

4

Determination of Stoichiometric Equations for Catabolism and Anabolism

4.1

Introduction

Chemical reactions can be traced by measuring the concentrations of educts as well as intermediate and final products by continuous or discontinuous measurements after taking samples. One condition is of high importance and can be used for checking the results: balances must be fulfilled for each element.

From a fundamental point of view, the same condition is valid for biological systems. Therefore, it is principally possible to study bioreactors using the same balances of elements. Two points must be considered which are typical for living systems. First, the mass of living organisms can increase by growing, it can decrease by endogenous respiration and by dying and new substrates can be produced by lysis as sources of carbon, hydrogen, nitrogen and phosphorous. The second point is typical for environmental microbiology. In one bioreactor, the number of different strains of bacteria is normally high and the composition may change during the process. Besides that, protozoa and other eukaryotes may grow in the same system as the bacteria and the bacteria are then eaten by protozoa.

Nevertheless, balances of total parameters such as COD, DOC and BOD₅, as well as balances of the elements C, O, H, N and P can be very helpful in studying and controlling environmental bioreactors.

First, we will start with simple balances, neglecting endogenous respiration, cell death, lysis, etc.; and we will consider only aerobic chemoorganoheterotrophic bacteria. Later on, we will expand these systems.

Consider that the following balances are totally independent of the kinetics and reaction engineering conditions. The question “How much mass is transferred in what time?” is of great significance, but we will delve into that question later.

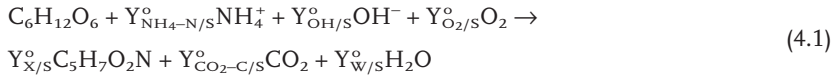
4.2

Aerobic Degradation of Organic Substances

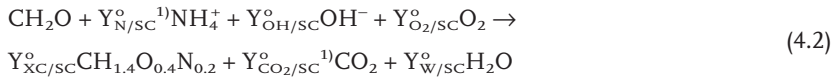
4.2.1

Degradation of Hydrocarbons Without Bacterial Decay

Let us start with the aerobic degradation of glucose, studying the stoichiometry of catabolism and anabolism:



and normalizing the glucose and the bacterial mass to *one* C atom:



Equation (4.2) is valid for substrates with the C-standardized composition CH_2O (hydrocarbons) and for bacteria with a mean composition $\text{CH}_{1.4}\text{O}_{0.4}\text{N}_{0.2}$.

Six true yield coefficients Y° must be determined. Biomass decay by endogenous respiration and bacterial death are not considered here. To fulfil the charge balance as required, we obtain:

$$Y_{\text{N}/\text{SC}}^\circ = Y_{\text{OH}/\text{SC}}^\circ \quad (4.3)$$

and, because of the following mass balances for four elements, we obtain all together five equations for the calculation of six yield coefficients:

$$\text{C balance: } 1 = Y_{\text{XC}/\text{SC}}^\circ + Y_{\text{CO}_2/\text{SC}}^\circ \quad (4.4)$$

$$\text{H balance: } 2 + 4 Y_{\text{N}/\text{SC}}^\circ + Y_{\text{OH}/\text{SC}}^\circ = 1.4 Y_{\text{XC}/\text{SC}}^\circ + 2 Y_{\text{W}/\text{SC}}^\circ \quad (4.5)$$

$$\text{O balance: } 1 + Y_{\text{OH}/\text{SC}}^\circ + 2 Y_{\text{O}_2/\text{SC}}^\circ = 0.4 Y_{\text{XC}/\text{SC}}^\circ + 2 Y_{\text{CO}_2/\text{SC}}^\circ + Y_{\text{W}/\text{SC}}^\circ \quad (4.6)$$

$$\text{N balance: } Y_{\text{N}/\text{SC}}^\circ = 0.2 Y_{\text{XC}/\text{SC}}^\circ \quad (4.7)$$

Five yield coefficients can be calculated using Eqs. (4.3) to (4.7):

$$Y_{\text{XC}/\text{SC}}^\circ = 3 - 4 Y_{\text{O}_2/\text{SC}}^\circ \quad (4.8)$$

$$Y_{\text{CO}_2/\text{SC}}^\circ = 4 Y_{\text{O}_2/\text{SC}}^\circ - 2 \quad (4.9)$$

$$Y_{\text{N}/\text{SC}}^\circ = 0.6 - 0.8 Y_{\text{O}_2/\text{SC}}^\circ \quad (4.10)$$

$$Y_{\text{OH}/\text{SC}}^\circ = 0.6 - 0.8 Y_{\text{O}_2/\text{SC}}^\circ \quad (4.11)$$

$$Y_{\text{W}/\text{SC}}^\circ = 0.4 + 0.8 Y_{\text{O}_2/\text{SC}}^\circ \quad (4.12)$$

