Tema 4 – Termodinámica biológica

Themodynamics

CI7115 – Biotecnología Ambiental

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Conceptos de termodinámica en biotecnología ambiental

Conservation of Energy - the First Law

- Energy balance on a bioreactor (digesters, landfills, compost)
- Heat of metabolism
- Energy recovery

Free Energy - the Second Law

- Feasible reactions
- Thermodynamic preferences
- Relationship between free energy and yield

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Energía

The capacity to do work, to make things move

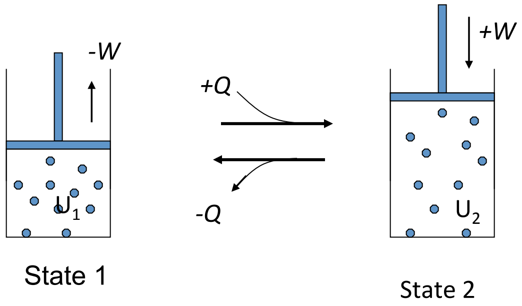
Energía interna U

Stored or "hidden" energy. The capacity to make things move at the scale of electrons, atoms, ions and molecules.

Units of Energy:

1 calorie raises a gram of water 4.184 joules = 1 calorie
1000 calories = 1 kCal = 1 Calorie (dietary calorie)

Primera ley: Conservación de energía



$$U_1 + Q - W = U_2$$

$$-W + Q = U_2 - U_1 = \Delta U$$

$$\Delta U = Q - W$$

Entalpía

Enthalpy - the "heat content" of the molecules, atoms, ions in a system at constant pressure

$H = U + PV$

$\Delta H = \Delta U + \Delta (PV) = \Delta U + \Delta P V + P \Delta V$

For a system at constant pressure, $\Delta P = 0$, so:

$\Delta H = \Delta U + P\Delta V = \Delta U + W = Q$

$\Delta H = H_{final} - H_{initial}$

$\Delta H < 0$ means the final state of the system has less energy than the initial state. Heat is released by the system ($Q < 0$). This is the case for biological reactions: they are exothermic.

UNITS FOR ENTHALPY: kJ/mol or kcal/mol

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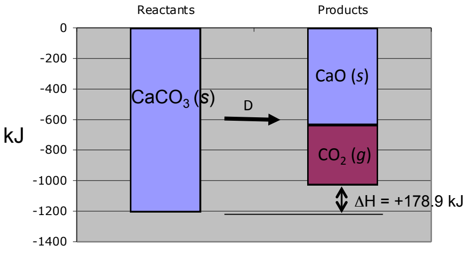
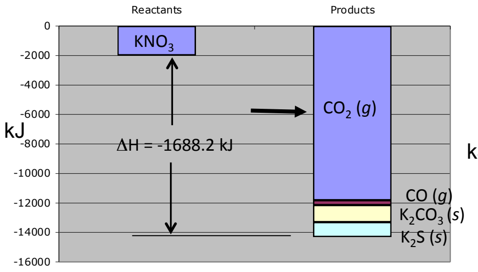
Enthalpy changes during chemical reactions. These changes reflect energy differences between the ground state of the products and reactants - i.e., the energy needed to make and break chemical bonds. This energy is released to the environment or taken up from the environment up as heat.

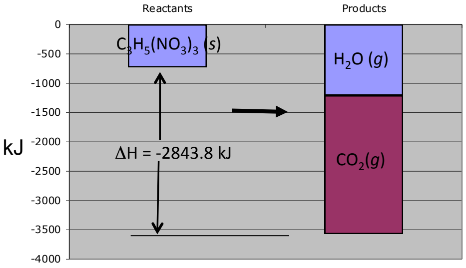
Quick lime production



Black powder explosion



Nitroglycerin explosion



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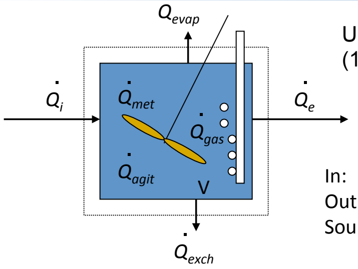
Balance de energía en un bioreactor



Units of $\dot{Q}$ are kcal/L-d or kJ/L-d
(1 calorie = 4.184 joules)

