the appropriate alkaline pH.

Example: The exergonic sulfate-reducing half-reaction (18 in table 1.3, $\Delta G^0_{r\,pH=0} = -192.2$ kJ/mol) will change into a strongly endergonic one at pH 12 (+ 424.3 kJ/mol). Acetate oxidation (16 in table 1.3), an endergonic half-reaction at pH 0 will become exergonic at pH 12 ($\Delta G^0_{r\,pH=12} = -407.618$ kJ/mol). The coupled proton consuming reaction (16 + 18) which is exergonic for standard conditions at pH 0 (− 120.34 kJ/mol) turns into an endergonic reaction at pH-values above 10.54.

Thus protons released or taken up by microbially mediated processes, regulate the course of reactions by altering ΔG_r. ΔG_r expressed as a function of pH is:

$$\Delta G_r = \Delta G_r^0 + 2.3026 \cdot R \cdot T \cdot (\log Q' - q \cdot pH_{act})$$

or (8)

$$\Delta G_r = 2.3026 \cdot R \cdot T \cdot (pK^0 + \log Q' - q \cdot pH_{act})$$

with

$$Q' = \frac{Q}{\{H^+\}^q_{act}} \quad \text{from} \quad Q = \frac{\prod_j \{P'_{j\,neq}\}^{v_j} \cdot \{H^+\}^q_{act}}{\prod_i \{S'_{i\,neq}\}^{v_i}}$$

1.3.5 Influence of microbial activity on solubility products. In biosynthesis and degradation microorganisms consume and produce dissolved ions. Thereby, the microbes *alter the ionic composition of the environment*. As a consequence ion activity products (IAP) and ionic strength (I) change which in turn affects equilibrium coefficients.

For the dissolution of a solid $X_xY_{y(s)}$ into its ionic products $X^{y+}_{(aq)}$ and $Y^{x-}_{(aq)}$:

$$X_xY_{y(s)} \Leftrightarrow x \cdot X^{y+}_{(aq)} + y \cdot Y^{x+}_{(aq)}$$

the equilibrium for standard conditions is

$$K_{eq} \mathrel{\hat{=}} K^0 = \frac{\{X\}^x \cdot \{Y\}^y}{\{X_xY_y\}}.$$

{ } designate activities. Subscripts and superscripts for charges and states are omitted for clarity. The activity of the solid phase is unity and the thermodynamic solubility product becomes thus $K^0_s = \{X\}^x \cdot \{Y\}^y$. For practical purposes the thermodynamic solubility product (K^0_s) is equal to the operational solubility product for standard conditions (esp. I = 0).

$$K^{0\prime}_s = [X]^x \cdot [Y]^y \tag{9}$$

([ ] designates concentrations.)

K^0_s and $K^{0\prime}_s$ are calculated from $\Delta G^0_r = -R \cdot T \cdot \ln K^0$. For reaction conditions in aqueous solutions, standard conditions are by convention those for which ionic strength and pH are 0. For conditions of I > 0 (but otherwise standard conditions), an actual solubility product is defined by

$$K'_s = [X]^x \cdot f^x_X \cdot [Y]^y \cdot f^y_Y \tag{10}$$

f_X and f_Y account for the activity changes of X and Y in a medium of I > 0. The actual solubility product thus becomes:

$$K'_s = K^{0\prime}_s \cdot f^x_X \cdot f^y_Y \tag{11}$$

Equation (11) can be transformed and written in the general form:

$$pK'_s = pK^{0\prime}_s - \log\left(\prod_j f_j^{v_j}\right) \equiv pK^{0\prime}_s - \sum_j v_j \log f_j \tag{12}$$

(j stands for the ionic reaction products, v_j designates their stoichiometries.)

Introducing activity correction factors (f_j) derived with the extended Debye-Hückel expression for ions in aqueous environments[18]

$$\log f_j = \frac{-A \cdot z_j^2 \cdot \sqrt{I}}{1 + a_j \cdot B \cdot \sqrt{I}} \tag{13}$$

(with z_j = charge, a_j = ion size parameter, A and B are parameters which depend on temperature and on ε_T, the temperature-dependent dielectric coefficient of water and I is ionic strength) into equation (12) gives

$$pK'_s = pK^{0\prime}_s + \sum_j \frac{v_j \cdot A \cdot z_j^2 \cdot \sqrt{I}}{1 + a_j \cdot B \cdot \sqrt{I}} \tag{14}$$

($pK^{0\prime}_s$ can of course be replaced by $\Delta G^0_r/2.3026 \cdot R \cdot T$). The operational solubility constant ($K^{0\prime}_s = 10^{-pK_s^{0\prime}}$) decreases with increasing ionic strength, thus actual solubility decreases. Microorganisms which consume or produce ions which are not reaction partners in the precipitation or dissolution reactions still influence these reactions by altering the ionic strength of the medium.

Example: A decrease in the ionic strength – measured for example as conductivity decrease in the epilimnion during photosynthesis – from $1.5 \cdot 10^{-2}$ mol-equivalents to 10^{-2} mol-equivalents increases $K^{0\prime}_s$ for calcite dissolution (reaction 22 in table 1.3) from $1.835 \cdot 10^{-9}$ to $2.135 \cdot 10^{-9}$ ($K^{0\prime}_s$ is $4.789 \cdot 10^{-9}$ for I = 0).

1.3.6 Influence of microbial activity on ion activity product (IAP). The role of microbes influencing precipitation and dissolution reactions by *altering the concentration of reactants* is illustrated with the formation of siderite ($FeCO_3$) which can take place in reducing environments. Siderite formation under standard conditions (reaction 24, table 1.3) has an operational solubility product $K^{0\prime}_s$ of $3.1935 \cdot 10^{-11}$ (for I = 0). The precipitation reaction is exergonic, above all due to the large entropy increase. The saturation concentrations for CO_3^{2-} and Fe^{2+} for the 1:1 stoichiometry in siderite are thus $5.65 \cdot 10^{-6}$ [mol/l] each. Dissolution or precipitation of siderite in an active habitat depends on the ratio of the actual ion activity product – valid for actual conditions of ionic strength – to the actual solubility product:

$$\Delta G_r = R \cdot T \cdot \ln \frac{\{Fe^{2+}\}_{act} \cdot \{CO_3^{2-}\}_{act}}{\{Fe^{2+}\}_{eq} \cdot \{CO_3^{2-}\}_{eq}}$$

$$= R \cdot T \cdot \ln \frac{IAP}{K'_s} \tag{15}$$

Dissolution of siderite requires that reaction 24 (table 1.3) proceeds from right to left exergonically. The boundary conditions for this reverse reaction are:

for dissolution: $IAP/K'_s < 1 (\Delta G_r < 0)$
for precipitation: $IAP/K'_s > 1 (\Delta G_r > 0)$
for saturation equilibrium: $IAP/K'_s = 1 (\Delta G_r = 0)$

Microbially mediated addition of Fe^{2+}-species to the habitat through ferric(hydr)oxide reduction (e.g., reactions 1, 2, 8, 9, 10 or 17 in table 1.3) will promote siderite formation. Uninhibited precipitation would require IAP < $3.1935 \cdot 10^{-11}$ [$\mathrm{mol}^2/\mathrm{l}^2$]. By supplying reactants the microbes make the dissolution reaction more endergonic.

The amount of carbonate in a habitat is regulated by the pH and by the amount of CO_2 produced during mineralization of organic matter. Siderite formation is thus also controlled by the bicarbonate-carbonate equilibrium. Combining reactions 21 and 24 (table 1.3) we get

$$Fe^{2+}_{(aq)} + HCO^-_{3\,(aq)} \Leftrightarrow FeCO_{3\,(s)} + H^+_{(aq)}$$

ΔG^0_r is -0.86 [kJ/mol], precipitation is thus slightly favored at standard conditions. The thermodynamic solubility product for the dissolution reaction from right to left is $K^0_s = 0.7069$. Decreasing the proton concentration on the right hand side of the reaction to pH = 8 changes ΔG^0_r by -45.665 [kJ/mol] and pK^0_s, calculated from $\Delta G^0_r = -46.525$, becomes thus -8.1507. At pH = 8, equal concentrations of $[Fe^{2+}_{(aq)}]$ and $[HCO^-_{3\,(aq)}]$ of $> 8.4075 \cdot 10^{-5}$ [mol/l] will lead to precipitation of siderite. Since the concentration of bicarbonate ions is influenced by the release of CO_2 stemming from the mineralization of organic substrates the actual bicarbonate concentration is calculated from the total content of dissolved inorganic carbon (C_T), the pH, the I and the T-corrected dissociation equilibrium constants (K'_1, K'_2). For the hydrogencarbonate buffer system one calculates HCO^-_3 according to

$$[HCO^-_3] = [C_T] \cdot \frac{K'_{a1} \cdot 10^{-pH}}{10^{-2pH} + K'_{a1} \cdot 10^{-pH} + K'_{a1} \cdot K'_{a2}} \quad (16)$$

The precipitation criterium for siderite for actual environmental conditions becomes:

$$IAP/K'_s = \frac{[Fe^{2+}_{(aq)}] \cdot f_{Fe^{2+}_{(aq)}} \cdot [C_T] \cdot 10^{-pH} \cdot K'_{a1} \cdot f_{HCO^-_{3(aq)}}}{K'_s \cdot (10^{-2pH} + K'_{a1} \cdot 10^{-pH} + K'_{a1} \cdot K'_{a2})}$$

Thus microorganisms regulate dissolution/precipitation reactions on three levels:

1) By producing or consuming reactants, thereby varying IAP directly.
2) By producing or consuming other ions, thereby altering ionic strength.
3) By producing or consuming protons, thereby changing acid-base equilibria which are linked to ion species distribution.

1.3.7 Influence of microbial activity on redox conditions. In metabolic oxidation-reduction processes microbes transfer electrons from a reductant (substrate) to an oxidant (substrate). The direction of electron transfer is also governed by laws of thermodynamics. The actual path of the electrons becomes more apparent if the overall transfer reaction is separated into two half-reactions. In the oxidizing half-reaction electrons are released, in the reducing one they are scavenged. By convention, electrons which are given off by the oxidative half-reaction have a negative sign, electrons which are consumed by the reductive half-reaction have a positive sign. The electrochemical potential (E) which is created in an electron transfer reaction between electron donor and electron acceptor is related to the Gibbs free energy of reaction for standard conditions by

$$\Delta G^0_r = -n \cdot F \cdot E^0 \quad (18)$$

(n = number of electrons exchanged, F = Faraday's constant = 96.48531 [kJ/V · mol], E^0 = standard electrochemical reference potential [V]).

For a reaction not at equilibrium, for which the free energy of reaction can be written as

$$\Delta G_r = \Delta G^0_r + R \cdot T \cdot \ln Q, \quad (19)$$

the actual electrochemical potential is related to ΔG_r by

$$\Delta G_r = -n \cdot F \cdot E \quad \text{or} \quad E = \frac{-\Delta G_r}{n \cdot F} \quad (20)$$

Combining eqs (19) and (20) leads to the Nernst equation:

$$E = \frac{-\Delta G^0_r}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln Q = E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln Q \quad (21)$$

which, when expressed with the equilibrium coefficient gives

$$E = \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{K^0}{Q} \quad (22)$$

Example: E for reaction 18 (table 1.3) is obtained from the Nernst equation:

$$E = \frac{-\Delta G^0_r}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\{HS^-_{(aq)}\} \cdot \{H_2O_{(l)}\}^4}{\{SO^{2-}_{4\,(aq)}\} \cdot \{e^-_{(aq)}\}^8 \cdot \{H^+_{(aq)}\}^9} \quad (23)$$

expressed as f(pH):

$$E = E^0 - \frac{2.3026 \cdot R \cdot T}{8 \cdot F} \cdot (9 \cdot pH + \log Q')$$

with $\log Q' = \log[\{HS^-_{(aq)}\} \cdot \{SO^{2-}_{4(aq)}\}^{-1} \cdot \{e^-_{(aq)}\}^{-8}]$. For standard state conditions of temperature and pressure and unit activity for water, SO^{2-}_4, HS^- and electrons, equation (23) becomes

$$E^{0\prime} = E^0 - 0.06656 \cdot pH \quad (24)$$

Increasing pH reduces standard electrochemical potential (E^0) in proportion to the number of protons exchanged (q) and the actual pH for an electron consuming reaction. A general formulation for E^0 as a function of pH (= $E^{0\prime}$) is

$$E^{0\prime} = E^0 - \frac{2.3026 \cdot R \cdot T}{F} \cdot \frac{q}{n} \cdot pH_{act} \quad (25)$$

for T = 298.15 [K] and unit activity for all reactants except protons:

$$E^{0\prime} = E^0 - 0.5916 \cdot \frac{q}{n} \cdot pH_{act}$$

and for disequilibrium conditions:

$$E = \frac{-2.3026 \cdot R \cdot T}{n \cdot F} \cdot (pK^0 + \log Q' - q \cdot pH_{act}) \quad (26)$$

Equations 25 and 26 are the basic relationships used for the construction of E/pH diagrams. They define the thermodynamic characteristics of a redox reaction within boundaries of pH and electrochemical potential.

Microbially mediated reactions are limited to a stability field confined to the pH-range 1 to 14 and limited in the E-coordinate by the stability functions of water.

The boundary reaction on the oxidized side:

$$1/2\, H_2O_{(l)} \Leftrightarrow 1/4\, O_{2\,(g)} + H^+_{(aq)} + e^-_{(g)}$$

is described by the equation:

$$E^{0\prime} = 1.229 - 0.05916 \cdot pH \quad (27a)$$

and on the reduced side by

$$e^-_{(g)} + H_2O_{(l)} \Leftrightarrow 1/2\, H_{2\,(g)} + OH^-_{(aq)} \text{ through}$$

$$E^{0\prime} = 0.0 - 0.05916 \cdot pH \text{ (for } T = 298.15 \text{ K).} \quad (27b)$$

Equation 27a describes the thermodynamic boundary of the E/pH-field below which gaseous O_2 present in the solution is reduced to water. The straight line which follows from equation 27b is the boundary above which gaseous H_2 in the solution is oxidized to water.

Redox conditions in a habitat can also be characterized using the pe-formalism. The concept summarizes electron activity of donor and acceptor reactions in a single term ($pe = -\log\{e^-\}$). Habitats with large positive pe-values express electron acceptor tendency; they are strongly oxidizing. Low and negative values for pe are characteristic of reducing habitat conditions.

Microbially mediated electron transfer reactions are conceptually again divided into an electron donor and an electron acceptor reaction. Surplus negative charges are balanced with protons. A pe-value can then be assigned to each half-reaction. From a generalized reduction half-reaction like

$$A_{ox} + n \cdot e^- + q \cdot H^+ \longrightarrow B_{red},$$

treated like an equilibrium reaction with

$$K^0 = \frac{\{B_{red}\}}{\{A_{ox}\} \cdot \{e^-\}^n \cdot \{H^+\}^q}$$

pe is derived as

$$pe = \frac{1}{n} \cdot \log K^0 + \frac{q}{n} \cdot \log\{H^+\} - \frac{1}{n} \cdot \log \frac{\{B_{red}\}}{\{A_{ox}\}} \quad (28)$$

in which $1/n \cdot \log K^0$ is chosen as reference state (pe^0). pe then becomes:

$$pe = pe^0 - \frac{q}{n} \cdot pH - \frac{1}{n} \cdot \log Q'_{red/ox} \quad \text{with}$$

$$Q'_{red/ox} = Q \cdot \{H^+\}^q \cdot \{e^-\}^n \quad \text{and} \quad (29)$$

$$Q = \frac{\prod_j \{P'_{j\,red}\}^{v_j}}{\{H^+\}^q \cdot \{e^-\}^n \cdot \prod_i \{S'_{i\,ox}\}^{v_i}}$$

pe is a function of pH, the reactant concentration and the equilibrium constant. Its value can be altered by the many microbial processes outlined above which influence these variables directly or indirectly.

Electrical potential and pe are connected by the expression

$$pe = \frac{F}{2.3026 \cdot R \cdot T} \cdot E^0 - \frac{q}{n} \cdot pH - \frac{1}{n} \cdot \log Q'_{red/ox} \quad (30)$$

or for the conversion of pe-units into volts by

$$E = \frac{2.3026 \cdot R \cdot T}{F} \cdot pe \quad [V] \quad (31)$$

(R in [kJ/K · mol], T in [K], F in [kJ/V · mol])

which gives a conversion factor applicable at 25 °C of

$$E = 0.05916 \cdot pe \quad [V] \quad (32)$$

E is connected with the Gibbs free energy of reaction via the relationship $\Delta G^0_r = -R \cdot T \cdot \ln K^0$:

$$pe = \frac{1}{n} \cdot \left[\frac{-\Delta G^0_r}{2.3026 \cdot R \cdot T} - q \cdot pH - \log Q'_{red/ox}\right] \quad (33)$$

The pe-concept is easy to use since it does not matter whether a half-reaction is looked at in the oxidizing or in the reducing direction. Solutions for pe include the + or − sign for electrons and protons. For aqueous environments pe, like E, are applicable up to the stability boundaries of water. For the oxidizing extreme of the reaction

$$\tfrac{1}{2} O_{2\,(g)} + 2\, e^-_{(g)} + 2\, H^+_{(aq)} \Leftrightarrow H_2O_{(l)}$$

electron activity becomes

$$pe = \tfrac{1}{2} \cdot \log K^0 - pH + \tfrac{1}{4} \cdot \log\{O_2\}. \quad (34)$$

For standard conditions of $pH = 0$ and O_2-pressure = 1 atm, pK^0 for the reaction above is −41.555. The stability function which describes the oxidation of water to O_2 for variable pH-values is thus

$$pe = 20.778 - pH. \quad (35)$$

An oxygen partial pressure of 10^{-6} [atm] at pH = 7 still corresponds to a pe of 12.28 (= +0.726 [V]) and the oxygen partial pressure would have to be lowered to $10^{-83.134}$ [atm] to attain pe = −7. For the reducing extreme of water stability, the reaction

$$H_2O_{(l)} + 2\, e^-_{(g)} + 2\, H^+_{(aq)} \longrightarrow H_{2\,(g)} + H_2O_{(l)}$$

simplifies to

$$e^-_{(g)} + H^+_{(aq)} \longrightarrow \tfrac{1}{2}H_{2\,(g)}\,.$$

The reduction of water is described by the function

$$pe = -pH \qquad (36)$$

which follows from the equation

$$pe = \log K^0 - pH - \tfrac{1}{2}\log\{H_2\} \qquad (37)$$

for standard conditions of $\{H_2\} = 1\,[\text{atm}]$

$\Delta G^0_r = 0$ and hence $pK^0 = 0$.

When the hydrogen partial pressure is diminished from 1 [atm] to 10^{-12} [atm], pe increases from -7 (-0.414 [V]) to -1 (-0.0592 [V]) for a pH of 7.

Example: Acetotrophic sulfate reduction in the pH-range 0–14.

Electron activity for the sulfate reducing half-reaction (table 1.3, reaction 18) is

$$pe = \frac{1}{8}\cdot\left(\log K^0 - 9\cdot pH - \log\frac{\{S_{T\,(aq)}\}}{\{L_{T\,(aq)}\}}\right) \qquad (38)$$

($S_T = [H_2S] + [HS^-] + [S^{2-}]$;
$L_T = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$)

and pe for the acetate oxidizing half-reaction (table 1.3, reaction 16) is

$$pe = \frac{1}{8}\cdot\left(-\log K^0 - 9\,pH - \log\frac{\{R_{T\,(aq)}\}}{\{C_{T\,(aq)}\}^2}\right). \qquad (39)$$

($R_T = [CH_3COOH] + [CH_3COO^-]$;
$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$, $H_2CO_3^*$ includes true H_2CO_3 and dissolved $CO_{2\,(aq)}$)

Nine equations for $Q'_{red/ox}$ are required to describe the entire pe/pH stability field for acetotrophic sulfate reduction if it is extended to include the various species of the acid-base-pairs of electron-acceptors and donors and their products. Equations which apply most appropriately to pH-values around 8.5 are

$$pe = 4.207 - 1.125\cdot pH - \log\frac{\{\gamma_1\cdot S_T\}}{\{\vartheta_2\cdot L_T\}} \qquad (40)$$

(γ_1 and ϑ_2 = acid-base distribution coefficients)

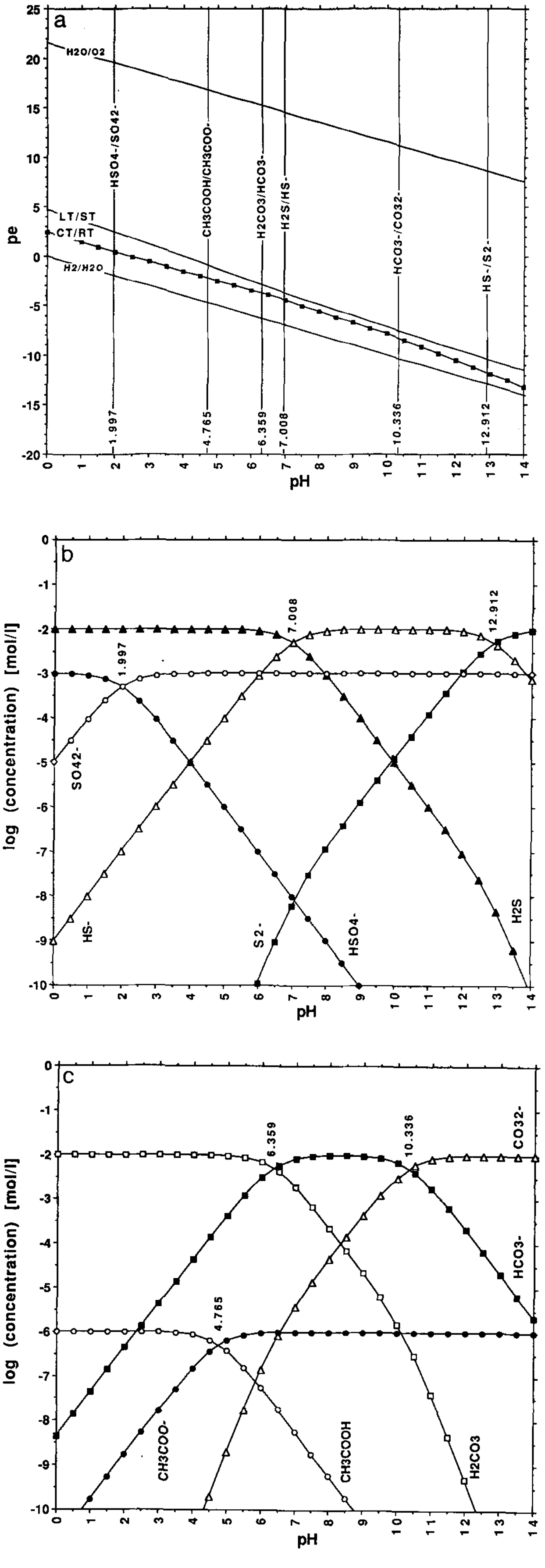


Figure 1.2. *a*) Electron-activity diagram (pe/pH) for acetotrophic sulfate reduction at 25 °C. Oxidizing and reducing boundaries of the stability field for water are drawn for 1 atm pressure of H_2 and O_2. Other boundary conditions are (in [mol/l]) $L_T = 10^{-3}$, $S_T = 10^{-2}$, $C_T = 10^{-2}$ and $R_T = 10^{-6}$. The vertical lines represent the pKa-values for the acid-base-pairs of electron donor and acceptor and their respective products. *b*) Concentration distribution of the electron-acceptor species (L_T) and their products (S_T) for the pH range 0–14, (total concentrations as in (*a*). *c*) Concentration distribution of the electron-donor species (R_T) and their products (C_T) for the pH range 0–14, (total concentrations as in (*a*)).

for sulfate reduction and

$$pe = 3.162 - 1.125 \cdot pH - \log \frac{\{\varepsilon_1 \cdot R_T\}}{\{\alpha_1 \cdot C_T\}^2} \qquad (41)$$

(ε_1 and α_1 = acid-base distribution coefficients)

for acetate oxidation. A graphical solution, valid for the entire pH-range, is illustrated in figure 1.2. Acetotrophic sulfate reduction is thermodynamically feasible under acidic, neutral and alkaline pH-values for the boundary conditions defined. Lower acetate ($R_T = 10^{-12}$ [mol/l]) and higher carbonate concentrations ($C_T = 10^{-1}$ [mol/l]) however, lead to thermodynamically unfavorable conditions within a certain pH-range (fig. 1.3).

