Fostering a Coordinated Teaching of the Experimental Sciences: Introduce Entropy and Chemical Potential from the Beginning!

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Abstract: Using a conceptual framework based a) on a model where energy is the regulating agent and b) on the introduction of conjugated intensive and extensive quantities, together with the introduction from the beginning of the concepts of entropy and chemical potential enables a variety of situations to be coherently modeled relating to didactically interesting examples referring to different disciplines.

Keywords: Chemical potential · Education · Energy · Entropy · Equilibrium

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The Context

In this contribution, which is the result of a recognition by the Swiss Chemical Society who intended to underscore the innovative character of our didactical approach, we present an overview of the development of our work during the past two decades and its current status. The implementation in Ticino of the reform of the Swiss Ordinance on the Recognition of the Baccalaureate at the end of the 1990s and the profound reorganization of the natural science teaching at high school level led to a total revision of the biology, chemistry and physics curricula with the objectives to arrive at a good coordination of the three subjects and to justify the introduction of a single grade. It was soon clear that we were in the presence of a unique opportunity to give a new impulse to the teaching of these branches, important and formative, but often feared and neglected by the students. The focus soon turned to the problem of how to organize the coordination and in particular how to follow up the desire to provide students with tools for thinking rather than individual notions, trying to highlight the overall coherence of the disciplinary framework.

In this context, instead of seeking for coordination based on a series of point requirements for individual disciplinary aspects (a model of propaedeuticity that proved ineffective), we focused our attention on the search for central ideas and transversal concepts as cognitive organizers, a choice that later proved extremely fruitful.[1-3] The adoption of an approach based on analogies and the conviction of the need for a profound revision, even at the level of disciplinary content, were then the first results that emerged from the reflections of the various groups working on this school reform.

Additionally, we chose to keep a strongly experimental didactic approach. We were convinced that it was necessary to ensure maximum rigour on both the epistemological and linguistic level. Finally, we also aimed to find tools (graphically and computationally) to conveniently support the quantitative dimension, especially for younger students. All this then resulted in the proposal of a conceptual framework that is essentially based on two distinct elements.

The first element is the model used to introduce the energy concept, the main objective being to underline its function as a *regulative principle*: through the balance equation, energy conservation allows one to analyze quantitatively processes which

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are manifestly not directly comparable, but are clearly linked by a cause and effect relationship.

The second element characterizes the proposed approach to a number of natural phenomena: hydraulic, mechanical, electrical, thermal, chemical. Here we notice the usefulness of introducing from the beginning a couple of physical conjugate quantities: intensive and extensive. By observing and discussing a number of wisely chosen experiments it is possible to develop, with the students, models and interpretations based on the idea that (a) the intensive quantity measures a *level*, while (b) the corresponding extensive quantity allows one to establish a *balance equation*. This choice highlights analogies and differences with respect to the traditional approach. In fact, while, for example, in electricity both quantities are traditionally presented (electric potential and electric charge), when considering thermal phenomena, temperature is present but entropy is usually avoided and similarly, when considering chemistry, chemical amount is present but chemical potential is missing. Thus, the traditional approach is not only quite different, but also completely asymmetrical, thereby ruling out the possibility of building a coherent and unified picture of natural phenomena.

This unsatisfying situation led us to explore a didactical approach which, by introducing the concepts of entropy and chemical potential, would allow us to introduce a conceptual frame allowing us to overcome these disciplinary barriers.

In the following, although only briefly, we will present a possible way to introduce the concepts of entropy and chemical potential from the very beginning. Then we will describe two more conceptual elements: the balance equation and the quantification of energy flows. Finally, we will discuss three typical examples in order to illustrate the potentiality of referring to different disciplines. With these examples, additionally, we can illustrate a further conceptual instrument very useful for modeling phenomena: the process diagrams.

Entropy from the Beginning: From Entropy Production to Process Irreversibility

A few simple experimental situations (such as thermal conduction, the approach to thermal equilibrium, the working of heat pumps, the melting of ice, a burning candle) will show the necessity to introduce (in addition to the *absolute temperature T* 'measuring' the thermal level) an extensive thermal quantity, the entropy *S*, characterized by the following properties: it may be stored, may flow from one object to another, *e.g.* in the presence of a temperature difference, may be produced (*e.g.* in the pres-

ence of mechanical friction, in a combustion) but it cannot be destroyed.[4,5] As we will see in detail later, this property allows one to distinguish two kinds of processes: *reversible* (no entropy production) and *irreversible* (with entropy production).