In: $[\dot{Q}_i + \dot{Q}_{agit} + \dot{Q}_{gas}]\, V\Delta t$
Out: $[\dot{Q}_{exch} + \dot{Q}_{evap} + \dot{Q}_e]\, V\Delta t$
Source: $\dot{Q}_{met} V\Delta t$

} Can be estimated using conventional chemical engineering relationships

$$\dot{Q}_{acc}\, V\Delta t = [\dot{Q}_i + \dot{Q}_{agit} + \dot{Q}_{gas}]\, V\Delta t - [\dot{Q}_{exch} + \dot{Q}_{evap} + \dot{Q}_e]\, V\Delta t + \dot{Q}_{met} V\Delta t$$

For steady state: $\dot{Q}_{acc} = 0 = \dot{Q}_i - \dot{Q}_e + \dot{Q}_{agit} + \dot{Q}_{gas} - \dot{Q}_{exch} - \dot{Q}_{evap} + \dot{Q}_{met}$

$$0 = \dot{Q}°C_p[T_i - T_e] + \dot{Q}_{agit} + \dot{Q}_{gas} - \dot{Q}_{exch} - \dot{Q}_{evap} + \dot{Q}_{met}$$

Can solve this for T_e.
C_p = heat capacity of water

For non-steady state $\dot{Q}_{acc} = c_{p,sys}\Delta T/\Delta t$ where $c_{p,sys}$ is the overall heat capacity of the system [kJ/L-°C].

What is $\dot{Q}_{met}$?

$\dot{Q}_{met} = \Delta H_{met}$ [kcal/g] x volumetric rate of consumption of substrate [g/L-d]

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Dos formas para estimar la entalpía del metabolismo (ΔH_{met})

1. Compute from balanced reaction for conversion of reactants, r, to products, p:

$$a_1r_1 + a_2r_2 + \dots a_nr_n \rightarrow b_1p_1 + b_2p_2 + \dots b_mp_m$$

$$\Delta H_{met} = \sum_{i=1}^{m} b_i H_{p,i} - \sum_{i=1}^{n} a_i H_{r,i}$$

where $H_{p,i}$ = standard enthalpy of products, $H_{r,i}$ = standard enthalpy of reactants

Uses standard molar enthalpy data
Not useful for mixed substrates.
Requires an estimate of the molar enthalpy of biomass $H_{biomass}$ ← Estimated at -3.72 kJ/g vss (Roels, 1980)

2. Estimate from heat of combustion data

ASSUMPTION: Heat of metabolism = heat released by combustion of electron donor minus the heat released by combustion of the reduced products of metabolism (biomass + reduced electron acceptor).

$$\Delta H_{met} = \Delta H_{c,donor} - [f_s\Delta H_{c,biomass} + f_e\Delta H_{c,reduced\ acceptor}]$$

ΔH_c = heat of combustion

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Entalpía de combustión ΔHc para algunas substancias*

	kcal/g	kcal/g O_2 eq
Carbohydrates		
glucose	-3.74	-3.51
Fats		
palmitic acid	-9.37	-3.26
tripalmitin	-9.28	-3.24
Protein		
glycine (amino acid)	-2.18	-3.41
Hydrocarbons		
decane	-11.34	-3.25
methane	-13.18	-3.30
Biomass	-6.9	-3.5
Hydrogen	-34.2	-4.27

* Assumes combustion with O_2 to CO_2(g), H_2O(l), HNO_3 (aq)

