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## **Entropy and Energy: Toward a Definition of Physical Sustainability**

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### **Abstract**

Sustainable development is a growing concern expressed by many businesses, organizations and individuals. Yet, no workable quantifiable definition of sustainability is available for evaluation of specific projects or operations. This paper attempts to set a framework for such a definition in terms of the first and second law of thermodynamics. Specifically, the proposed description of sustainability relates the fundamental processes of chemical, physical or biological transformation, and mass transport to energy and entropy changes. Unlike previous applications of these concepts, the proposed definition is focused on the smallest unit operations and processes while allowing for aggregation into larger systems. The proposed description also explicitly considers the time horizon for sustainability. An example of sustainability analysis for a water treatment process is included.

### **Sustainability - Lack of a Definition**

Sustainability of human activities (predominantly production and consumption) is a growing concern among businesses, customers, governments, international bodies and non-governmental organizations. These concerns are often linked to energy efficiency, reduction of environmentally harmful emissions, ecosystem preservation and other "save the Earth" efforts. They are becoming a part of a "triple bottom line" for business accounting: financial, social and environmental (EBF, 2002). Despite its increasing importance, current definitions of "sustainability" are somewhat vacuous. The most commonly accepted description was provided by the World Commission on Environment and Development (1987) in the so-called "Brundtland Report". According to this report, the goal of sustainability is to "meet the needs of the present generation without compromising the ability of future generations to meet their own needs". Other descriptions are similarly phrased and often confuse sustainability with environmental protection and other lofty goals that, strictly speaking, are not required for sustainable operation.

If sustainability is to be incorporated in common business and societal activities, it must have a reasonably simple and quantitative definition, somewhat akin to financial descriptors like price or cost. If such a description is developed for each activity, similarly to a dollar tag, it could then be used to compare alternatives. It could also be aggregated to evaluate more complicated systems such as an industry sector or a national economy. The ultimate goal of so-defined sustainability definition is not to pass a judgement on which activities are "better" or "worse" but rather to provide a framework for a meaningful comparison. Not every product that is less expensive is necessarily more desirable. Similarly, not every activity that is more "sustainable" is better whatever metric is applied. In both cases, the metric itself, whether financial or sustainability, cannot be substituted for judgement but can help reaching such a judgement.

Several different approaches have been proposed as a proxy for sustainability in the past. In one type of approach, the flow of materials in any activity or a system is evaluated (Graedel and Klee, 2002; Bouman et al., 2000; Hjalmarsson et al., 1996; van der Voet et al., 1999). It is often proposed that processes that use more materials are less sustainable. However, just the mass of a product (even with the mass of the associated waste) does not provide a good measurement of sustainability. Simply speaking, just adding the mass of gravel, steel and silicon chips does not make much sense. To improve on this approach, adjustment coefficients were devised to create what some proponents call an "environmental rucksack" (Schmidt-Bleek, 1993). The major problem with the adjustment coefficients (and thus with the whole mass approach) is the arbitrary nature of the adjustments that are not transparent to the end user and often not easily available. Sometimes, the basis for adjustment is so completely subjective (e.g., based on fiscal penalties levied for unauthorized discharge of compounds to the environment - Wang and Feng, 2000) as to make them irrelevant.

Another approach to assess the sustainability is based on the energy. This approach should not be confused with energy efficiency and energy minimization. Rather, it considers that the Earth's ecosystem, taken globally with its individual or societal human activities, depends on the flow of energy. This fact was recognized a long time ago (see Cleveland, 1999 for an interesting historical review) but for many decades it did not create any concerns since the sources of energy were deemed practically inexhaustible. Only relatively recently a realization that the sources of energy (and especially fossil fuels) are finite came to a forefront of public discussion. Although many previous estimates of the extent of fossils fuel stores turned out misguided and a vigorous debate is carried out about the exact endpoint of oil, gas and coal reserves, the conclusion that they will not last forever is inescapable. Thus, life on Earth depends on the flow of energy either currently available (e.g., wind, solar, hydropower, biomass - plants and animals) or stored as fossil fuels. All the above forms are eventually derived from the energy of the Sun. The significant differences are in the rates of generation, possibility of storage, availability, and ease of utilization. Strictly speaking, another ultimate energy source, nuclear power, also relies on use of energy stored as matter in the Big Bang. Theoretically, energy available from mass conversion is practically limitless. However, only few isotopes may be used for nuclear power generation. Since a substantial energy input is needed for their extraction, further enrichment, processing and disposal, this type of energy is also subject to a sustainability analysis.

