Thermodynamic Laws, Gibbs Free Energy & pE/pH

or how to predict chemical reactions without doing experiments

OCN 623 – Chemical Oceanography

Definitions

- Extensive properties
  - Depend on the amount of material
  - e.g. # of moles, mass or volume of material
  - examples in chemical thermodynamics:
  - G -- Gibbs free energy
  - H -- enthalpy

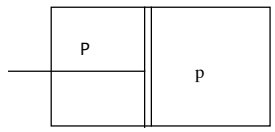
Intensive properties

- Do not depend on quantity or mass
  e.g.
  - temperature
  - pressure
  - density
  - refractive index

Reversible and irreversible processes

- Reversible process occurs under equilibrium conditions

  e.g. gas expanding against a piston



$p = P + \partial p$ reversible
$p = P + \Delta p$ irreversible

- No friction or other energy dissipation
- System can return to its original state
- Very few processes are really reversible in practice
  - e.g.

    Daniell Cell

    $Zn + CuSO_4 = ZnS0_4 + Cu$

    with balancing external emf

    Compression of gases

    Vaporisation of liquids
- Is a concept used for comparison

Spontaneous processes

- Occur without external assistance
  - e.g.

    expansion of a gas from region of high pressure to low pressure

    diffusion of a solute in a solvent

  Are irreversible by definition -- occur at a finite rate

1st law of thermodynamics

- Energy cannot be created or destroyed
  - when one kind of energy disappears it is transformed into an equivalent quantity of another kind

$$\Delta U = q - w$$
$$dU = dq - dw$$

dU = change in internal energy of the system
dq = heat absorbed by the system +
dw = work done by the system +

- U is a thermodynamic function

  dU depends only on the initial and final states of the system-not the path taken

  q and w are NOT thermodynamic functions

Internal energy of system is increased by gaining heat (q)

Internal energy of system is decreased when work is done by the system

$$dU = dq - dw$$

$w_{rev.} > w_{irrev.}$

- Work done by system during irreversible process is less than could be obtained if process was reversible

  e.g. if piston moved at finite rate, friction dissipates energy

Chemical thermodynamics

HEAT

- Heat (q) is measured in terms of:
  amount of substance x molar heat capacity x temp rise
- For phase change
  q = moles of substance x molar latent heat
- q is the heat of reaction

WORK

- Work of expansion

$$= P \Delta V$$

where P = pressure and ΔV is change in volume
at constant volume $\Delta V = 0$,
therefore w = 0 no work is done

Electrical work

- Occurs in electrical cells e.g.
  $Zn + Cu^{2+} = Zn^{2+} + Cu$

- Electrical energy = I * E * t
  E is the emf (voltage), t = time, I = current flowing
  It=zF for 1 mol
  z= # of electrons transferred,
  F (Faraday)= 96,490 Coulombs/mol

  Electrical energy = zEF

- System at constant volume

  (all non-gas reactions are at constant volume)

  $P\Delta V = w = 0$

  $$\Delta \mathbf{U} = \mathbf{q_v}$$

  $q_{v=}$ heat at constant volume

- System at constant pressure

  (all reactions open to atmosphere)

  $$\Delta \mathbf{U} = \mathbf{q_p} - \mathbf{P\Delta V}$$

Ideal gas law $P\Delta V = \Delta nRT$

R is the gas constant = 8.314 Joules mol^{-1} K^{-1}

therefore $\Delta U = q_p - \Delta nRT$

rearranging $q_p = \Delta U + \Delta nRT$

- q_p is called the enthalpy H

  change in enthalpy $\Delta H = \Delta U + P\Delta V$

  in absolute terms

  $$H = U + PV$$

- H is a thermodynamic property,

  is defined in terms of thermodynamic functions: U, P and V

  For an infinitesimal change at constant pressure:

  $$dH = dU + PdV$$

- $\Delta H_f{}^o{}_{298}$
  is the heat of formation of 1 mole of a compound from its elements at 298°K