¹⁾ Instead of $Y_{\text{CO}_2-\text{C}/\text{SC}}^\circ$ we write $Y_{\text{CO}_2-\text{SC}}^\circ$ and instead of $Y_{\text{NH}_4-\text{N}}^\circ$ we write $Y_{\text{N}/\text{SC}}^\circ$.

At first, we conclude that one of the six yield coefficients must be unknown without experiments. But after elimination of $Y_{O_2/SC}^\circ$ from Eq. (4.6):

$$Y_{O_2/SC}^\circ = 0.2 Y_{XC/SC}^\circ + Y_{CO_2/SC}^\circ + 0.5 Y_{W/SC}^\circ - 0.5 Y_{OH/SC}^\circ - 0.5 \quad (4.13)$$

and, combining Eqs. (4.8), (4.9), (4.11) and (4.12) into Eq. (4.13), a further equation for the calculation of $Y_{O_2/SC}^\circ$ is available:

$$Y_{O_2/SC}^\circ = Y_{CO_2/SC}^\circ + 0.2 Y_{XC/SC}^\circ + 0.5 (Y_{W/SC}^\circ - Y_{OH/SC}^\circ - 1) \quad (4.14)$$

Now the system of the six equations (Eq. (4.3) to (4.7) and (4.14)) can be solved; and we are able to predict all yield coefficients:

$$Y_{XC/SC}^\circ = 1/3 \frac{\text{mol C}}{\text{mol C}}; \quad Y_{CO_2/SC}^\circ = 2/3 \frac{\text{mol C}}{\text{mol C}}; \quad Y_{N/SC}^\circ = 0.067 \frac{\text{mol N}}{\text{mol C}}$$

$$Y_{OH-/SC}^\circ = 0.067 \frac{\text{mol OH}^-}{\text{mol C}}; \quad Y_{W/SC}^\circ = 0.93 \frac{\text{mol H}_2\text{O}}{\text{mol C}}; \quad Y_{O_2/SC}^\circ = 2/3 \frac{\text{mol O}_2}{\text{mol C}}$$

For mol C we can write: mol DOC.

From a fundamental point of view, it should be possible to determine an unknown oxygen and hydrogen content of a substrate $\text{CH}_{\text{SH}}\text{O}_{\text{SO}}$, if two yield coefficients are measured, in this case $Y_{XC/SC}^\circ$ and $Y_{CO_2/SC}^\circ$. Apart from the fact that the CO_2 formed is only determined if the change in concentrations of dissolved CO_2 , HCO_3^- and CO_3^{2-} is known (see Section 4.3), it can be shown that only two equations are available to calculate SH as well as $Y_{W/SC}^\circ$, which cannot be measured using aqueous substrate solutions.

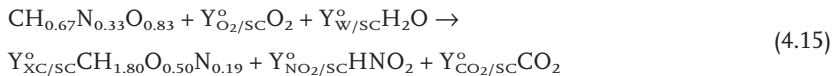
Because of the constancy of the elementary composition of most wastewater mixtures, the calculation of SH, SO, SN and SP is mostly only of academic interest.

4.2.2

Mineralization of 2,4-Dinitrophenol

2,4-Dinitrophenol (2,4-DNP) is used together with other nitroaromatic compounds for the production of dyes, explosives and photographic materials. It can be mineralized by some aerobic bacteria which need nitroaromatic compounds as a source of not only carbon but also nitrogen. At high concentrations, it is very toxic and acts as an insecticide and fungicide.

Here, only the stoichiometric equation of its aerobic mineralization should be of interest. For this purpose, the catabolic and anabolic reactions are summarized, as already shown for glucose in Section 4.2.1. Writing this equation not as $\text{C}_6\text{H}_3\text{OH}(\text{NO}_2)_2$ (2,4-DNP), but for the standardized molecule $\text{CH}_{0.67}\text{N}_{0.33}\text{O}_{0.83}$ (after dividing by the number of C atoms, see Eq. 4.2), the normalized stoichiometric equation is (Heinze 1997):



Comparing Eq. (4.15) with Eq. (4.2), three differences can be discovered:

- The consideration of the equilibria $\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$ and $\text{OH}^- + \text{H}^+ = \text{H}_2\text{O}$ leads to a stoichiometry equation without ions.
- Nitrogen must not be added because of the high content in the substrate molecule.
- The composition of the bacteria (Behrendt 1994) differs a little from that used in Eq. (4.2).