Thus, from this perspective, a better definition of sustainability could be based on the concept of energy debt incurred against energy stocks stored earlier. In this approach, the changes of energy stock formation and depreciation are directly accounted for, and the time required for the debt repayment (if any) is explicitly specified. For example, windpower is essentially instantly replaced (if the wind continues to blow). Water discharged from a reservoir to generate electricity may be replaced in the next hydrologic year. But if a growing tree is chopped down and used for fuel, the time for its replacement is typically measured in years or decades. Oil, natural gas and coal, on the other hand, were created on a geological time scale and, for all practical purposes, are irreplaceable. Thus, the energy debt due from using a tree as an energy source may be repaid within one human generation while burned oil or coal will remain as a debt.

Fundamentally, energy consumption is a misnomer since the first law of thermodynamics asserts that energy is neither lost nor gained. What is commonly understood under the term of "energy consumption" is utilization of "high quality" energy. This idea was quantified through the concept of exergy proposed by several authors and formalized by Szargut et al. in 1988. Exergy (sometimes called essergy) is defined as "useful energy" that can be applied to a process to perform work. For purely chemical systems it is equal to the Gibbs free energy. Formally, exergy is characterized as an excess of energy (in different forms) above an accepted reference level or "a departure of the state of the system from that of the environment" (Moran, 1999). Exergy has been extensively used in the analysis of thermal processes such as heating, combustion, engines, electric power generation. In this context, exergy  $Ex$  can be expressed as (Ahern, 1980):

$$Ex = (H - H_0) - T_0 (S - S_0) + p_0 (V - V_0)$$

where  $H$ ,  $S$ ,  $p$  and  $V$  are enthalpy, entropy, pressure and volume, respectively; the subscript 0 denotes the reference level (i.e., the environment). The usual definition of exergy can be extended to include chemical potential or other forms of energy (Szargut et al., 1988; Ayres, 1998) but in its practical applications to thermal processes these forms have been often excluded.

Exergy was applied in industrial ecology (Ayres, 1978; Ayres and Ayres, 1998; Ayres et al., 1998; Dewulf and Van Langenhove, 2002) as a measure of sustainability. This application recognizes that in every process, energy is transformed and part of it is degraded with respect to its ability to perform useful work. However, applications of exergy generally do not consider dilution or concentration of material flows during production or consumption. For example, when natural gas is burned in a turbine that drives an electric power generator, the chemical energy contained in gas molecules is partially transformed into electrical energy and the rest remains as thermal and potential energy of the exhaust gas. This residual energy, which depends on the exhaust gas pressure and temperature can be further utilized, for example to heat water. When the exhaust gas reaches the pressure and the temperature of the environment, no more useful work can be extracted without further expenditure of energy. Exergy does not account for dilution of carbon from its high concentration in natural gas to its low concentration in atmospheric carbon dioxide.

Exergy can be a useful characteristic of the "quality" of an energy source and its potential for exploitation. Typically, in the history of human development, energy sources of higher "quality" (generally of higher exergy) were utilized first (e.g., higher quality fuel sources were used and depleted before lower quality was used). Of course, this general rule was, and is, the subject of social, political and technological constraints (such as territorial control of the resource or availability of technical methods for extraction). In this sense, wood was used first before coal since coal mining required substantial technological improvements (excavation and drainage). However, where there was a choice, richer coal deposits were mined and depleted before moving to poorer sites.

While the material balance or the energetic approaches to quantification of human activities have been promoted as indices of "sustainability," neither of them is theoretically sound nor easy to use. Each considers only one side of the issue and does not allow for evaluation of alternatives where

higher energy use could be offset by lower consumption of materials and vice versa. Moreover, a simple material balance does not account for differences in the ways the materials are used and transformed in a production and consumption process. For example, the material balance approach will not differentiate between one process that produces mixed and diluted by-products (waste) and another that generates separate and concentrated streams of the same by-products. Yet in the second case, any further by-product utilization or re-use is much easier than in the first case. Even if these by-products or wastes are not currently reused, their containment and mitigation of potential environmental impacts are also easier.