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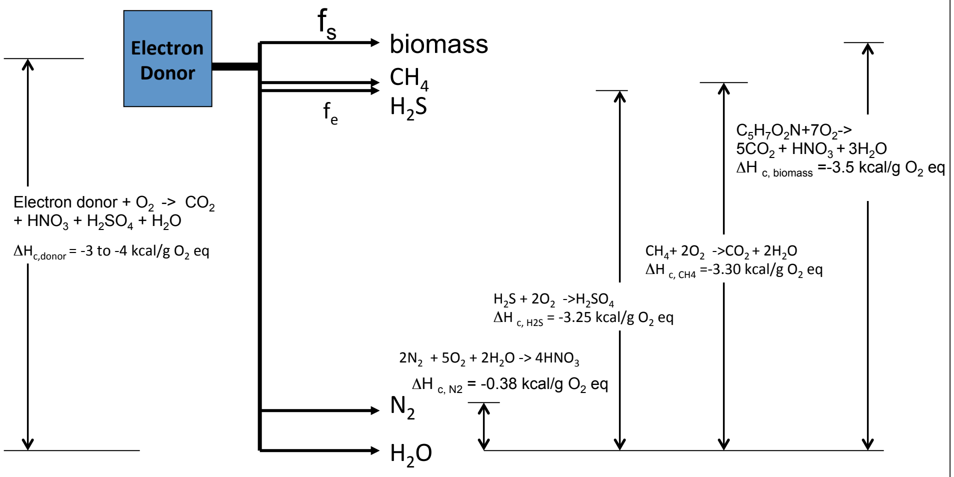
$$\Delta H_{met} = \Delta H_{c,donor} - [f_s \Delta H_{c,biomass} + f_e \Delta H_{c,reduced\ acceptor}]$$



ΔH_c is the specific heat of combustion of the reduced species (in kcal/g O_2 eq), assuming oxidation with O_2 to produce H_2O, HNO_3, H_2SO_4, CO_2.(g)

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Composting

Aerobic Thermophilic Degradation

- Stabilization
  - o Reduce odors
  - o Decrease rate of decay
- Decrease mass
- Reduce pathogens

Disadvantages

Area intensive
Costly - labor intensive
Incomplete disinfection

Composting Windrows

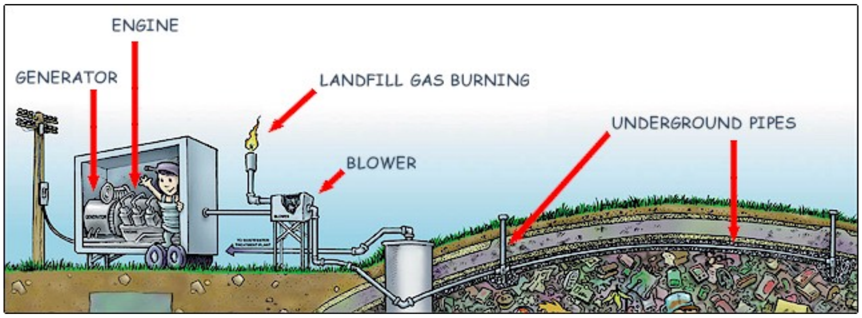
Composting

The heat of combustion (~3.4 kcal/g COD) from decay aids in drying the compost

Water vapor rising from compost piles with forced aeration

Landfills

Biogenic methane gas can be recovered from landfills and burned for energy



Source: City of Ann Arbor, MI
http://www.ci.ann-arbor.mi.us/PublicServices/FieldOperations/SolidWaste/education/rrc/landfill.html

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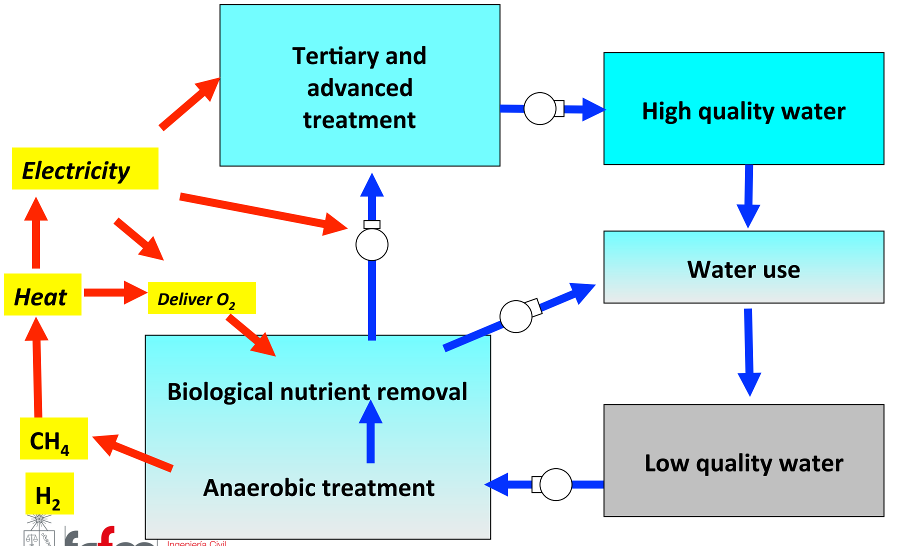
Recuperación de recursos - Puede el tratamiento de ARes ser “energy neutral”?