Microbial alteration of redox conditions (E, pe) takes place on three levels: on the number of electrons and protons transferred, on the electron acceptor and donor capacity of oxidants and reductants respectively and on the activities of oxidants and reductants under habitat conditions.

1.4 Biomass formation

Energy for growth of microorganisms is extracted from the free energy released by exergonic reactions. The efficiency of the transformation of free energy of reactions into high energy bonds of biological energy transfer molecules (ATP etc.) or into bioelectrochemical gradients depends on the biochemical pathways employed for substrate conversion.

Thermodynamic analyses of growth requires thermochemical values for biomass. I have made the following assumptions for a simplified thermochemical and stoichiometric description of biomass:

1) Only C, H and O which can account for 80–90% of the dry weight are considered.
2) The stoichiometric composition of an average molecular 'biomass unit' is taken as $\langle C_4H_7O_3 \rangle$. Biomass would consist of y such units.
3) Determination of enthalpy and entropy of formation is based on the structural formula

   $R-[-CHOH-CH_2-CHOH-COH]$.

   Hf^0 and Sf^0 are determined with the group increment method with values from table A.3.:

   $$Hf^0 = 2 \cdot [C(H)(O)(C)_2] + [C(H)_2(C)_2] + [CO(H)(C)] + 2 \cdot [O(H)(C)].$$

   No structural or statistical corrections are needed. The values for Hf^0 and Sf^0 are -519.76 [kJ/mol] and $+335.65$ [J/K · mol] respectively.
4) Gibbs free energy of formation ($Gf^0 = -385.294$ [kJ/mol]) follows from the combustion reaction

   $$\langle C_4H_7O_3 \rangle + 4\tfrac{1}{4} O_{2(g)} \longrightarrow 4\,CO_{2(aq)} + 3\tfrac{1}{2} H_2O_{(l)}$$

   employing the Hf^0 and Sf^0 values calculated above and in conjunction with $\Delta Gf^0 = \Delta Hf^0 - T \cdot \Delta Sf^0$ (see eq. 47, section 3).
5) A total of 17 electrons are freely exchangeable which gives an average oxidation state of -0.25 for the carbon atoms.

Biomass formation can thus be written as half-reaction:

$$\boxed{4\,CO_{2(aq)} + 17\,e^-_{(g)} + 17\,H^+_{(aq)} \longrightarrow \langle C_4H_7O_3 \rangle + 5\,H_2O_{(l)}.}$$

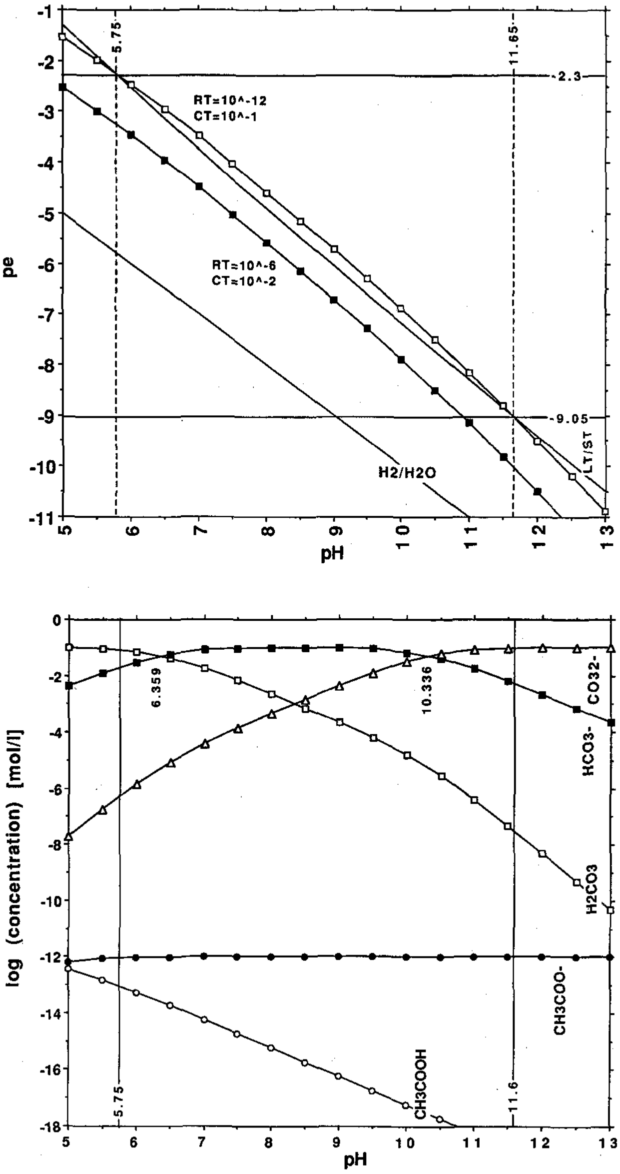


Figure 1.3. *a*) Electron-activity diagram for total concentrations of $C_T = 10^{-1}$ and $R_T = 10^{-12}$ [mol/l] and the pH range between 5 and 13. The reaction (□) is endergonic for 5.75 < pH < 11.65 which corresponds to $-2.3 < pe < -9.05$. Conditions for L_T and S_T (full line) as well as for C_T and R_T of the exergonic reaction (■) and the lower boundary for the water stability are the same as in fig. 1.2. *b*) Concentration distribution of the electron-donor species and their products for the reaction which becomes endergonic within the pH interval 5.75–11.65. The concentration distributions for the other conditions are the same as in fig. 1.2b and c.

ΔGr_r^0 is -27.12 [kJ/mol] based on the value derived above and those listed in table A.1. Growth associated with fermentative acetate dissimilation which corresponds to a stoichiometric coupling of reaction 36 (table 1.3.) with reaction 16 would be thermodynamically unfavorable under standard conditions (reaction 37). It is more endergonic at pH 7. Growth on toluene under standard conditions (reaction 38) would require coupled dissimilation reactions with a free energy change larger than -207.31 [kJ/mol] to make reaction 38 exergonic. Sulfate reducing dissimilation of toluene (reaction 7) could support biomass synthesis (reactions 39 and 40) if reactions 7 and 38 would be coupled at a ratio larger than 0.56:1.

These purely thermodynamic considerations can only insufficiently account for the growth patterns observed in nature. ΔG_r for growth combined with the physiological yield coefficient Y, however, allows one to make useful growth predictions for a great number of different conditions.

1.5 Electron acceptor diversity

The microbes represent the entire potential needed to balance global metabolism. The full enzymatic capacity for the immense variety of transformation processes is distributed on a great number of different organisms of the microbial world and no single microbe possesses them all.

Different physiological types of life can best be classified according to the conditions under which the organisms thrive and to the oxidants chosen to mediate electron transfer. A selection of microbially mediated reduction reactions is summarized for standard conditions in table 1.4. For the basic concept it is unimportant whether an electron acceptor is supplied to the microbial cell externally or whether electrons are transferred to an intracellular metabolic intermediate as is the case for fermentation reactions. The Gibbs free energy of reaction varies, depending on the oxidant employed in conjunction with a particular electron source. Reactions 2, 3 and 7 (table 1.3) illustrate the point. From table 1.4. it can also be deduced that oxygen and gases of nitrogen oxides lead to large free energy gains while carbon oxides and protons give small ones. Basically, reduction reactions are associated with an entropy decrease which diminished ΔG_r. Redox-reactions are thermodynamically feasible, as long as the oxidation half-reactions coupled with reduction half-reactions listed in table 1.4. give exergonic overall-processes.

Oxidants most frequently used by microorganisms are limited to compounds of the major elements employed in biology: C,H,O,N,S,Fe and Mn (see section 1.1). The reduction by microorganisms of a few additional heavy metals (Hg, As, etc.) are interesting curiosities which might become quantitatively important in certain waste repositories. The maximal biological reduction span, expressed as the number of mol-equivalents of electrons accepted per mol of oxidant, is 8 for C, N and S, 2 for O and Mn, 1 for H and Fe and 0 for P[5]. While C, N and S are capable of exchanging all the electrons in their 2s/2p or 3s/3p orbitals respectively, O only varies its redox span by exchanging 2 electrons of the 2p orbital. P is not involved in redox changes at all, it is always present in biological compounds and in the natural environment with 'empty' 3s/3p orbitals but a 'full Neon-core'. The curious anomalies of O and P in biological processes are not understood yet.

Electron transport is coupled to an equivalent transfer of positive charges. This leads to the formation of electrochemical gradients. On a cellular level these gradients are formed across cell membranes where they form the link

Table 1.4. Stoichiometries and standard thermodynamic values for major microbially mediated electron-acceptor reactions

			$\frac{q}{n}$	ΔGr^0 [kJ/mol] (1)	ΔHr^0 [kJ/mol] (2)	$\log K^0$ (3)	E^0 [V] (4)	pe^0 (5)	$pe^{0\prime}$ pH = 7 (6)
1	$4e^- + O_{2(g)} + 4H^+_{(aq)}$	$\longrightarrow 2H_2O_{(l)}$	1	− 474.4	− 571.6	83.11	1.229	20.78	+13.78
2	$2e^- + 2H^+_{(aq)}$	$\longrightarrow H_{2(g)}$	1	0	0	0	0	0	− 7
3	$2e^- + H_2O_{2(aq)} + 2H^+_{(aq)}$	$\longrightarrow 2H_2O_{(l)}$	1	− 608.4	− 380.4	106.59	3.153	53.29	+46.29
4	$2e^- + NO^-_{3(aq)} + 2H^+_{(aq)}$	$\longrightarrow NO^-_{2(aq)} + H_2O_{(l)}$	1	− 158.1	− 183.0	27.70	0.8193	13.85	+ 6.85
5	$4e^- + 2NO^-_{2(aq)} + 6H^+_{(aq)}$	$\longrightarrow N_2O_{(g)} + 3H_2O_{(l)}$	$1\frac{1}{2}$	− 543.0	− 566.2	95.13	1.407	23.78	+13.28
6	$8e^- + 2NO_{2(g)} + 8H^+_{(aq)}$	$\longrightarrow N_{2(g)} + 4H_2O_{(l)}$	1	−1051.4	−1209.6	184.2	1.362	23.02	+16.02
7	$4e^- + 2NO_{(g)} + 4H^+_{(aq)}$	$\longrightarrow N_{2(g)} + 2H_2O_{(l)}$	1	− 647.6	− 752	113.5	1.678	28.36	+21.36
8	$2e^- + N_2O_{(g)} + 2H^+_{(aq)}$	$\longrightarrow N_{2(g)} + H_2O_{(l)}$	1	− 341.4	− 367.8	59.81	1.769	29.91	+22.91
9	$6e^- + N_{2(g)} + 8H^+_{(aq)}$	$\longrightarrow 2NH^+_{4(aq)}$	$1\frac{1}{3}$	− 158.8	− 266.5	27.82	0.2743	4.637	− 4.697
10	$6e^- + R-NO_2 + 6H^+_{(aq)}$	$\longrightarrow R-NH_2 + 2H_2O_{(l)}$	1						
11	$2e^- + S_{(S)} + H^+_{(aq)}$	$\longrightarrow HS^-_{(aq)}$	$\frac{1}{2}$	+ 12.1	− 17.6	−2.120	−0.0627	−1.060	− 4.560
12	$8e^- + S^{2-}_{3+2(aq)}{}^{(7)} + 5H^+_{(aq)}$	$\longrightarrow 5HS^-_{(aq)}$	$\frac{5}{8}$	− 5.20	− 109.3	0.911	0.0067	0.114	− 4.261
13	$8e^- + S_{1+1}O^{2-}_{3(aq)}{}^{(8)} + 8H^+_{(aq)}$	$\longrightarrow 2HS^-_{(aq)} + 3H_2O_{(l)}$	1	− 164.9	− 244.1	28.89	0.2136	3.611	− 3.389
14	$4e^- + S_{1+1}O^{2-}_{3(aq)}{}^{(8)} + 6H^+_{(aq)}$	$\longrightarrow 2S_{(S)} + 3H_2O_{(l)}$	$1\frac{1}{2}$	− 189.1	− 208.9	33.13	0.490	8.282	− 2.218

Table 1.4. Continued.

			$\frac{q}{n}$	ΔGr^0 [kJ/mol] (1)	ΔHr^0 [kJ/mol] (2)	$\log K^0$ (3)	E^0 [V] (4)	pe^0 (5)	$pe^{0\prime}$ pH = 7 (6)
15	$S_{1+1}O^{2-}_{3(aq)}{}^{(8)}$	$\longrightarrow SO^{2-}_{3(aq)} + S_{(S)}$	0	+ 35.9	+ 13.0	−6.289	−0.093	−1.572	− 1.572
16	$10e^- + S_2O^{2-}_{4(aq)} + 10H^+_{(aq)}$	$\longrightarrow 2HS^-_{(aq)} + 4H_2O_{(l)}$	1	− 324.3	− 424.9	56.814	0.336	5.681	− 1.319
17	$16e^- + S_{2+1}O^{2-}_{6(aq)}{}^{(9)} + 15H^+_{(aq)}$	$\longrightarrow 3HS^-_{(aq)} + 6H_2O_{(l)}$	$\frac{15}{16}$	− 428.9	− 598.8	75.139	0.278	4.696	− 1.866
18	$14e^- + S_2O^{2-}_{6(aq)} + 14H^+_{(aq)}$	$\longrightarrow 2HS^-_{(aq)} + 6H_2O_{(l)}$	1	− 433.0	− 576.8	75.857	0.321	5.418	− 1.582
19	$6e^- + SO_{2(g)} + 5H^+_{(aq)}$	$\longrightarrow HS^-_{(aq)} + 2H_2O_{(l)}$	$\frac{5}{6}$	− 162.1	− 292.4	28.398	0.280	4.733	− 1.100
20	$4e^- + SO_{(g)} + 3H^+_{(aq)}$	$\longrightarrow HS^-_{(aq)} + H_2O_{(l)}$	$\frac{3}{4}$	− 205.3	− 309.66	35.967	0.532	8.992	+ 3.742
21	$6e^- + SO^{2-}_{3(aq)} + 7H^+_{(aq)}$	$\longrightarrow HS^-_{(aq)} + 3H_2O_{(l)}$	$1\frac{1}{6}$	− 212.9	− 239.5	37.298	0.368	6.216	− 1.950
22	$8e^- + SO^{2-}_{4(aq)} + 9H^+_{(aq)}$	$\longrightarrow HS^-_{(aq)} + 4H_2O_{(l)}$	$1\frac{1}{8}$	− 192.1	− 251.2	33.654	0.249	4.207	− 3.668
23	$4e^- + R_1{-}SO{-}R_2 + 4H^+_{(aq)}$	$\longrightarrow R_1{-}SH + H{-}R_2 + H_2O_{(l)}$	1						
24	$6e^- + R_1{-}SO_2{-}R_2 + 6H^+_{(aq)}$	$\longrightarrow R_1{-}SH + H{-}R_2 + 2H_2O_{(l)}$	1						
25	$1e^- + Fe^{3+}_{(aq)}$	$\longrightarrow Fe^{2+}_{(aq)}$	0	− 74.3	− 40.6	13.017	0.770	13.017	13.017
26	$1e^- + Fe(OH)^+_{2(aq)} + H^+_{(aq)}$	$\longrightarrow Fe(OH)^+_{(aq)} + H_2O_{(l)}$	1	− 57.4	− 59.2	10.056	0.595	10.056	3.056
27	$1e^- + Fe(OH)^{2+}_{(aq)}$	$\longrightarrow Fe(OH)^+_{(aq)}$	0	− 48.0	− 33.9	8.409	0.497	8.409	8.409
28	$1e^- + Fe(OH)^0_{3(aq)} + 2H^+_{(aq)}$	$\longrightarrow Fe(OH)^+_{(aq)} + 2H_2O_{(l)}$	2	− 92.4		16.188	0.958	16.188	2.188
29	$1e^- + FeO(OH)_{(S)} + 2H^+_{(aq)}$	$\longrightarrow Fe(OH)^+_{(aq)} + H_2O_{(l)}$	2	− 24.2	− 51.5	4.240	0.251	4.240	− 9.760
30	$1e^- + FePO_4 \cdot 2H_2O_{(S)}$	$\longrightarrow Fe(OH)^+_{(aq)} + HPO^{2-}_{4(aq)} + H_2O_{(l)}$	0	+ 53.8	− 14.4	−9.425	−0.558	−9.425	− 9.425
31	$1e^- + Mn^{3+}_{(aq)}$	$\longrightarrow Mn^{2+}_{(aq)}$	0	− 142.6	− 120.3	24.982	1.478	24.982	24.982
32	$1e^- + Mn(OH)^0_{3(aq)}$ $+ HCO^-_{3(aq)} + 3H^+_{(aq)}$	$\longrightarrow Mn(HCO_3)^+_{(aq)} + 3H_2O_{(l)}$	3	− 200.4		35.108	2.077	35.108	14.108
33	$1e^- + MnO(OH)_{(S)}$ $+ HCO^-_{3(aq)} + 3H^+_{(aq)}$	$\longrightarrow Mn(HCO_3)^+_{(aq)} + 2H_2O_{(l)}$	3	− 150.2		26.314	1.557	26.314	5.314
34	$2e^- + Mn_2O_{3(S)}$ $+ 2HCO^-_{3(aq)} + 6H^+_{(aq)}$	$\longrightarrow 2Mn(HCO_3)^+_{(aq)} + 3H_2O_{(l)}$	3	− 296.6		51.962	1.537	25.981	4.981
35	$2e^- + MnO_{2(S)}$ $+ HCO^-_{3(aq)} + 4H^+_{(aq)}$	$\longrightarrow Mn(HCO_3)^+_{(aq)} + 2H_2O_{(l)}$	2	− 242.4		42.466	1.256	21.233	7.233
36	$1e^- + MnO(OH)_{(S)} + 2H^+_{(aq)}$	$\longrightarrow Mn(OH)^+_{(aq)} + H_2O_{(l)}$	2	− 84.9	− 121.1	14.874	0.880	14.874	0.874
37	$2e^- + MnO_{2(S)} + 3H^+_{(aq)}$	$\longrightarrow Mn(OH)^+_{(aq)} + H_2O_{(l)}$	$1\frac{1}{2}$	− 177.1	− 216.4	31.026	0.918	15.513	5.013
38	$8e^- + HCO^-_{3(aq)} + 9H^+_{(aq)}$	$\longrightarrow CH_{4(g)} + 3H_2O_{(l)}$	$1\frac{1}{8}$	− 175.5	− 240.2	30.746	0.227	3.843	− 4.032
39	$8e^- + 2HCO^-_{3(aq)} + 9H^+_{(aq)}$	$\longrightarrow CH_3COO^-_{(aq)} + 4H_2O_{(l)}$	$1\frac{1}{8}$	− 144.4	− 245.2	25.298	0.187	3.162	− 4.713
40	$2e^- + CO_{(g)} + 2H^+_{(aq)}$	$\longrightarrow \langle HCHO\rangle_{(aq)}{}^{(10)}$	1	+ 6.7	− 39.7	−1.174	−0.0347	−0.587	− 7.587
41	$4e^- + CO_{2(g)} + 4H^+_{(aq)}$	$\longrightarrow \langle HCHO\rangle_{(aq)}{}^{(10)} + H_2O_{(l)}$	1	+ 26.7	− 42.5	−4.678	−0.0692	−1.169	− 8.169
42	$8e^- + CS_{2(g)} + 6H^+_{(aq)}$	$\longrightarrow CH_{4(g)} + 2HS^-_{(aq)}$	$\frac{3}{4}$	− 93.8	− 227.4	16.433	0.122	2.054	− 3.196
43	$8e^- + COS_{(g)} + 7H^+_{(aq)}$	$\longrightarrow CH_{4(g)} + HS^-_{(aq)} + H_2O_{(l)}$	$\frac{7}{8}$	− 106.6	− 236.1	18.675	0.138	2.334	− 3.791
44	$2e^- + R{-}COOH + 2H^+_{(aq)}$	$\longrightarrow R{-}CHO + H_2O_{(l)}$	1						
45	$2e^- + R{-}CHO + 2H^+_{(aq)}$	$\longrightarrow R{-}CH_2OH$	1						
46	$2e^- + R{-}CH_2OH + 2H^+_{(aq)}$	$\longrightarrow R{-}CH_3 + H_2O_{(l)}$	1						
47	$2e^- + R_1{-}CHOH{-}R_2 + 2H^+_{(aq)}$	$\longrightarrow R_1{-}CH_2{-}R_2 + H_2O_{(l)}$	1						
48	$2e^- + R_1{-}CO{-}R_2 + 2H^+_{(aq)}$	$\longrightarrow R_1{-}CHOH{-}R_2$	1						
49	$2e^- + R_1{-}(CH)_2{-}R_2 + 2H^+_{(aq)}$	$\longrightarrow R_1{-}(CH_2)_2{-}R_2$	1						
50	$2e^- + CCl_{4(g)} + H^+_{(aq)}$	$\longrightarrow CHCl_{3(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 141.0	− 167.3	24.702	0.731	12.351	8.851
51	$2e^- + CHCl_{3(g)} + H^+_{(aq)}$	$\longrightarrow CH_2Cl_{2(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 126.7	− 156.5	22.197	0.657	11.098	7.598
52	$2e^- + CH_2Cl_{2(g)} + H^+_{(aq)}$	$\longrightarrow CH_3Cl_{(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 118.2	− 155.4	20.708	0.613	10.354	6.854
53	$2e^- + CH_3Cl_{(g)} + H^+_{(aq)}$	$\longrightarrow CH_{4(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 124.6	− 161.1	21.829	0.646	10.914	7.414
54	$2e^- + CCl_2CCl_{2(g)} + H^+_{(aq)}$	$\longrightarrow CHClCCl_{2(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 135.8	− 162.8	23.791	0.704	11.895	8.395
55	$2e^- + CHClCCl_{2(g)} + H^+_{(aq)}$	$\longrightarrow CHClCHCl_{(l)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 121.9	− 182.4	21.356	0.632	10.678	7.178
56	$2e^- + CHClCHCl_{(l)} + H^+_{(aq)}$	$\longrightarrow CH_2CHCl_{(g)} + Cl^-_{(aq)}$	$\frac{1}{2}$	− 106.6	− 108.4	18.675	0.552	9.338	5.838

(1) follows from $\Delta G^0_r = \sum_j Gf^0_{P_j} - \sum_i Gf^0_{S_i}$ with values from tables A.1 and A.2.

(2) follows from $\Delta H^0_r = \sum_j Hf^0_{P_j} - \sum_i Hf^0_{S_i}$

(3) follows from $\Delta G^0_r = -2.3026 \cdot R \cdot T \cdot \log K^0$

(4) follows from $E^0 = -\Delta Gr^0_r / n \cdot F$

(5) follows from $pe^0 = \frac{1}{n} \cdot \log K^0$

(6) follows from $pe^{0\prime} = pe^0 - \frac{q}{n} \cdot pH_{act}$

(7) Pentasulfide contains sulfur atoms with oxidation states I− and 0.