The five true yield coefficients were calculated in the same way, as described by Heinze (1997). First, four equations are obtained by element balances:

$$\text{C balance: } 1 = Y_{\text{XC/SC}}^\circ + Y_{\text{CO}_2/\text{SC}}^\circ \quad (4.16)$$

$$\text{H balance: } 0.67 + 2 Y_{\text{W/SC}}^\circ = 1.8 Y_{\text{XC/SC}}^\circ + Y_{\text{NO}_2/\text{SC}}^\circ \quad (4.17)$$

$$\text{O balance: } 0.83 + 2 Y_{\text{O}_2/\text{SC}}^\circ + Y_{\text{W/SC}}^\circ = 0.5 Y_{\text{XC/SC}}^\circ + 2 Y_{\text{NO}_2/\text{SC}}^\circ + 2 Y_{\text{CO}_2/\text{SC}}^\circ \quad (4.18)$$

$$\text{N balance: } 0.33 = 0.19 Y_{\text{XC/SC}}^\circ + Y_{\text{NO}_2/\text{SC}}^\circ \quad (4.19)$$

An additional equation follows if $Y_{\text{XC/SC}}^\circ$ is eliminated from Eq. (4.18) and (4.19).

$$Y_{\text{O}_2/\text{SC}}^\circ = 0.019 - 0.316 Y_{\text{N/SC}}^\circ - 0.5 Y_{\text{W/SC}}^\circ + Y_{\text{CO}_2/\text{SC}}^\circ \quad (4.20)$$

This system of five equations with five unknown true yield coefficients can be solved as already discussed in Section 4.2.1, resulting in:

$$Y_{\text{XC/SC}}^\circ = 0.3 \frac{\text{mol C}}{\text{mol C}}; \quad Y_{\text{CO}_2/\text{SC}}^\circ = 0.7 \frac{\text{mol C}}{\text{mol C}}; \quad Y_{\text{NO}_2/\text{SC}}^\circ = 0.27 \frac{\text{mol N}}{\text{mol C}}$$

$$Y_{\text{W/SC}}^\circ = 0.07 \frac{\text{mol H}_2\text{O}}{\text{mol C}}; \quad Y_{\text{O}_2/\text{SC}}^\circ = 0.60 \frac{\text{mol O}_2}{\text{mol C}}$$

Although the substrate is of a completely different type, most of the yield coefficients do not differ remarkably from those of Section 4.2.1.

Heinze (1997) investigated the aerobic mineralization of 2,4-DNP in a bioreactor filled with solid porous particles (polyurethane cubes with sides of 0.9 cm) operated with recycle flow. The particle-free overflow was aerated and dissolved oxygen was measured before and after flowing through the fixed bed. By considering the measured flow rate, the oxygen consumption rate $r_{\text{O}_2,\Sigma}$ could be predicted, which changed with the flow rate and was plotted versus the 2,4-DNP removal rate r_s (Fig. 4.1). The observed straight line intersects the ordinate at a positive value, giving the rate of endogenous respiration $r_{\text{O}_2,e}$.

The straight line can be described by:

$$r_{O_2,\Sigma} = r_{O_2} + r_{O_2,e} = Y_{O_2/SC} \cdot r_{SC} \quad (4.21)$$

with:

$$Y_{O_2/SC} = \frac{r_{O_2} + r_{O_2,e}}{r_{SC}} \quad (4.22)$$

as the real yield coefficient. Considering:

$$r_{SC} = \frac{\mu X}{Y_{XC/SC}^0} \quad (4.23)$$

$$r_{O_2} = \frac{\mu X}{Y_{XC/O_2}^0} \quad (4.24)$$

$$r_{O_2,e} = \frac{k_e X}{Y_{XC/O_2}^0} \quad (4.25)$$

the following relation between real and true yield coefficient can be applied:

$$Y_{O_2/SC} = Y_{O_2/SC}^0 \left(1 + \frac{k_e}{\mu} \right) \quad (4.26)$$

If bacteria grow at a high rate μ , the coefficient k_e/μ can be neglected. Otherwise, a relatively large amount of the oxygen consumed is needed for endogenous respiration. In our stoichiometric consideration of Sections 4.2.1 and 4.2.2, it was neglected.