Chemical Potential from the Beginning: From Spontaneous Chemical Reactions to Chemical Equilibrium

For the description of processes involving the transformation of substances, in addition to the usual extensive quantity, the *chemical quantity n*, it is very useful to explicitly introduce the intensive quantity describing its level, the *chemical potential μ*. Experimental observations allow one to determine its properties: it describes the tendency of a substance to react with other substances, to change its state, or to spread out in the available volume. For example, if we wish to examine a chemical reaction, given the stoichiometry of the process to examine (assuming that for the substances involved we have the information necessary to determine the variation of their chemical potential with temperature, pressure and concentration changes) we can determine the total chemical potential of the reactants {r} as well as that of the products {p}. Their difference:

$$\Delta\mu_R = \mu_{\{p\}} - \mu_{\{r\}}$$

provides simply and clearly the necessary condition for a *spontaneous* process:

$$\Delta\mu_R < 0$$

Similarly, the requirement of zero driving force, $\Delta\mu_R = 0$, characterizes the final situation reached by the system, when the process tends towards chemical equilibrium. With $\mu_{\{p\}}^{eq} = \mu_{\{r\}}^{eq}$, given the external constraints of temperature and total pressure, we may determine the compositions of the reactants at equilibrium, as well as the law of mass action and the equilibrium constant. With the temperature dependence of the equilibrium constant we can, at least qualitatively, predict the system's response to equilibrium perturbations (Le Châtelier's principle).[6,7]

The Balance Equation

A powerful instrument underlining the usefulness of our conceptual picture and of quantitative approaches is the *balance equation* relating the variations of a given quantity to the exchanges occurring between system and outside world and to production (or destruction) processes occurring within the system.[8,9] Fig. 1 shows the situation for the three extensive quantities of interest in this work: chemical quantity *n*, entropy *S* and energy *E*.
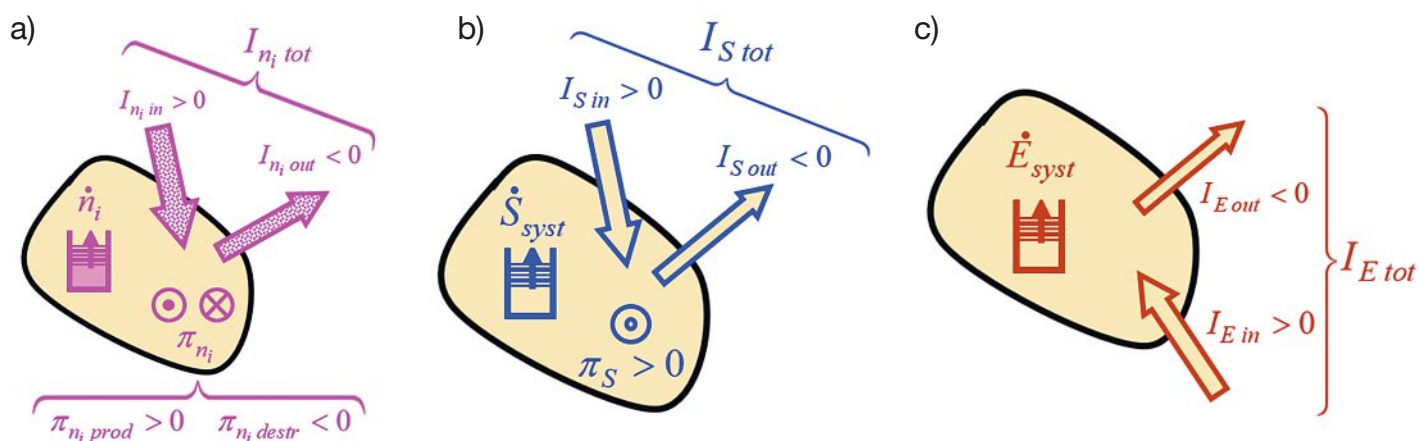

Fig. 1. Schematic representation of the elements used in process modeling: a) chemical quantity *n*; b) entropy *S*; c) energy *E*. All three cases represent a situation where the instantaneous rate of change of the quantity (represented respectively by $\dot{n}(t)$, $\dot{S}(t)$, and $\dot{E}(t)$) is positive. Exchanges between the system and the environment are represented by arrows: the intensities *I*(*t*) are taken positive for incoming flows, negative for outgoing flows. The width of the arrows increases with increasing flow magnitude. $\pi(t)$ is the internal production rate (positive) or destruction rate (negative) of the quantity.