(8) Thiosulfate contains sulfur atoms with oxidation states I− and V+.

(9) Trithionate contains sulfur atoms with oxidation states 0 and V+.

(10) $\langle HCHO\rangle_{(aq)}$ represents organic matter with oxidation state 0 for the C-atom; $Gf^0 = -130.5$, $Hf^0 = -150.2$ [kJ/mol].

Activities are 1 [molal] for aqueous species and 1 [atm] for gaseous species.

for the conversion of thermodynamic free energy into the electromotive force (emf) for biological work and biosynthesis. On the niveau of the entire ecosystem, electron and associated charge transfers lead to alterations in environmental state parameters (see 1.3).

1.6 Conclusions from section 1

For thermodynamic treatments of microbial ecosystems we acknowledge the following results:

1) All mass transformation reactions can be described by *stoichiometric mass equations.*
2) Reactions for which balanced equations can be written will actually take place.
3) The *likelihood* of a reaction occurring in a closed system may be described by the free energy equation $\Delta G_r = \Delta H_r - T \cdot \Delta S_r$.
4) The *direction* in which a reaction will proceed is described by the deviation of the activity of the reactants from equilibrium activity conditions as expressed by the disequilibrium equation:

$$Q = \frac{\prod_j \{P_{j\,neq}\}^{v_j}}{\prod_i \{S_{i\,neq}\}^{v_i}} = K^0 \cdot \exp\left[\frac{\Delta Gr}{R \cdot T}\right]$$

or

$$Q = K^0 \cdot \exp\left[\frac{-E \cdot n \cdot F}{R \cdot T}\right]$$

5) The *rate* by which a reaction will proceed depends
   a) on the physico-chemical reaction conditions (temperature, pH, etc.) and
   b) on the presence or absence of catalysts (enzymes, reactive surfaces, etc.).
6) Reactions involve the breaking and forming of bonds and possibly the *transfer of electrons and protons.*
7) Microbes mediate electron and proton transfer. They *live from the free energy* made available as reactions proceed towards equilibrium.
8) Microbial life can exist in an ecosystem as long as *differences in chemical potentials* are maintained.
9) Progressing reactions lead to *changes in the conditions* of closed systems. If microbes are reaction mediators changes will take place more rapidly.
10) Environmentally forced and metabolically induced changes of *state parameters regulate the thermodynamics of reactions.* A few equations describing microbially induced changes in ecological state parameters are summarized in table A.4 in the appendix.

2. Thermodynamic treatment of degradation in waste repositories

In this section I will apply thermodynamic considerations to possible processes in mixed waste repositories. I realize of course that the complexity of the numerous interacting processes cannot be resolved by a simple comprehensive approach. The discussion will be limited to an evaluation of a few individual reactions which are characteristic for nuclear waste repositories. Bitumen is selected as the model substrate.

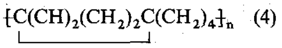
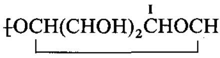
The reactive waste-containing 'cell' is treated as a closed system. It contains organic matter in the form of bitumen and polymers from ion-exchange resins, other synthetics and cellulose (table 2.1). Thermochemical values are calculated for 'polymer-unit' molecules applying the rules of the group increment method and values of table A.3. Further calculations with the values listed allow one to make predictions about the likelihood and the direction of reactions involving the organic compounds as substrates. The microbes are unimportant for these purely thermodynamic considerations. But their presence will determine reaction rates and directions and changes in environmental conditions and they will efficiently mediate the coupling between different reactions. From the discussion in section 1 it becomes clear that any reaction which is basically endergonic, when treated as an individual reaction, can be made to proceed in the unlikely direction if it is efficiently coupled to a strongly exergonic reaction.

In model calculations for waste repositories which include microbes as a parameter, it is assumed that the nutrients required for microbial growth are present – albeit in small concentrations – and that microbial contamination of waste cells is inevitable. It is also assumed that oxidation-reduction reactions which lead to a net gain of free energy can always be coupled by microbes and the reaction rates are thus accelerated. This view discounts the earlier concept that only reactions which surpass a certain minimal free energy gain will be coupled by microorganisms[19]. The sequence of processes that occur follows the rule that reactions with large free energy gains are favored against those with small gains[5]. Aerobic microbes would thus rapidly consume the small amount of oxygen present in the trapped air. Further degradation would then proceed fermentatively and be coupled to methane production or to sulfate reduction. The latter process would be important in alkaline, cement-containing matrixes where the pH might rise to 12. Steel iron is assumed to be oxidized and the assumption that iron oxidation can be coupled to sulfate reduction after oxic corrosion has ceased will be examined below (2.2). Accumulating metabolites alter redox conditions (pe), pH and other state parameters discussed in section 1.3, which will in turn influence reaction conditions.

2.1 Bitumen degradation

Elemental analyses of bitumen give an average composition of C:H:O:N:S of 200:280:1:1:3. Assigning 0 and III- as oxidation states to sulfur and nitrogen respectively, one calculates an average oxidation state of − 1.375 for the carbon atoms. Aerobic degradation of bitumen would thus follow the stoichiometry

Table 2.1. Thermochemical values of the major organic compounds in low and intermediate level radioactive wastes.

Compound [sum formula]	Assumed structural formula of formal polymer unit (2)	Hf^0 [kJ/mol] (3)	Sf^0 [J/K · mol] (3)	Average oxidation state of carbon atoms
Bitumen (1) $\{C_{200}\overset{I+}{H}_{280}\overset{II-}{O}_1\overset{III-}{N}_1\overset{0}{S}_3\}_n$ $\approx\{C_{10}H_{14}\}_{20n}$ (4)	 $\{C(CH)_2(CH_2)_2C(CH_2)_4\}_n$ (4)	+ 61.7	+214.6	−1.375 −1.4
Resin (1) $\{C_{19}H_{20}O_4\overset{III-}{N}_1\overset{V+}{S}_1\}_n^+$ (5)	$\{C_2H_2-C_6H_3(SO_3H)C_2H_2\overset{I}{C}_6H_2(OH)N^+(CH_3)_3]_n$ (5)	−417.5	+681	−0.68421
Cellulose $\{C_6H_{10}O_5\}_n$	 $\{OCH(CHOH)_2\overset{I}{C}HOCHCH_2OH]_n$	−892.4	+320.5	0
Polyvinylchloride PVC-unit $\{C_2H_3Cl\}_n$	$\{CH_2CHCl\}_n$	− 82.55	+112.05	−1.0
Polyethylene PE-unit $\{C_2H_4\}_n$	$\{CH_2CH_2\}_n$	− 41.26	+ 76.82	−2.0
Polystyrol PS-Unit $\{C_8H_8\}_n$	$\{CH_2\overset{I}{C}H(C_6H_5)]_n$	+ 67.37	+196.6	−1.0

(1) Based on elemental analysis.
(2) Calculations of Hf^0 and Sf^0 are based on the structures which have been assigned to the monomers in their gaseous state.
(3) Calculated according to the group increment method with values listed in table A.3; obvious correction terms have been considered (see table 3.1).
(4) O, N and S which account for 4.5% of the molecular weight of a formal "bitumen monomer unit" have been neglected in the bitumen hydrocarbon.
(5) O, N and S have been included in the formal "resin monomer unit" since they account for 31% of the molecular mass. Oxidation states of N and S are III− and V+ respectively.

$$\boxed{\begin{array}{l}\langle C_{200}H_{280}O_1N_1S_3\rangle_y + 275\tfrac{1}{4}\cdot y\,O_2 \\ \qquad\qquad\downarrow \\ 200\cdot y\,CO_2 + 7\cdot y\,H^+ + y\,NO_3^- + 3\cdot y\,SO_4^{2-} \\ \quad + 136\tfrac{1}{2}\cdot y\,H_2O.\end{array}}$$

Neglecting O, N, and S which account for 4.5% (= 126 Da) of the total molecular weight (2806 Da) allows one to describe a simplified 'molecular unit'of bitumen as a hydrocarbon with composition $[-C_{10}H_{14}-]$. C has an oxidation state of − 1.4. From the structural formula designed in table 2.1, one can calculate Hf^0 and Sf^0 employing values from table A.3. The following groups were added:

$$2\cdot[C_d(C)_2] + 2\cdot[C_d(H)\,(C)] + 4[C(H)_2(C)\,(C_d)] + 2\cdot[C(H)_2(C)_2].$$

Corrections for 1,3 cyclohexadiene (+ 20.08 [kJ]mol]) and for cis-alkane (+ 4.184 [kJ/mol]) were considered for Hf^0, σ and W were assigned values of 2 and 10 respectively. Values for Hf^0 and Sf^0 are given in table 2.1. Gf^0 is + 286.83418 [kJ/mol] calculated with formula 47 explained in section 3. Aerobic degradation is a strongly exergonic reaction ($\Delta G_r^0 = -5665.4$ [kJ/mol]) for standard conditions. It remains exergonic as long as $|T\cdot\Delta S_r^0| < |\Delta H_r^0|$ (case B, table 1.2). The system entropy (ΔS_r^0) would have to increase by a factor of 20, the entropy of formation (Sf^0) 90-fold to make the reaction endergonic for standard conditions (Hf^0 = constant, case C, table 1.2). The estimates for the thermochemical values of bitumen are made for $[-C_{10}H_{14}-]$ as a gaseous entity. Solidification into an amorphous mass is unlikely to decrease Sf^0 by so much that ΔG_r^0 of the oxidation reaction changes substantially.

The degradation reaction under oxic conditions is assumed to take place under the following initial boundary conditions:

$$[-C_{10}H_{14}-] + 13\tfrac{1}{2}\,O_{2(aq)} + 3\,H_2O_{(l)} \rightarrow 10\,HCO^-_{3\,(aq)} + 10\,H^+_{(aq)}$$

T = 298.15 K (as in all examples in this section), pH = 8.4, $[HCO^-_{3\,(aq)}] = 10^{-2}$ [mol/l], $pO_2 = 0.21$ [atm] (approximately 0.28 · 10^{-3} [mol/l] = 9 [mg/l] dissolved in the aqueous milieu. Calculations are based on $[O_{2(aq)}] = K_H\cdot pO_{2(g)}$, K_H being Henry's law constant, and $pO_{2(g)} = R\cdot T\cdot nO_{2(g)}/V_0$) and $[-C_{10}H_{14}-] = 10^{-12}$ [mol/l]. The conditions take into account that bitumen is accessible preferentially to the organisms which adhere to the bitumen surface[24]. The concentration of free bitumen monomer is assumed to be very low (10^{-12} [mol/l]). Thermodynamically the reaction will proceed in the direction as written as long as $Q/K^0 < 1$ and $\Delta G_r < 0$ (as derived in section 1.3). ΔG_r for the actual conditions is − 5808.38 [kJ/mol]. More alkaline pH-values make ΔG_r of the proton producing reaction more negative. The reaction is still exergonic with $\Delta G_r = -5265.8$ [kJ/mol] if pO_2 is reduced to $7.47\cdot10^{-10}$ [atm] ($\triangleq 10^{-12}$ [mol/l] dissolved O_2). Although this seems to be a low oxygen partial pressure the condition still represents a redox potential of + 0.598 [V] corresponding to a pe of + 10.102. The few calculations indicate that there are no thermodynamic restrictions to the aerobic breakdown of bitumen.

A comparison of several anaerobic degradation sequences is made by coupling half-reactions 1 and 2 (table 2.2), which represent complete and incomplete bitumen oxidation, to hydrogenic, methanogenic, acetogenic, and sulfidogenic electron acceptor half-reactions 5 to 8 (table 2.2). Gibbs free energy can be calculated from the values listed, by stoichiometrically combining the appropriate reactions. Degradation associated with hydrogen gas production will turn into an exergonic reaction at $pH > 8.9$ and $[H_{2(aq)}] \leq 10^{-6}$ [mol/l] (corresponding to a partial pressure for H_2 of $1.212 \cdot 10^{-3}$ [atm]).

ΔG_r^0 for the homoacetogenic breakdown of bitumen is − 15.42 [kJ/mol]. Increasing pH to 8.4 and to 12 makes the standard reaction more exergonic. The ΔG_r^0 values are − 171.25 and − 238.04 [kJ/mol], respectively. The reaction remains exergonic even if acetate accumulates to very high concentrations.

Methanogenic degradation at pH 8.4 is exergonic ($\Delta G_r^{0\prime} = -434.78$ [kJ/mol]) at a partial pressure of methane of 1 [atm] and high bicarbonate concentration (1 [mol/l]). Increasing the pH makes this reaction more favorable.

ΔGr_r^0 for sulfidogenic bitumen breakdown follows when reaction 1 (table 2.2) is stoichiometrically combined with reaction 8. Under standard conditions a ΔGr_r^0-value of − 337.23 [kJ/mol] is obtained. The value increases to − 522.74 [kJ/mol] at pH 10 where almost all of the sulfide formed is present as HS^-. $\Delta G_r^{0\prime}$ becomes − 769.0 [kJ/mol], if ferrous ions (10^{-6} [mol/l] react with the sulfide to form pyrrhotite (reaction 20, table 1.3), the available bitumen concentration remains at 10^{-12} [mol/l] and sulfate and bicarbonate are present at 10^{-3} [mol/l]. Thermodynamically there are no reasons for bitumen to be as stable as it seems to be when tested in short-term microbial experiments.

The rates of degradation might be slow, but bitumen is thermodynamically destined to decay and given enough time it will be oxidized via aerobic and anaerobic processes[24].

2.2 Corrosion

Metal iron, present in waste packaging material, represents an additional source of reducing power. For oxic conditions half-reactions 3 and 4 (table 2.2) describe acid catalyzed iron oxidation:

$$Fe_{(s)} + \tfrac{1}{2} O_{2(g)} + H^+_{(aq)} \rightarrow Fe(OH)^+_{(aq)}$$

At initially low concentrations of $Fe(OH)^+$ [10^{-6} mol/l], a pO_2 of 0.21 [atm] and at pH = 12, the reaction is exergonic ($\Delta G_r = -241.15$ [kJ/mol]). Also the acid-independent oxic corrosion which is associated with goethite precipitation,

$$Fe_{(s)} + \tfrac{3}{4} O_{2(g)} + \tfrac{1}{2} H_2O_{(l)} \rightarrow Fe\,O(OH)_{(s)}$$

is strongly exergonic at $pO_2 = 0.21$ [atm] ($\Delta G_r = -367.22$ [kJ/mol]). For anoxic conditions the possibility of corrosion promoting electron transfer from iron to sulfate was investigated thermodynamically. It is assumed that iron oxidation can be mediated by sulfate reducing bacteria which metabolize acetate as their main source of energy and carbon. It is further assumed that the free ferrous iron forms pyrrhotite according to:

$$Fe_{(s)} + SO^{2-}_{4(aq)} + \tfrac{3}{4} CH_3COO^-_{(aq)} + 1\tfrac{1}{4} H^+_{(aq)}$$
$$\rightarrow FeS_{(s)} + 1\tfrac{1}{2} HCO^-_{3(aq)} + H_2O_{(l)}$$

The coupled processes for the boundary conditions, $[HCO_3^-] = [SO_4^{2-}] = 10^{-3}$ [mol/l], $[CH_3COO^-] = 10^{-6}$ [mol/l] give $\Delta G_r = -119.64$ [kJ/mol] and − 93.95 [kJ/mol] for pH 8.4 and 12 respectively and are thus exergonic. Temperature changes between 0 °C and 50 °C do not alter the direction of the reaction.

Under the conditions defined packaging and waste materials form reactive systems in repositories. The free energy released by the exergonic reactions can support microbial existence. Deterioration of the materials and environmental changes associated with them are mediated and thus accelerated by microorganisms until the repository system has reached a thermodynamically stable state.

Table 2.2. Half-reactions considered for bitumen degradation(1)

Nr.	Stoichiometric half-reaction equation	ΔH_r^0 [kJ/mol]	ΔS_r^0 [J/K · mol]	ΔG_r^0 [kJ/mol]
1	$\{C_{10}H_{14}\} + 30\,H_2O_{(l)} \longrightarrow 10\,HCO^-_{3(aq)} + 54\,e^- + 64\,H^+_{(aq)}$	+1592.28	+2121.18	+959.85
2	$\{C_{10}H_{14}\} + 10\,H_2O_{(l)} \longrightarrow 5\,CH_3COO^-_{(aq)} + 14\,e^- + 19\,H^+_{(aq)}$	+ 366.28	+ 432.17	+237.42
3	$Fe_{(s)} + H_2O_{(l)} \longrightarrow Fe(OH)^+_{aq} + 2e^- + 1\,H^+_{(aq)}$	− 38.90	+ 4.20	− 40.15
4	$Fe(OH)^+_{(aq)} + H_2O_{(l)} \longrightarrow Fe\,O(OH)_{(s)} + 1\,e^- + 2\,H^+_{(aq)}$	+ 75.70	+ 167.40	+ 25.80
5	$e^- + H^+_{(aq)} \longrightarrow \tfrac{1}{2} H_{2(aq)}$	− 2.10	− 36.35	+ 8.74
6	$e^- + 1\tfrac{1}{8} H^+_{(aq)} + \tfrac{1}{8} HCO^-_{3(aq)} \longrightarrow \tfrac{1}{8} CH_{4(aq)} + \tfrac{3}{8} H_2O_{(l)}$	− 31.80	− 39.93	− 19.90
7	$e^- + 1\tfrac{1}{8} H^+_{(aq)} + \tfrac{1}{4} HCO^-_{3(aq)} \longrightarrow \tfrac{1}{8} CH_3COO^-_{(aq)} + \tfrac{1}{2} H_2O_{(l)}$	− 30.65	− 42.23	− 18.06
8	$e^- + 1\tfrac{1}{8} H^+_{(aq)} + \tfrac{1}{8} SO^{2-}_{4(aq)} \longrightarrow \tfrac{1}{8} HS^-_{aq} + \tfrac{1}{2} H_2O_{(l)}$	− 31.40	− 24.75	− 24.02

(1) gaseous compounds are considered to be dissolved in the aqueous matrix.
Standard conditions: T = 298.15 K, concentrations 1-molal, pH = 0, I = 0.

3. Free energy of formation (Gf^0), enthalpy of formation (Hf^0) and entropy of formation (Sf^0) of organic compounds

Thermochemical values for numerous inorganic compounds are more easily available (table A.1) than those for the innumerable organic ones (table A.2). Since thermodynamic analyses applied to microbial ecology are aimed at investigating the coupling between inorganic and organic reactants, methods are needed which permit an accurate estimate of the thermochemical values of almost any organic molecule. Gf^0_A, Hf^0_A and Sf^0_A are defined for the oxidation of compound A (e.g., an organic substrate containing C, H and O atoms) with O_2 according to the stoichiometry

$$\boxed{\begin{aligned}&C_aH_bO_{c(g)} + 1/4\,(4a + b - 2c)O_{2\,(g)}\\ &\quad\longrightarrow a\,CO_{2\,(g)} + b/2\,H_2O_{(l)}\end{aligned}}$$

If Hf^0 and Sf^0 of substrate $C_aH_bO_{c(g)}$ can be determined one can calculate Gf^0 employing the known thermochemical values for $CO_{2(g)}$, $H_2O_{(l)}$ and $O_{2(g)}$ (table A.1). Following the relationships (42) to (45),

$$\Delta Gf^0 = \Delta Hf^0 - T \cdot \Delta Sf^0 \tag{42}$$

$$\begin{aligned}\Delta Gf^0 &= \sum_j v_j \cdot Gf^0_{P_j} - \sum_i v_i \cdot Gf^0_{S_i} \\ &= a \cdot Gf^0_{CO_{2\,(g)}} + \frac{b}{2} \cdot Gf^0_{H_2O_{(l)}} \\ &\quad - \frac{1}{4} \cdot (4a + b - 2c) \cdot Gf^0_{O_{2\,(g)}} - Gf^0_{C_aH_bO_{c\,(g)}}\end{aligned} \tag{43}$$

$$\begin{aligned}\Delta Hf^0 &= \sum_j v_j Hf^0_{P_j} - \sum_i v_i \cdot Hf^0_{S_i} \\ &= a \cdot Hf^0_{CO_{2\,(g)}} + \frac{b}{2} \cdot Hf^0_{H_2O_{(l)}} \\ &\quad - \frac{1}{4} \cdot (4a + b - 2c) \cdot Hf^0_{O_{2\,(g)}} - Hf^0_{C_aH_bO_{c\,(g)}}\end{aligned} \tag{44}$$

$$\Delta Sf^0 = \sum_j v_j \cdot Sf^0_{P_j} - \sum_i v_i \cdot Sf^0_{S_i} \tag{45}$$

(= analogous to ΔHf^0 and ΔGf^0)

free energy of formation of $C_aH_bO_{c\,(g)}$ becomes

$$\begin{aligned}Gf^0_{C_aH_bO_{c\,(g)}} &= a \cdot Gf^0_{CO_{2\,(g)}} + \frac{b}{2} \cdot Gf^0_{H_2O_{(l)}} \\ &\quad - \frac{1}{4} \cdot (4a + b - 2c) \cdot Gf^0_{O_{2\,(g)}} - Hf^0_{C_aH_bO_{c\,(g)}} \\ &\quad + T \cdot \Delta Sf^0_{C_aH_bO_{c\,(g)}}.\end{aligned} \tag{46}$$

Numerical values for 298.15 K from table A.1 introduced into eq. (46) yield the equation for the calculation of the free energy of formation:

$$\begin{aligned}Gf^0_{C_aH_bO_{c\,(g)}} &= 62.815 \cdot a + 34.720 \cdot b \\ &\quad - 15.280 \cdot (4a + b - 2c) + Hf^0_{C_aH_bO_{c\,(g)}} \\ &\quad - 0.29815 + Sf^0_{C_aH_bO_{c\,(g)}}.\end{aligned} \tag{47}$$

Example: Gf^0 for toluene ($C_7H_{8(g)}$) and acetic acid ($C_2H_4O_{2(g)}$) are calculated with corresponding entropy and enthalpy values from table A.2 inserted into equation (47):

$Gf^0_{toluene(g)} = + 122.1$ [kJ/mol]
$Gf^0_{acetic\ acid(g)} = - 374.1$ [kJ/mol]

The comparative values listed by Weast et al.[23] are 122.3 and − 374.0 [kJ/mol] respectively for toluene and acetic acid in the gaseous state.

Calorimetric measurements on heat of combustion and heat capacity as well as spectral data on electronic states have been determined for a large number of particular compounds. For comparative studies, the consistency of these data is often insufficient if they stem from individual experimental determinations.

Two methods for calculating Hf^0 and Sf^0 values are compared below. Enthalpy and entropy of formation are related to free energy of formation at constant temperature by relationship 42 above. Gf^0 and ΔGf^0 are the terms which are used most often. I have used Gf^0 exclusively. Gf^0 represents in a single term the combined contributions of enthalpy and entropy of formation of a compound.