- ΔH is -ve = exothermic reaction
- ΔH is +ve = endothermic reaction
  (seen from system perspective)
- ΔH is proportional to amount of material
  is an extensive property

- ΔH is equal in magnitude but opposite in sign for the reverse reaction, because it is a thermodynamic quantity

$$\Delta H_{products} - \Delta H_{reactants}$$

ΔH for reaction is same regardless of number of steps between reactants and products

$$\Delta H = \Delta U + \Delta nRT$$

- Can use component reactions to calculate enthalpy change for unknown reaction

Reaction	Enthalpy
$H_2 + 0.5\ O_2 = H_2O$ (a)	$\Delta H = -285.8$ kJ mol^{-1}
$C + O_2 = CO_2$ (b)	$\Delta H = -393.3$ kJ mol^{-1}
$C_2H_6 + 3.5\ O_2 = 2\ CO_2 + 3H_2O$ (c)	$\Delta H = -1559.8$ kJ mol^{-1}

can use above to calculate ΔH for ethane formation

2*b + 3*a - c

$2C + 2O_2 + 3H_2 + 1.5\ O_2 - C_2H_6 - 3.5\ O_2 = 2CO_2 + 3H_2O - 2\ CO_2 - 3H_2O$

canceling yields

$2C + 3\ H_2 = C_2H_6$ $\Delta H = 2^* -393.3 + 3^* -285.8 - (-1559.8)$ $= -84.2$ kJ mol^{-1}

- But enthalpy change alone is insufficient to allow prediction of likelihood of reaction
- Entropy change is also needed

2nd law of thermodynamics

$$dS = \frac{dq_{rev}}{T}$$

change in entropy = amount of reversible heat absorbed by system divided by temperature

- Entropy is the degree of disorder of the system
  chance of finding something in a fixed volume- higher pressure, greater chance, liquid lower entropy than gas, solid lower than liquid
- Change in entropy measures capacity for spontaneous change diffusion of a solute from high concentration to low concentration, or a gas from high pressure to low pressure
- A system undergoing spontaneous change is moving to a greater degree of disorder

- Entropy is an extensive property
- Units heat/temperature = J(oules) K^{-1} mol^{-1}
  for solids dq = moles x molar heat capacity x temperature rise
  $dq = C_m dT$

- For phase change

$$\Delta S = \frac{L}{T}$$

where L is the latent heat of fusion

e.g. for water L = 6 kJ mol^{-1}

$\Delta S = \frac{6000}{273.1} = 22.0$ J $K^{-1}mol^{-1}$ for melting ice

- reversible reaction the net change in entropy is zero
- irreversible reaction there is a net increase in entropy

- Since nearly all reactions are irreversible, entropy is increasing -- called times arrow
- always increasing --cannot run time backwards

Third law of thermodynamics

The entropy of a perfectly crystalline material at the absolute zero (-273.1° C) is zero

- entropy allows prediction of the feasibility of reactions

Gibb's free energy

- Gibbs function G = H - TS

equals the enthalpy - temperature x entropy
at constant volume q = ΔU

- Tendency of reaction to occur is combination of energy and entropy change
- Reactions proceed in direction that minimises the internal energy, i.e. H is lowered
- Reactions proceed to maximise degrees of freedom i.e. entropy increases
- ΔG is negative for a spontaneous reaction

- $G = H - TS$
- at constant temperature: $dG = dH - TdS$

G is a thermodynamic function

ΔG for a reaction = $\Delta G_{products} - \Delta G_{reactants}$

Spontaneity of reactions

sign of ΔG	ΔH	ΔS	Comments
always -	-	+	Spontaneous at all T; reverse never spontaneous
always +	+	-	Never spontaneous at any T reverse reaction occurs
High T - Low T +	+	+	spontaneous at High T only
low T - high T +	-	-	Spontaneous at low T reverse rx at high T

- For an electrical system

$$\Delta G = -zEF$$

where:

E = the emf of the cell (or half cell)