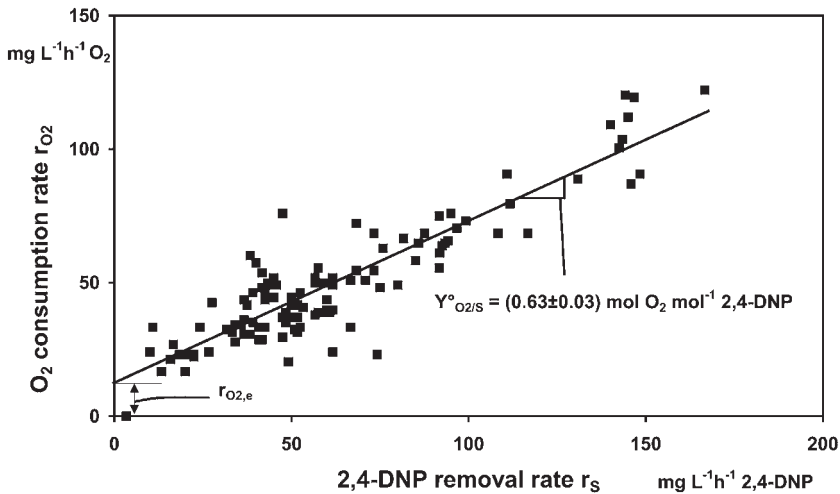


Fig. 4.1 Biodegradation of 2,4-DNP in a fixed bed reactor: oxygen consumption rate as a function of substrate removal rate (Heinze 1997).

4.2.3

Degradation of Hydrocarbons with Bacterial Decay

To this point, endogenous respiration and the death of aerobic bacteria have been neglected, although in Fig. 4.1 the influence of endogenous respiration on total oxygen consumption could be detected. This may be allowed so long as the specific growth rate μ is large compared to the decay rate k_d . Otherwise, we must write (Herbert 1958):

$$r_{XC} - r_{XC,d} = \mu X - k_d X = \mu X - (k_e + k_s) X \quad (4.27)$$

$$r_{CO_2} + r_{CO_2,e} = \frac{\mu X + k_e X}{Y_{XC/CO_2}^o} \quad (4.28)$$

$$r_{SC} = \frac{\mu X}{Y_{XC/SC}^o} \quad (4.29)$$

where μ is the specific growth rate, k_d is the coefficient of decay, k_s is the coefficient of death and k_e is the coefficient of endogenous respiration.

These processes cannot be neglected if the growth rate is reduced as a result of substrate limitation or inhibition. A part of the bacteria will be inactive and no longer involved in substrate consumption and growth. They are dying at rate $k_s X$. Another part loses cell mass at the rate $k_e X$ and uses oxygen at the respiration rate of $k_e X / Y_{XC/O_2}^o$ during the consumption of the cell mass (see Eqs. 4.27 and 4.28).

We will assume here that the dying cells do not release organics for the growth of living cells, so that the stoichiometric Eq. (4.2) is not changed, with the exception of the yield coefficients. Instead of the true yield coefficients Y^o , now the real yield coefficients Y must be considered, which differ the more greatly the less μ is compared to k_d and k_e , respectively.

In the first step, the real yield coefficients are defined as:

$$Y_{XC/SC} = \frac{r_{XC} - r_{XC,d}}{r_{SC}} \quad (4.30)$$

$$Y_{CO_2/SC} = \frac{r_{CO_2} + r_{CO_2,e}^{1)}}{r_{SC}} \quad (4.31)$$

$$Y_{O_2/SC} = \frac{r_{O_2} + r_{O_2,e}}{r_{SC}} \quad (4.32)$$

which can be transformed with the help of Eqs. (4.27) and (4.28) into:

$$Y_{XC/SC} = Y_{XC/SC}^o \left(1 - \frac{k_d}{\mu} \right) \quad (4.33)$$

¹⁾ We will write $CO_2 - C = CO_2$ only for reasons of simplicity.