3.1 Calculation of enthalpy of formation (Hf^0) from heat of combustion (ΔH^0_c)

The heats of combustion of organic compounds are standard reaction enthalpy changes which occur when the substrates are oxidized with $O_{2(g)}$ to $CO_{2(g)}$, $H_2O_{(l)}$, $N_{2(g)}$ and $SO_{2(g)}$. The products of halogenated (X) and phosphorus containing compounds are dilute aqueous solutions of HX and H_3PO_4 respectively. For a generalized combustion equation (oxidation states of S, N, P and X in the substrate molecule are − I, − III, + V and − I respectively),

$$\boxed{\begin{aligned}&\langle C_aH_bO_cN_dP_eS_fX_g\rangle + \tfrac{1}{4}(4a + b - 2c + 5e + 4f - g)\,O_2\\ &\rightarrow a\,CO_2 + d/2\,N_2 + f\,SO_2 + e\,H_3PO_4 + g\,HX\\ &\qquad + \tfrac{1}{2}(b - 3e - g)\,H_2O\end{aligned}}$$

heat of combustion is calculated from the sum of the enthalpies of formation of the products minus the sum of Hf^0 of the substrates:

$$\Delta H^0_c = \sum_j v_j \cdot Hf^0_{product(j)} - \sum_i v_i \cdot Hf^0_{substrate(i)} \tag{48}$$

with $v_{j,i}$ representing stoichiometric coefficients.

Conventionally the following enthalpies of formation of the products are used for calculations (values given in kJ/mol): $CO_{2(g)} = -393.5$, $H_2O_{(l)} = -285.8$, $N_{2(g)} = 0$, $O_{2(g)} = 0$, $SO_{2(g)} = -296.8$, $H_3PO_{4\,(dil.\,aq.)} = -1288.3$ and $HCl_{(dil.\,aq.)} = -166.7$.

Example: Hf^0 for toluene, can be calculated from its $\varDelta H^0$-value (from ref. 8) according to:

$$C_7H_{8\,(l)} + 9\,O_{2\,(g)} \longrightarrow 7\,CO_{2\,(g)} + 4\,H_2O_{(l)}$$

$$\begin{aligned} Hf^0_{C_7H_{8\,(l)}} &= 7 \cdot Hf^0_{CO_{2\,(g)}} + 4 \cdot Hf^0_{H_2O_{(l)}} - 0 - \varDelta H^0{}_{C_7H_{8\,(l)}} \\ &= 7 \cdot (-393.5) + 4 \cdot (-285.8) - (-3920.4) \\ &= +22.7\,[\text{kJ/mol}] \end{aligned}$$

Benson[1] lists a value for toluene(g) of + 50.208, Weast et al.[23] give + 49.99, and Hf^0 calculated according to the molecular group increment method outlined below yields $+49.93$ $(= 5 \cdot [C_B(H)] + [C_B(C)] + [C(H)_3(C_B)]$. Kharash[8] has offered simple equations for the calculation of heats of combustion of a large number of organic compounds. His values seem to be in relatively good agreement with data from other sources as illustrated for linear, saturated hydrocarbons in figure 3.1 a. Small differences in these large heat of combustion values express themselves more dramatically however in the much smaller enthalpy values which are calculated from them. Hf^0-values calculated for linear hydrocarbons with the group increment method compare well with those listed in Weast et al.[23]. They do not agree however with the corresponding values calculated with Kharash's method (fig. 3.1 b). Thus values for heat of combustion should only be used for the calculation of Hf^0 if it can be ascertained that the enthalpy values so obtained are consistent with like values derived by other methods.

3.2 Calculation of enthalpy (Hf^0) and entropy (Sf^0) of formation by the group increment method

Unfortunately no easily applicable thermodynamic relationship exists which would allow one to calculate enthalpy and entropy or Gibbs energy of formation for polyatomic molecules from simple molecular parameters. Empirical concepts have been developed however which make approximate calculations of molecular energy levels possible. The approach is based on the observation that chemical and physical properties of molecules are the sum of structural, as well as size and mass contributions of individual atoms, the bonds between them, the oxidation state and the interactions between neighboring functional groups within the more complex molecules. The concept has led to the formulation of the additivity rules for the determination of thermochemical molecular properties of organic compounds. Some rules of the group increment method are summarized below. They are explained in more detail by Benson[1]. For enthalpy of formation they are:

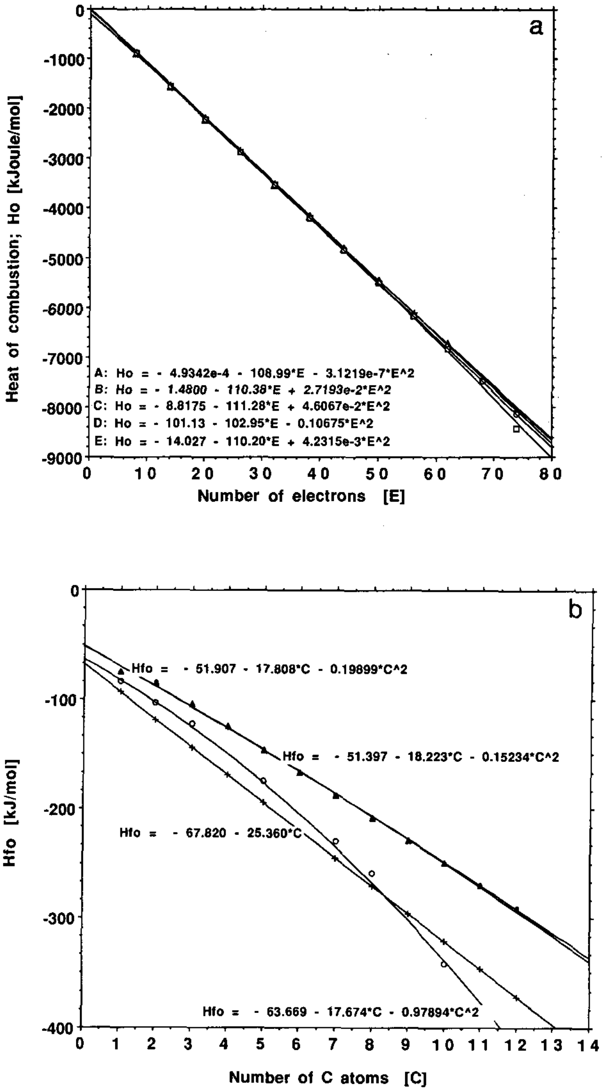


Figure 3.1. Enthalpy of formation (Hf^0) for saturated hydrocarbons calculated from heat of combustion (H_c^0). *a*) There are only small relative deviations between H_c^0-values compiled from different sources for hydrocarbons with $10 <$ electrons < 50. + calculated acc. to Kharash's formula (A); ◆ Kharash's experimental values (B); △ Ho as listed in Weast et al.[23] (C); □ calculated from enthalpies of formation (Hf^0) as listed in Weast et al.[23] (D); ○ calculated from Hf^0-values obtained from group property additions (E). *b*) Hf^0-values obtained from H_c^0 in (*a*), however, give unacceptable differences when they are calculated with the generalized equations used by Kharash[8]; ▲ Hf^0 as listed in Weast et al.[23]; ◆ Hf^0 calculated from group properties; + Hf^0 calculated from heat of combustion according to Kharash's formula; ○ Hf^0 calculated from heat of combustion with Kharash's experimental values.

$$\begin{aligned} Hf^0 &= \sum_{(i)} Hf^0_{\text{atomic group (i)}} + \sum\nolimits^{\text{positional}}_{\text{corrections}} \\ &= \sum_{(i)} Hf^0_{\text{atomic group (i)}} + Hf^0_{\text{gauche}} + Hf^0_{\text{cis}} + Hf^0_{\text{ortho}} \\ &\quad + Hf^0_{\text{ring strain}} \end{aligned} \tag{49}$$

and for entropy of formation:

$$\begin{aligned} Sf^0 &= \sum_{(i)} Sf^0_{\text{atomic group (i)}} + \sum^{\text{statistical}}_{\text{corrections}} + \sum^{\text{positional}}_{\text{corrections}} \\ &= \sum_{(i)} Sf^0_{\text{atomic group (i)}} + R \cdot \ln W - v_i \cdot R \cdot \ln \sigma + Sf^0_{\text{cis}} \\ &\quad + Sf^0_{\text{ortho}} + Sf^0_{\text{ring strain}} \,. \qquad (50) \end{aligned}$$

(R = gas constant, W = configurational possibilities, σ = symmetry factor, v_i = stoichiometry coefficient.)

Enthalpy and entropy values of atoms and functions with ≥ 2 covalent bond-possibilities are listed in table A.3. The values apply for gaseous states and standard conditions. The valencies of the group atoms or functions are occupied by the ligand atoms H, O, N, P, S, C or halogens (X).

Cis-trans isomerization, gauche configuration and conformational influences within ring compounds are structural interactions which cannot be included in the group property value a priori. Their contribution to the thermochemical values are considered by adding appropriate correction terms, some of which are summarized in table 3.1. The gauche corrections apply to atoms and functional groups other than H-atoms. If values for the usually more stable trans isomers are tabulated, the values for corresponding cis isomers are obtained by adding the correction term. Enthalpy of formation for the trans isomer of the ethylene functional group listed in table 3.2 for example is calculated from $2 \cdot [C_d(H)(C)] = 2 \cdot 35.94 = +71.88$ [kJ/mol]. Adding the cis correction gives $Hf^0_{cis} = 71.88 + 4.184 = +76.06$ [kJ/mol]. The corresponding entropy values are + 66.70 [J/K · mol] if the ethylene group is part of a 2-ene, + 64.19 if it is in a 3-ene and + 71.22 in but-2-ene. Applications of the group property correction rules are illustrated in the examples and in table 3.3. The total number of distinguishable configuration possibilities (W) statistically increase entropy by $R \cdot \ln W$. The total number of independent permutations of identical groups or atoms in a molecule that can be obtained by rotation of the entire molecule about its center of mass reduces entropy by $-R \cdot \ln \sigma$. Values for σ are: 1 for linear molecules without end-to-end symmetry like HCl, CO, CH_2CHCl, etc., 2 for linear or angular molecules with end-to-end symmetry like O_2, H_2S, CO_2, H_2O, NO_2, SO_2, CHClCHCl, etc., 3 for pyramidal and planar groups like NH_3, H_3O^+, $-CH_3$, NO_3^-, CO_3^{2-}; 4 · 3 for CH_4 and CCl_4; 4 for tetrahedral groups like SO_4^{2-}; 6 for cyclohexane, 10 for cyclopentane and 12 for the benzene ring. Thus the Sf^0-correction for a methyl group always amounts to $8.3145 \cdot \ln 3 = -9.1344$ [J/K · mol].

Table 3.1. Major positional correction terms

Correction[a]	Hf^0_{298} [kJ/mol]	Sf^0_{298} [J/K · mol]	other
A) *for non-next-nearest neighbor*			
– *gauche corrections for rotational isomers:*			
Alk*ane*	+ 3.347		
Alk*ene*	+ 2.092		
Ether oxygen	+ 2.092		
Oxygen	0		
Cl	+ 4.184		
– *cis corrections for geometrical double bond isomers:*			
(Hydrocarb.)	+ 4.184	0	for 2 enes
(Hydrocarb.)			
		– 2.510	for 3 enes
		+ 5.021	for but-2 ene
(Cl) (Cl)	– 1.255		
(Alkane) (Cl)	– 3.347		
– *ortho corrections for ring positions:*			
Hydrocarbons	+ 2.385	– 6.763	
Oxygen	0		
(Cl) (Cl)	+ 9.205		
(Alkane) (Cl)	+ 2.510		
B) *for ring – strain energy*			
Cyclopentane	+26.359	+114.223	$\sigma = 10$
Cyclohexane	+ 0.837	+ 76.567	$\sigma = 6$
Furan	–24.267		$\sigma = 1$
Tetrahydrofuran	+24.686		$\sigma = 1$
Dioxan	+13.807		$\sigma = 2$
Thiophene	+ 7.113	+ 98.742	$\sigma = 1$
Benzene[b]			$\sigma = 12$

[a] They need to be applied to particular configurations of compounds whose thermochemical values are obtained by the addition of group property values. σ = symmetry number (For details see ref. (1) and examples).

[b] Corrections are included in the group property value $[C_B(H)]$ of table A.3.

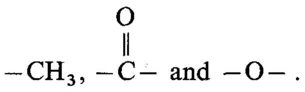
The following procedure is recommended for the determination of enthalpy and entropy of formation of organic compounds with the group increment method:

1) Draw the structure of the molecule.
2) Determine the number of polyvalent (≥ 2) atoms.
3) Assign group functions to the polyvalent atoms.
4) Add the group values from table A.3 for Hf^0 and Sf^0.
5) Determine cis, trans and ortho positions, gauche configurations, ring strain, symmetry factor (σ) and configurational possibilities (W).
6) Add correction values from table 3.1.

Thermochemical values for molecules consisting of 2 or more polyvalent atoms can also be obtained by the addition of the values of its functional groups some of which are compiled in table 3.2. The use of tables A.3 and 3.2 is illustrated with three examples:

Example 1:

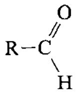
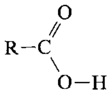
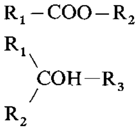
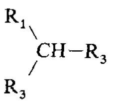
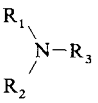
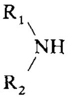
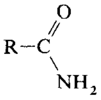
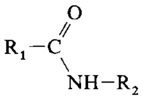
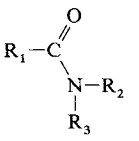
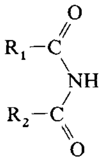
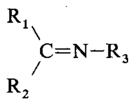
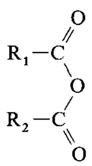
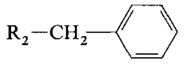
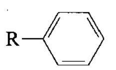
Pyruvic acid consists of six polyvalent atoms which form the following 3 groups:



$$-CH_3,\ -\overset{\overset{\displaystyle O}{\|}}{C}-\ \text{and}\ -O-\,.$$

They are written with the formalism applied to the listing in table A.3 as $[C(H)_3(CO)]$ for the methyl group attached to a carbonyl carbon, $[CO(C)(CO)]$ for the ketogroup attached to a methyl and a carboxyl carbon, $[CO(O)(CO)]$ for the carboxy group attached to a car-

Table 3.2. Enthalpies of formation (Hf^0) and entropies of formation (Sf^0) of major functional groups present in microbiologically and environmentally relevant compounds

Functional group	Hf^0_{298} (1) [kJ/mol]	Sf^0_{298} (1) [J/K mol]	Group name
$R-CH_3$	-42.17	$+118.11$ (3)	Methyl
$R-CH_2OH$	-192.46	$+162.63$	Alcohol, prim.
 $R-C(=O)-H$	-121.75	$+146.02$	Aldehyde
 $R-C(=O)-O-H$	-389.95	$+164.43$	Carboxyl
$R_1-CH_2-R_2$	-20.63	$+38.41$	Methylene
$R_1-CH_2O-R_2$	-130.96	$+77.32$	
$R_1-CHOH-R_2$	-188.69	$+75.61$	Alcohol, sec.
R_1-CO-R_2	-131.38	$+62.76$	Keto
$R_1-COO-R_2$	-327.19	$+97.07$	Ester
 $(R_1)(R_2)COH-R_3$	-186.18	-18.79	Alcohol, tert.
 $(R_1)(R_3)CH-R_3$	-7.95	-50.50	Methine
$R-OCH_3$	-139.24	$+154.43$ (3)	Methoxy
$R-OC_2H_5$	-173.13	$+195.43$ (3)	Ethoxy
$R-CH=CH_2$	$+62.13$	$+148.87$	Vinyl
$R_1-CH=CH-R_2$cis	$+76.06$	$+66.70$ (2)	Ethylene
$R_1-CH=CH-R_2$trans	$+71.88$	$+66.70$	
$R-OH$	-158.57	$+121.63$	Hydroxyl
$R-O-R$	-97.07	$+36.32$	Ether
 $(R_1)(R_2)N-R_3$	$+102.09$	-56.32	Amine, tert.
 $(R_1)(R_2)NH$	$+64.43$	$+37.40$	Amine, sec.
$R-NH_2$	$+20.08$	$+124.31$	Amine, prim.
$R-NO_2$	-63.20		Nitro
 $R-C(=O)-NH_2$	-199.58	$+171.08$	Amine, prim.
 $R_1-C(=O)-NH-R_2$	-155.65	$+84.10$	Amine, sec.
 $R_1-C(=O)-N(R_3)-R_2$	-35.15	$+11.46$	Amine, tert.
 $R_1-C(=O)-NH-C(=O)-R_2$	-351.88	$+172.96$	Imide
 $(R_1)(R_2)C=N-R_3$	$+132.37$	-109.46	Imine
 $R_1-C(=O)-O-C(=O)-R_2$	-488.28	$+158.99$	Anhydride
	-71.77	$+242.35$ (4)	Benzyl
	-92.10	$+203.30$ (4)	Phenyl

(1) values are valid for R = alkane carbon
(2) see text for deviation
(3) symmetry correction for methyl group included
(4) ring symmetry corrections included

bonyl carbon and [O(H)(CO)] for the hydroxy group attached to the carboxy carbon.

The thermochemical values for pyruvic acid are then calculated from table A.3 as

$$\begin{aligned} Hf^0_{\text{pyruvic acid}} &= Hf^0[C(H)_3(CO)] + Hf^0[CO(C)(CO)] \\ &\quad + Hf^0[CO(O)(CO)] + Hf^0[O(H)(CO)] \\ &= -42.17 - 122.17 - 122.59 - 243.09 \\ &= -530.02\ [\text{kJ/mol}] \end{aligned}$$

and

$$\begin{aligned} Sf^0_{\text{pyruvic acid}} &= Sf^0[C(H)_3(CO)] + Sf^0[CO(C)(CO)] \\ &\quad + Sf^0[CO(O)(CO)] \\ &\quad + Sf^0[O(H)(CO)] - R \cdot \ln 3 \\ &= +127.24 + 62.76 + 61.92 + 102.51 - 9.13 \\ &= +345.3\ [\text{J/K} \cdot \text{mol}] \end{aligned}$$

The values from table 3.2 cannot be used for this calculation since they were determined for 'R' representing alkane carbon atom(s) only.

Example 2:

Lactic acid contains five groups with the polyvalent atoms $[C(H)_3(C)]$, $[C(H)(O)(C)(CO)]$, $[CO(O)(C)]$, $[O(H)(CO)]$ and $[O(H)(C)]$ which can be merged for this special case into three functional groups: a methyl, a secondary alcohol and a carboxyl group. For the calculation of the thermochemical values of lactic acid the functional group values of table 3.2 may now be applied:

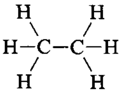
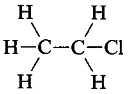
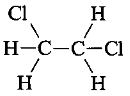
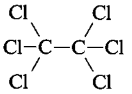
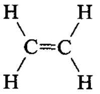
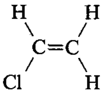
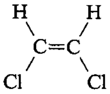
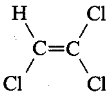
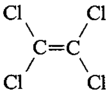
$$\begin{aligned} Hf^0_{\text{lactic acid}} &= Hf^0(-CH_3) + Hf^0(-CHOH) \\ &\quad + Hf^0(-COOH) \\ &= -42.17 - 188.69 - 389.95 \\ &= -620.81\ [\text{kJ/mol}] \end{aligned}$$

$$\begin{aligned} Sf^0_{\text{lactic acid}} &= Sf^0(-CH_3) + Sf^0(-CHOH) \\ &\quad + Sf^0(-COOH) \\ &= +118.11 + 75.61 + 164.43 \\ &= +358.15\ [\text{J/K} \cdot \text{mol}] \end{aligned}$$

Comparison with the calculations based on values from table A.3 illustrates the consistency of the two methods. Enthalpy and entropy of formation for lactic acid calculated from atomic group values are:

$$\begin{aligned} Hf^0_{\text{lactic acid}} &= Hf^0[C(H)_3(C)] + Hf^0[C(H)(O)(C)(CO)] \\ &\quad + Hf^0[CO(O)(C)] + Hf^0[O(H)(CO)] \\ &\quad + Hf^0[O(H)(C)] \\ &= -42.17 - 30.12 - 146.86 - 243.09 \\ &\quad - 158.57 \qquad = -620.81\ [\text{kJ/mol}] \end{aligned}$$

Table 3.3. Examples which illustrate the group increment method applied to organic compounds

Compound (gaseous state)	Additive group properties and correction terms	Hf^0 [kJ/mol]	Sf^0 [J/K · mol]	Hf^0 [kJ/mol]	Sf^0 [J/K · mol]
		Calculated values (for gaseous state)		Tabulated values in ref. (23)	
Ethane 	$2\cdot[C(H)_3(C)]$ $W = 1$ $\sigma = 3 + 2$ $-2R\cdot\ln 3 - R\cdot\ln 2$	− 84.34	230.448	− 84.684	229.492
Ethylchloride 	$[C(H)_3(C)] + [C(H)_2(C)(Cl)]$ $W = 1$ $\sigma = 3$ $-R\cdot\ln 3$	−111.210	276.266	−112.173	275.893
1,2-Dichlorethane 	$2\cdot[C(H)_2(C)(Cl)] + 2\cdot$gauche (Cl) $W = \frac{1}{2}\cdot 3!$ $+R\cdot\ln 3$ $\sigma = 2$ $-R\cdot\ln 2$	−129.788	313.928	−129.788	308.277
Hexachlorethane 	$2\cdot[C(C)(Cl)_3] + 6\cdot$ gauche (Cl) $W = 1$ $\sigma = 3 + 2$ $-2R\cdot\ln 3 - R\cdot\ln 2$	−148.116	397.708	−147.695	396.643
Ethene 	$2\cdot[C_d(H)_2]$ $W = 1$ $\sigma = 2$ $-2R\cdot\ln 2$	− 52.38	219.514	+ 52.258	219.451
Vinylchloride 	$[C_d(H)Cl)] + [C_d(H)_2] + 1$ gauche (Cl) $W = 1$ $\sigma = 1$	+ 25.344	263.63	+35.564	263.885
1,2 Dichlorethylene 	$2\cdot[C_d(H)Cl)] + 2$ gauche (Cl) + [cis(Cl)(Cl)] $W = 2$ $+R\cdot\ln 2$ $\sigma = 2$ $-R\cdot\ln 2$	− 1.672	296.22	−	−
Trichlorethylene 	$[C_d(H)Cl)] + [C_d(Cl)_2] + 1$ gauche $W = 1$ $\sigma = 1$	− 8.366	324.26	− 7.782	324.678
Tetrachlorethylene 	$2\cdot[C_d(Cl)_2] + 1$ gauche $W = 1$ $\sigma = 2$ $-2\cdot R\cdot\ln 2$	− 10.876	340.774	− 12.134	340.996

$$\begin{aligned} Sf^0_{\text{lactic acid}} &= +127.24 - 46.02 + 61.92 + 102.51 \\ &\quad + 121.63 - 9.13 \\ &= +358.15\ [\text{J/K} \cdot \text{mol}] \end{aligned}$$

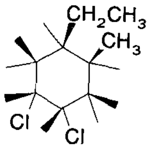
which corresponds to the values above.

A third example and the comparisons among the chlorinated hydrocarbons (table 3.3) illustrate the use of the correction terms as listed in table 3.1.

Parks and Huffmann[13] suggested rules to account for changes in entropy and free energy of formation accompanying structural modifications of a large number of compounds. Many of the thermochemical data which were available to these authors at the time no longer agree with the more precise values which have been determined since then. I have included their values in table A.2 only if no newer data could be found.