F = Faraday (a positive number)

z = number of electrons involved in the reaction

- Thermodynamics applied to redox speciation
- Redox speciation has profound effects on chemical and biological processes
- Photosynthetic organisms, altered Earth's redox conditions from reducing to oxidising
- Profound consequences for life
- Anoxic conditions exist today

- Circulation changes may have resulted in limited anoxia in basins
- Removal rate of geochemical species affected by redox speciation
- Equilibrium thermodynamics can be used to predict redox speciation as a function of pH and pε

Definitions

- pH -- from the German, potens Hydrogen ion -- strength of the hydrogen ion

$pH = -\log \{H^+\}$ Note: is activity not concentration

$pH = 2$ (acid) $= -\log \{H^+\}$

or $\{H^+\} = 10^{-2}$ M = 0.01 M (10 millimolar)

pH = 9 (alkaline)

$\{H^+\} = 10^{-9}$ M (1 nanomolar)

Also tendency of a solution to accept or transfer protons

high pH = low $\{H^+\}$ but high tendency to accept H^+

Predict speciation of ions as a function of pH and redox conditions

pH

- For a general acid dissociation reaction

$$HA + H_2O = H_3O^+ + A^- \quad K_1$$

$$-\log \{H^+\} = -\log K_1 - \log \frac{\{HA\}}{\{A^-\}}$$

$$pH = pK_1 + \log \frac{\{A^-\}}{\{HA\}}$$

- Can relate the pH of the solution to the equilibrium constant for the dissociation constant and the ratio of the base to the conjugate form

General case reaction

$H_nB + nH_2O = nH_3O^+ + B^{-n}$ K_n

$$pH = \frac{1}{n} pK_n + \frac{1}{n} \log \frac{\{B^{-n}\}}{\{H_nB\}}$$

since $\Delta G = -RT \ln K$

Rearrange and convert ln to log

$$pK = \frac{\Delta G}{2.303\ RT}$$

$$pH = \frac{\Delta G}{2.303\ RT} + \log \frac{\{A^-\}}{\{HA\}}$$

Shows the relationship between ΔG, the base, the conjugate form and pH

Redox speciation

- Oxidation/reduction is transfer of electrons from one species to another
- Define redox intensity of solution

$$p\varepsilon = -\log \{e^-\}$$

$p\varepsilon$ is the hypothetical tendency of a solution to accept or donate electrons, analogous to pH

Oxidation--the increase in the oxidation number
e.g. Fe (II) to Fe (III)

- increase in charge on charged species
  e.g. Co^{2+} to Co^{3+}

Reduction is the reverse

Oxidation-reduction reactions occur together
One component is oxidised, the other is reduced

Component that is reduced is the oxidising agent
Component that is oxidised is the reducing agent

Reducing solution --

electron activity is high

$p\varepsilon$ is low

high tendency to donate electrons

Oxidising solution--

electron activity is low

$p\varepsilon$ is high

high tendency to accept electrons

Can treat in same way as pH

Reduction of Fe by hydrogen

$$Fe^{3+} + 1/2\ H_{2(g)} = Fe^{2+} + H^{+} \quad K_1$$

$$p\varepsilon = \frac{-\Delta G}{2.303\ RT} + \log \frac{\{Fe^{3+}\}}{\{Fe^{2+}\}}$$

$$p\varepsilon = \frac{-\Delta G}{2.303\ RT} + \log \frac{\{ox\}}{\{red\}}$$

General reaction where n electrons are involved

$$ox + n/2\ H_2 = red + ne^- + nH^+$$

$$p\varepsilon = \frac{1}{n} \log K + \frac{1}{n} \log \frac{\{ox\}}{\{red\}}$$

Relationship to Eh electrode or redox potential

$$\Delta G = -nE_{cell}F$$

At standard conditions $\Delta G^0 = -nE^0F$
where E^0 = std redox potential of cell

$$\text{so} \quad p\varepsilon_{cell} = \frac{E_{cell}F}{2.303RT}$$

E_{cell} is the sum of the 1/2 cell potentials

Can now use the pH and pε relationships to predict the stability of species under various pH/ pε conditions