Tertiary and advanced treatment

High quality water

Electricity

Water use

Heat

Deliver O_2

Biological nutrient removal

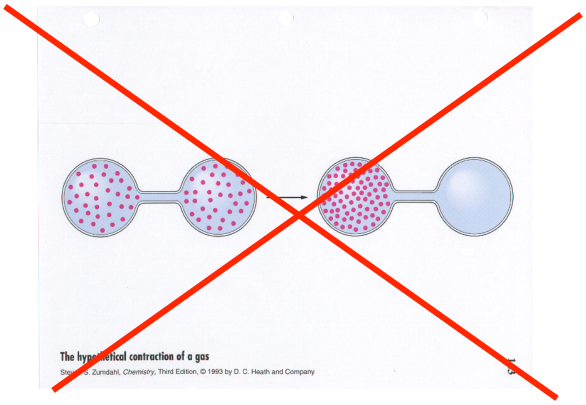
CH_4

Anaerobic treatment

Low quality water

H_2

Energía libre – La segunda ley



The hypothetical contraction of a gas

Steven S. Zumdahl, *Chemistry*, Third Edition, © 1993 by D. C. Heath and Company

In the absence of outside energy inputs, energy flows from being concentrated in one place to diffuse and spread out. $\Delta S_{univ} > 0$ for any change.

Energía libre y Entropía (S)

For a given macrostate (V, T, P, composition), he number of microstates is a measure of S. Microstates are specific configurations of energy within a molecules or a system of molecules.

Think of temperature T as a measure of the **average energy per microstate**. If we add an amount of energy *Q* to a system at constant temperature, the number of microstates will change by *Q/T*, so $\Delta S_{system} = \frac{Q}{T}$.

$$\Delta H_{system} = Q_{system} = - Q_{environment}$$

so $\Delta S_{environment} = -\frac{\Delta H_{system}}{T}$

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{environment}$$

$$\Delta S_{univ} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

$$\boxed{\Delta G_{system} = \Delta H_{system} - T\Delta S_{system} = -T\Delta S_{univ}}$$

Energía libre y Equilibrio

$$a_1r_1 + a_2r_2 + \ldots a_nr_n \rightarrow b_1p_1 + b_2p_2 + \ldots b_mp_m$$

Standard conditions (25°C, all concentrations =1 M or 1 atm)

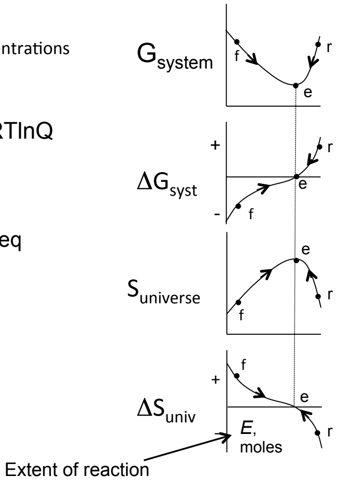
$$\Delta G^\circ = \sum_{i=1}^{m} b_i G^o_{p,i} - \sum_{i=1}^{n} a_i G^o_{r,i}$$

Actual measured concentrations

$$\Delta G = \Delta G^\circ + RT\ln\left[\frac{(p_1)^{b_1}(p_2)^{b_2}\ldots(p_m)^{b_m}}{(r_1)^{a_1}(r_2)^{a_2}\ldots(r_n)^{a_n}}\right] = \Delta G^\circ + RT\ln Q$$