Example 3:

Calculation of enthalpy and entropy of formation for cis-1-ethyl,2-methyl,cis-4,5-dichlor-cyclohexane:



Addition of group properties:

	Hf^0	Sf^0
ethyl: $[C(H)_3C] + [C(H)_2(C)_2]$	$-42.17 - 20.63$	$+127.24 + 38.41$
methyl: $[C(H_3)(C)]$	-42.17	$+127.24$
C_1 and C_2: $2 \cdot [C(H)(C)_3]$	$2 \cdot (-7.95)$	$2 \cdot (-50.50)$
C_3 and C_6: $2 \cdot [C(H)_2(C)_2]$	$2 \cdot (-20.63)$	$2 \cdot (38.41)$
C_4 and C_5: $2 \cdot [C(H)(C)_2(Cl)]$	$2 \cdot (-61.92]$	$2 \cdot (73.64)$
Corrections:		
cis-correction for alkyl: C_1C_2	$+4.184$	0
cis-correction for (Cl) (Cl): C_4C_5	-1.255	
gauche-correction for alkyl: C_1C_2	$+3.347$	
gauche-correction for (Cl) (Cl): C_4C_5	$+4.184$	
C_6-ring correction	$+0.837$	$+76.567$
σ and W are each 1; $-2 \cdot R \cdot \ln 3$ accounts for the two methyl groups		-18.269
	-274.67 [kJ/mol]	$+474.29$ [J/K · mol]

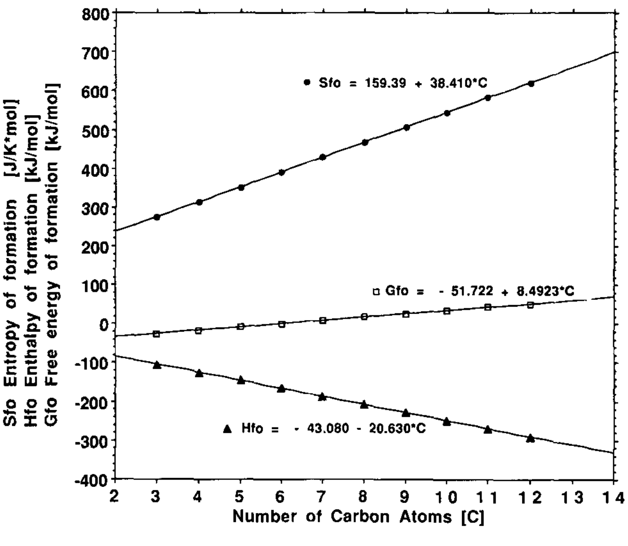


Figure 3.2. Deduction of the elongation rule for the introduction of methylene groups into a hydrocarbon chain. The slopes of the lines (− 20.630, 38.410 and 8.4923) represent the increments in Hf^0, Sf^0 and Gf^0 for $-CH_2-$, respectively. The corresponding increment values for the methylene group calculated from Weast's data[23] are: 38.530 for Sf^0, − 20.783 for Hf^0 and 8.3609 for Gf^0.

Modification rules which are applicable to today's data are contained in tables 3.2 and A.3. A very general one can be deduced from figure 3.2 which is based on values for saturated n-hydrocarbons. The values were calculated by applying the group increment method. Insertion of a methylene group into a hydrocarbon chain alters Hf^0 and Sf^0 by −20.63 [kJ/mol] and +38.41 [J/K · mol] respectively. The corresponding value for Gf^0 is +8.49 [kJ/mol]. The rules apply for n-hydrocarbons with more than 2 carbon atoms. With the three modification terms one can also calculate Gf^0, Hf^0 and Sf^0 for the gaseous state of straight chain primary alcohols with $C > 2$ and analogous mono- and dicarboxylic acids larger than propionic acid and succinic acid respectively. The group additivity rules are the most practical means for the determination of the thermochemical values for a large number of organic compounds. Hf^0 values are estimated to lay within ± 2.09 and ± 12.55 [kJ/mol], those of Sf^0 within ± 1.26 and ± 6.28 [J/K · mol] respectively. The upper limits apply to heavily substituted compounds[1].

Table A.2 contains a selection of common microbial substrates and products. Some of the values for gaseous states (labeled 'a' in the reference column) have been compiled with the group increment method employing values of table A.3.

3.3 Alternative approaches

Three additional methods for the calculation of thermochemical values should be mentioned:

a) Gf^0 derived from equilibrium constants,
b) Gf^0 derived from electrochemical potentials and
c) the additivity rules for chemical bond properties.

a) The change in standard Gibbs free energy (ΔGf^0) for the conversion of substrate A, in its standard state, into products X and Y in their respective standard states is related to the equilibrium constant (K^0) by:

$$\Delta Gf^0 = Gf^0_X + Gf^0_Y - Gf^0_A = -R \cdot T \cdot \ln K^0. \qquad (51)$$

For reactions which proceed rapidly enough towards equilibrium, K^0 (= dissociation coefficient for acids (K_a), solubility product for solids (K_s), etc.) can be determined experimentally. If the free energy of formation of all the reaction partners except one are known, the missing Gf^0 may be calculated from equation (51):

$$Gf^0_A = Gf^0_X + Gf^0_Y + R \cdot T \cdot \ln K^0 \qquad (52)$$

Example:

Gf^0 for anhydrite may be derived from standard conditions from $Gf^0_{SO^{-2}_{4(aq)}}$ (− 744.6), $Gf^0_{Ca^{2+}(aq)}$ (− 553.6) and the solubility product for anhydrite ($K_{CaSO_{4(s)}} = 7.1 \cdot 10^{-5}$)[23]:

$$\begin{aligned} Gf^0_{CaSO_{4(s)}} &= (-533.6) + (-744.6) \\ &\quad + 8.3145 \cdot 298.15 \cdot 10^{-3} \cdot \ln(7.1 \cdot 10^{-5}) \\ &= -1321.88 \text{ [kJ/mol]} \end{aligned}$$

(the value listed in table A.1 is − 1321.8 kJ/mol)

Measured equilibrium values (K^0) obtained from experiments at various temperatures are graphically related to the inverse of the temperature (1/T) by

$$\log K^0 = \frac{\Delta Sf^0}{2.3026 \cdot R} - \frac{\Delta Hf^0}{2.3026 \cdot R} \cdot \frac{1}{T}. \qquad (53)$$

ΔHf^0 is calculated from the slope (m), ΔSf^0 from the intercept (y_1) of a linear plot of $\log K^0$ versus $1/T$[17]:

$$\Delta Hf^0 = -2.3026 \cdot R \cdot m$$
$$\Delta Sf^0 = +2.3026 \cdot y_1$$

The unknown enthalpy and entropy of formation of substrate A is then obtained from

$$Hf^0_A = Hf^0_X + Hf^0_Y + 2.3026 \cdot R \cdot m \qquad (54)$$

$$Sf^0_A = Sf^0_X + Sf^0_Y - 2.3026 \cdot R \cdot y_1 \qquad (55)$$

b) Thermochemical values can also be obtained through voltage change measurements which occur as a consequence of a redox-reaction taking place in an electrical cell under constant conditions of pressure and temperature. The voltage change (E^0) expresses the tendency of the two half-reactions to lose and gain electrons. Faraday's constant (F = 96.485309 [kJ/V · mol]) is used to convert volts into kilojoules. The energy which is released while n mol-equivalents of electrons pass from reductant to oxidant is defined as

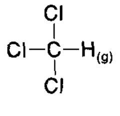
$$-n \cdot F \cdot E^0 = \Delta G^0_r. \qquad (56)$$

By convention, electrons which are lost by the oxidation half-reaction have a negative sign, electrons which are gained by the reduction half-reaction have a positive sign. E^0 is thus proportional to the Gibbs free energy of reaction for standard state conditions. Thermochemical values may be calculated from ΔG^0_r as outlined under (3.3a) above. In combination with the equation $\Delta G^0 = -R \cdot T \cdot \ln K^0$, the equilibrium constant may be deduced directly from electrochemical measurements:

$$\log K^0 = \frac{n \cdot F \cdot E^0}{2.3026 \cdot R \cdot T} \qquad (57)$$

c) Thermochemical values for small molecules in their gaseous state may also be estimated by the addition of individual bond properties. As with the group increment method, symmetry and isomeric corrections have to be accounted for separately. As an illustration, Hf^0 and Sf^0 are calculated with the bond enthalpy and entropy values listed by Benson[1] for chloroform and toluene.

Chloroform:



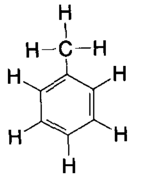
$Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}H_{(g)}$

$$\triangleq 3 \cdot [C{-}Cl] + 1 \cdot [C{-}H]; \quad \sigma = 3$$

$$\begin{aligned} Hf^0 &= 3 \cdot [-30.96] + [-16.02] \\ &= -108.9 \text{ [kJ/mol]} \\ Sf^0 &= 3 \cdot [82.42] + [53.97] - R \cdot \ln 3 \\ &= 292.1 \text{ [J/K} \cdot \text{mol]} \end{aligned}$$

The corresponding values in table A.2 are − 103.1 and 295.6 respectively.

Toluene:



$$\hat{=} 5 \cdot [\mathrm{Ar-H}] + [\mathrm{Ar-C}] + 3 \cdot [\mathrm{C-H}]; \quad \sigma = 3 + 2$$

$$Hf^0 = 5 \cdot [13.6] + [30.33] + 3 \cdot [-16.02]$$

$$= 50.27\,[\mathrm{kJ/mol}]$$ (to be compared with corresponding values discussed in section 3.1)

$$Sf^0 = 5 \cdot [48.95] + [-72.8] + 3 \cdot [53.97] - R \cdot [\ln 3 + \ln 2]$$

$$= 318.96\,[\mathrm{J/K \cdot mol}]$$

Values in table A.2 are 49.99 and 319.7 for Hf^0 and Sf^0 respectively.

The bond addition method works well for small molecules but it is less applicable to heavily branched and substituted compounds with bond partner atoms of different electronegativities.

4. Conclusion

It is intended to design repositories for radioactive waste in such a way that the nuclides will be retained for very long periods of time. No radioactive material should escape and find its way into any of the ecospheres which are linked to life. Repositories are thus designed as closed ecosystems. Since contamination with microbes cannot be prevented, the repositories become habitats where microorganisms can evolve physiological activities under appropriate conditions. Geological formations are frequently considered as sites for repositories since, from a thermodynamic point of view, rocks are normally rather stable solid phases. Many dissolution reactions are endergonic and remain so even when brought in contact with stabilized waste. Changing conditions, however, can lead to accelerated erosion and hence to destruction of the containment barriers and the repository location.

Evaluating the long-term stability of repositories entails defining the state of reactivity of the waste system and the reaction rates. The state of reactivity can be judged from chemical characteristics of the matter present and from its thermodynamic behavior under defined boundary conditions. The rates by which the matter is transformed are determined by the activation energy, the temperature, the number of catalytic sites and the concentration of substrates and products. State parameters thus influence rates and *vice versa*. In this presentation I have emphasized the effect of state parameters on the reactivity of the system and the role microbes play in altering state parameters.

A system which is in a thermodynamic nonequilibrium state with regard to possible reactions between its components is a potentially reactive system and therefore labile. The labile system may change into a meta-stable one if all the reactions have attained equilibrium states under the prevailing conditions. Any change in the conditions, however, can displace the equilibrium into a labile one again. Equilibria reached under anoxic conditions are always meta-stable states in relation to the oxic world. They remain stable as long as access of oxygen is prevented. A repository has reached a stable state if all reactions have progressed to equilibrium and if changes in the conditions will not lead to a reactivation of the system. In a non-reactive system all components are fully oxidized, water being the only reduced species. An external input of energy is needed to reactivate a thermodynamically stable system.

A mixed waste system containing oxidizable matter and oxidants is a thermodynamically unstable system. Its components are destined to react and the reaction products will lead to alterations in the conditions and possibly also in the habitat. Changing state parameters like pH, pe, E, T, I, a_w, addition of substrates and removal of products, will alter thermodynamic states and therefore the reactivity of a system. Microbes which mediate conversion reactions regulate the stability of the system through their influence on state parameters. In turn, microbes which convert part of the free energy of reaction via biochemical pathways into work and chemical bond energy of biosyntheses products, need reactive systems to live. Microorganisms surviving in meta-stable systems might become active again once the system changes into a labile one.

Conditions leading to exergonic reactions are a prerequisite for a process to take place but do not alone suffice for the reaction to be mediated by microbes. Recalcitrant and xenobiotic compounds, for example, will not be transformed biologically. Evolution is yet progressing to the point where all organic molecules, both natural and man-made, can be degraded by microbial enzymes. But rates of changes in today's microbial inadequacy cannot be predicted for the future.

Thermodynamic considerations are a means of forecasting *directions* and *probabilities* of reactions. *Reaction rates* cannot be deduced and hence the time scale for alterations cannot be predicted. Forecasts based on thermodynamic considerations are valid only for the chosen set of boundary conditions. Alterations in these state parameters will lead to variations in the scenario.

Equations derived from thermodynamic laws represent ecological state functions (table A.4). They are well suited to describe the energetic conditions within a particular ecosystem. Applied to microbial ecology of nuclear waste repositories they:

- provide a means for quantitative description of the chemical non-equilibrium state,
- might clarify relationships between ecological state parameters and their variabilities,
- can be used to calculate the thermodynamic functions from which directions of reactions are predicted,
- guide in selecting the proper parameters to be measured in the environment,

- permit one to design model calculations about possible or expected reactions under changing conditions or to eliminate impossible processes, and
- help in designing experiments and in choosing the appropriate kind of observations to be pursued in the natural environment and in artificial microbial ecosystems.

Abbreviations

a, b, c, d, e, f, g, x, y, z	stoichiometric coefficients
act	*act*ual conditions, e.g. T_{act}
a_j	ion size parameter in $[10^{-8}$ cm]
(am)	*am*orphous state
(aq)	*aq*ueous state
[atm]	standard atmosphere: 1 [atm] $\hat{=}$ 101 325 [Pa] $\hat{=}$ 760 [Torr] $\hat{=}$ 1.01325 [bar]
a_w	water activity
bar	1 [bar] $\hat{=}$ 10^5 [Pa] $\hat{=}$ 0.986923 [atm] $\hat{=}$ 750.062 [Torr]
c	denotes *c*ombustion, e.g. ΔH_c^0
c_i	concentration of chemical species i
c_i^0	standard concentration of species j [1 mol/dm^3]
e^-	electron
e	base of natural logarithm = 2.71828183
emf	electromotive force
eq	*eq*uilibrium
exp	*exp*onential function to base e
f	denotes thermochemical quantity associated with the formation of a substance from elements in their reference state, e.g. Gf, Hf, Sf
f_j	Debye-Hückel activity correction factor
(g)	*g*aseous state
h	surplus charge of biomolecule
i, j	chemical species designation
(l)	*l*iquid state
[l]	liter
ln	natural logarithm = 2.302585 · $_{10}$ log
ln 10	natural logarithm of 10 = 2.302585
m	slope of a linear function
n	number of electrons transferred
neq	*n*on-*eq*uilibrium
ox	*ox*idized
p	pressure
p^0	standard state pressure 1 [atm] (earlier), 1 [bar] (today)
pe	$-\log \{e^-\}$; electron activity
pe^0	electron activity reference state $= \frac{1}{n} \cdot \log Keq \hat{=} F \cdot E^0/2.3026 \cdot R \cdot T$
pK	$-\log K$
$\pm q$	number of protons transferred, + if they are produced, − if they are consumed
r	denotes thermodynamic quantity associated with a *r*eaction, e.g. ΔG_r, ΔH_r, ΔS_r
ref	*ref*erence state e.g. T_{ref} = 298.15 [K]
red	*red*uced
(s)	*s*olid state
$v_{i,j}$	stoichiometric coefficients of species i, j
x, y, z	stoichiometric coefficients
y_1	intercept on y-axes
z_j	charge of species j
[ ]	designates concentration, or monomer unit
{ }	designates activity
< >	designates hypothetical unit molecule, e.g. for biomass
$[-C_aH_b-]$	designates repetitive molecular fragment e.g. monomer molecule
$[C(H)_2(C)(CO)]$	designates group increment
$\alpha_0, \alpha_1, \alpha_2$	acid-base pair distribution coefficients
$\gamma_0, \gamma_1, \gamma_2$	for mono- and diprotic acids
$\varepsilon_0, \varepsilon_1$	
$\vartheta_0, \vartheta_1, \vartheta_2$	
Σ	sum of terms
Π	product of terms
ε_T	temperature-dependent dielectric coefficient of water
σ	symmetry factor
I +, II −, V +, U, R, etc.	designates oxidation states
+, −, 2 −, 3 + h etc.	designates ionic charges
^{0}	denotes standard state conditions with reactants in their pure state present at a pressure of 1 [atm] if the reactants are gases or 1-molal concentrations if the reactants are solutes
$^{0\prime}$	denotes standard state except for 1 reactant (e.g. $\mathrm{pH} \neq 0$)
A, B, C, D, ... X, Y, Z	chemical species
A, B	Debye-Hückel-Onsager parameters $A = 1.82 \cdot 10^6 (\varepsilon_T \cdot T)^{-3/2}$ $B = 50.3 \cdot (\varepsilon_T \cdot T)^{-1/2}$
A^-, A^{2-}	anions of mono and diprotic acids
[°C]	temperature in degree Celsius = T/K − 273.15
C_T	sum of inorganic carbonate species $= [CO_{2(aq)}] + [H_2CO_{3(aq)}] + [HCO_{3\ (aq)}^-]$ $+ [CO_{3\ (aq)}^{2-}]$
C, H, O, N, P, S	most common chemical elements in organic biomolecules
[Da]	Dalton
E	electrochemical potential in [V] = emf
E^0	standard emf = electrochemical reference potential [V] $= -\Delta G_r^0/n \cdot F \hat{=} 2.3026 \cdot RT \cdot p_e{}^0/F$
$E^{0\prime}$	standard emf at $\mathrm{pH} \neq 0$
F	Faraday's constant = 96.485309 $[kJ \cdot mol^{-1} \cdot V^{-1}]$
Gf^0	standard free energy of formation [kJ/mol]
ΔGf^0	standard Gibbs free energy change of formation
ΔG_r^0	change of Gibbs free energy of reaction at standard conditions $= -R \cdot T \cdot \ln K^0$
$\Delta G_r^{0\prime}$	change of Gibbs free energy of reaction at standard conditions except for one reactant (e.g. at $\mathrm{pH} \neq 0$)
ΔG_r	change of Gibbs free energy of reaction at actual conditions
H^+	proton
Hf^0	standard enthalpy of formation [kJ/mol]
ΔHf^0	standard enthalpy change of formation
ΔH_r^0	change of enthalpy of reaction at standard conditions

ΔH_r	change of enthalpy of reaction at actual conditions
ΔH_c^0	change of standard heat of combustion
HA, H_2A	mono- and diprotic acids, protonated
I	ionic strength $= \frac{1}{2}\sum_j c_j \cdot z_j{}^2$ [mol/l]
IAP	ion activity product
[J]	Joule
[K]	temperature in Kelvin degree
K	dissociation, equilibrium or solubility coefficient
K'_1, K'_2	temperature and/or ionic strength corrected dissociation coefficient
K_a^0	thermodynamic acid dissociation coefficient
K_D	Ostwald coefficient $= K_H \cdot R \cdot T$ [–]
$K_{eq} \triangleq K^0$	thermodynamic equilibrium coefficient
log Keq	$= -\Delta G_r^0/2.3026 \cdot R \cdot T$
K_H	Henry's law constant [mol $\cdot 1^{-1} \cdot$ atm^{-1}]
K_s^0	thermodynamic solubility product for standard conditions
K'_s	actual solubility product for $I \neq 0$
$K_s^{0'}$	operational solubility product for standard conditions at $I = 0$
K_w	dissociation coefficient of water
[kJ]	kilojoule $= 10^3$ Joule
L_T	sum of inorganic sulfate species $= [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$
M	sum of minor elements in organic molecule
P	reaction-product
[Pa]	1 Pascal $\triangleq 9.86923 \cdot 10^{-6}$ [atm] $\triangleq 7.50062 \cdot 10^{-3}$ [Torr]
Q	ratio of actual activity products of reactants
Q′	ratio of actual activity products of reactants excluding protons (or/and electrons in half-reactions)
–R–	rest of organic molecule, mostly C-entity
R^+	average oxidation state of M
R	gas constant $= 8.31451 \cdot 10^{-3}$ [kJ $\cdot$ mol$^{-1} \cdot$ K^{-1}] (concentration basis) $= 82.057844 \cdot 10^{-3}$ [atm $\cdot$ l $\cdot$ mol$^{-1} \cdot$ K^{-1}] (pressure basis)
R_T	sum of acetate and acetic acid $= [CH_3COO^-] + [CH_3COOH]$
S	substrate
Sf^0	standard entropy of formation [J/K $\cdot$ mol]
ΔSf^0	standard entropy change of formation
ΔS_r^0	change of entropy of reaction at standard conditions
ΔS_r	change of entropy of reaction at actual conditions
S_T	sum of inorganic sulfide species $= [H_2S] + [HS^-] + [S^{2-}]$
T	thermodynamic temperature in [K]
U	oxidation state (number) of carbon in an organic molecule
[V]	volt
V_0	molar volume of ideal gas (at $p^0 = 1$ bar, $T = 273.15$ K) $= 22.71108$ [l $\cdot$ mol^{-1}], $\triangleq 22.41409$ [l $\cdot$ mol^{-1}] for $p^0 = 1$ [atm] and $T = 273.15$ K; for $p^0 = 1$ [atm] and $T = 298.15$ K, $V_0 = 24.46554$ [l $\cdot$ mol^{-1}]
W	number of possible structural configurations
X, Y	chemical species

Appendix

Unless indicated otherwise the values listed in tables A.1–A.3 are valid for standard conditions of pressure (p = 101 325 Pascal = 1 atm) and temperature (T = 298.15 K = 25 °C). The physical states are labeled with g for gaseous, l for liquid, am for amorphous, s for solid and aq if the compound is dissolved in water. Hf_T^0, Sf_T^0 and Gf_T^0 represent the changes in enthalpy and entropy of formation and the Gibbs free energy of formation respectively when 1 gram-mol of the compound in its standard state is formed isothermally at the indicated temperature T from the elements in their standard reference state. The standard state free energy and enthalpy-values ($Gf_{298.15}^0$ and $Hf_{298.15}$) for the elements are zero.

The change of a substance from its gaseous to its liquid state is associated with an entropy decrease (increased order) and an increase in the absolute value of the enthalpy. Entropies of vaporization for most of the substances listed in table A.2 vary between 40 and 120 [J/K $\cdot$ mol], those for enthalpies of vaporization between 5 and 40 [kJ/mol][3]. The values are deduced from measurements of heat of vaporization. Dissolution of a solute in water and the formation of ions and aquo-complexes may produce or absorb heat. Heats of solution and ionization are therefore also linked to entropy and enthalpy changes. Although proper thermochemical values for aqueous states are important for the application of thermodynamics to natural systems, their calculation would go beyond the limit of this presentation.

The standard state for an aqueous solution of dissolved solute j is defined for a hypothetical ideal solution containing 1 mol of solute (1 molal). Hf^0 of j in the 1-molal solution is the same as in the indefinitely dilute real solution; enthalpy of dilution is then zero. Hf^0-values for solutes in their standard state are thus the apparent molal enthalpies of formation of the compound in the infinitely dilute real solution (ionic strength I = 0).