TABLE 7.1
Standard Electrode Potentials for Selected Half-Reactions

Reaction	*Log K at 25°C*	*Standard Electrode Potential (V) at 25°C*
$Na^+ + e^- = Na(s)$	−46	−2.71
$Zn^{2+} + 2e^- = Zn(s)$	−26	−0.76
$Fe^{2+} + 2e^- = Fe(s)$	−14.9	−0.44
$Co^{2+} + 2e^- = Co(s)$	−9.5	−0.28
$V^{3+} + e^- = V^{2+}$	−4.3	−0.26
$2H^+ + 2e^- = H_2(g)$	0.0	0.00
$S(s) + 2H^+ + 2e^- = H_2S$	+4.8	+0.14
$Cu^{2+} + e^- = Cu^+$	+2.7	+0.16
$AgCl(s) + e^- = Ag(s) + Cl^-$	+3.7	+0.22
$Cu^{2+} + 2e^- = Cu(s)$	+11.4	+0.34
$Cu^+ + e^- = Cu(s)$	+8.8	+0.52
$Fe^{3+} + e^- = Fe^{2+}$	+13.0	+0.77
$Ag^+ + e^- = Ag(s)$	+13.5	+0.80
$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + 3H_2O$	+17.1	+1.01
$IO_3^- + 6H^+ + 5e^- = \frac{1}{2}I_2(s) + 3H_2O$	+104	+1.23
$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	+43.6	+1.29
$Cl_2(g) + 2e^- = 2Cl^-$	+46	+1.36
$Co^{3+} + e^- = Co^{2+}$	+31	+1.82

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TABLE 7.2
Computing E^0_{cell} from E^0_h's[a]

Location	*Reaction*	E^0_h *(V)*
Cathode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
Anode	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	+0.76
Redox reaction	$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$	+1.10

[a]The redox reaction and E^0_{cell} are calculated by summing the half-reactions and E^0_h's, respectively.

SO_4^{2-} and S^{2-} important diagenesis reaction

$SO_4^{2-} + 8H^+ + 6e^- = S_{(s)} + 4H_2O$

$$p\varepsilon = \frac{1}{6}\log K + \frac{1}{6}\log \frac{\{SO_4\}\ \{H^+\}^8}{\{S\}\ \{H_2O\}^4}$$

look up log K or get it from ΔG use 36.2

Activity of $\{H_2O\} = 1$ $\{S\} = 1$(a solid)

$$p\varepsilon = \frac{1}{6}(36.2) + \frac{1}{6}\log \{SO_4^{2-}\}\{H^+\}^8$$

seawater $\{SO_4^{2-}\} = \sim 30$ mmolar

$$p\varepsilon = 6.03 + \frac{1}{6}\log (30 \times 10^{-3}) + \frac{8}{6}\log\{H^+\}$$

