Writing half reactions – example

example 1) Glucose oxidation

Step 1) $CO_2 \rightarrow C_6H_{12}O_6$

Step 2) $CO_2 + H_2O + e^- \rightarrow C_6H_{12}O_6$

in redox reactions, water is almost always a reactant or a product

because we write half reactions in the direction of reduction, e- always appear on the left

Step 3) $6CO_2 + H_2O + e- \rightarrow C_6H_{12}O_6$

Step 4) $6CO_2 + e^- \rightarrow C_6H_{12}O_6 + 6H_2O$

Step 5) $6CO_2 + 24H^+ + e^- \rightarrow C_6H_{12}O_6 + 6H_2O$

Step 6) $6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$

Step 7) $(1/4)CO_2 + H^+ + e^- \rightarrow (1/24)C_6H_{12}O_6 + (1/4)H_2O$

example 2) Nitrate reduction

Step 1) $NO_3^- \rightarrow N_2$

Step 2) $NO_3^- + H_2O + e^- \rightarrow N_2$

Step 3) $2NO_3^- + H_2O + e^- \rightarrow N_2$

Step 4) $2NO_3^- + e^- \rightarrow N_2 + 6H_2O$

Step 5) $2NO_3^- + 12H^+ + e^- \rightarrow N_2 + 6H_2O$

Step 6) $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$

Step 7) $(1/5)NO_3^- + (6/5)H^+ + e^- \rightarrow (1/10)N_2 + (3/5)H_2O$

Textbook example: Alanine oxidation

$(1/4)CO_2 + (1/12)NH_3 + H^+ + e^- \rightarrow (1/12)CH_3CHNH_2COOH + (1/3)H_2O$

Eq. [2.22] to [2.25] in the textbook: slightly different equations depending on different forms of carbonate species and ammonia, and different source of hydrogen (all are correct)

Ammonia $pK_a = 9.25$ → mostly in NH_4^+ in neutral pH

Carbonate $pK_{a1} = 6.3$, $pK_{a2} = 10.3$ → mostly in HCO_3^- with some in H_2CO_3 in neutral pH

Thus, some find it better to use NH_4^+ and HCO_3^- to write reactions, but some prefer others for different reasons

Overall reactions for bacterial growth

We can write up overall reactions for bacterial growth, which involves reactions for energy production and cell synthesis → full stoichiometry of what's happening when you grow bacteria in a growth medium!

- Combining electron donor and acceptor half reactions, we get the overall reaction for respiration (energy reaction)

  $R_e = R_a - R_d$ (- sign on R_d because R_d is written in the direction of reduction)

  ex) Benzoate respiration using nitrate as an electron acceptor (textbook)

  R_a: $(1/5)NO_3^- + (6/5)H^+ + e^- \rightarrow (1/10)N_2 + (3/5)H_2O$

  $-R_d$: $(1/30)\ C_6H_5COO^- + (13/30)H_2O \rightarrow (1/5)CO_2 + (1/30)HCO_3^- + H^+ + e^-$

  R_e: $(1/30)C_6H_5COO^- + (1/5)NO_3^- + (1/5)H^+ \rightarrow (1/5)CO_2 + (1/10)N_2 + (1/30)HCO_3^- + (1/6)H_2O$

- Combining cell synthesis and electron donor half reactions, we get the overall reaction for cell synthesis using a specific electron donor (synthesis reaction)

  $R_s = R_c – R_d$

  ex) Use of benzoate to synthesize cell with generic cell formula (textbook)

  R_c: $(1/5)CO_2 + (1/20)NH_4^+ + (1/20)HCO_3^- + H^+\ e^- \rightarrow (1/20)C_5H_7O_2N + (9/20)H_2O$

  $-R_d$: $(1/30)\ C_6H_5COO^- + (13/30)H_2O \rightarrow (1/5)CO_2 + (1/30)HCO_3^- + H^+ + e^-$

  R_s: $(1/30)\ C_6H_5COO^- + (1/20)NH_4^+ + (1/60)HCO_3^- \rightarrow (1/20)C_5H_7O_2N + (1/60)H_2O$

- Now, note that for the overall reactions for bacterial growth, R_e occurs with a fraction of f_e and R_s occurs with a fraction of f_s. Therefore,

  $R = f_eR_e + f_sR_s$ [Eq (1)]

ex) Overall cell synthesis reaction for benzoate as an electron donor and nitrate as an electron acceptor (textbook)

when $f_s = 0.40$,

$f_e = 1 – f_s = 0.60$

$R = 0.60 \times R_e + 0.40 \times R_s$

R: $0.0333C_6H_5COO^- + 0.12\ NO_3^- + 0.02\ NH_4^+ + 0.12\ H^+ \rightarrow 0.2C_5H_7O_2N + 0.06N_2 +$ $+ 0.12CO_2 + 0.0133HCO_3^- + 0.1067H_2O$

→ Full stoichiometry obtained!

If you plug in the expressions for R_e and R_s in Eq (1),

$R = f_e(R_a – R_d) + f_s(R_c – R_d) = f_eR_a + f_sR_c – R_d$

So, instead of calculating the energy and cell synthesis reactions separately, you can use the equation above to make the overall reaction.