When $\Delta G = 0$, then $\Delta G^\circ = -RT\ln Q_{eq}$

$Q_{eq} = K =$ equilibrium constant



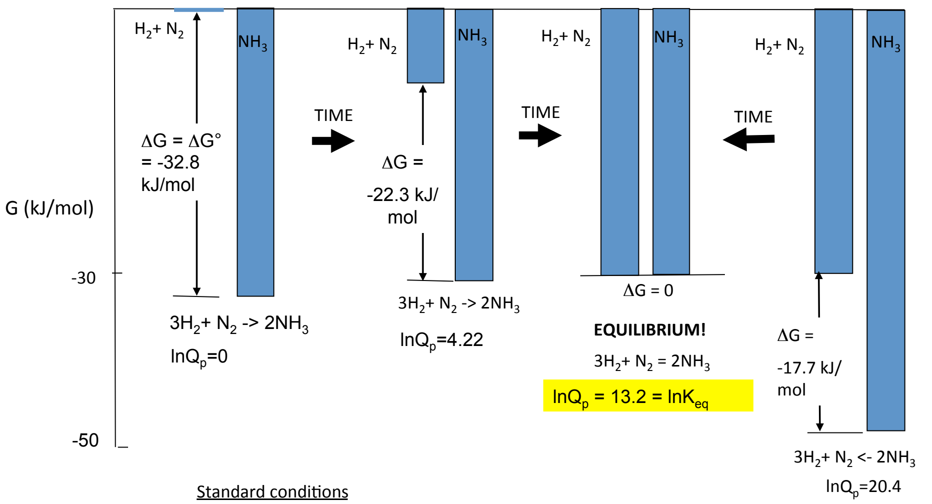
El proceso Haber:

$$3H_2 + N_2 = 2NH_3$$

$$\mathbf{\Delta G = \Delta G^\circ + RT\ln Q_p}$$

$$Q_p = \frac{P_{NH_3}^{\;2}}{P_{H_2}^{\;3}P_{N_2}}$$

$$K_{eq} = e^{13.2} \quad @\ 25°C$$



G (kJ/mol)

-30

-50

H_2+ N_2

NH_3

ΔG = ΔG° = -32.8 kJ/mol

$3H_2$+ N_2 -> $2NH_3$

$\ln Q_p$=0

TIME

H_2+ N_2

NH_3

ΔG = -22.3 kJ/mol

$3H_2$+ N_2 -> $2NH_3$

$\ln Q_p$=4.22

TIME

H_2+ N_2

NH_3

ΔG = 0

EQUILIBRIUM!

$3H_2$+ N_2 = $2NH_3$

$\ln Q_p = 13.2 = \ln K_{eq}$

TIME

H_2+ N_2

NH_3

ΔG = -17.7 kJ/mol

$3H_2$+ N_2 <- $2NH_3$

$\ln Q_p$=20.4

Standard conditions

T=298 K

	Partial pressure (atm)
H_2	1.0
N_2	1.0
NH_3	1.0

	Partial pressure (atm)
H_2	0.34
N_2	0.78
NH_3	1.44

	Partial pressure (atm)
H_2	0.02
N_2	0.673
NH_3	1.654

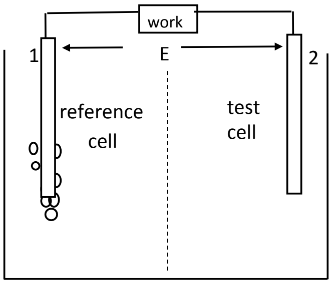
	Partial pressure (atm)
H_2	0.002
N_2	0.667
NH_3	1.665

Energía libre y Voltaje

Nernst equation ΔG = -nFE
n = number of electron equivalents transferred
F = Faraday's constant (96,493 coulombs/eq)

Free energy per mole of electrons is directly proportional to voltage. The proportionality constant is Faraday's constant.

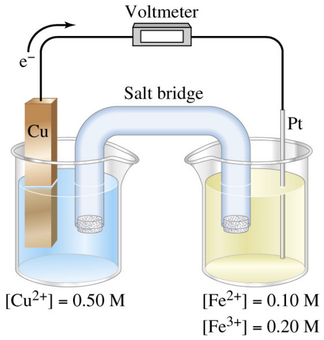
Reference Cell



{H+} = 1
H_2 = 1 atm
pH=0

$1/2H_2 = H^+ + e^-$

Real Cell



Reacciones factible

Standard half reaction reduction potentials for electrode reactions at 25°C (from Bockris and Reddy, 1977)