$$p\varepsilon = 6.03 - \frac{1.5}{6} - \frac{8}{6}\,pH$$

$$p\varepsilon = 5.78 - \frac{4}{3}\,pH$$

Can use to construct pε/pH relationship predictions for S system

pε/pH of various biologically important species

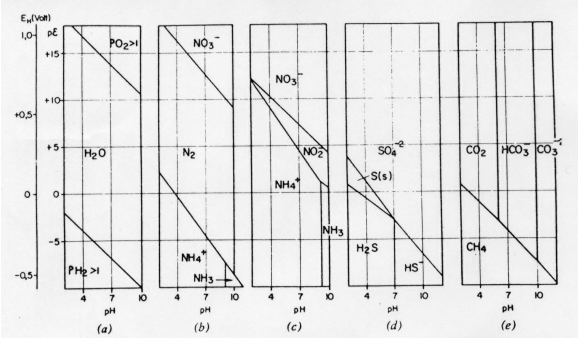

Figure 7.8 pε–pH diagrams for biologically important elements (25°C). (*a*) The upper and lower lines represent equations 44 and 43, respectively, the oxygen and hydrogen equilibria with water. (*b*) The nitrogen system, considering only stable equilibria. The only oxidation states involved are (-III), the elemental state, and (V). (*c*) NH_4^+, NH_3, NO_3^- and NO_2^- are treated as species metastable with regard to N_2; that is, N_2 is treated as a redox inert component (cf. Figure 9.10c and text). (*d*) Sulfur species stable for assumed conditions are SO_4^{2-}, elemental sulfur, and sulfides (cf. Figure 7.5 and Example 7.7). (*e*) The thermodynamically possible existence of elemental *C* (graphite) is ignored.

- can use pε to determine ratio of species under given conditions
- e.g. oxidation of S^{2-} by oxygen

$$\frac{1}{4} O_2 + H^+ + e^- = \frac{1}{2} H_2O$$

and $\frac{1}{8} SO_4^{2-} + \frac{9}{8} H^+ + e^- = \frac{1}{8} HS^- + \frac{1}{2} H_2O$

pε° for oxygen reduction is +20.75

larger than the sulphate reduction (+4.25)

So oxygen gets reduced and the S gets oxidised

TABLE 7.3
Log K, pe^0_w, and $E^0_h(w)$ of Redox Processes[a]

Reaction	pe^0 (=log K)	$pe^{0\,a}_w$	$E^0_h(w)$
(1) $\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	+20.75	+13.75	+0.81
(2) $\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+21.05	+12.65	+0.75
(3) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-(10^{-3}M) + \frac{3}{2}H^+ + e^- = \frac{1}{2}MnCO_3(s) + \frac{3}{8}H_2O$	—	+3.9[b]	+0.23
(4) $\frac{1}{2}NO_3^- + H^+ + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	+14.15	+7.15	+0.42
(5) $\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.90	+6.15	+0.36
(6) $\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+15.14	+5.82	+0.34
(7) $\frac{1}{2}CH_3OH + H^+ + e^- = \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$	+9.88	+2.88	+0.17
(8) $\frac{1}{4}CH_2O + H^+ + e^- = \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$	+6.94	−0.06	+0.00
(9) $FeOOH(s) + HCO_3^-(10^{-3}M) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	—	−0.8[b]	−0.05
(10) $\frac{1}{2}CH_2O + H^+ + e^- = \frac{1}{2}CH_3OH$	+3.99	− 3.01	−0.18
(11) $\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^- = \frac{1}{6}S(s) + \frac{2}{3}H_2O$	+6.03	−3.30	−0.20
(12) $\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	+5.25	−3.50	−0.21
(13) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	−3.75	−0.22
(14) $\frac{1}{2}S(s) + H^+ + e^- = \frac{1}{2}H_2S(g)$	+2.89	−4.11	−0.24
(15) $\frac{1}{8}CO_2(g) + H^+ + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+2.87	−4.13	−0.24
(16) $\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^- = \frac{1}{3}NH_4^+$	+4.68	−4.68	−0.28
(17) $\frac{1}{2}(NADP^+) + \frac{1}{2}H^+ + e^- = \frac{1}{2}(NADPH)$	−2.0	−5.5	−0.33
(18) $H^+ + e^- = \frac{1}{2}H_2(g)$	0.0	−7.00	−0.41
(19) Oxidized ferredoxin + e^- = reduced ferredoxin	−7.1	−7.1	−0.42
(20) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{24}(glucose) + \frac{1}{4}H_2O$	−0.20	−7.20	−0.43
(21) $\frac{1}{2}HCOO^- + \frac{3}{2}H^+ + e^- = \frac{1}{2}CH_2O + \frac{1}{2}H_2O$	+2.82	−7.68	−0.45
(22) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	−1.20	−8.20	−0.48
(23) $\frac{1}{2}CO_2(g) + \frac{1}{2}H^+ + e^- = \frac{1}{2}HCOO^-$	−4.83	−8.33	−0.49

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1970 by John Wiley & Sons, Inc., New York, p. 318. Reprinted by permission. See Stumm and Morgan (1970) for data sources.
[a]Values for pe^0_w apply to the electron activity for unit activities of oxidant and reductant in neutral water, that is, at pH = 7.0 for 25°C.
[b]These data correspond to $(HCO_3^-) = 10^{-3}$ M rather than unity and so are not exactly pe^0_w; they represent typical aquatic conditions more nearly than pe^0_w values do.