## **Fundamental Analysis**

The goal of this study is to develop a workable, quantifiable definition of physical sustainability. To achieve this objective, we focus on simple systems commonly called unit operation and processes (UOP) by chemical engineers. Such operations and process can usually be well defined and their performance measured and controlled. Thus, they provide an advantage for quantification of any sustainability description. They can also be aggregated up to a desired scale level allowing for a meaningful comparisons of larger project alternatives.

On a basic level, each UOP can be characterized by transport of mass and transformation of input components. These two features can be characterized by energy flux and the changes of entropy. The concept of energy flux is simple. It is the sum of all energy inputs or outputs (mechanical, chemical, electrical, thermal, etc.) although practical accounting may sometimes pose problems. If the "quality of energy" is considered, exergy described in the previous section may be used. For some systems, energy flux may be sufficient for a complete description without considering the entropy. For example, water pumping can be described (with some idealization) only in energy (or exergy) terms. Electrical energy supplied to the pump motor is converted into mechanical energy of the pump impeller and eventually conveyed to water. As water is moved to a higher elevation or acquires higher pressure this energy is stored as potential energy. In real applications, some of the supplied energy is not conveyed to water but dissipates as heat due to friction or electrical resistance. Thus, a careful setting of system boundaries is important. Considering only a pump will yield different energy fluxes compared with a system consisting of a pump with an electrical motor and a variable frequency converter.

In other UOP, the flux of energy may be insignificant and the system is better characterized by entropy changes. For example, mixing by diffusion of two non-reacting components (with the same temperature and density) may not involve energy fluxes but the endproduct will have considerably different entropy. Although the notion of entropy dates back to the advances of thermodynamics in the 19th century, it has only recently come of use in the ecological area (e.g., Singh and Fiorentino, 1992; Rechberger and Brunner, 2002; Huesemann, 2001, 2003). Entropy can be defined in the thermodynamical terms following the seminal work of Rudolf Clausius in the 19th century. It does not require that the current "standard" environment (or any arbitrary standard) be assumed as a reference level. From a theoretical point of view, dispensing with an assumed reference state has an advantage because it does not predicate that the present state of the environment is somehow

preferred or desirable. Another definition of entropy follows the Boltzmann's approach rooted in the statistical mechanics where it is related to the probability distribution of the micro-states of a system. If all  $W$  micro-states are equally probable, entropy  $S$  is given as

$$S = k_B \ln W$$

where  $k_B$  is the Boltzmann constant. In this form, the definition of entropy is mathematically identical with that proposed by Shannon in 1949 in the context of the information theory. The only mathematical difference is that, following Shannon's approach,  $k_B = \ln 2$  to give entropy units in bits.

Such diverse and yet ultimately equivalent formulations of entropy make it especially appealing for a sustainability analysis since it allows, in principle, to account for various forms of energy (thermal, potential, kinetic) and for transformation of materials (and their dilution or concentration). Therefore, entropy can be used to characterize the changes of both the energy and the matter. In many cases, ecological problems may be related to an entropy increase, for example as a result of transformation of "high quality" energy in fossil fuels to dispersed heat. Many processes generate wastes and yield diluted streams of increased entropy. Such diluted materials can be reconcentrated (and the associated entropy decreased) through the expenditure of energy.

While changes of input components can be analyzed easier at a level of UOP (see Rechberger and Brunner, 2002 for applications to waste incineration), it can also be conceptually applied to bigger problems of global changes and resource management. For example, mitigation of a current increase of atmospheric carbon dioxide concentrations was proposed either by liquefying  $\text{CO}_2$  and storing at the ocean floor or by sequestration in geological formations. In both cases, the diluted  $\text{CO}_2$  would be concentrated (thus decreasing its entropy) but at a price of energy utilization. Another example may involve production of copper. This metal can be smelted from the native ore moving elementary copper from the dispersed state (high entropy) to the concentrated metallic form (low entropy). The metallic form could be also harvested from communication cables made obsolete by optical fiber. Locally, i.e., in the cable, copper is in a highly concentrated form but geographically possibly quite dispersed leading to quite different entropy estimates. Energy fluxes will also be significantly different for smelting and cable scavenging. This hypothetical example emphasizes both the possible usefulness of entropy-energy definition of sustainability as well as the need for careful a setup of space and time boundaries.