Electrode reaction	E°, V	Electrode reaction	E°, V
$Li^+ + e^- = Li$	-3.01	$Cd^{2+} + 2e^- = Cd$	-0.40
$Rb^+ + e^- = Rb$	-2.98	$In^{3+} + 3e^- = In$	-0.34
$Cs^+ + e^- = Cs$	-2.92	$Ti^+ + e^- = Ti$	-0.34
$K^+ + e^- = K$	-2.92	$Co^{2+} + 2e^- = Co$	-0.27
$Ba^{2+} + 2e^- = Ba$	-2.92	$Ni^{2+} + 2e^- = Ni$	-0.23
$Sr^{2+} + 2e^- = Sr$	-2.89	$Sn^{2+} + 2e^- = Sn$	-0.14
$Ca^{2+} + 2e^- = Ca$	-2.84	$Pb^{2+} + 2e^- = Pb$	-0.13
$Na^+ + e^- = Na$	-2.71	$D^+ + e^- = 0.5D_2$	-0.003
$Mg^{2+} + 2e^- = Mg$	-2.38	**$H^+ + e^- = 0.5H_2$**	**0.00**
$Ti^{2+} + 2e^- = Ti$	-1.75	$Cu^{2+} + 2e^- = Cu$	0.34
$Be^{2+} + 2e^- = Be$	-1.70	$0.5O_2 + H_2O + 2e^- = 2OH^-$	0.40
$Al^{3+} + 3e^- = Al$	-1.66	$Cu^+ + e^- = Cu$	0.52
$V^{2+} + 2e^- = V$	-1.50	$Hg^{2+} + 2e^- = Hg$	0.80
$Mn^{2+} + 2e^- = Mn$	-1.05	$Ag^+ + e^- = Ag$	0.80
$Zn^{2+} + 2e^- = Zn$	-0.76	$Pb^{2+} + 2e^- = Pb$	0.83
$Ga^{3+} + 3e^- = Ga$	-0.52	$Ir^{3+} + 3e^- = Ir$	1.00
$Fe^{3+} + 3e^- = Fe$	-0.44	$O_2 + 4H^+ + 4e^- = 2H_2O$	1.23

How could you design a system to remove copper from solution?

Combustibles (donadores de e^-)

Organic molecules are good fuels. For CO_2/organic molecule couples, E°' <0 (so they are >0 when the organic is oxidized to CO_2). When coupled to reduction half reactions for oxidants, the resulting whole reactions have positive voltages E >0.

Some inorganics are also good fuels:

best

e^- donor	Half reaction	E°' (V)
HSO_3^-	$SO_4^{2-} + 3H^+ + 2e^- = HSO_3^- + H_2O$	-0.51
H_2	$2H^+ + 2e^- = H_2$	-0.41
$S_2O_3^{2-}$	$2SO_4^{2-} + 10H^+ + 8e^- = S_2O_3^{2-} + 5H_2O$	-0.25
HS^-	$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$	-0.22
S	$SO_4^{2-} + 8H^+ + 6e^- = S + 4H_2O$	-0.20
AsO_3^{3-}	$AsO_4^{3-} + 4H^+ + 2e^- = H_2AsO_3^- + H_2O$	+0.15
Cu^+	$Cu^{2+} + e^- = Cu^+$	+0.16
Se	$SeO_4^{2-} + 8H^+ + 6e^- = Se + 4H_2O$	+0.33
NH_4^+	$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$	+0.36
Mn (II)	$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+0.47
Fe (II)	$Fe^{3+} + e^- = Fe^{2+}$	+0.77

worst

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Oxidantes (receptores de e^-)