Formally, we are dealing with the following equations (for more details see, for example, Ch. 4 in ref. [8] and Ch. 3 in ref. [9]):

– the balance equation for the *chemical amount* connects the rate of change $\dot{n}(t)$ with the production/destruction rate $\pi_{n\,tot}(t)$ (which takes negative values when the species under consideration is a reactant, positive if it is a product) and with the total strength of exchanges between the system and its environment $I_{n\,tot}(t)$ (accounted positive when incoming and negative when outgoing):

$$\dot{n}(t) = I_{n\,tot}(t) + \pi_{n\,tot}(t) \qquad (1)$$

– the balance equation for *entropy* has the same basic structure with the important difference that the rate of internal production, because of the second principle of thermodynamics, it *can never be negative*. It is zero for *reversible* and positive for *irreversible* processes:

$$\dot{S}_{syst}(t) = I_{S\,tot}(t) + \pi_S(t) \quad \text{with} \quad \pi_S(t) \geq 0 \qquad (2)$$

– since *energy* is a *conserved quantity*, production or destruction terms *never* appear in the balance equation. Therefore, any change in internal energy of the system under consideration must necessarily be linked to exchanges with the environment:

$$\dot{E}_{syst}(t) = I_{E\,tot}(t) \qquad (3)$$

Energy Flows, Released and Uploaded Power and Second Law Efficiency

The connection between energy and extensive quantities is established by considering the fact that all energy exchanges between a system and its surroundings are accompanied by the exchange of at least one other extensive quantity (which may therefore be called energy carriers). For example, for *thermal exchanges* due to conduction, we have (see ref. [8] Ch. 4, or ref. [10] p. 318):

$$I_{E\,therm}(t) = T(t)I_S(t) \qquad (4)$$

where T is the absolute temperature (the 'thermal level') of the entry (or exit) 'point' of the entropy into (or out of) the system at the considered time. For a *convective exchange* of a given chemical substance i we have:

$$I_{E\,chem}(t) = \mu_i(t)\,I_{n_i}(t) \qquad (5)$$

where μ_i represents the chemical potential at which the chemical species under consideration is *exchanged* (*i.e.* enters or leaves the system at the time under consideration).

Aiming to develop a quantitative description valid in the presence of dissipative processes too, we introduce the following three concepts:

– *released power* $\mathcal{P}_{rel}^{\nearrow}$: this allows to account for the fact that not necessarily all the energy that enters the system is of itself useful: the amount is often limited by some law of nature. This is, for example, the situation for thermal engines, for which the impossibility of destroying entropy means that – at steady state – in addition to the incoming flow of entropy there must also be an outgoing flow that takes with it part of the energy that had entered the engine. The value of the rate at which energy is released can then be expressed as the difference between incoming and outgoing energy flows: in the example of the heat engine, we will therefore have

$$\mathcal{P}_{therm}^{\nearrow} = I_{E\,therm\,in} - \left| I_{E\,therm\,out} \right|$$

or in the case of a chemical reactor:

$$\mathcal{P}_{chem}^{\nearrow} = I_{E\,chem\,in} - \left| I_{E\,chem\,out} \right|$$

– *uploaded power* $\mathcal{P}_{up}^{\nwarrow}$ to obtain the rate at which energy is actually made available by the process under consideration, it must be taken into account that not all of the energy released can be uploaded to the desired energy carrier, since any process is generally non-ideal, *i.e.* accompanied by dissipative effects (entropy production). Notice that in order to deal with positive values – which makes things much easier for students – the arrow in the symbol is reversed: obviously $\mathcal{P}_{up}^{\nwarrow} = -\mathcal{P}_{up}^{\nearrow}$.

– *second law efficiency ε*: finally, we define the *second law efficiency* ε of a process as the ratio of uploaded to released power:

$$\varepsilon = \frac{\mathcal{P}_{up}^{\nwarrow}}{\mathcal{P}_{rel}^{\nearrow}}$$

This value tells us how close the concrete realisation of the process comes to the ideal case ($\varepsilon = 1$) and in general it is related to the technological level used to carry out the process.