The thermochemical values of ions in aqueous solutions are based on the convention that Hf^0, Gf^0 and Sf^0 for the proton (aqueous standard state, 1-molal) are zero. Values for undissociated acids (labeled 'b' in table A.2) are calculated from the Gf^0-values of the dissociated forms and the dissociation coefficients:

$$HA \Leftrightarrow A^- + H^+;\ \Delta G_r^0 = Gf_{A^-}^0 + Gf_{H^+}^0 - Gf_{HA}^0$$
$$= -R \cdot T \cdot \ln K_a^0$$

Since $Gf_{H^+}^0 = 0$ (table A.1):

$$Gf_{HA}^0 = Gf_{A^-}^0 + R \cdot T \cdot \ln K_a^0$$
$$= Gf_{A^-}^0 - 2.3026 \cdot R \cdot T \cdot pK_a^0 \qquad (1\,A)$$

and for diprotic acids:

$$Gf_{H_2A}^0 = Gf_{A^{2-}}^0 - 2{,}3026 \cdot R \cdot T \cdot (pK_{a1}^0 + pK_{a2}^0) \qquad (2\,A)$$

The following dissociation equilibrium constants were used (values given as $pK_a^0 = -\log K_a^0$): propionic acid 4.88; butyric acid 4.81; succinic acid $pK_{a1}^0 = 4.16$,

Table A 1. Molar standard Gibbs free energy (Gf^0), enthalpy (Hf^0) and entropy (Sf^0) of formation of some inorganic compounds relevant in natural ecosystems. (Sequence of arrangement: H, O, C, N, P, S, Halogen, Fe, Mn, Ca, Mg, Na, K, Al, Si)

Element: Hydrogen

Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Electron	e^-		g/aq	0	0	+65.25	
Proton	H^+ (pH = 0)		aq	0	0	0	22
Hydrogen	H_2		g	0	0	+130.5	22
			aq	17.55	−4.16	+57.7	

Element: Oxygen

Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Oxygen	O_2		g	0	0	+205.0	22
			aq	+16.4	−11.7	+110.9	22
Water	H_2O		l	−237.2	−285.8	+69.9	22, 23
			g	−228.6	−241.8	+188.7	22, 23
Hydroxyl	OH^-		aq	−157.3	−230.0	−10.7	22, 23
Ozone	O_3		g	+135.6	+143.2	+238.8	23, 1
Hydrogen peroxide	H_2O_2		aq	+134.0	−191.2	+143.9	22
			g	+105.4	−136.1	+232.9	1

Element: Carbon

Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Graphite	C		s	0	0	+5.74	22
Carbon dioxide	CO_2		g	−394.4	−393.5	+213.7	22, 1
			aq	−386.0	−413.8	+117.6	22
Carboxylic acid	H_2CO_3	undissoc.	aq	−623.2	−699.6	+187.4	22, 23
Bicarbonate	HCO_3^-		aq	−586.9	−692.0	+91.2	22, 23
Carbonate	CO_3^{2-}		aq	−527.9	−677.1	−56.9	22, 23
Carbon monoxide	CO		g	−137.2	−110.5	+197.6	22, 23
			aq	−119.9	−121.0	+104.6	23
Carbondisulfide	CS_2		l	+65.3	+89.7	+151.3	23
			g	+67.2	+117.4	+237.7	23
			aq	+89.1			
Carbonoxisulfide	COS		g	−169.3	−142.1	+231.5	23
Methane	CH_4		g	−50.8	−74.8	+186.2	23
			aq	−34.4	−89.0	+83.7	23

Element: Nitrogen

Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Nitrogen	N_2		g	0	0	+191.5	22, 23
			aq	+18.2	−10.5	+95.4	12
Nitrogen oxide	NO		g	+86.6	+90.2	+210.8	22, 23
Dinitrogen oxide	N_2O		g	+104.2	+82.0	+219.8	22, 23
Nitrogen dioxide	NO_2		g	+51.3	+33.2	+240.0	22, 23
Ammonia	NH_3		g	−16.5	−46.1	+192.7	22, 23
		undissoc.	aq	−26.6	−80.3	+111.3	22, 23
Ammonium	NH_4^+		aq	−79.4	−133.3	+111.2	22, 23
Nitrous acid	HNO_2	undissoc.	aq	−50.6	−119.2	+135.6	22
			g	−46.0	−76.6 (300 K)	+249.4 (300 K)	1, 21
Nitrite	NO_2^-		aq	−32.2	−104.6	+123	22, 23
Nitric acid	HNO_3	undissoc.	aq	−111.3	−207.4	+146.4	22, 23
			g	74.8	−134.3 (300 K)	+266.5 (300 K)	21, 1
(dilute acid solution)	$HNO_{3\ \mathrm{dil}}$		aq		−202.9		23
Nitrate	NO_3^-		aq	−111.3	−207.4	+146.9	14, 22, 23

Element: Phosphorus

Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Phosphorus white	P	undissoc.	s	0	0	+41.1	23
Phosphoric acid	H_3PO_4		aq	−1142.6	−1288.3	+158.2	22
Dihydrogenphosphate	$H_2PO_4^-$		aq	−1130.3	−1296.3	+90.4	22
Hydrogenphosphate	HPO_4^{2-}		aq	−1089.1	−1292.1	−33.5	22
Phosphate	PO_4^{3-}		aq	−1018.8	−1277.4	−222.0	22
Hydroxiapatite	$Ca_{10}(PO_4)_6OH_2$		s	−12677.0	−13477.0	+780.7	22
Brushite	$CaHPO_4 \cdot 2H_2O$		s	−2154.8	−2403.6	+189.5	22, 23
Monetite	$CaHPO_4$		s	−1681.3	−1814.4	+111.4	22
Calcium hydrogenphosphate	$Ca(HPO_4)$		aq	−1642.8	−1835.0	−86.6	23
Ca-dihydrogenphosphate prec.	$Ca(H_2PO_4)_2$		s	−2812.0	−3114.6	+189.5	9

Table A 1. Continued

Element: Phosphorus cont. Compound name	Formula	State	$Gf^0_{(298)}$ [kJ·mol⁻¹]	$Hf^0_{(298)}$ [kJ·mol⁻¹]	$Sf^0_{(298)}$ [J·K⁻¹·mol⁻¹]	Ref.
Ca-dihydrogenphosphate	$Ca(H_2PO_4)_2$	aq	− 2814.3	− 3135.4	+127.6	23
Ca-dihydrogenphosphate prec.	$Ca(H_2PO_4)_2 \cdot H_2O$	s	− 3058.4	− 3409.7	+259.8	23
Ca-phosphate	$Ca_3(PO_4)_2$	s	− 3884.8	− 4120.8	+236.0	23
	$Ca_3(PO_4)_2$	aq	− 3698.2	− 4183.2	−602.5	23
Strengite	$FePO_4 \cdot 2H_2O$	s	− 1657.5	− 1888.2	+171.3	22, 23
Heterosite	$FePO_4$	s	− 1184.9	− 1297.5	+100.8	12
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	s	− 4377.2			20
Ferrous hydrogenphosphate (ion pair)	$Fe(HPO_4)^0$	aq				-
Ferrous dihydrogenphosphate ion	$Fe(H_2PO_4)^+$	aq				-
Berlinite	$AlPO_4$	s	− 1617.9	− 1733.9	+ 90.8	22
Variscite	$AlPO_4 \cdot 2H_2O$	s	− 2111.4	− 2353.3	+134.5	12
Manganesephosphate prec.	$Mn_3(PO_4)_2$	s	− 2858.0	− 3226.0	+299.6	9
Farringtonite	$Mg_3(PO_4)_2$	s	− 3538.7	− 3780.7	+189.2	22
Magnesiumhydrogenphosphate	$Mg(HPO_4)^0$	aq	− 1563.4			22
Magnesiumdihydrogenphosphate-ion	$Mg(H_2PO_4)^+$	aq				-
Magnesiumphosphate-ion	$Mg(PO_4)^-$	aq				-
Phosphine	PH_3	g	+13.39	+ 5.44	+210.12	23
		aq	+25.31	− 9.50	+120.08	23

Element: Sulfur Compound name	Formula		State	$Gf^0_{(298)}$ [kJ·mol⁻¹]	$Hf^0_{(298)}$ [kJ·mol⁻¹]	$Sf^0_{(298)}$ [J·K⁻¹·mol⁻¹]	Ref.
Sulfur	S^0 (rhombic)		s	0	0	+ 32.1	22, 23
	S^0 (monoclinic)		s	+ 0.1	+ 0.3	+ 32.6	22, 12
	S^0 (cyclo)		s	-	+ 102.5 (300 K)	+ 431 (300 K)	1
Dihydrogen sulfide	H_2S		g	− 33.6	− 20.6	+ 205.8	22, 23
		undissoc.	aq	− 27.9	− 39.7	+ 121.0	22
Hydrogen sulfide	HS^-		aq	+ 12.1	− 17.6	+ 62.8	22
Sulfide	S^{2-}		aq	+ 85.8	+ 33.1	− 14.6	22
Disulfide	S_2^{2-}		aq	+ 79.5	+ 30.1	+ 28.5	22
Trisulfide	S_3^{2-}		aq	+ 73.7	+ 25.9	+ 66.1	22
Tetrasulfide	S_4^{2-}		aq	+ 69.1	+ 23.0	+ 103.3	22
Pentasulfide	S_5^{2-}		aq	+ 65.7	+ 21.3	+ 140.6	22
Polysulfide	S_n^{2-}						-
Thiosulfate	$S_2O_3^{2-}$		aq	− 522.5	− 648.5	+ 67.0	10, 22
Hydrogenthiosulfate	$HS_2O_3^-$		aq	− 523.6	− 624.7	+ 162.8	12
Dihydrogenthiosulfate	$H_2S_2O_3$	undissoc.	aq	− 527.0	− 604.4	+ 242.2	12
Dithionate	$S_2O_6^{2-}$		aq	− 966	−1173.2	+ 126	9
Trithionate	$S_3O_6^{2-}$		aq	− 958.0	−1167.0	+ 138.0	10, 9
Tetrathionate	$S_4O_6^{2-}$		aq	−1040.4	−1224.2	+ 257.3	10, 22
Pentathionate	$S_5O_6^{2-}$		aq	− 956.0	−1176.0	+ 167	10, 9
Polythionate	$S_nO_6^{2-}$						-
Dithionite (Hydrosulfite)	$S_2O_4^{2-}$		aq	− 600.3	− 753.5	+ 92.0	22
Hydrogendithionite	$HS_2O_4^-$		aq	− 614.5			22
Dihydrogendithionite	$H_2S_2O_4$	undissoc.	aq	− 616.6			22
Disulfite (Pyrosulfite)	$S_2O_5^{2-}$		aq	− 791.0	− 971	+ 105	9
Dithionate	$S_2O_6^{2-}$		aq	− 966	−1173.2	+ 126	9
Peroxidisulfate	$S_2O_8^{2-}$		aq	−1114.9	−1344.7	+ 244.3	22
Dihydrogenperoxidisulfate	$H_2S_2O_8$	undissoc.	aq	−1096	−1356.9	+ 146	9
Sulfur dioxide	SO_2		g	− 300.2	− 296.8	+ 248.1	22, 1
			aq	− 300.7	− 323.0	+ 162.0	21
Sulfur trioxide	SO_3		g	− 371.1	− 395.7	+ 256.8	22, 1
Sulfur monoxide	SO		g	− 19.8	6.26	+ 221.8	22, 1
Sulfurous acid	H_2SO_3	undissoc.	aq	− 537.8	− 608.8	+ 232.2	22
Hydrogen sulfite	HSO_3^-		aq	− 527.7	− 626.2	+ 139.7	22
Sulfite	SO_3^{2-}		aq	− 486.6	− 635.5	− 29.3	22, 23
Sulfuric acid	H_2SO_4	undissoc.	aq	− 744.6	− 909.3	− 20.1	23
Sulfuric acid (dil. aqueous sol.)	$H_2SO_{4\ \mathrm{dil.}}$	undissoc.	aq		− 893.5		23
Hydrogen sulfate	HSO_4^-		aq	− 756	− 887.3	+ 131.8	22, 23
Sulfate	SO_4^{2-}		aq	− 744.6	− 909.6	+ 18.8	22, 23

Table A 1. Continued

Elements: Halogens

Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Chloride	Cl^-	aq	−131.2	−167.1	+ 56.7	22
Fluoride	F^-	aq	−278.8	−335.4	− 13.2	22
Bromide	Br^-	aq	−104.0	−121.5	+ 82.8	22
Iodide	I^-	aq	− 51.6	− 56.9	+106.7	22
Hydrogenchloride	HCl	g	− 95.3	− 92.3	+186.8	22
Hydrogenchloride (dil. aqueous sol.)	HCl	aq	−131.2	−166.7	+ 55.1	15, 23
Hydrogenbromide	HBr	g	− 53.4	− 36.4	+198.6	22
Hydrogenbromide (dil. aqueous sol.)	HBr	aq		−121.2		23
Hydrogenfluoride	HF	g	−273.2	−273.3	+173.7	22
Hydrogenfluoride (dil. aqueous sol.)	HF	aq	−296.8	−320.1	+ 88.7	22, 23
Hydrogeniodide	HI	g		+ 26.4	+206.5	23
Hydrogeniodide (dil. aqueous sol.)	HI	aq		− 54.8		23

Element: Iron

Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Iron metal	Fe	s	0	0	+ 27.3	22
Ferrous ion	$Fe(II+)^{2+}$	aq	− 78.9	− 89.1	−137.7	22
Ferric ion	$Fe(III+)^{3+}$	aq	− 4.6	− 48.5	−315.9	22, 23
Ferric tetrahydroxi ion	$Fe(OH)_4^-$	aq	− 843.9			12
Ferric dihydroxi ion	$Fe(OH)_2^+$	aq	− 457.2	− 551.3	−18.0	11
Ferric hydroxi ion	$Fe(OH)^{2+}$	aq	− 229.4	− 290.8	−142	22
Ferrous hydroxi ion	$Fe(OH)^+$	aq	− 277.4	− 324.7	− 29	22
Ferrous trihydroxi ion	$Fe(OH)_3^-$	aq	− 614.9			22
Ferrous oxi(hydroxi) ion	$FeO(OH)^-$	aq	− 379.1			25
Ferrous tetrahydroxi ion	$Fe(OH)_4^{2-}$	aq	− 769.7			22
Ferrous hydroxide (Amakinite)	$Fe(OH)_2$	s	− 493.0	− 573.2	+ 92.5	12
prec. white	$Fe(OH)_2$	s	− 486.6	− 569.0	+ 87.9	22, 23
ion pair	$Fe(OH)_2^0$	aq	− 459.2			12
Ferric-hydroxide prec.	$Fe(OH)_3$	s	− 696.6	− 823.0	+106.7	22, 23
ion pair	$Fe(OH)_3^0$	aq	− 659.4			22, 23
Goethite	α-FeO(OH)	s	− 490.4	− 559.0	+ 67.4	12
Ferric (hydr)oxide	FeO(OH)	am	− 462			9
Ferric oxide ion	$Fe_2O_4^{2-}$	aq	− 464.4			25
Haematite	α-Fe_2O_3	s	− 742.2	− 824.2	+ 87.4	22
Magnetite	Fe_3O_4	s	−1015.5	−1118.4	+146.4	22, 23
Siderite	$FeCO_3$	s	− 666.7	− 740.6	+ 92.9	22
Ferrous hydrogen-carbonate ion	$Fe(HCO_3)^+$	aq				
Pyrrhotite	FeS	s	− 100.8	− 100.4	+ 60.3	7
Pyrrhotite iron rich	FeS	s	− 100.4	− 100.0	+ 60.3	22
Pyrrhotite iron poor = sulfur rich	$Fe_{0.877}S$	s	− 93.6	− 92.0	+ 60.7	22
Pyrite	FeS_2	s	− 166.9	− 178.2	+ 52.9	22
Marcasite	FeS_2	s	− 158.4	− 169.4	+ 53.9	14
Strengite	$FePO_4 \cdot 2H_2O$	s	−1657.5	−1888.2	+171.3	22, 23
Heterosite	$FePO_4$	s	−1184.9	−1297.5	+100.8	12
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	s	−4377.2			20
Ferrous sulfate	$FeSO_4$	s	− 820.8	− 928.4	+107.5	22
Melanterite	$FeSO_4 \cdot 7H_2O$	s	−2509.9	−3014.6	+409.2	22
Ferric sulfate	$Fe_2(SO_4)_3$	s	−2250.0	−2576.9	+282.8	14
Ferric sulfate ion	$Fe(SO_4)^+$	aq	− 775.6			22

Element: Manganese

Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Manganese	Mn	s	0	0	+ 32.0	23
Manganese (II+) ion	$Mn(II+)^{2+}$	aq	− 228.0	− 220.7	− 73.6	22, 23
Manganese (III+) ion	$Mn(III+)^{3+}$	aq	− 85.4	− 100.4	− 213.0	12
Manganese (II+) hydroxi ion	$Mn(OH)^+$	aq	− 405.0	− 450.6	− 17.0	22
Manganese oxi(hydroxi) ion	$MnO(OH)^-$	aq	− 505.8			9
Manganese trihydroxide	$Mn(OH)_3$	s	− 757.0	− 887.0	+ 99.6	9
ion pair	$Mn(OH)_3^0$	aq	− 744.3			21
Pyrochroite	$Mn(OH)_2$	s	− 616.7	− 702.1	+ 81.6	12

Table A 1. Continued

Element: Manganese cont. Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Manganese dihydroxide prec.	$Mn(OH)_2$	am	− 615.1	− 695.4	+ 99.2	22, 23
Manganite	α-MnO(OH)	s	− 557.3	− 615.3		16
Bixpyite	Mn_2O_3	s	− 881.2	− 959.0	+110.5	22, 23
Hausmannite	Mn_3O_4	s	−1283.2	−1387.8	+155.6	22
Pyrolusite	γ-MnO_2	s	− 465.1	− 520.0	+ 53.0	22
Manganosite	MnO	s	− 362.9	− 385.2	+ 59.7	22
Rhodochrosite natural	$MnCO_3$	s	− 816.7	− 894.1	+ 85.8	22
prec.	$MnCO_3$	s	− 813.0	− 887	+ 99.6	9
Manganese carbonate	$Mn(CO_3)^0$	aq	− 751.4	− 895.0	−136.8	15
Manganese hydrogencarbonate ion	$Mn(HCO_3)^+$	aq	− 820.0			22
Alabandite green	MnS	s	− 218.4	− 214.2	+ 78.2	22
prec.	MnS	s	− 223.0			9
Hauerite	MnS_2	s	− 232.2	− 244.6	+ 54.0	12
Manganese sulfate	$MnSO_4$	s	− 957.4	−1065.2	+112.1	22
Manganese phosphate prec.	$Mn_3(PO_4)_2$	s	−2858.0	−3226.0	+299.6	9

Element: Calcium Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Calcium	Ca	s	0	0	+ 41.4	23
Calcium ion	Ca^{2+}	aq	− 553.6	− 542.8	− 53.1	22
Calcium hydroxide ion	$Ca(OH)^+$	aq	− 717.0	− 764.3	− 14.6	12
Calcium carbonate (ion pair)	$Ca(CO_3)^0$	aq	−1098.9			12
Calcium hydrogencarbonate ion	$Ca(HCO_3)^+$	aq	−1145.0			4
Calcium sulfate (ion pair)	$Ca(SO_4)^0$	aq	−1310.4	−1448.5	+ 20.5	12
Calcite	$CaCO_3$	s	−1128.8	−1206.9	+ 92.9	22
Aragonite	$CaCO_3$	s	−1127.8	−1207.1	+ 88.7	22
Dolomite	$CaMg(CO_3)_2$	s	−2163.9	−2326.3	+155.2	22
Anhydrite	$CaSO_4$	s	−1321.8	−1434.1	+106.7	22
Gypsum	$CaSO_4 \cdot 2H_2O$	s	−1797.6	−2022.6	+194.1	22
Calcium sulfide (Oldhamite)	CaS	s	−477.4	− 482.4	+ 56.5	22
Calcium phosphates see 'Phosphorus'.						

Element: Magnesium Compound name	Formula	State	Gf$^0_{(298)}$ [kJ·mol^{-1}]	Hf$^0_{(298)}$ [kJ·mol^{-1}]	Sf$^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Magnesium	Mg	s	0	0	+ 32.7	23
Magnesium ion	Mg^{2+}	aq	− 454.8	− 466.8	−138.1	22
Magnesium hydroxide ion	$Mg(OH)^+$	aq	− 626.7			22
Magnesium dihydroxide	$Mg(OH)_2$	s	− 833.7	− 924.7	+ 63.1	15
Magnesium carbonate (i.p.)	$Mg(CO_3)^0$	aq	−1002.5			12
Magnesium hydrogencarbonate ion	$Mg(HCO_3)^+$	aq	−1047.2			22
Magnesium sulfate (i.p.)	$Mg(SO_4)^0$	aq	−1212.2	−1356.0	− 7.1	22
	$MgSO_4$	s	−1170.6	−1284.9	+ 91.6	22
Magnesium sulfide	MgS	s	− 341.8	− 346.0	+ 50.3	22
Magnesite	$MgCO_3$	s	−1012.1	−1095.8	+ 65.7	22
Faringtonite	$Mg_3(PO_4)_2$	s	−3538.7	−3780.7	+189.2	22
Magnesium hydrogenphosphate (ion pair)	$Mg(HPO_4)^0$	aq				
Magnesium dihydrogenphosphate ion	$Mg(H_2PO_4)^+$	aq				
Struvite	$MgNH_4PO_4 \cdot 6H_2O$	s	−3051.1	−3681.9		20
Magnesium-montmorillonite	$Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	s	−5336	−5707.6	+256.1	6

Table A 1. Continued

Element: Sodium

Compound name	Formula	State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Sodium	Na	s	0	0	+51.2	23
Sodium ion	Na^+	aq	−261.9	−240.3	+58.4	22
Sodium carbonate ion	$Na(CO_3)^-$	aq	−792.8	−935.9	−49.8	22
Sodium hydrogencarbonate	$Na(HCO_3)$	aq	−849.7	−943.9	+113.8	22
Sodium sulfate	$Na(SO_4)^-$	aq	−1010.6	−1144.7	+108.8	22
Sodium carbonate	Na_2CO_3	s	−1044.4	−1130.7	+135.0	22
(ion pair)	$Na_2(CO)_3^0$	aq	−1051.9			9
Sodium chloride	$NaCl$	s	−384.1	−411.1	+72.1	22
(ion pair)	$Na(Cl)^0$	aq	−393.0	−642.6	+115.5	15

Element: Potassium

Compound name	Formula	State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Potassium	K	s	0	0	+64.2	23
Potassium ion	K^+	aq	−283.3	−252.2	+101.0	22
Potassium sulfate ion	$K(SO_4)^-$	aq	−1032.7	−1157.4	+151.0	22
Potassium carbonate	K_2CO_3	s	−1063.5	−1151.0	+155.5	22
Potassium chloride	KCl	s	−409.1	−436.7	+82.6	22
(ion pair)	$K(Cl)^0$	aq	−413.4	−418.7	+157.7	15

Element: Aluminum

Compound name	Formula	State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Aluminum	Al	s	0	0	+28.3	23
Aluminumion	Al^{3+}	aq	−485.0	−531.0	−321.7	22
Aluminum hydroxide ion	$Al(OH)^{2+}$	aq	−700.6	−767.0	−156.9	12
	$Al(OH)_2^+$	aq	−907.4			12
	$Al(OH)_4^-$	aq	−1305.3	−1502.5	+102.9	22
Aluminum oxide ion	AlO_2^-	aq	−839.7			24
Aluminum oxidihyroxide ion	$AlO(OH)_2^-$	aq	−1077.0			24
Aluminum oxide	Al_2O_3	s	−1582.3	−1675.7	+50.9	22
Gibbsite	$Al_2O_3 \cdot 3H_2O$	s	−2287.4			23
Aluminum hydroxide (Gibbsite)	$Al(OH)_3$	s	−1155.1	−1293.3	+68.4	22
		am	−1142.2	−1276.1	+82.8	12
Boehmite	$AlO(OH)$ $=Al_2O_3 \cdot H_2O$	s	−915.8	−990.4	+48.4	22
Aluminum sulfate	$Al_2(SO_4)_3$	s	−3099.9	−3440.8	+239.3	22
Aluminum phosphate (Berlinite)	$Al(PO_4)$	s	−1617.9	−1733.8	+90.8	22
Variscite	$Al(PO_4) \cdot 2H_2O$	s	−2111.4	−2353.3	+134.5	12
Kyanite	Al_2SiO_5	s	−2443.9	−2594.3	+83.8	22
Kaolinite	$Al_2Si_2O_5(OH)_4$ $=Al_2Si_2O_7 \cdot 2H_2O$	s	−3799.7	−4119.6	+205.0	22