best

e^- acceptor	Half reaction	E°' (V)
N_2O	$N_2O + 2H^+ + 2e^- = N_2 + H_2O$	+1.31
ClO_3^-	$ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$	+1.04
NO_2^-	$2NO_2^- + 8H^+ + 6e- = N_2 + 4H_2O$	+0.94
O_2	$O_2 + 4H^+ + 4e^- = 2H_2O$	+0.82
Fe^{3+}	$Fe^{3+} + e^- = Fe^{2+}$	+0.77
NO_3^-	$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$	+0.74
NO_3^-	$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$	+0.43
NO_3^-	$NO_3^- + 10H^+ + 8\,e^- = NH_4^+ + 3H_2O$	+0.36
$C_6H_4ClCOO^-$	$C_6H_4ClCOO^- + H^+ + 2e^- = C_6H_5COO^- + Cl^-$	+0.26
$(CH_3)_2SO$	$(CH_3)_2SO + 2H^+ + 2e- = (CH_3)_2S + H_2O$	+0.23
$S_2O_3^{2-}$	$S_2O_3^{2-} + 8H^+ + 8e^- = 2HS^- + 3H_2O$	-0.21
SO_4^{2-}	$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$	-0.22
CO_2	$CO_2 + 8H^+ + 8e- = CH_4 + 2H_2O$	-0.24
S	$S + H^+ + 2e^- = HS^-$	-0.27

worst

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Energía libre y Yield

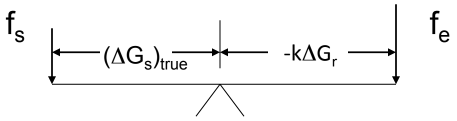
Why do some microorganisms have a lower yield than others?

Microorganisms “prefer” to convert all their substrate into biomass (f_s = 1.0), but some substrate must be burned to give energy for synthesis.

When energy reactions yield very little energy per equivalent, most of the electrons must be used to produce energy for cell synthesis (f_e must be large). For these reactions, f_s and yield will be small.

Other energy reactions generate considerable energy per equivalent. Fewer equivalents can generate sufficient energy for cell synthesis (f_e can be small). For these reactions, f_s and yield will be large.

Balance de energía libre de McCarty y fs



For a balance to be achieved, $f_s(\Delta G_s)_{true} = -f_e k\Delta G_r$

ΔG_s = Energy required to synthesize one eq of cells from a carbon source

ΔG_r = Energy obtained by combining the electron donor and acceptor

$$f_s(\Delta G_s)_{true} = -f_e k\Delta G_r \qquad f_e = 1 - f_s$$

$$f_s\left(\Delta G_s\right)_{true} = -k\Delta G_r + f_s k\Delta G_r$$

$$f_s\left(\Delta G_s\right)_{true} - f_s k\Delta G_r = -k\Delta G_r$$

$$f_s\left[\left(\Delta G_s\right)_{true} - k\Delta G_r\right] = -k\Delta G_r$$

$$\boxed{f_s = \frac{-k\Delta G_r}{-k\Delta G_r + \left(\Delta G_s\right)_{true}}}$$

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For synthesis, assume that carbon from the donor is converted to pyruvate then to the cell.

$$\left(\Delta G_s\right)_{true} = \frac{\Delta G_p}{k^m} + \frac{\Delta G_{pc}}{k} \qquad \begin{array}{l} m = -1 \text{ if } \Delta G_p < 0 \\ m = +1 \text{ if } \Delta G_p > 0 \end{array}$$

ΔG_p = Energy required to convert the carbon source to pyruvate

ΔG_r = Energy required to convert pyruvate carbon to cells

Estimación of fs°

Superscript ° indicates that this f_s is a maximum value (I.e., no decay)

Electron donor: acetate
Electron acceptor: nitrate
N source: nitrate

		$\Delta G^{\circ\prime}$(kJ/eq)	
R_d:	$\frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O = \frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$	-27.40	(as written)
R_a:	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2 + \frac{3}{5}H_2O$	-72.20	

ΔG_r = Energy released = -27.40-72.20 = -99.62 KJ/eq

Energy required for synthesis = $\Delta G_p + \Delta G_{pc}$

ΔG_p is obtained by combining R_d with the pyruvate half reaction:

	$\Delta G^{\circ\prime}$(kJ/eq)
$\frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e^- = \frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O$	+35.09

ΔG_p=-27.40+(+35.09)=7.69 KJ/eq

Assume k=0.6, ΔG_{pc}=13.4 kJ/eq for nitrate N source

$$f_s^{\circ} = \frac{-k\Delta G_r}{-k\Delta G_r + \frac{\Delta G_{pc} + \Delta G_p}{k}} = \frac{-0.6(-99.60)}{-0.6(-99.60) + \frac{13.4+7.69}{0.6}} = 0.63$$

f_e=1-0.63=0.37

$$Y = 0.63\frac{4.04^\circ g^\circ vs/eq}{\left(1/8\right)59^\circ g^\circ acetate/eq} = \frac{0.35^\circ gvs}{g^\circ acetate}$$