As suggested by the examples above, both entropy and energy should be included in the desired definition of sustainability. Since the Earth's ecosystem is maintained by the flow of energy, it seems that by analogy the rate of entropy change combined with the energy flux may be a reasonable measure of sustainability. In general, changes of entropy resulting from transformation, concentration or dilution of individual constituents can be calculated using a common thermodynamical approach. These changes can be positive indicating an entropy increase (e.g., as a result of dilution) or negative (e.g., resulting from segregation of a mixed stream into its components). From a sustainability viewpoint, the processes that increase entropy are less sustainable. Although a complete reversal of entropy increases is not possible (Huesemann, 2003), lowering the rate of its increase is desirable. In some cases, a local entropy decrease can be also achieved.

Entropy changes must be compared with the associated energy fluxes. Unlike entropy, the quantity of energy remains unchanged but its forms may (and do) undergo transformations. We propose to use in the sustainability assessment only this part of the total energy flux that changes form in association with the changes of entropy. For example, water flowing through a treatment plant contains (large) thermal energy. This energy would be not counted in our proposed analysis unless water temperature changes significantly. Similarly, only that portion of the potential energy of water pressure that is used to overcome headloss would be used in the assessment. The comparison of entropy changes with energy fluxes can be facilitated by a combined criterion  $\Omega$

$$\Omega = \Delta E + T \cdot \Delta S \quad (1)$$

where  $\Delta S$  is change of entropy,  $\Delta E$  - associated energy flux, and  $T$  - absolute temperature. Processes that result in large positive entropy changes  $\Delta S \gg 0$  or use large amounts of energy  $\Delta E \gg 0$  are deemed less sustainable (perhaps unsustainable) and are characterized by  $\Omega \gg 0$ . Highly positive values of  $\Delta S$  indicate unsustainable processes as they “degrade” the quality of materials (e.g., by significant dilution or dispersion). Conversely, processes with smaller values of  $\Omega$  (ideally  $\Omega \ll 0$ ) are more sustainable.

One of the novel elements in the proposed approach is the scale of application. Previous quantitative analyses of sustainability (whether by entropy or exergy) were applied to whole industrial sectors or large geographic areas. Thus, they were not directly useful for individual producers and consumers as tools and guidelines in their activities. The approach described in this work focuses on smaller scales of individual unit processes and operations and on evaluation of energy and material inputs and outputs at that level. Further advancement of this approach will develop a framework for aggregation of results and evaluation of larger systems. This methodology is similar to cost estimating in manufacturing where unit costs of each part are brought together to yield the total cost of the finished product.

### **Application Example**

A simplified example of this analysis is presented for two processes used for water treatment: membrane filtration and conventional coagulation-flocculation. It is assumed that both processes can produce treated water with the same quality. For the sake of simplicity, in this example only one water quality parameter, concentration of dissolved organics, is considered. At this stage of the methodological development, the following example makes use of several, clearly identified assumptions that may or may not be applicable in a specific application. First, it is assumed that all processes occur at an ambient pressure of 100 kPa (1 bar) and temperature of 298 K. These values represent standard thermodynamic conditions but all calculations can be adjusted to other conditions. For the purpose of this example, a water volume  $V$  of 1 L is treated by each process. Pertinent operating conditions as shown in Fig. 1. For each process, the values of energy and entropy change are calculated as shown in the following sections.