We would like to briefly illustrate these ideas with three concrete examples.

Example 1: Thermal Engines: First and Second Law Efficiency – Process Diagrams

Eqn. (4) tells us that, in the case of conductive heat exchanges, a given entropy flow is associated with an energy flow whose value depends on the temperature at which it occurs. Consider the example of an *ideal* thermal engine (for instance a reversible Carnot engine, without entropy production) working in a stationary state between two reservoirs at temperatures T_h and T_c. Then the entropy balance equation tells us that the magnitudes of the incoming and outgoing flows are equal: $\left| I_{S\,out} \right| = I_{S\,in} = I_S$. This implies that in addition to the incoming thermal energy flow $I_{E\,therm\,in} = T_h I_S$, there is *necessarily* also an outgoing thermal energy flow $I_{E\,therm\,out} = T_c I_S$: this directly *explains* the reason why (taking up the Kelvin-Planck's formulation of the *second principle* of thermodynamics) it is impossible to carry out a process whose only result is the transformation of heat taken from a uniform source into work. It is then straightforward to find out the efficiency of such an engine by noticing that energy conservation implies that the useful mechanical energy is:

$$I_{E\,mech} = I_{E\,therm\,in} - \left| I_{E\,therm\,out} \right| = I_S T_h - I_S T_c \qquad (6)$$

By defining as usual the *first law efficiency* η of the engine with the ratio of the mechanical energy made available to the thermal energy furnished to the engine, we get:

$$\eta = \frac{\left| I_{E\,mech} \right|}{I_{E\,therm\,in}} = \frac{I_S\,T_h - I_S\,T_c}{I_S\,T_h} = \frac{T_h - T_c}{T_h} < 1 \qquad (7)$$

a well-known result, which may be derived in this approach in all its generality rapidly and efficiently.

In the case of the ideal thermal engine (Carnot cycle) energy conservation requires that the released thermal power is given by:

$$\mathcal{P}_{therm}^{\nearrow} = I_{E\,therm\,in} - \left| I_{E\,therm\,out} \right| = I_S\,T_h - I_S\,T_c = I_S\left[T_h - T_c\right] = -I_S\,\Delta T \qquad (8)$$

Fig. 2a illustrates the situation: since there is no entropy production and therefore $\left| I_{S\,out} \right| = I_{S\,in} = I_S$, in the $I_E(T) = I_S T$ graph the points representing the situation at the entry and the one at the exit from the engine lie on a unique (blue) line.

Further, since the considered process is reversible, 100% of the released thermal power (vertical yellow downward arrow) may be used, *i.e.* for the uploaded mechanical power (the yellow upward arrow in Fig. 2a) we have: $\mathcal{P}_{mech} = \mathcal{P}_{therm}$. This means that the *second law efficiency* of this process is 100%.

Fig. 2b shows the *process diagram*: red arrows indicate the energy exchanges between the system (grey area) and its surroundings, while the green and pink lines with arrows represent the flows of the energy carriers. The yellow downward (upward) arrows represent the released (thermal) and uploaded (mechanical) power.

These representations are particularly useful when the processes occurring within the system are partially or totally dissipative, *i.e.* when there is entropy production. Considering again only stationary states, the outflow of entropy will therefore be larger than the inflow $\left| I_{S\,out} \right| = I_{S\,in} + \pi_S$, so that the thermal energy outflow will be larger than in the reversible case and the available mechanical energy will be less. Taking into account the dissipated power $\mathcal{P}_{diss}$, we now have:

$$\mathcal{P}_{therm} = \mathcal{P}_{mech} + \mathcal{P}_{diss}. \tag{9}$$

With the second law efficiency ε of the process, the uploaded power becomes $\mathcal{P}_{mech} = \varepsilon\,\mathcal{P}_{therm}$, while the dissipated power is $\mathcal{P}_{diss} = [1-\varepsilon]\,\mathcal{P}_{therm}$. One can show that the dissipated power is related to the entropy production rate by:

$$\mathcal{P}_{diss} = T_c\,\pi_S \tag{10}$$

where T_c is the temperature at which the entropy leaves the system. Figs. 3a and 3b show the situation in the presence of partial dissipation, $(0 < \varepsilon < 1)$, as is the case in a *real thermal engine*. In Figs. 3c and 3d we consider the extreme situation where all the released power is dissipated ($\varepsilon = 0$), *i.e.* where the maximum possible entropy production occurs. An example is *thermal conduction*, a process totally irreversible and dissipative.