All rates r and yield coefficients Y can be written using mol or g.

and:

$$Y_{\text{CO}_2/\text{SC}} = Y_{\text{CO}_2/\text{SC}}^{\circ} \left(1 + \frac{k_e}{\mu} \right) \quad (4.34)$$

Starting with Eq. (4.30):

$$r_{\text{SC}} - r_{\text{XC},d} = Y_{\text{XC}/\text{C}} \cdot r_{\text{SC}} \quad (4.35)$$

and considering Eq. (4.32) we obtain:

$$r_{\text{XC}} - r_{\text{XC},d} = Y_{\text{XC}/\text{SC}}^{\circ} \left(1 - \frac{k_d}{\mu} \right) r_{\text{SC}} \quad (4.36)$$

According to that:

$$r_{\text{CO}_2} + r_{\text{CO}_2,e} = Y_{\text{CO}_2/\text{SC}}^{\circ} \left(1 + \frac{k_e}{\mu} \right) r_{\text{SC}} \quad (4.37)$$

Equation (4.26) results. Equations (4.35) and (4.36) can be compared with the results of Section 4.2 (Eqs. 4.18 and 4.19). The real growth rate and CO_2 production rate differ by the relation of bacterial decay and endogenous respiration to specific growth rate from the true rates.

Using the C balance:

$$r_{\text{SC}} = r_{\text{XC}} - r_{\text{XC},e} + r_{\text{CO}_2} + r_{\text{CO}_2,e} \quad (4.38)$$

introducing Eq. (4.30):

$$r_{\text{SC}} = r_{\text{SC}} Y_{\text{XC}/\text{SC}} + r_{\text{CO}_2,\Sigma} \quad (4.39)$$

$$r_{\text{SC}} = \frac{r_{\text{CO}_2,\Sigma}}{1 - Y_{\text{XC}/\text{SC}}} \quad (4.40)$$

and considering Eq. (4.33):

$$r_{\text{SC}} = \frac{r_{\text{CO}_2,\Sigma}}{1 - Y_{\text{XC}/\text{SC}}^{\circ} \left(1 - \frac{k_d}{\mu} \right)} \quad (4.41)$$

follows. According to this consideration:

$$r_{\text{SC}} = \frac{r_{\text{O}_2,\Sigma}}{1 - Y_{\text{XC}/\text{SC}}^{\circ} \left(1 + \frac{k_e}{\mu} \right)} \quad (4.42)$$

can be obtained from the O balance ($\text{C}/\text{O} = 1$ for hydrocarbon molecules).

From Eqs. (4.41) and (4.42) k_d/μ and k_e/μ can be easily eliminated after some conversions:

$$\frac{k_d}{\mu} = \frac{Y_{XC/SC}^o + \frac{r_{CO_2,\Sigma}}{r_{SC}} - 1}{Y_{XC/SC}^o} \quad (4.43)$$

$$\frac{k_e}{\mu} = \frac{1 - \frac{r_{O_2,\Sigma}}{r_{SC}} - Y_{XO/SC}^o}{Y_{XO/SC}^o} \quad (4.44)$$

Note that only measurements of DOC for r_{SC} and O_2 as well as CO_2 reaction rate using gas analysis are needed. However, it is necessary to point out that the CO_2 formed is in equilibrium with HCO_3^- and CO_3^{2-} , which is influenced by all other ions. This will be discussed in the next chapter.

4.3

Measurement of O_2 Consumption Rate $r_{O_2,\Sigma}$ and CO_2 Production Rate $r_{CO_2,\Sigma}$

As explained in Section 4.2.3, $r_{O_2,\Sigma}$ or $r_{CO_2,\Sigma}$ are needed to measure the substrate removal rate r_{SC} and to calculate real yield coefficients, as well as k_e/μ and k_d/μ .

The measurement of $r_{O_2,\Sigma}$ is not complicated for closed aeration tanks, conducting a small bypass exhaust air flow through an O_2 gas analyzer, such as an ABB Magnos 16. For steady-state conditions and a completely mixed tank, $r_{O_2,\Sigma}$ can be calculated using:

$$r_{O_2,\Sigma} = \frac{Q_G (c_{O_2,0} - c_{O_2})}{V_R} \quad (4.45)$$

after measuring c_{O_2} in the exhaust gas. The change in the dissolved oxygen concentration is very low compared with the respiration rate because of the high Henry coefficient H , which is defined by Henry's law, see Eq. (5.6):

$$\frac{c_{O_2}}{H} = c_{O_2}^* \quad (4.46)$$

where c_{O_2} is the O_2 concentration in the gas and $c_{O_2}^*$ is the O_2 concentration at the border gas/liquid at equilibrium.