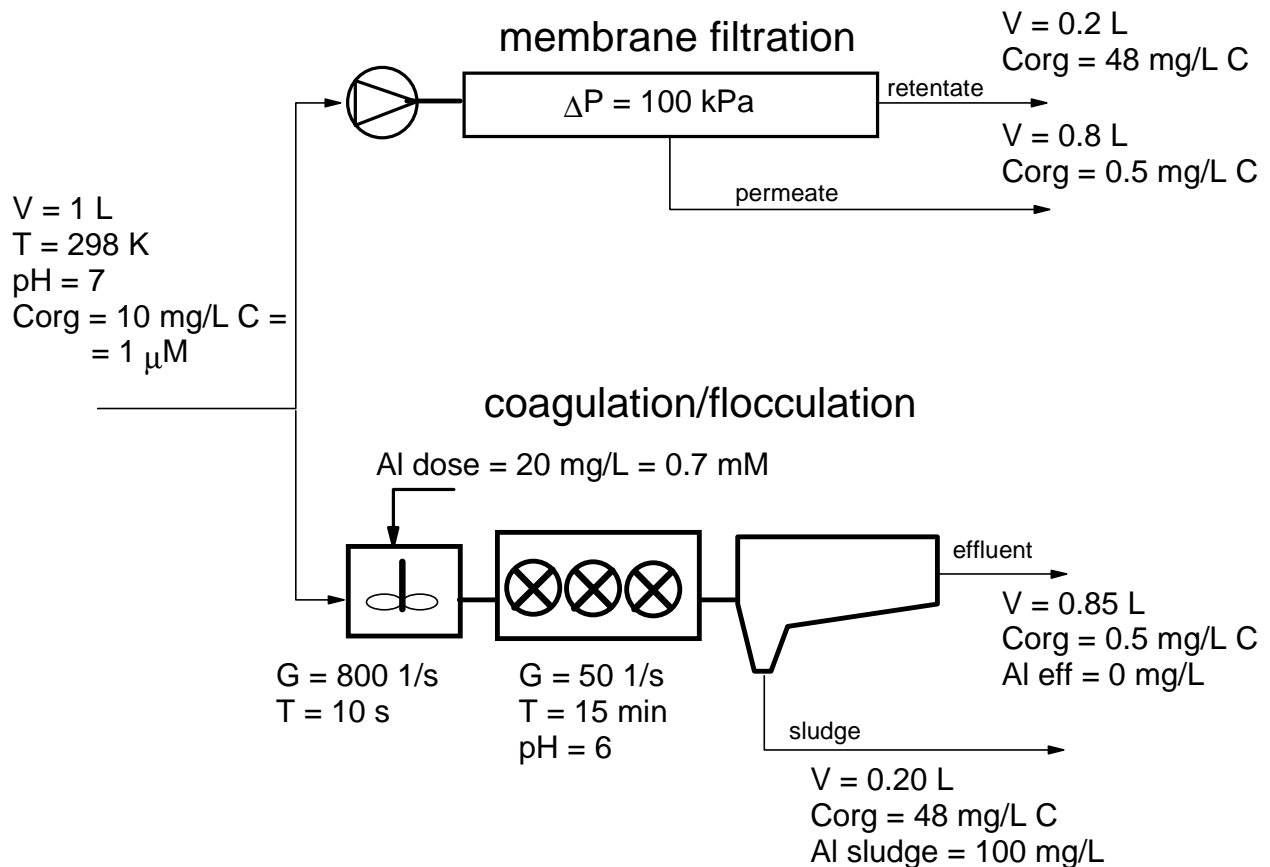


Figure 1 Process Conditions for Two Treatment Schemes

### Membrane Filtration

In this simple example, the energy  $\Delta E_{MF}$  is characterized solely by transmembrane pressure  $\Delta P$  assumed 100 kPa. Thus,

$$\Delta E_{MF} = V \Delta P = 1 \text{ L} \cdot 100 \text{ kPa} = 100 \text{ J} \quad (2)$$

In more realistic calculations, other energy changes need to be accounted for. They may include energy changes associated with less than 100% efficiency of an electrical motor and pump, dissipation of the kinetic energy of the water, etc.

Since generic organics are the only component of water considered in this example, the change of entropy is only associated with separation of organics present in the influent at  $C_{MF \text{ in}} = 10 \text{ mg/L}$  into two streams: a more diluted permeate ( $C_{MF \text{ perm}}$  assumed at 0.5 mg/L) and the more concentrated retentate. It is also assumed that 80% of water ends up in the permeate stream, thus

$$C_{MF \text{ ret}} = \frac{C_{MF \text{ in}} - 0.8 C_{MF \text{ perm}}}{1 - 0.8} = 48 \text{ mg/L} \quad (3)$$



We assume that no chemical transformation of organics occur and the change of entropy  $\Delta S$  is purely due to changes of concentrations. Such change of entropy **per mole** of compound is

$$\Delta S = -R \ln\left(\frac{C_{final}}{C_{initial}}\right) \quad (4)$$

where  $R$  is the universal gas constant. Accounting for the amount of organics in each of the effluents (permeate and retentate), the change of entropy associated with processing of  $V = 1$  L of water is

$$\Delta S_{MF} = -R \left[ 0.8 V C_{MF perm} \ln\left(\frac{C_{MF perm}}{C_{MF in}}\right) + (1 - 0.8) V C_{MF ret} \ln\left(\frac{C_{MF ret}}{C_{MF in}}\right) \right] \quad (5)$$