Element: Silicon

Compound name	Formula	State	$Gf^0_{(298)}$ [kJ·mol^{-1}]	$Hf^0_{(298)}$ [kJ·mol^{-1}]	$Sf^0_{(298)}$ [J·K^{-1}·mol^{-1}]	Ref.
Silicon	Si	s	0	0	+18.8	23
Silicic acid	$H_4SiO_4=Si(OH)_4$	aq	−1316.6	−1468.6	+180	22
Silicate	$H_3SiO_4^-=SiO(OH)_3^-$	aq	−1253.9	−1426.2	+112.5	12
Quartz	SiO_2	s	−856.6	−910.9	+41.5	22
		am	−850.7	−903.5	+46.9	22
Muscovik	$KAl_3Si_3O_{10}(OH)_2$	s	−5608.4	−5984.4	+306.3	22
K-Montmorillonite	$K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	s	−5356.4	−5730.3	+265.4	6
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	s	−5445.9	−5821.9	+278.0	6
Na-Montmorillonite	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$	s	−5346.1	−5718.8	+262.8	6

Table A2. Molar standard thermochemical values of some organic compounds of microbiological interest

Compound	Formula	State	Gf^0_{298} [kJ/mol]	Hf^0_{298} [kJ/mol]	Sf^0_{298} (c) [J/K·mol]	Ref.
Hydrocarbons & derivatives						
Methane	CH_4	g	−50.8	−74.8	186.2	23
		aq	−34.4	−89.0	83.7	23
Ethane	C_2H_6	g	−32.9	−84.7	229.5	23
		aq	−17.1	−102.1	118.4	23
Propane	C_3H_8	g	−23.5	−103.8	269.9	23
n-Butane	C_4H_{10}	g	−15.7	−124.7	310.0	23
n-Pentane	C_5H_{12}	g	−8.20	−146.4	348.4	23
n-Hexane	C_6H_{14}	l	+0.21	−167.2	386.8	23
n-Heptane	C_7H_{16}	l	+8.75	−187.8	425.3	23
n-Octane	C_8H_{18}	l	+17.3	−208.4	463.7	23
n-Nonane	C_9H_{20}	l	+25.9	−229.0	502.1	23
n-Decane	$C_{10}H_{22}$	l	+34.4	−249.7	540.5	23
n-Undecane	$C_{11}H_{24}$	l	+43.0	−270.3	578.9	23
n-Dodecane	$C_{12}H_{26}$	l	+51.6	−290.6	617.3	a
Cyclopentane	C_5H_{10}	g	+38.6	−77.2	292.9	23
Cyclohexane	C_6H_{12}	g	+31.8	−123.1	298.2	23
		l	+28.5			13
Benzene	C_6H_6	g	+129.7	+82.9	269.2	23
		l	+123.0			13
Toluene	$C_6H_5CH_3$	g	+122.3	+49.99	319.7	23
o-Xylene	$C_6H_4(CH_3)_2$	g	+122.1	+18.99	352.8	23
		l	+114.2			13
m-Xylene	$C_6H_4(CH_3)_2$	g	+118.8	+17,2	357.7	23
		l	+113.0			13
p-Xylene	$C_6H_4(CH_3)_2$	g	+121.1	+17.9	352.4	23
		l	+97.1			13
1,3,5-Trimethylbenzene	$C_6H_3(CH_3)_3$	g	+117.9	−16.1	385.6	23
O-containing aromatics						
Methoxybenzene	$C_6H_5OCH_3$	g	+19.6	−73.1	352.9	a
Benzaldehyde	C_6H_5CHO	g	+16.0	−37.2	355.1	a
Benzylalcohol	$C_6H_5CH_2OH$	g	−13.2	−100.4	371.2	a
Benzoic acid	C_6H_5COOH	g	−133.5	−211.7	373.5	a
		l	−247.5			13
unionized		aq	−242.5			13
ionized		aq	−218.6			13
o-Hydroxybenzoic acid	$C_6H_4OHCOOH$	g	−388.2	−487.8	404.3	a
m-Hydroxybenzoic acid		g				
p-Hydroxybenzoic acid		g				
Phenol	C_6H_5OH	g	−29.7	−93.3	314.4	a
		s	−46.0			13
Catechol	$C_6H_4(OH)_2$	g	−187.1	−272.0	345.3	a
		s	−215.1			13
Hydrochinone	$C_6H_4(OH)_2$	s	−220.5			13
Resorcinol	$C_6H_4(OH)_2$	s	−222.6			13
Carboxylic acids, aldehydes, ketones, ethers, esters						
Formaldehyde	HCHO	g	−113.0	−117.2	218.7	23
		aq	−130.5	−150.2		23, 1, 2
Formic acid	HCOOH	l	−361.4	−424.7	129.0	23
		g	−349.8	−377.4	248.5	a
unionized		aq	−372.4	−425.4	163.2	23
ionized		aq	−351.0	−425.6	92.0	23
Acetic acid	CH_3COOH	l	−389.9	−484.5	159.8	23
		g	−374.0	−432.2	282.4	23
unionized		aq	−396.6	−485.8	178.7	23
ionized		aq	−369.4	−486.0	86.6	23
Glycolic acid	$CH_2OHCOOH$	s		−664.0		23
ionized		aq		−652.3		23
Glyoxylic acid	$CH(OH)_2COOH$	s		−835.5		23
Dichloroacetic acid	$CHCl_2COOH$	l		−497.9		23
unionized		aq		−503.8		23
ionized		aq		−512.1		23
Trichloroacetic acid	CCl_3COOH	s		−505.0		23
ionized		aq		−516.3		23
Propionic acid	CH_3CH_2COOH	g	−367.3	−453.9	322.6	a
unionized		aq	−389.0			b
ionized		aq	−361.1			2

Table A2. Continued

Compound	Formula	State	Gf^0_{298} [kJ/mol]	Hf^0_{298} [kJ/mol]	Sf^0_{298} (c) [J/K·mol]	Ref.
n-Butyric acid	$CH_3(CH_2)_2COOH$	g	– 358.7	−474.5	361.0	a
		l	– 382.8			13
unionized		aq	– 380.1			b
ionized		aq	– 352.6			2
iso-Butyric acid	$(CH_3)_2CHCOOH$	g		−481.4	366.5	a
n-Valeric acid	$CH_3(CH_2)_3COOH$	g	– 350.2	−495.1	399.4	a
ionized		aq	– 344.3			19
n-Caproic acid	$CH_3(CH_2)_4COOH$	g	– 341.8	−515.8	437.8	a
ionized		aq	– 336.0			19
n-Heptanoic acid	$CH_3(CH_2)_5COOH$	g	– 333.2	−536.3	476.2	a
n-Octanoic acid	$CH_3(CH_2)_6COOH$	g	– 324.6	−557.0	514.2	a
n-Nonanic acid	$CH_3(CH_2)_7COOH$	g	– 316.4	−577.7	553.1	a
n-Palmitic acid	$CH_3(CH_2)_{14}COOH$	g	– 256.9	−722.1	821.9	a
		l	– 328.7			13
		s	– 334.7			13
Oxalic acid	$(COOH)_2$	s	– 694.13	−827.2		13, 23
unionized		aq	– 674.0	−825.1	45.6	23
one ionization		aq	– 698.4	−818.4	149.4	23
two ionizations		aq	– 674.0	−825.1	45.6	23
Succinic acid unionized	$(CH_2)_2(COOH)_2$	aq	– 746.0			b
doubly ionized		aq	– 690.2			2
Fumaric acid unionized	$(CH)_2(COOH)_2$	aq	– 646.8			b
doubly ionized		aq	– 604.2			2
L-malic acid ionized	$CHOHCH_2(COO^-)_2$	aq	– 845.12			2
unionized		aq	– 893.6			13
Oxalacetic acid ionized	$CH_2CO(COO^-)_2$	aq	– 797.2			2
α-Ketoglutaric acid ionized	$(CH_2)_2CO(COO^-)_2$	aq	– 797.6			2
Lactic acid	$CH_3CHOHCOOH$	g	– 514.2	−620.8	358.2	a
		l	– 520.5			13
unionized		aq	– 539.0			b
ionized		aq	– 517.1			2
Pyruvic acid	$CH_3COCOOH$	g	– 458.4	−530.0	345.3	a
ionized		aq	– 474.6			2
Glyceric acid ionized	$CH_2OHCHOHCOO^-$	aq	– 658.1			19
Glyceraldehyde	$CH_2OHCHOHCHO$	aq	– 437.7			19
Acetaldehyde	CH_3CHO	g	– 133.9			13
		l	– 133.4			13
Dihydroxyacetone	$(CH_2OH)_2CO$	aq	– 455.2			19.
Acetone	CH_3COCH_3	g	– 152.6	−215.7	299.0	a
Diethylether	$(CH_3CH_2)_2O$	l	– 118.4			13
Ethylacetate	$CH_3CH_2OCOCH_3$	l	– 324.7			13
Alcohols						
Methanol	CH_3OH	l	– 166.4	−238.7	126.8	23
		g	– 162.2	−200.7	239.7	a, 23
		aq	– 175.4	−245.9	133.1	23
Ethanol	C_2H_5OH	l	– 174.9	−277.7	160.7	23
		g	– 168.8	−235.1	282.6	a, 23
		aq	– 181.8	−288.3	148.5	23
n-Propanol	$CH_3(CH_2)_2OH$	g	– 159.3	−255.3	319.2	a
		l	– 171.1			13
		aq	– 175.8			2
iso-Propanol	$(CH_3)_2CHOH$	g	– 174.8	−273.0	311.8	a
		l	– 184.1			13
		aq	– 185.9			2
n-Butanol	$CH_3(CH_2)_3OH$	g	– 150.8	−275.9	357.6	a
		l	– 169.0			13
		aq	– 171.8			21
tert. Butanol	$(CH_3)_3COH$	l	– 188.3			13
n-Pentanol	$CH_3(CH_2)_4OH$	g	– 143.3	−296.5	396.0	a
n-Hexanol	$CH_3(CH_2)_5OH$	g	– 134.8	−317.2	434.4	a
n-Heptanol	$CH_3(CH_2)_6OH$	g	– 126.4	−337.8	472.8	a
n-Octanol	$CH_3(CH_2)_7OH$	g	– 117.9	−358.4	511.2	a
Glycerol	$(CH_2OH)_2CHOH$	l	– 477.1			2
		aq	– 488.5			2
Mannitol	$(CH_2OH)_2(CHOH)_4$	aq	– 942.6			2
Sorbitol	$(CH_2OH)_2(CHOH)_4$	aq	– 942.7			2

Table A2. Continued

Compound	Formula	State	Gf^0_{298} [kJ/mol]	Hf^0_{298} [kJ/mol]	Sf^0_{298} (c) [J/K·mol]	Ref.
Carbohydrates						
α-D-Glucose	$CH_2OH(CHOH)_4CHO$	aq	−917.2			2
α-D-Galactose	$CH_2OH(CHOH)_4CHO$	aq	−923,5			2
D-Fructose	$(CH_2OH)_2CO(CHOH)_3$	aq	−915.4			2
Sucrose	$C_{12}H_{22}O_{11}$	aq	−1551.9			2
Glycogen	$\{C_6H_{10}O_5\}$ unit	aq	−662.3			2
N-containing compounds						
Methylamine	CH_3NH_2	l	+35.6	−47.3	150.2	23
		g	+32.1	−23.0	243.3	23
unionized		aq	+20.7	−70.2	123.4	23
ionized	$CH_3NH_3^+$	aq	−40.0	−124.9	142.7	23
Dimethylamine	$(CH_3)_2NH$	l	+69.9	−43.9	182.3	23
		g	+68.4	−18.5	273.0	23
unionized		aq	+57.9	−70.6	133.1	23
ionized	$(CH_3)_2NH_2^+$	aq	+3.35			21
Trimethylamine	$(CH_3)_3N$	l	+100.8	−46.0	208.4	23
		g	+99.0	−24.3	287.0	23
unionized		aq	+93.0	−76.0	133.5	23
ionized	$(CH_3)_3NH^+$	aq	+37.2	−112.9	196.6	23
Ethylamine	$C_2H_5NH_2$	l		−74.1		23
		g		−47.2		23
Diethylamime	$(C_2H_5)_2NH$	l		−103.3		23
		g		−71.4		23
Ethylenediamine	$NH_2CH_2CH_2NH_2$	l		−24.4		23
Acetamide	CH_3CONH_2	s		−318.0		23
Nitromethane	CH_3NO_2	g		−74.9	28.5 (for 300 K)	1
Nitroethane	$C_2H_5NO_2$	l		−140.2		23
Glycine	NH_2CH_2COOH	s	−368.6	−528.1	103.5	23
ionized		aq	−315.0	−469.8	119.4	23
unionized		aq	−370.8	−514.0	158.3	23
Other amino acids see ref.						23, 19
Urea	$CO(NH_2)_2$	s	−196.8	−332.9	104.6	23
		aq	−203.84			13
Ammoniumacetate	CH_3COONH_4	aq	−448.3	−618.5	200.0	23
N-Dimethylaniline	$C_6H_5N(CH_3)_2$	g		+92.2	380.6	a
Aniline	$C_6H_5NH_2$	l	−148.1			13
S-containing compounds						
Methylsulfide	CH_3SH	l	−7.74	−46.4	169.2	23
		g	−9.33	−22.3	255.1	23
Dimethylsulfide	$(CH_3)_2S$	g		−36.2	286.4	a
Dimethyldisulfide	$(CH_3)_2S_2$	g		−25.3	334.9	a
Ethanethiol	C_2H_5SH	l	−5.36	−73.3	207.0	23
		g	−4.39	−45.8	296.1	23
Diethylsulfide	$(C_2H_5)_2S$	l	+11.8	−119.0	269.3	23
		g	+18.2	−83.1	368.0	23
Thiourea	$CS(NH_2)_2$	s		−88.3		23
Dimethylsulfoxide	$(CH_3)_2SO$	l	−99.2	−203.3	188.3	23
		g	−81.5	−150.5	306.3	23
Dimethylsulfone	$(CH_3)_2SO_2$	s	−302.5	−451.0	142.3	23
Halogenated hydrocarbons and precursors						
Methane	CH_4	g	−50.8	−74.8	186.2	23
Chlormethane	CH_3Cl	g	−57.4	−80.8	234.5	23
		aq	−51.5	−101.7	144.8	23
Methylenechloride	CH_2Cl_2	l	−67.3	−121.5	177.8	23
		g	−65.9	−92.5	270.1	23
Chloroform	$CHCl_3$	l	−73.7	−134.5	201.7	23
		g	−70.4	−103.1	295.6	23
		aq		−143.5		23
Carbontetrachloride	CCl_4	l	−65.3	−135.4	216.4	23
		g	−60.6	−102.9	309.7	23
Ethane	C_2H_6	g	−32.9	−84.7	229.5	23
		aq	−17.1	−102.1	118.4	23
Ethylchloride	CH_3CH_2Cl	l	−59.4	−136.5	190.8	23
		g	−60.5	−112.2	275.9	23
1,2-Dichlorethane	CH_2ClCH_2Cl	l	−79.6	−165.2	208.5	23
		g	−73.9	−129.8	308.3	23
Hexachlorethane	C_2Cl_6	g		−147.7	396.6	a
Ethene (Ethylene)	C_2H_4	g	+68.1	+52.3	219.5	23
		aq	+81.3	+36.4	122.2	23

Table A2. Continued

Compound	Formula	State	Gf^0_{298} [kJ/mol]	Hf^0_{298} [kJ/mol]	Sf^0_{298} (c) [J/K·mol]	Ref.
Vinylchloride	CH_2CHCl	l		+ 14.6		23
		g	+ 51.9	+ 35.6	263.9	23
1,2-Dichlorethylene cis	CHClCHCl	l	+ 22.0	− 27.6	198.4	23
trans		l	+ 27.3	− 23.1	195.9	23
Trichlorethylene	$CHClCCl_2$	l	+ 12.1	− 42.3	228.4	23
		g	+ 18.0	− 7.78	324.7	23
Tetrachlorethylene	C_2Cl_4	l	+ 4.60	− 52.3	266.9	23
		g	+ 22.6	− 12.1	341.0	23
Chlorobenzene	C_6H_5Cl	l	+ 116.3			13

a Calculated for the gaseous state with the group increment method (values see table A.3);
b Values for undissociated acids are calculated from Gf^0 of dissociated acid and pK^0_a (see text);
c All values in this column are positive (+).

Table A 3. Values for the calculation of enthalpy of formation (Hf^0) and entropy of formation (Sf^0) by the group increment method (1)

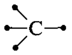
Group atom or function	Ligand atoms covalently bound to group atom or function H	O	N	P	S	C	X	Thermochemical values Hf^0_{298} [kJ/mol]	Sf^0_{298} [J/K·mol]
C: 						$(C)_4$		+ 2.09	−146.86
	$(H)_3$					(C)		− 42.17	+127.24
	$(H)_2$					$(C)_2$		− 20.63	+ 38.41
	(H)					$(C)_3$		− 7.95	− 50.50
	$(H)_3$					(CO)		− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$					$(C)(C_d)$		− 19.92	+ 41.00
	(H)					$(C)_2(CO)$		− 7.11	− 50.21
	(H)					$(C)_2(C_B)$		− 4.10	− 50.84
	$(H)_3$					(C_d)		− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$					(C)(CO)		− 21.76	+ 40.17
	$(H)_2$					$(C)(C_B)$		− 20.33	+ 39.08
	$(H)_3$					(C_B)		− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_3$	(O)						− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$	$(O)_2$						− 67.36	+ 26.00*
	$(H)_2$	(O)				(C)		− 33.89	+ 41.00
	$(H)_2$	(O)				(C_B)		− 33.89	+ 40.58
	(H)	(O)				$(C)_2$		− 30.12	− 46.02
	(H)	$(O)_2$				(C)		− 68.20	+ 26.00*
	(H)	(O)				(C)(CO)		− 30.12$^{2)}$	− 46.02$^{2)}$
		(O)				$(C)_3$		− 27.61	−140.42
	$(H)_2$		(N)			(C)		− 27.61	+ 41.00
	(H)		(N)			$(C)_2$		− 21.76	− 48.95
	(H)		(N)			(C)(CO)		− 21.76$^{3)}$	− 48.95$^{3)}$
	$(H)_3$		(N)					− 42.14$^{1)}$	+127.24$^{1)}$
			(N)			$(C)_3$		− 13.39	−142.67
	$(H)_2$		(N_I)			(C)		− 27.61$^{4)}$	+ 41.00$^{4)}$
	(H)		(N_I)			$(C)_2$		− 21.76$^{3)}$	− 48.95$^{3)}$
	$(H)_3$			(PO)				− 42.14$^{1)}$	+127.24$^{1)}$
	$(H)_2$			(PO)		(C)		− 14.23	+ 40.17$^{5)}$
	$(H)_3$				(S)			− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$				(S)	(C)		− 20.63$^{6)}$	+ 38.41$^{6)}$
	(H)				(S)	$(C)_2$		− 7.95$^{7)}$	− 50.50$^{7)}$
					(S)	$(C)_3$		+ 2.09$^{8)}$	−146.86$^{8)}$
	$(H)_2$				(S)	(C_B)		− 33.89$^{9)}$	+ 40.58$^{9)}$
	$(H)_3$				(SO)			− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$				(SO)	(C)		− 32.30	+ 40.17$^{5)}$
	$(H)_3$				(SO_2)			− 42.17$^{1)}$	+127.24$^{1)}$
	$(H)_2$				(SO_2)	(C)		− 32.13	+ 40.17$^{5)}$
	(H)				(SO_2)	$(C)_2$		− 10.96	− 50.21$^{10)}$
						(C)	$(Cl)_3$	− 86.61	+210.87
	(H)					(C)	$(Cl)_2$	− 79.08	+182.84
	$(H)_2$					(C)	(Cl)	− 69.04	+158.16
	(H)	(O)				(C)	(Cl)	− 90.37	+ 66.53
						(C)	$(F)_3$	−662.75	+177.82
	(H)					(C)	$(F)_2$	−428.02	+163.59
	$(H)_2$					(C)	(F)	−215.48	+148.11
						(C)	$(Cl)(F)_2$	−444.76	+169.45
	(H)					$(C)_2$	(Cl)	− 61.92	+ 73.64
CO: 	(H)					(C)		−121.75	+146.02
	(H)					(C_B)		−121.75$^{11)}$	+146.02$^{11)}$
	(H)	(O)						−134.31	+146.02
		(O)				(C)		−146.86	+ 61.92

Table A 3. Continued

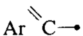
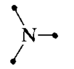
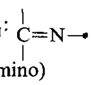
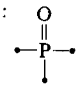
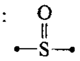
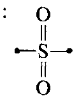
Group atom or function	Ligand atoms covalently bound to group atom or function							Thermochemical values	
	H	O	N	P	S	C	X	Hf^0_{298} [kJ/mol]	Sf^0_{298} [J/K·mol]
		(O)				(C_B)		-153.13	+61.92 [12]
		(O)				(CO)		-122.59	+61.92 [12]
	(H)		(N)					-123.85	+146.15
			(N)			(C)		-137.24	+67.78
			$(N)_2$					-131.38 [13]	+62.76 [13]
					(S)	(C)		-132.05	+64.18
						$(C)_2$		-131.38	+62.76
						(C)(C_B)		-129.29	+62.76 [13]
						(C)(CO)		-122.17	+62.76 [13]
	$(H)_2$							-108.78	+218.82
C_d: $\bullet\!-\!\overset{\|}{C}\!-\!\bullet$	(H_2)							+26.19	+115.52
	(H)					(C_d)		+28.37	+26.69
(double)	(H)					(C_B)		+28.37	+26.69
	(H)					(C)		+35.94	+33.35
	(H)	(O)						+35.98	+33.47
		(O)				(C)		+37.15 [14]	-61.09 [14]
		(O)				(C_d)		+37.15 [14]	-61.09 [14]
		(O)				(CO)		+48.53	-61.09 [14]
						$(C)_2$		+43.26	-53.14
	(H)		(N)					+35.94 [15]	+33.35 [15]
			(N)			(C)		+43.26 [16]	-53.14 [16]
	(H)		(N_I)					+28.37 [17]	+26.69 [17]
			(N)(N_I)					+37.15 [14]	-61.09 [14]
			(N_I)			(C)		+37.15 [14]	-61.09 [14]
	(H)						(Cl)	-5.02	+148.11
						(C)	(Cl)	-8.79	+62.76
							$(Cl)_2$	-7.53	+176.15
	(H)						(F)	-157.32	+137.24
							$(F)_2$	-324.26	+156.06
						(C)(C_d)		+37.15	-61.09
C_B: 	(H)							+13.81	+48.24
		(O)						-3.77	-42.68
(Benzene)			(N)					-2.09	-40.54
				(PO)				+15.48 [19]	-32.17 [19]
					(S)			-7.53	+42.68
					(SO)			+15.48 [19]	-32.17 [19]
					(SO_2)			+15.48 [19]	-32.17 [19]
						(C)		+23.05	-32.17
						(C_d)		+23.77	-32.64
						(CO)		+15.48	-32.17 [18]
						(C_B)		+20.75	-36.15
							(Cl)	-15.90	+79.08
							(F)	-179.08	+67.36
O: •—O—•						$(C)_2$		-97.07	+36.32
						(C)(CO)		-180.33	+35.15
						$(CO)_2$		-194.56	+35.15 [21]
	(H)					(C)		-158.57	+121.63
	(H)					(CO)		-243.09	+102.51
	(H)					(C_B)		-158.57	+121.75
						(C)(C_B)		-96.23	+36.32 [20]
	(H)			(PO)				-271.96	+102.51 [22]
				(PO)		(C)		-170.29	+35.15 [21]
				$(PO)_2$				-228.03	+35.15 [21]
	(H)				(SO)			-158.57 [28]	+121.75 [28]
	(H)				(SO_2)			-243.09 [29]	+102.51 [29]
N: 	$(H)_2$					(C)		+20.08	+124.31
	(H)					$(C)_2$		+64.43	+37.40
						$(C)_3$		+102.09	-56.32
	$(H)_2$					(C_d)		+20.08 [23]	+124.31 [23]
	(H)					(C_d)		+20.08 [23]	+124.31 [23]
	(H)					(C)(C_d)		+64.43 [24]	+37.40 [24]
	$(H)_2$					(CO)		-62.34	+103.30
	(H)					(C)(CO)		-18.41	+16.32
	(H)					(CO)(C_B)		+1.67	
	$(H)_2$					(C_B)		+20.08 [23]	+124.31 [23]