In comparison to $r_{O_2,\Sigma}$, $r_{CO_2,\Sigma}$ is more difficult to measure for two reasons:

- The solubility of CO_2 in water is much higher than that of O_2 .
- The soluted $CO_{2,L}$ reacts rapidly with water, forming carbonic acid.



However, the equilibrium constant following from:

$$k_1 S_{CO_2,L} \cdot S_{H_2O} = k_2 S_{H_2CO_3} \quad (4.48)$$

$$K'_e = \frac{k_2}{k_1} = \frac{S_{H_2CO_3}}{S_{CO_2,L} \cdot S_{H_2O}} \quad (4.49)$$

$$K_e = S_{H_2O} \cdot K'_e = \frac{S_{H_2CO_3}}{S_{CO_2,L}} = 1.58 \cdot 10^{-3} \quad (4.50)$$

is very low, showing that only ~0.16% of the soluted CO_2 is present in the form H_2CO_3 . Following the concept of Nazaroff and Alvarez-Cohen (2001), we summarize $CO_{2,L}$ and H_2CO_3 by writing:

$$r_{H_2CO_3,\Sigma} = r_{CO_2,L} + r_{H_2CO_3} \quad (4.51)$$

or rather as “carbonic acid” concentration, considering Eq. (4.50):

$$S_{H_2CO_3,\Sigma} = S_{CO_2,L} + S_{H_2CO_3} = S_{CO_2,L} (1 + K_e) \quad (4.52)$$

Depending on the pH, “carbonic acid” dissociation reactions display the following equilibria:



which are strongly influenced by S_{H^+} or $pH = -\log S_{H^+}$:

$$K_1 = \frac{S_{H^+} \cdot S_{HCO_3^-}}{S_{H_2CO_3,\Sigma}} = 4.47 \cdot 10^{-7} \text{ mol L}^{-1} \quad (4.55)$$

$$K_2 = \frac{S_{H^+} \cdot S_{CO_3^{2-}}}{S_{HCO_3^-}} = 4.68 \cdot 10^{-11} \text{ mol L}^{-1} \quad (4.56)$$

A fraction α_i of each species $S_{H_2CO_3,\Sigma}$, $S_{HCO_3^-}$ and $S_{CO_3^{2-}}$ related to the total concentration:

$$S_{C\Sigma} = S_{H_2CO_3,\Sigma} + S_{HCO_3^-} + S_{CO_3^{2-}} \quad (4.57)$$

can be calculated using Eqs. (4.55) and (4.56). (Note: $S_{H_2CO_3,\Sigma} \approx S_{CO_2}$):

$$\alpha_{H_2CO_3,\Sigma} = \frac{S_{H_2CO_3,\Sigma}}{S_{C\Sigma}} = \frac{S_{H^+}^2}{S_{H^+}^2 + K_1 K_2 + K_1 S_{H^+}} \quad (4.58)$$

$$\alpha_{HCO_3^-} = \frac{S_{HCO_3^-}}{S_{C\Sigma}} = \frac{K_1 S_{H^+}}{S_{H^+}^2 + K_1 K_2 + K_1 S_{H^+}} \quad (4.59)$$

$$\alpha_{CO_3^{2-}} = \frac{S_{CO_3^{2-}}}{S_{C\Sigma}} = \frac{K_1 K_2}{S_{H^+}^2 + K_1 K_2 + K_1 S_{H^+}} \quad (4.60)$$

For $\alpha_{\text{H}_2\text{CO}_3, \Sigma} = \alpha_{\text{HCO}_3^-} = 0.5$ and for $\alpha_{\text{HCO}_3^-} = \alpha_{\text{CO}_3^{2-}} = 0.5$, the pH values are called pK_1 and pK_2 , showing characteristic values ($\text{pK}_1 = 6.33$; $\text{pK}_2 = 10.33$).

Equations (4.58) to (4.60) are plotted in Fig. 4.2, presenting some important results:

- At $\text{pH} < 4.5$, all dissolved carbon is in the form of $\text{H}_2\text{CO}_3, \Sigma \approx \text{CO}_2$.
- At $4.3 < \text{pH} < 8.3$, $\text{H}_2\text{CO}_3, \Sigma \approx \text{CO}_2$ and HCO_3^- dominates.
- At $8.3 < \text{pH} < 12.3$, HCO_3^- and CO_3^{2-} dominate.
- At $\text{pH} > 12.3$, all dissolved carbon is in the form of CO_3^{2-} .

This equilibrium can be influenced by temperature and the concentration of other anions.