Energía libre de formación

ΔG_f^o = Free energy of formation, under standard conditions (pH7, 25^{o}C, all reactants at 1M)

- if <u>negative</u>, reaction is energy yielding and will proceed favorably (**exergonic**)

- if <u>positive</u>, reaction is energy consuming and will <u>not</u> proceed favorably (**endergonic**)

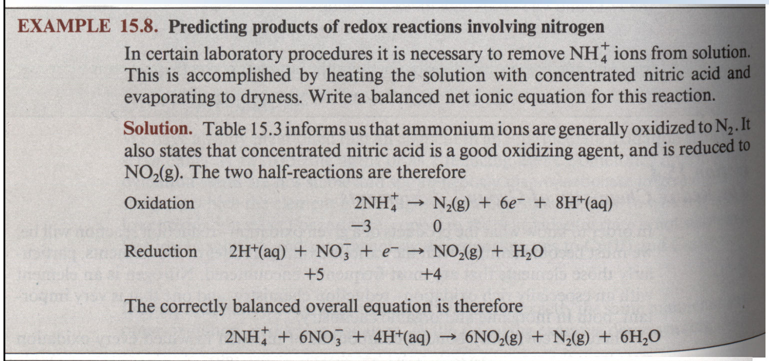
Energía libre de reacción

$\Delta G^{o'}$ = Free energy of reaction, under standard conditions (pH7, 25^{o}C, all reactants at 1M)

- if <u>negative</u>, reaction is energy yielding and will proceed favorably (**exergonic**)

- if <u>positive</u>, reaction is energy consuming and will <u>not</u> proceed favorably (**endergonic**)

Reacciones medias REDOX de Nitrogen



EXAMPLE 15.8. Predicting products of redox reactions involving nitrogen

In certain laboratory procedures it is necessary to remove NH_4^+ ions from solution. This is accomplished by heating the solution with concentrated nitric acid and evaporating to dryness. Write a balanced net ionic equation for this reaction.

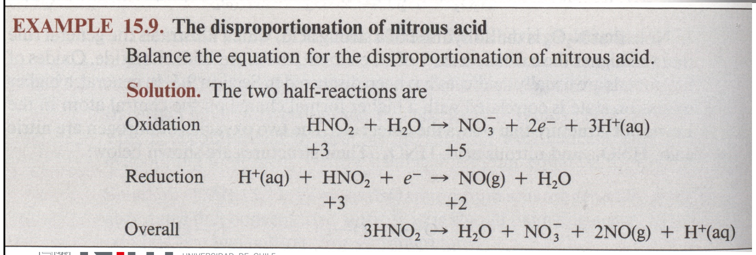
Solution. Table 15.3 informs us that ammonium ions are generally oxidized to N_2. It also states that concentrated nitric acid is a good oxidizing agent, and is reduced to $NO_2(g)$. The two half-reactions are therefore

Oxidation $\underset{-3}{2NH_4^+} \rightarrow \underset{0}{N_2(g)} + 6e^- + 8H^+(aq)$

Reduction $2H^+(aq) + \underset{+5}{NO_3^-} + e^- \rightarrow \underset{+4}{NO_2(g)} + H_2O$

The correctly balanced overall equation is therefore

$$2NH_4^+ + 6NO_3^- + 4H^+(aq) \rightarrow 6NO_2(g) + N_2(g) + 6H_2O$$



EXAMPLE 15.9. The disproportionation of nitrous acid

Balance the equation for the disproportionation of nitrous acid.

Solution. The two half-reactions are

Oxidation $\underset{+3}{HNO_2} + H_2O \rightarrow \underset{+5}{NO_3^-} + 2e^- + 3H^+(aq)$

Reduction $H^+(aq) + \underset{+3}{HNO_2} + e^- \rightarrow \underset{+2}{NO(g)} + H_2O$

Overall $3HNO_2 \rightarrow H_2O + NO_3^- + 2NO(g) + H^+(aq)$

Segal, Chemistry: experiment and theory. 1985