Substituting the appropriate values, we obtain  $\Delta S_{MF} = -1.15 \cdot 10^{-5}$  J/K. The first term in this formula expresses entropy changes due to “dilution” of organics in the permeate. It is positive and equal to  $9.96 \cdot 10^{-7}$  J/K. The second term describes concentrating the organics in the retentate. It is negative at  $-1.25 \cdot 10^{-5}$  J/K and dominates the overall entropy change. As expected, the overall entropy change is negative and presumably makes the process physically sustainable but at an expense of energy flux.

The calculated values of  $\Delta E_{MF}$  (expressed in J) and  $\Delta S_{MF}$  (in J/K) can be compared by forming a parameter  $\Omega$  defined in Eq. 1. In our microfiltration example is  $\Omega = +99.997$  J (three decimals are shown to indicate the effects of entropy). As stated in the previous section, values of  $\Omega < 0$  characterize sustainable processes that use small amounts of energy while  $\Omega > 0$  shows large energy use.

### ***Coagulation-Flocculation***

While membrane filtration is predominantly a physical process, physical and chemical processes interact in the conventional coagulation-flocculation. They both contribute to energy and entropy changes. At the rapid-mix stage, a coagulant is added and mixed with the treated water. We assume that only  $\text{Al}_2(\text{SO}_4)_3$  is used according to the following reaction



or expressed per one mole of Al



In this reaction, all soluble Al species are neglected. It is also assumed that solid aluminum sulfate is added although in practice the solid would be dissolved before its addition to the rapid-mix tank. The flocs are formed in the slow-mix tank and eventually settled in the sedimentation tank. The overall process is very complicated and many parts of it are still not fully understood. In our analysis, we focus on major aspects for which we analyze energy and entropy changes.

Energy is used to mix water with the coagulant in the rapid-mix tank and to assist flocculation in the slow-mix chamber. Figure 1 list the assumed values of the velocity gradient  $G$  in each tank and the corresponding detention times. The velocity gradient is related to power input  $P$ , tank volume  $V$  and dynamic water viscosity  $\mu$

$$G = \sqrt{\frac{P}{V \mu}} \quad (6)$$

In our calculations, we maintain  $V = 1$  L and using the values from Figure 1 calculate the amount of energy for rapid mix

$$E_{rapid} = G^2 \mu V T_{rapid} = 6.4 J \quad (7)$$

and for slow mixing

$$E_{slow} = G^2 \mu V T_{slow} = 2.3 J \quad (8)$$

The total energy imparted by mixing  $E_{mix}$  is 8.7 J.

An additional amount of energy is associated with settling of sludge in the sedimentation tank. In this process, solid particles fall to the bottom of the sedimentation tank losing their potential energy. If sludge has to be pumped back to the water level, this energy has to be supplied back to the system. To calculate this value, we assume that the volume of sludge after settling is equal to 20% of the volume of treated water, i.e., treatment of 1 L of raw water produces 200 mL of sludge containing removed organics and all of the coagulant. The actual volume of sludge generated and removed from the system at the bottom of the sedimentation tank will vary depending of the settling characteristics of flocs. The energy change involved in settling depends on the actual configuration of the outlet and bottom sludge withdrawal. For example, if 20% of water flow is discharged as sludge at the bottom of the sedimentation tank, the change of potential energy will correspond to the sedimentation tank height. However, if sludge flows under hydrostatic pressure and is discharged at a level above the sedimentation tank bottom, the corresponding energy change will be smaller.