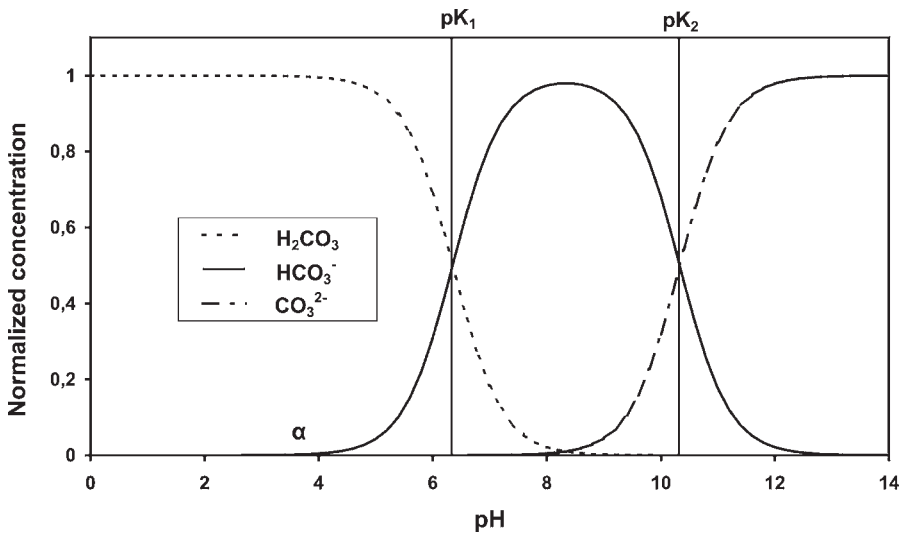


Fig. 4.2 Normalized concentrations α_i of the dissociation products of “carbonic acid” $\text{H}_2\text{CO}_3, \Sigma$, HCO_3^- and CO_3^{2-} as a function of pH (Nazaroff and Alvarez-Cohen 2001); $T = 20^\circ\text{C}$.

PROBLEM 4.1

An industrial wastewater is polluted mostly by polysaccharides ($\text{C}_n\text{H}_{2n}\text{O}_n$ or for $n=1$ CH_2O , respectively). The composition of the bacteria is given by $\text{C}_5\text{H}_7\text{O}_2\text{N}$. The flow rate is $10\,000 \text{ m}^3 \text{ d}^{-1}$, the concentration of the influent is $S_0 = 2000 \text{ mg L}^{-1} \text{ DOC}$; and 90% removal should be achieved.

Calculate the amount of nitrogen which must be added.

How much sludge must be treated?

The specific growth rate μ is large compared to the decay coefficient k_d .

In Section 4.2.1, $Y_{\text{N/SC}}^\circ = 0.067 \text{ mol N (mol DOC)}^{-1}$ and $Y_{\text{XC/SC}}^\circ = 1/3 \text{ mol C (mol DOC)}^{-1}$ was calculated for aerobic degradation of hydrocarbons.

Solution

$$Y_{N/SC}^o = \frac{r_N V}{r_{SC} V} = 0.067 \frac{\text{mol N}}{\text{mol DOC}} = 0.067 \cdot \frac{14}{12} \text{ g N (g C)}^{-1} = 0.078 \frac{\text{g N}}{\text{g C}} =$$

$$0.078 \text{ t N (t C)}^{-1}$$

$$r_{SC} V = Q_w (S_o - S) = 10^4 \cdot 1800 \text{ g d}^{-1} = 18 \text{ t d}^{-1} \text{ DOC}$$

$$r_N V = r_{SC} V \cdot Y_{N/SC}^o = 18 \cdot 0.078 = 1.4 \text{ t N d}^{-1} \text{ nitrogen must be added.}$$

$$Y_{XC/SC}^o = 1/3 \frac{\text{mol C}}{\text{mol DOC}} = 0.33 \text{ g C (g DOC)}^{-1}$$

$$Y_{XC/SC}^o = \frac{r_{XC}}{r_{SC}} ;$$

$$r_{XC} = r_{SC} Y_{XC/SC}^o ; r_{XC} V = r_{SC} V Y_{XC/SC}^o$$

$$r_{XC} V = r_{SC} V Y_{XC/SC}^o = 18,000 \cdot 0.33 = 5940 \text{ kg C d}^{-1}$$

50% C per mass MLVSS

$$r_{MLVSS} V = 2 r_{XC} V \approx 12 \text{ t MLVSS d}^{-1} \text{ sludge must be treated.}$$