Table A 3. Continued

Group atom or function	Ligand atoms covalently bound to group atom or function H	O	N	P	S	C	X	Thermochemical values Hf^0_{298} [kJ/mol]	Sf^0_{298} [J/K·mol]
	(H)					(C)(C_B)		+ 62.34	+ 37.40[24]
						$(C)_2(C_B)$		+109.62	− 56.32[25]
	(H)					$(CO)_2$		− 77.40	+ 37.40[24]
	$(H)_2$		(N)					+ 47.70	+121.88
	(H)		(N)			(C)		+ 87.45	+ 40.21
			(N)			$(C)_2$		+122.17	− 57.74
N_I:  $C{=}N{-}\bullet$ (Imino)	(H)							+ 68.20	+ 37.40[24]
						(C)		+ 89.12	− 56.32[25]
						(C_B)		+ 69.87	− 56.32[25]
PO:  $\bullet{-}P({=}O)({-}\bullet){-}\bullet$		$(O)_3$						−437.65	(+209)
		$(O)_2$				(C)		−416.31	
						$(C_B)_3$		−221.33	
S: $\bullet{-}S{-}\bullet$	(H)					(C)		+ 19.33	+136.94
	(H)					(CO)		− 5.90	+130.54
	(H)					(C_B)		+ 50.04	+ 52.97
						$(C)_2$		+ 48.16	+ 55.02
					(S)	(C)		+ 29.50	+ 51.76
					$(S)_2$			+ 12.59	+ 56.07
SO:  $\bullet{-}S({=}O){-}\bullet$						$(C)_2$		− 60.29	+ 75.73
						$(C_B)_2$		− 50.21	+ 75.73[26]
SO_2:  $\bullet{-}S({=}O)_2{-}\bullet$						$(C)_2$		−291.79	+ 87.45
						(C)(C_B)		−302.46	+ 87.45[27]
						$(C_B)_2$		−286.94	+ 87.45[27]
		(O)				(C_B)		−291.79[27]	+ 87.45[27]

The valencies of the group atom or function which need to be combined with ligand atoms are marked —•. The following assumptions are made for combinations for which no thermochemical values are available (= assigned values):

1) ≡ $C(H)_3(C)$ ≡ $C(H)_3CO$
2) ≡ $C(H)(O)(C)_2$
3) ≡ $C(H)(N)(C)_2$
4) ≡ $C(H)_2(N)(C)$
5) ≡ $C(H)_2(C)(CO)$
6) ≡ $C(H)_2(C)_2$
7) ≡ $C(H)(C)_3$
8) ≡ $C(C)_4$
9) ≡ $C(H)_2(O)(C_B)$
10) ≡ $C(H)(C)_2(CO)$
11) ≡ CO(H)(C)
12) ≡ CO(O)(C)
12) ≡ $CO(C)_2$
14) ≡ $C_d(C)(C_d)$
15) ≡ $C_d(H)(C)$
16) ≡ $C_d(C)_2$
17) ≡ $C_d(H)(C_d)$
18) ≡ $C_B(C)$
19) ≡ $C_B(CO)$
20) ≡ $O(C)_2$
21) ≡ O(C)(CO)
22) ≡ O(H)(CO)
23) ≡ $N(H)_2(C)$
24) ≡ $N(H)_2(C)$
25) ≡ $N(C)_3$
26) ≡ $S(C)_2$
27) ≡ $SO_2(C)_2$
28) ≡ O(H)(C)
29) ≡ O(H)(CO)
* = author's estimate

The benzene ring consists of 6·$[C_B(H)]$ for $Hf^0 = (6 \cdot 13.81)$ and for $Sf^0 = (6 \cdot 48.24)$. Ring corrections are included in these values, symmetry corrections ($\ln \sigma$) for Sf^0 are not.

Table A4. Summary of equations describing ecological state parameters (1)

Free energy equation:

$$\Delta G_r = \Delta H_r - T \cdot \Delta S_r$$

Equilibrium equation:

$$\Delta G_r = 0;\ \Delta G_r^0 = -R \cdot T \cdot \ln K^0 \qquad \Delta G_r^0 = \sum_j v_j Gf^0_{P_j} - \sum_i v_i Gf^0_{S_i} \quad (2)$$

or

$$K^0 = \exp\left[\frac{-\Delta G_r^0}{R \cdot T}\right]$$

Disequilibrium equation:

$$\Delta G_r = \Delta G_r^0 + R \cdot T \cdot \ln Q \qquad \Delta G_r < 0 \qquad (3)$$

or

$$\Delta G_r = R \cdot T \cdot \ln \frac{Q}{K^0} \qquad \frac{Q}{K^0} < 1$$

or

$$Q = K^0 \cdot \exp\left[\frac{\Delta G_r}{R \cdot T}\right]$$

or

$$Q = K^0 \cdot \exp\left[\frac{-E \cdot n \cdot F}{R \cdot T}\right]$$

Influence of temperature changes on equilibrium equation:

$$\Delta G^0_{r,T_{act}} = \Delta G^0_{r,T_{ref}} \cdot \frac{T_{act}}{T_{ref}} + \Delta H^0_{r,T_{ref}} \cdot \frac{T_{ref} - T_{act}}{T_{ref}}$$

Influence of temperature changes on equilibrium constant:

$$pK^0_{T_{act}} = pK^0_{T_{ref}} + \frac{\Delta H^0_{r/T_{ref}}}{2.3026 \cdot R} \cdot \frac{T_{ref} - T_{act}}{T_{ref} \cdot T_{act}}$$

Table A4. Continued

Influence of pH-changes on equilibrium equation:

$$\Delta G_r^{0\prime} = \Delta G_r^0 - 2.3026 \cdot R \cdot T \cdot q \cdot pH_{act} \qquad (4)$$

Influence of pH-changes on disequilibrium equation:

$$\Delta G_r = \Delta G_r^0 + 2.3026 \cdot R \cdot T \cdot (\log Q'_{neq} - q \cdot pH_{act}) \qquad (5)$$

or

$$\Delta G_r = 2.3026 \cdot R \cdot T \cdot (pK^0 + \log Q'_{neq} - q \cdot pH_{act}) \qquad (5)$$

Influence of changes in solute concentrations on solubility products: (follows from equilibrium equation):

$$pK'_S = pK_S^{0\prime} - \log \left(\prod_j f_j^{v_j}\right)$$

or

$$pK'_S = pK_S^{0\prime} + \sum_j \frac{v_j \cdot A \cdot z_j^2 \cdot \sqrt{I}}{1 + a_j \cdot B \cdot \sqrt{I}}$$

Influence of changes in solute concentrations on precipitation-dissolution reactions: (follows from disequilibrium equation):

$$\Delta G_r = R \cdot T \cdot \ln \frac{IAP}{K'_S} \qquad \text{dissolution if } \Delta G_r < 0 \text{ or } \frac{IAP}{K'_S} < 1.$$

$$\text{precipitation if } \Delta G_r > 0 \text{ or } \frac{IAP}{K'_S} > 1.$$

$$\text{saturation equilibrium if } \Delta G_r = 0 \text{ or } \frac{IAP}{K'_S} = 1.$$

Influence of changes in pH, I and T on the species composition of the carbonate-bicarbonate-carbonic acid equilibrium:

$$[CO_3^{2-}] = [C_T] \cdot \frac{K'_{a_1} \cdot K'_{a_2}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}$$

$$[HCO_3^-] = [C_T] \cdot \frac{K'_{a_1} \cdot 10^{-pH}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}$$

$$[H_2CO_3] = [C_T] \cdot \frac{10^{-2pH}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}.$$

Influence of changes in solute concentrations on disequilibrium redox potentials:

$$E = \frac{-\Delta G_r}{n \cdot F}$$

or

$$E = \frac{-\Delta G_r^0}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln Q \qquad (6)$$

or

$$E = E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln Q$$

or

$$E = \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{K^0}{Q}$$

Influence of changes in pH on standard redox potentials:

$$E^{0\prime} = E^0 - \frac{2.3026 \cdot R \cdot T}{F} \cdot \frac{q}{n} \cdot pH \qquad (4)$$

Influence of changes in pH and/or solute concentrations on disequilibrium redox potential:

$$E = -\frac{\Delta G_r^0}{n \cdot F} - \frac{2.3026 \cdot R \cdot T}{n \cdot F} \cdot (\log Q'_{red/ox} - q \cdot pH_{act}) \qquad (8)\ (7),\ (4)$$

or

$$E = E^0 - \frac{2.3026 \cdot R \cdot T}{n \cdot F} \cdot (\log Q'_{red/ox} - q \cdot pH_{act})$$

or

$$E = \frac{-2.3026 \cdot R \cdot T}{n \cdot F} \cdot (pK^0 + \log Q'_{red/ox} - q \cdot pH_{act})$$

Influence of changes in solute concentrations or/and pH on disequilibrium electron activity:

$$pe = \frac{1}{n} \cdot \log K^0 - \frac{q}{n} \cdot pH - \frac{1}{n} \cdot \log Q'_{red/ox} \qquad (7),\ (4),\ (9)$$

---

(1) See list of abbreviations for meaning of terms.

(2) $K^0 \triangleq K_{eq} = \frac{\prod_j \{P_{j\,eq}\}^{v_j}}{\prod_i \{S_{i\,eq}\}^{v_i}}$

(3) $Q = \frac{\prod_j \{P_{j\,neq}\}^{v_j}}{\prod_i \{S_{i\,neq}\}^{v_i}}$

(4) q is − for H^+-consuming and + for H^+-producing reactions respectively.

(5) From $Q = \frac{\prod_j \{P'_{j\,neq}\}^{v_j} \cdot \{H^+\}^q}{\prod_i \{S'_{i\,neq}\}^{v_i}} = Q'_{neq} \cdot \{H^+\}^q$ follows: $Q'_{neq} = \frac{Q}{\{H^+\}^q}$

(6) $Q = \frac{\prod_j \{P_{j\,red}\}^{v_j}}{\prod_i \{S_{i\,ox}\}^{v_i}}$

(7) From $Q = \frac{\prod_j \{p^-_{j\,red}\}^{v_j}}{\prod_i \{S'_{i\,ox}\}^{v_i} \cdot \{H^+\}^q \cdot \{e^-\}^n} = Q'_{red/ox} \cdot \{H^+\}^{-q} \cdot \{e^-\}^{-n}$

follows: $Q'_{red/ox} = Q \cdot \{H^+\}^q \{e^-\}^n$.

(8) electrons which are given off by oxidation half-reactions are assigned *a negative sign, electrons which are consumed by reduction half-reactions have a positive sign.*

(9) n is always + in the pe-formalism.

$pK_{a2}^0 = 5.61$; fumaric acid $pK_{a1}^0 = 3.03$, $pK_{a2}^0 = 4.44$; lactic acid 3.83[23]. 4.184 [kJ/kcal] was used for the conversion of [kcal/mol] into [kJ/mol].

Enthalpy of formation and free energy of formation of the electron are 0 by convention. A numerical value for its entropy of formation ($Sf_{e^-}^0$) follows from $Sf_{H_2(g)}^0$ or $Sf_{H_2(aq)}^0$ (table A.1). ΔG_r^0 and ΔH_r^0 of the half-reaction

$$2\,e^-_{(g)} + 2\,H^+_{(aq)} \leftrightarrow H_{2\,(g)}$$

are 0 and ΔS_r^0 calculated from

$$\Delta S_r^0 = -\frac{1}{T} \cdot (\Delta G_r^0 - \Delta H_r^0)$$

thus also becomes 0. $Sf_{e^-_{(g)}}^0$ emerges from

$$\Delta S_r^0 = Sf_{H_2(g)}^0 - 2\,Sf_{e^-_{(g)}}^0 - 2\,Sf_{H^+(aq)}^0 = 0$$

as

$$Sf_{e^-_{(g)}}^0 = \tfrac{1}{2} \cdot Sf_{H_2(g)}^0 = 65.25\ [J/K \cdot mol]$$

Entropy of formation of the "aqueous state of the electron ($e^-_{(aq)}$)" follows from

$$2\,e^-_{(aq)} + 2\,H^+_{(aq)} \leftrightarrow H_{2\,(aq)}.$$

Since all three thermochemical values are 0 for the proton, $Sf^0_{e^-_{(aq)}}$ can be calculated from $Gf^0_{H_2(aq)}$, $Hf^0_{H_2(aq)}$ and $Sf^0_{H_2(aq)}$ according to

$$\begin{aligned} Sf^0_{e^-_{(aq)}} &= \frac{1}{2 \cdot T} \cdot (Gf^0_{H_2(aq)} - Hf^0_{H_2(aq)} + T \cdot Sf^0_{H_2(aq)}) \\ &= \frac{10^3}{596.3} \cdot (17.55 + 4.16 + 0.29815 \cdot 57.7) \\ &= 65.25(78)\ [\mathrm{J/K \cdot mol}]. \end{aligned}$$

No distinction needs to be made between $e^-_{(g)}$ and $e^-_{(aq)}$ in thermodynamic considerations since $Gf^0_{e^-_{(g)}} \equiv Gf^0_{e^-_{(aq)}} = 0$, $Hf^0_{e^-_{(g)}} \equiv Hf^0_{e^-_{(aq)}} = 0$ and $Sf^0_{e^-_{(g)}} \equiv Sf^0_{e^-_{(aq)}} = 65.25\ [\mathrm{J/K \cdot mol}]$.

The internal consistency of the values for Gf^0, Hf^0 and Sf^0 listed in table A.1 can be examined by comparing changes in the standard Gibbs free energy of reaction calculated in different ways. Consistency requires a relationship between substances A and B which can be expressed in a stoichiometric equation:

$$a \cdot A = b \cdot B + c \cdot C.$$

It will have to satisfy the thermodynamic relation

$$(\Delta Gf^0)_T = (\Delta Hf^0)_T - T \cdot (\Delta Sf^0)_T$$

which corresponds to

$$\begin{aligned} & b \cdot Gf^0_B + c \cdot Gf^0_c - a \cdot Gf^0_A \\ &\quad = (b \cdot Hf^0_B + c \cdot Hf^0_C - a \cdot Hf^0_A) \\ &\qquad - T \cdot (b \cdot Sf^0_B + c \cdot Sf^0_C - a \cdot Sf^0_A). \end{aligned}$$

or

$$(\sum_j v_j Gf^0_{P_j} - \sum_i v_i Gf^0_{S_i})$$

$$= (\sum_j v_j Hf^0_{P_j} - \sum_i v_i Hf^0_{S_i}) - T \cdot (\sum_j v_j Sf^0_{P_j} = \sum_j v_i Sf^0_{S_i})$$

Consistency is illustrated for 4 cases of the carbon dioxide – bicarbonate – carbonate – equilibria, involving gas dissolution, acid formation, dissociation and precipitation:

1 Dissolution of gaseous CO_2 in water:
$CO_{2(g)} \Leftrightarrow CO_{2(aq)}$
2 Formation of carboxylic acid:
$CO_{2(aq)} + H_2O_{(l)} \Leftrightarrow H_2CO_{3(aq)}$
3 Dissociation of carboxylic acid to hydrogencarbonate:
$H_2CO_{3(aq)} \Leftrightarrow HCO^-_{3\,(aq)} + H^+_{(aq)}$
4 Precipitation of calciumcarbonate as calcite:
$CO^{2-}_{3\,(aq)} + Ca^{2+}_{(aq)} \Leftrightarrow CaCO_{3(s)}$

Employing the corresponding values from table A.1 one calculates for the 4 examples:

$$\begin{aligned} 1\ & Gf^0_{CO_{2(aq)}} - Gf^0_{CO_{2(g)}} = (Hf^0_{CO_{2(aq)}} - Hf^0_{CO_{2(g)}}) - T \cdot (Sf^0_{CO_{2(aq)}} - Sf^0_{CO_{2(g)}}) \\ & (-386.0 + 394.4) = -413.8 + 393.5) - 298.15 \cdot (0.1176 - 0.2137) \\ & \quad +8.4 \approx +8.352\ [\mathrm{kJ/mol}] \end{aligned}$$

$$\begin{aligned} 2\ & Gf^0_{H_2CO_{3(aq)}} - Gf^0_{CO_{2(aq)}} - Gf^0_{H_2O_{(l)}} \\ & = (Hf^0_{H_2CO_{3(aq)}} - Hf^0_{CO_{2(aq)}} - Hf^0_{H_2O_{(l)}}) \\ & \quad - T \cdot (Sf^0_{H_2CO_{3(aq)}} - Sf^0_{CO_{2(aq)}} - Sf^0{}_{H_2O_{(l)}}) \\ & \quad - 632.2 + 386 + 237.2 = (699.6 + 413.8 + 285.8) \\ & \quad - 298.15 \cdot (0.1874 - 0.1176 - 0.0699) \\ & 0 \approx +0.0298\ [\mathrm{kJ/mol}] \end{aligned}$$

$$\begin{aligned} 3\ & Gf^0_{HCO^-_3\,(aq)} + Gf^0_{H^+{}_{(aq)}} - Gf^0_{H_2CO_{3(aq)}} \\ & = (Hf^0_{HCO_3{}^-{}_{(aq)}} + Hf^0_{H^+(aq)} - Hf^0_{H_2CO_{3(aq)}}) - T \cdot (Sf^0_{HCO_3{}^-{}_{(aq)}} \\ & \quad + Sf^0{}_{H^+{}_{(aq)}} - Sf^0{}_{H_2CO_{3(aq)}}) \\ & \quad - 586.9 + 0 + 623.2 = (-692.0 + 0 + 699.6) \\ & \quad - 298.15 \cdot (0.0912 + 0 - 0.1874) \\ & \quad + 36.3 \approx +36.28\ [\mathrm{kJ/mol}] \end{aligned}$$

$$\begin{aligned} 4\ & Gf^0_{CaCO_{3(s)}} - Gf^0_{Ca^{2+}{}_{(aq)}} - Gf^0_{CO_3{}^{2-}{}_{(aq)}} \\ & = (Hf^0_{CaCO_{3(s)}} - Hf^0_{Ca^{2+}{}_{(aq)}} - Hf^0_{CO_3{}^{2-}{}_{(aq)}}) - T \cdot (Sf^0_{CaCO_{3(s)}} \\ & \quad - Sf^0_{Ca^{2+}{}_{(aq)}} - Sf^0_{CO_3{}^{2-}{}_{(aq)}}) \\ & \quad - 1128.8 + 553.6 + 527.9 = (-1206.9 + 543.1 + 677.1) \\ & \quad - 298.15 \cdot (0.0929 + 0.0531 + 0.0569) \\ & \quad - 47.3 \approx -47.19\ [\mathrm{kJ/mol}] \end{aligned}$$

The agreement for all 4 examples is better than 99% for ΔG^0_r.

The equation for acetoclastic methanogenesis serves to illustrate the consistency of the values of table A.2:

$$CH_3COOH_{(aq)} = CH_{4(aq)} + CO_{2(aq)}$$

$$\Delta Gf^0 = -34.4 - 386.0 + 396.6 = -23.8\ [\mathrm{kJ/mol}]$$

$$\begin{aligned} \Delta Hf^0 - T \cdot \Delta Sf^0 & \\ &= (-89.0 - 413.8 + 485.8) \\ &\quad - 298.15 \cdot (83.7 + 117.6 - 178.7) \cdot 10.^{-3} \\ &= -23.74\ [\mathrm{kJ/mol}] \end{aligned}$$

There is good agreement between the values also if the above reaction is formulated for other physical states:

$$CH_3COOH_{(g)} \Leftrightarrow CH_{4(g)} + CO_{2(g)}$$

$$\Delta Gf^0 = -71.2\ [\mathrm{kJ/mol}];$$

$$\Delta Hf^0 - T \cdot \Delta Sf^0 = -71.13\ [\mathrm{kJ/mol}]$$

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \Leftrightarrow CH_{4(aq)} + HCO^-_{3\,(aq)}$$

$$\Delta Gf^0 = -14.7\ [\mathrm{kJ/mol}];$$

$$\Delta Hf^0 - T \cdot \Delta Sf^0 = -14.69\ [\mathrm{kJ/mol}]$$

$$CH_3COOH_{(l)} + H_2O_{(l)} \Leftrightarrow CH_{4(g)} + HCO^-_{3(aq)} + H^+_{(aq)}$$

$$\Delta Gf^0 = -10.6\ [\mathrm{kJ/mol}];$$

$$\Delta Hf^0 - T \cdot \Delta Sf^0 = -10.72\ [\mathrm{kJ/mol}]$$

Although there is good agreement between values from the same source, table A.2 is generally less consistent than table A.1. Before particular combinations of values from different sources are made, the consistency of the data should be ascertained if possible. References listed in the tables identify the source.

Values labeled with 'a' in the reference column are calculated for gaseous states with the group increment method, employing values from table A.3. Corresponding Gf^0-values were estimated with equation 47 (section 3).

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Synthesis and metabolism of vertebrate-type steroids by tissues of insects: A critical evaluation

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Summary. This review covers the synthesis and the metabolism of vertebrate-type steroids (progesterone, testosterone, estradiol, corticosteroids) by insect tissues and discusses the significance of the reactions for insect physiology. Biosynthesis of vertebrate-type steroids from cholesterol hitherto has been demonstrated in only two insect species, i.e. the water beetle *Acilius sulcatus* (Coleoptera) and the tobacco hornworm *Manduca sexta* (Lepidoptera). In *Acilius*, steroid synthesis is associated with exosecretion (chemical defense). Nothing, however, is known about a physiological role of the C_{21} steroid conjugate present in ovaries and eggs of *Manduca*.

No synthesis of vertebrate-type steroids was observed in any other insect investigated to date. Most metabolic conversions of steroids by insects concerned oxidoreduction of oxygen groups (hydroxysteroid dehydrogenase activity) and (polar and apolar) conjugate formation. All important enzymatic steps involved in synthesis and catabolism, as known from studies with tissues of vertebrates, were not, or hardly observed.

The conclusion is drawn that typical vertebrate-type (C_{21}, C_{19} and C_{18}) steroids probably do not act as physiologically active substances in insects.

Key words. Vertebrate-type steroids; insects; metabolism; hormones.

Introduction

In recent years, it has become clear that the endocrine system of insects is much more complicated than previously assumed and, in addition, that it shares many common features with that of vertebrates[16, 18, 106]. Thus, several families of peptides have members in both verte-