Textbook example: Nitrification [Ex 2.4]

Step 1)

R_d (Table 2.2, I-1): 0.125NO3- + 1.25H+ + $e^- = 0.125NH_4^+ + 0.375H_2O$

R_a (Table 2.2, I-14): $0.25O_2 + H^+ + e^- = 0.5H_2O$

R_c (Table 2.3, O-20): $0.2CO_2 + 0.05NH_4^+ + 0.05HCO_3^- + H^+ + e^- = 0.05\ C_5H_7O_2N + 0.45H_2O$

Step 2)

$f_e = 0.10$, $f_s = 0.90$

Step 3-4)

f_eR_a: $0.225O_2 + 0.9H^+ + 0.9e^- \rightarrow 0.45H_2O$

f_sR_c: $0.02CO_2 + 0.005NH_4^+ + 0.005HCO_3^- + 0.1H^+ + 0.1\ e^- \rightarrow 0.005\ C_5H_7O_2N + 0.045H_2O$

$-R_d$: $0.125NH_4^+ + 0.375H_2O \rightarrow 0.125NO_3^- + 1.25H^+ + e^-$

R: $0.13NH_4^+ + 0.225O_2 + 0.02CO_2 + 0.005HCO3- \rightarrow 0.005C_5H_7O_2N + 0.125NO_3^- + 0.25H^+ + 0.12H_2O$

Textbook example: methanogenesis from wastewater [Ex 2-5]

Wastewater empirical formula given in the example: $C_8H_{17}O_3N$

R_d from [Table 2.3], O-19:

$d = 4 \times 8 + 17 - 2 \times 3 - 3 \times 1 = 40$

R_d: $(1/40)NH_4^+ + (1/40)HCO_3^- + (7/40)CO_2 + H^+ + e^- \rightarrow (1/40)\ C_8H_{17}O_3N + (7/20)H_2O$

R_a from [Table 2.4], O-12

- For methanogenesis, e- donor produces CO2, and CO2 is also acts as an e-acceptor. CO2 is converted to CH4, getting 8 e- eq/mol. This is an energy-consuming process. Why does it happen? – No good electron acceptor (cf: O_2 to H_2O or CO_2: energy producing while accepting electrons)

R_c from Table 2.3, O-20

$f_e = 0.92$, $f_s = 0.08$

f_eR_a: $0.115CO_2 + 0.92H^+ + 0.92e^- \rightarrow 0.115CH_4 + 0.23H_2O$

f_sR_c: $0.0116CO_2 + 0.004NH_4^+ + 0.004HCO_3^- + 0.08H^+ + 0.08e^- \rightarrow 0.004C_5H_7O_2N + 0.036H_2O$

$-R_d$: $0.025\ C_8H_{17}O_3N + 0.35H_2O \rightarrow 0.025NH_4^+ + 0.025HCO_3^- + 0.175CO_2 + H^+ + e^-$

R: $0.025\ C_8H_{17}O_3N + 0.084H_2O \rightarrow 0.004C_5H_7O_2N + 0.115CH_4 + 0.044CO_2 + 0.021NH_4^+ + 0.021HCO_3^-$

Percent methane in the produced gas = 0.115/(0.115+0.044) = 72%

Simple fermentation

Ex) Glucose fermentation to ethanol

First, let's think about energy production (R_e)

Electron donor half reaction (R_d – [Table 2.3] O-7):

$(1/24)C_6H_{12}O_6 + (1/4)H_2O \rightarrow (1/4)CO_2 + H^+ + e^-$

Taking reduction of CO_2 to ethanol for electron acceptor half reaction (R_a – [Table 2.3] O-5):

$(1/6)CO_2 + H^+ + e^- \rightarrow (1/12)CH_3CH_2OH + (1/4)H_2O$

$R_e = R_a - R_d = (1/24)C_6H_{12}O_6 \rightarrow (1/12)CH_3CH_2OH + (1/12)CO_2$

- Note: The reaction actually does not happen in the two steps, but with a complex pathway to partition electrons in glucose to ethanol and CO_2. But with this calculation, we obtain a reaction that will end up with the same reactants and products as the actual fermentation. You can also calculate how much energy is produced by this reaction.

Now, for an overall bacterial growth equation with $f_s = 0.22$,
f_aR_a: $0.13CO_2 + 0.78H^+ + 0.78e^- \rightarrow 0.065CH_3CH_2OH + 0.195H_2O$
f_sR_c: $0.044CO_2 + 0.011NH_4^+ + 0.011HCO_3^- + 0.22H^+ + 0.22e^- \rightarrow 0.011C_5H_7O_2N + 0.099H_2O$
$-R_d$: $0.0417C_6H_{12}O_6 + 0.25H_2O \rightarrow 0.25CO_2 + H^+ + e^-$
R: $0.0417C_6H_{12}O_6 + 0.011NH_4^+ + 0.011HCO_3^- \rightarrow 0.011C_5H_7O_2N + 0.065CH_3CH_2OH + 0.076CO_2 + 0.044H_2O$