PROBLEM 4.2

In a completely mixed (stirred) tank reactor (CSTR), a wastewater loaded with organics and without inorganic carbon is treated aerobically. For this process, carried out in a steady state, the following data are given:

$$\text{Wastewater flow rate } Q_w = 1000 \text{ m}^3 \text{ d}^{-1}$$

$$\text{Air flow rate } Q_A = 7500 \text{ m}^3 \text{ d}^{-1}$$

$$\text{Reactor volume } V = 1000 \text{ m}^3, \text{ pH } 8$$

Henry's law is given by

$$p = H_g c^*$$

(Nazareff and Alvrez-Cohen 2001).

For CO_2 and 25°C $H_g = 29 \text{ atm (mol/L)}^{-1}$ is given. In order to get Henry coefficient H in its dimensionless form

$$p = RTc$$

must be introduced giving

$$c = \frac{H_g}{RT} c^* = H c^*$$

$$\text{With } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 82.05 \cdot 10^{-6} \text{ m}^3 \text{ atm (mol K)}^{-1}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$H = \frac{29}{82.05 \cdot 10^{-6} \cdot 298} = 1.19 \text{ follows.}$$

$\text{CO}_2/\text{HCO}_3^-$ equilibrium constant $K_1 = 4.47 \cdot 10^{-7} \text{ mol L}^{-1}$

CO_2 production rate $r_{\text{CO}_2} = 9000 \text{ g m}^{-3} \text{ d}^{-1}$

Calculate the portion of carbon:

produced as CO_2 in the air leaving the reactor and

produced as CO_2 , HCO_3^- and CO_3^{2-} in the water leaving the reactor.

Solution

C balance in water:

$$0 = - \underbrace{\frac{Q_w}{V} (S_{\text{CO}_2} + S_{\text{HCO}_3^-} + S_{\text{CO}_3^{2-}})}_{\text{dissolved in the effluent water}} - \underbrace{\frac{Q_A}{V} c_{\text{CO}_2}}_{\text{stripped out with air}} + \underbrace{r_{\text{CO}_2}}_{\text{produced}} \quad (4.61)$$

$S_{\text{CO}_3^{2-}}$ can be neglected (pH 8)

$$S_{\text{HCO}_3^-} = K_1 \frac{S_{\text{H}_2\text{CO}_3, \Sigma}}{S_{\text{H}^+}} \approx K_1 \frac{S_{\text{CO}_2}}{S_{\text{H}^+}} \quad (4.62)$$

$$\text{Henry's law } S_{\text{CO}_2} = c^* = \frac{c_{\text{CO}_2}}{H} \quad (4.63)$$

From (4.61) we obtain with Eqs. (4.62) and (4.63)

$$S_{\text{CO}_2} = \frac{r_{\text{CO}_2}}{\frac{Q_w}{V} \left(1 + \frac{K_1}{S_{\text{H}^+}} \right) + \frac{Q_A}{V} H} \quad (4.64)$$

$$K_1 = 4.47 \cdot 10^{-7} \text{ mol L}^{-1}, M_{\text{HCO}_3^-} = 61 \text{ g mol}^{-1}$$

$$K_1 = 4.47 \cdot 61 \cdot 10^{-7} = 272.67 \cdot 10^{-7} \text{ g L}^{-1}$$

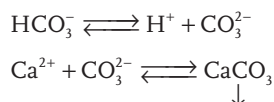
$$S_{\text{H}^+} = 10^{-8} \text{ mol L}^{-1} = 10^{-8} \text{ g L}^{-1}, H = 1.19$$

$$S_{\text{CO}_2} = \frac{9000}{1 \left(1 + \frac{272.67 \cdot 10^{-7}}{10^{-8}} \right) + 7.5 \cdot 1.19} = \frac{9000}{2744.6} = 3.29 \text{ g m}^{-3}$$

With Eq. (4.61) the different parts can be calculated

$$\underbrace{9000 \text{ g m}^{-3} \text{ h}^{-1}}_{\text{CO}_2 \text{ produced}} \approx \underbrace{3.29}_{\text{CO}_2 \text{ trans-ported with water}} + \underbrace{8970.8}_{\text{HCO}_3^- \text{ trans-ported with water}} + \underbrace{29.36}_{\text{CO}_2 \text{ stripped with air}}$$

In reality two further reactions are of importance, which reduce HCO_3^- -concentration:



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