Even in this simplified example, careful and precise definition of system boundaries, both in terms of geometry and energy is very important. For our calculations, we assume that the energy change associated with solids settling corresponds to the movement of the solids mass from the center of the sedimentation tank to the center of a sludge blanket (Figure 2). The mass of solids is virtually equal to the mass of  $Al(OH)_3$  formed as a main component of flocs and the energy change is equal to the change of its potential energy

$$E_{separ} = C_{AlOH3} V g \left( \frac{H_{sed}}{2} - \frac{H_{sludge}}{2} \right) \quad (9)$$

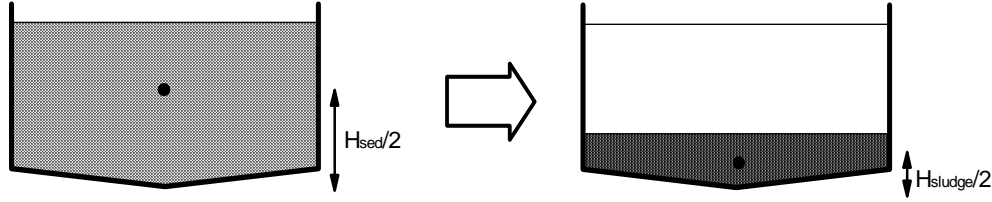


Figure 2 Schematics of Sludge Sedimentation

Using the values from Fig. 1,  $H_{sed} = 3.66$  m (12 ft) and  $H_{sludge} = 0.73$  m (2.4 ft) the separation energy  $E_{separ} = 4.9 \cdot 10^{-4}$  J. This energy is much smaller than other energetic constituents and it was included in our analysis for demonstration of a principle.

A bigger amount of energy is associated with the withdrawal of water in the sludge at the bottom of the sedimentation tank. The fraction of water flow withdrawn with the sludge has been previously assumed at 20%; thus for each liter of water entering the sedimentation tank, 200 mL exits through the bottom. This withdrawal contributes to the loss of potential energy  $E_{sed}$

$$E_{sed} = 0.2V\rho g H_{sed} \quad (10)$$

In our calculations,  $E_{sed} = 7.2$  J (assuming water density  $\rho = 1000$  kg/m<sup>3</sup>)

The final component of energy calculations is due to hydraulic headlosses of water flowing through the tanks. These headlosses occur mostly at the transition from one tank to another. Assuming a typical value of  $\Delta H_{local} = 20$  cm, the total energy change for two transitions (rapid-mix to slow-mix and slow-mix to sedimentation tank) is

$$E_{local} = 2V\rho g \Delta H_{local} \quad (11)$$

The value of  $E_{local}$  is 3.9 J. The total amount of energy is equal to the sum of the above components and is  $E_{CFtotal} = 19.8$  J, much less than the energy associated with the membrane filtration example.

Two types of processes contribute to entropy changes: chemical transformations and physical diluting or concentrating. Similarly to membrane filtration, organic matter is present in the incoming water stream at concentration  $C_{CFin} = 10$  mg/L as C. The organics are separated; the concentration in the effluent (treated water) is  $C_{CFout} = 0.5$  mg/L and the remaining organics are incorporated into the sludge. If chemical transformations of organics are not considered, the change of entropy due to separation of organics can be calculated the same way as in Eqs. (2) and (4). Since the volume of treated water is 80% of the incoming water (set on purpose at the same value as for the membrane process), organics concentration in the sludge withdrawn at the bottom of the sedimentation tank is

$C_{CF\ sludge} = 48\ \text{mg/L}$ . The change of entropy due to organics separation is also the same as in the membrane system  $\Delta S_{CF\ separ} = -1.15 \cdot 10^{-5}\ \text{J/K}$ .

During coagulation, aluminum sulfate is converted to  $\text{Al(OH)}_3$  solid and dissolved ionic species. Entropy change can be calculated by subtracting the entropy of the reactants from the entropy of the products. At standard thermodynamic conditions, entropy of the chemical species involved has the values shown in the third column of Table 1 (Lattimer, 1952; Daubert, 1989-1992)

**Table 1. Entropies of chemical species**

Species	Concentration, mM	Standard entropy $S^0$ , J/K·mole	Actual entropy $S$ , J/K·mole
$\text{H}_2\text{O}$	-	70.05	70.05
$\text{Al}_2(\text{SO}_4)_3\ (\text{s})$	-	239	239
$\text{Al(OH)}_3\ (\text{s})$	0.74	68.4	161.2
$\text{SO}_4^{2-}$	1.11	17.17	73.7
$\text{H}^+$	$10^{-3}$	0	114.9

