

2.2 EVALUATION OF PARAMETERS USING CHEMICAL ENERGY

In this section, we will attempt to relate the parameters used to quantify the concentration of organic material (COD, BOD and TOC) to the chemical energy contained in the material. To do so, it will be necessary to introduce a basic thermodynamic concept. Free energy is defined as the amount of useful energy released during a chemical reaction, for example during oxidation of organic material. Values of the free energy release of many compounds can be found in thermodynamic tables. In Table 2.4 it is shown that the values of the released free energy, expressed as $\text{kJ}\cdot\text{mol}^{-1}$, vary enormously for different chemical compounds. However, when the released free energy per unit mass of theoretical COD is calculated, the value is more or less constant for the different compounds. The only substantially different values are those for the first two from the list: oxalic acid ($21.6 \text{ kJ}\cdot\text{g}^{-1}$ COD) and formic acid ($18.0 \text{ kJ}\cdot\text{g}^{-1}$ COD). If these two compounds are excluded, an average value of 13.7 kJ is calculated for all other compounds and none of the individual values deviates more than 10 percent from this average value.

Table 2.4 Free energy release / electron transfer upon oxidation of selected compounds

Component	I	II	III	IV	V
	($\text{kJ}\cdot\text{mol}^{-1}$)	($\text{kJ}\cdot\text{g}^{-1}$ COD _t)	($\text{kJ}\cdot\text{g}^{-1}$ TOC _t)	(N _{eq})	(N _{el})
Oxalic acid	344.4	21.55	14.45	2	1
Formic acid	285.6	18.02	23.98	2	2
Citric acid	722.4	15.04	30.07	6	3
Glucose	2881.2	14.99	40.03	24	4
Lactic acid	1369.2	14.24	38.01	12	4
Acetic acid	869.4	13.57	36.20	8	4
Glycerine	1625.4	14.49	39.44	14	$4\frac{2}{3}$
Phenol	3036.6	13.52	42.04	28	$4\frac{2}{3}$
Ethyl. glycol	1180.2	14.74	49.10	10	5
Benzene	3196.2	13.31	44.31	30	5
Acetone	1722	13.44	51.16	16	$5\frac{1}{3}$
Palmitic acid	9819.6	13.36	51.16	92	$5\frac{3}{4}$
Cyclohexane	3784.2	13.10	52.42	36	6
Ethylene	1318.8	13.73	54.94	12	6
Ethanol	1310.4	13.65	54.60	12	6
Methanol	693	14.45	57.79	6	6
Ethane	1444.8	12.89	60.19	14	7
Methane	802.2	12.52	65.44	8	8

Headings: I = free energy content; II = energy content per g COD; III = energy content per g TOC,
IV = number of electron equivalents per mol compound and V = number of electrons transferred per C-atom.

The large differences for oxalic and formic acid can be explained by taking into account the oxidation state of these compounds, which is reflected by the number of electrons transferred per carbon atom during the oxidation process. In Eq. (2.1a) the number of electron equivalents transferred during the oxidation of 1 mol of $C_xH_yO_z$ (N_{eq}) is given by:

$$N_{eq} = 4x + y - 2z \quad (2.7)$$

As 1 mol of $C_xH_yO_z$ contains x moles of carbon, it can be calculated that the number of electron equivalents per mol C or the number of electrons per carbon atom N_{el} is equal to:

$$N_{el} = (4x + y - 2z)/x \quad (2.8)$$

The values of N_{eq} and N_{el} are presented in Table 2.4 as well. Fig. 2.2 is a graphical representation of the released free energy of the organic compounds in Table 2.4 as a function of the number of electrons released per C-atom.

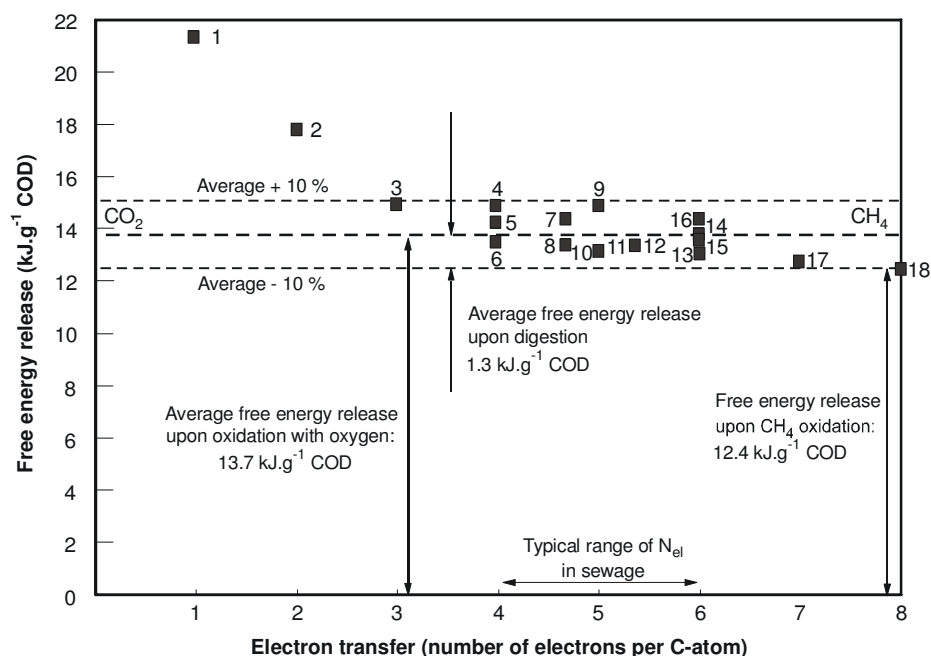


Figure 2.2 Value of the released free energy as a function of the number of transferred electrons per C-atom (the numbers in Fig 2.2 correspond to the compounds listed in Table 2.4)

There is a tendency for the free energy release to decrease as the number of transferred electrons increases, but for numbers above $N_{el} = 3$ electrons per C-atom, this tendency is not very significant and an approximately constant value of $13.7 \text{ kJ.g}^{-1} \text{ COD}$ is maintained. The exceptions to the rule are oxalic and formic acid, with N_{el} values of 1 and 2 respectively. The overwhelming majority of the compounds in waste waters have N_{el} values in the range of 4 electrons per C-atom (carbohydrates, proteins) to 6 electrons per C-atom (lipids). Hence it can be justified to assume that for organic material in waste waters the free energy content will be $13.7 \text{ kJ.g}^{-1} \text{ COD} \pm 10\%$.

The compounds in Table 2.4 and Fig. 2.2 represent the entire spectrum from the most reduced organic material (methane, $N_{e|} = 8$ electrons per C atom) to the most oxidised organic material (oxalic acid, $N_{e|} = 1$ electron per C atom). Purposely, the compounds were chosen for their very different nature: the series has saturated aliphatics (alkanes, alcohols, aldehydes, fatty acids) and unsaturated aliphatics (alkenes), aromatic compounds and a carbohydrate. The objective of such a diverse selection is to show that the released free energy per unit mass of oxidised COD is practically constant. Based on this data it can be concluded that the COD is a good parameter to estimate the chemical energy present in organic material.