Write equation

$$\frac{1}{8}HS^- + \frac{1}{4}O_2 = \frac{1}{8}SO_4^{2-} + \frac{1}{8}H^+$$

Can predict reaction products using

$$p\varepsilon^\circ_1 - p\varepsilon^\circ_2 = \frac{1}{n}\log K_{cell}$$

(full derivation Libes P114)

$$13.75-(-3.75) = \frac{1}{1}\ \mathrm{Log}\ \frac{\{SO_4^{2-}\}^{1/8}}{P_{O2}^{1/4}}\ \frac{\{H^+\}^{1/8}}{\{HS^-\}^{1/8}}$$

$$17.5 = \frac{1}{8}\log\frac{\{SO_4^{2-}\}}{\{HS^-\}} - \frac{1}{8}pH - \frac{1}{4}\log PO_2$$

- Assuming pH = 8 and a PO_2 of 0.21 atm
  (partial pressure of 0.21 atm)

  Calculate:

  $$\frac{\{SO_4^{2-}\}}{\{HS^-\}} = 10^{149}$$

i.e. no HS^- present

Calculate the energy released from reaction

ΔG -99.91 kJ/mole

In presence of oxygen S will be oxidised to SO_4^{2-}

Energy can be gained from the reaction

Is the basis of the life forms around hydrothermal vents

Micro-organisms make a living oxidising sulphide to sulphur in an oxic environment

The half reaction with the highest $p\varepsilon$ will force the other reactions to proceed as oxidations

- The greater the difference in pε between the oxidising and reducing agents the greater the free energy yield for the reaction

- can construct a series of favourable oxidants for organic matter

  Greatest free energy yield is from the oxidation of organic matter by oxygen reduction

  $CH_2O + O_2 = CO_2 + H_2O \quad \Delta G = -125.31$ kJ/mole (-29.95 kcal/mole)

Oxidation sequence on the redox scale

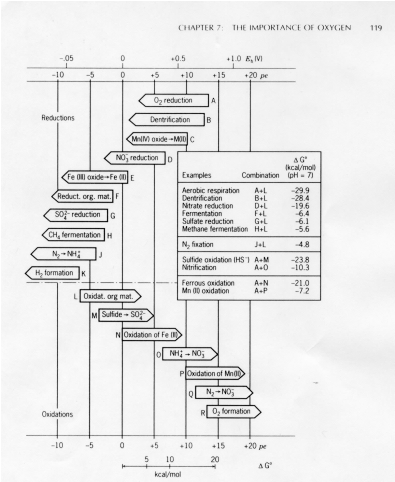

FIGURE 7.4. Sequence of microbially mediated redox reactions. The arrows point in the direction of the spontaneous redox reaction. The originating point of the arrows indicates the redox energy associated with each half-reaction. No information is contained in the relative length of the arrows. *Source:* From *Aquatic Chemistry*, W. S. Stumm and J. J. Morgan, copyright © 1981 by John Wiley & Sons, Inc., New York, p. 460. Reprinted by permission.

- Can determine which would be the next most favoured substrate to oxidise in the absence of organic matter
- Sulphide is next
- Sunlight is ultimate energy source driving these reactions (not hydrothermal sulphide)
- The net energy from the oxidation of the carbon is a result of the energy from sunlight being originally used to reduce oxidised carbon to organic carbon

Photosynthetic organisms started a disproportionation in the thermodynamic state of matter

Produced two large pools of material that are thermodynamically unstable in each others presence -- organic matter and oxygen

Kinetics allows co-existence!

https://www.youtube.com/watch?v=VnbiVw_1FNs