These standard values must be adjusted to actual concentrations (strictly speaking, activities) in the system

$$S = S^0 - R \ln\left(\frac{C_{actual}}{C_{reference}}\right) \quad (12)$$

For simplicity, the temperature of the process is assumed to be equal to the standard temperature (298 K). At the alum dose  $C_{Al\ in}$  of 20 mg/L as Al (or 0.74 mM), the resulting concentrations are listed in the second column of Table 1 and actual entropies in the last column. The system is assumed to be maintained at pH=6, yielding  $[\text{H}^+]$  of  $10^{-3}$  mM although the reactions leading to this pH are not considered for the sake of simplicity. Entropies of water and solid aluminum sulfate are not adjusted as these compounds are in their thermodynamic reference state (Lattimer, 1952).

The total change of entropy due to chemical transformation  $\Delta S_{CF\ chem}$  is obtained by adding the entropies of individual components with appropriate stoichiometric coefficients

$$\begin{aligned} \Delta S_{CF\ chem} &= V C_{Al\ in} (1.5S_{\text{SO}_4} + 3S_{\text{H}^+} + 1S_{\text{Al(OH)}_3} - 3S_{\text{H}_2\text{O}} - 0.5S_{\text{alum}}) \\ \Delta S_{CF\ chem} &= 0.21\ \text{J/K} \end{aligned} \quad (13)$$

After coagulation, water with flocs passes to a sedimentation tank, where the sludge settles and is concentrated at the bottom. This process contributes to entropy changes  $\Delta S_{thick}$  and can be calculated

based on the ratio of Al in coagulated water  $C_{Al\ in}$  and in the sludge  $C_{Al\ sludge}$ . Using the assumed volume of sludge equal to 20% of treated water

$$\Delta S_{thick} = -V C_{Al\ in} R \ln\left(\frac{C_{Al\ sludge}}{C_{Al\ in}}\right) \quad (14)$$

The resulting value of  $\Delta S_{thick}$  is  $-9.9 \cdot 10^{-3}$  J/K. The total entropy change in the coagulation-flocculation process  $\Delta S_{CF\ total}$  is equal to the sum of its individual components and  $\Delta S_{CF\ total} = \Delta S_{CF\ chem} + \Delta S_{thick} = 0.203$  J/K.

For comparison, entropy changes and energy associated with individual steps of both treatment processes are summarized in Table 2 for one liter of treated water.

**Table 2. Entropy Changes and Energy for Individual Process Elements**

Source	Energy $E$ J	Entropy $\Delta S$ J/K	$\Omega$ J
<i>Membrane Filtration</i>			
- organics separation in permeate		+ $9.96 \cdot 10^{-7}$	
- organics concentration in retentate		- $1.25 \cdot 10^{-5}$	
<b>Total</b>	100	- $1.15 \cdot 10^{-5}$	+99.997*
<i>Coagulation-Flocculation</i>			
- rapid mix: chemical transformations	6.4	+ 0.21	+69.7
- slow mix	2.3	0**	+2.3
- sedimentation: sludge thickening	$4.9 \cdot 10^{-4}$	- $9.92 \cdot 10^{-3}$	-2.96
- sedimentation: potential energy loss	7.2		+4.22***
- hydraulic energy losses	3.9		
- separation of organics		- $1.15 \cdot 10^{-5}$	
<b>Total</b>	19.7	+ 0.203	+80.1
* - three decimal places shown to indicate the contribution of $\Delta S$			
** - entropy changes due to floc formation (aggregation) neglected			
*** - combined for sludge thickening and potential energy loss			

Membrane filtration process yields a negative change of entropy due to concentrating the organics in a much smaller volume of the retentate. However, that decrease of entropy is associated with a substantial energy expenditure. In contrast, the energy expenditure for the conventional coagulation-

flocculation process is much smaller but the overall entropy change is large and positive, primarily due to conversion of concentrated coagulant dosed to the system into much less concentrated chemical sludge. Thus, thanks to its lower energy utilization, the process is less unsustainable within the conceptual framework developed in this work (although not sustainable strictly speaking). As the two examples show, rigorously defined thermodynamic functions of entropy and energy can be used for quantitative assessment of physical sustainability at the level of individual unit operations and processes. Such results can be aggregated to a desired level (e.g., process stream, plant) to compare technical alternatives. The value of  $\Omega$  may be used for comparisons, with smaller values indicating more a desirable choice.

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