Example 2: The Electrochemical Cell and Nernst's Law

We consider an electrochemical zinc/silver cell operating (at constant temperature) according to the following reaction:

$$2\,Ag^+_{(aq)} + Zn_{(s)} \quad \rightarrow \quad Zn^{2+}_{(aq)} + 2\,Ag_{(s)}$$
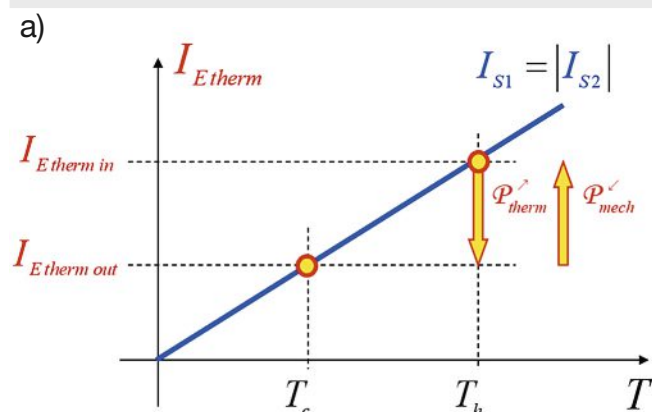
Based on the chosen stoichiometry, the transformation rates π_{ni} of the different chemical species involved are related to each other by:

$$\pi_{n(R)} = \frac{\left| \pi_{n(Ag^+)} \right|}{2} = \frac{\left| \pi_{n(Zn)} \right|}{1} = \frac{\pi_{n(Zn^{2+})}}{1} = \frac{\pi_{n(Ag)}}{2} \tag{11}$$

By the oxidation of one mole of Zn(s) and the reduction of two moles of Ag$^+$ ions, 2 moles of electrons e$^-$ flow across the electrodes. Therefore the electrical current I_Q flowing in the circuit is:

$$I_Q = (z\,e\,N_A)\,\pi_{n(R)} = z\,\mathcal{F}\,\pi_{n(R)} \tag{12}$$

where $N_A = 6.022 \times 10^{23}$ mol^{-1} is Avogadro's constant, $e = 1.602 \times 10^{-19}$ C is the elementary charge, $\mathcal{F} = 9.65 \times 10^4$ C mol^{-1} is Faraday's constant and z is the number of electrons exchanged between the reducing agent and the oxidant, according to stoichiometry. In this case $z = 2$.

To simplify matters somewhat, we assume a constant temperature and that the processes taking place are reversible (*i.e.* without entropy production). Fig. 4 shows the resulting process diagram for the electro-chemical part (for simplicity, entropic aspects are not represented).

Under the assumed conditions the efficiency is 100%, so that all the released chemical power can be uploaded to the external circuit: $\mathcal{P}_{chem} = \mathcal{P}_{el} = \Delta\varphi\,I_Q$. Therefore:

$$-\Delta\mu_R\,\pi_{n(R)} = \Delta\varphi\,z\,\mathcal{F}\,\pi_{n(R)} \tag{13}$$

Since the cell operates at constant temperature and the chemical potentials of solids remain constant during the process, adopting the usual first order approximations for chemical potential for the ions in the solution, we obtain for $\Delta\mu_R$[4,7]

$$
\begin{aligned}
\Delta\mu_R &= \left\{ \mu_{Zn^{2+}} + 2\,\mu_{Ag} \right\} - \left\{ \mu_{Zn} + 2\,\mu_{Ag^+} \right\} \\
&= \left\{ \mu^o_{Zn^{2+}} + RT\ln\left[Zn^{2+} \right] + 2\,\mu^o_{Ag} \right\} - \left\{ \mu^o_{Zn} + 2\,\mu^o_{Ag^+} + 2\,RT\ln\left[Ag^+ \right] \right\} \\
&= \Delta\mu^o_R + RT\ln\frac{\left[Zn^{2+} \right]}{\left[Ag^+ \right]^2}
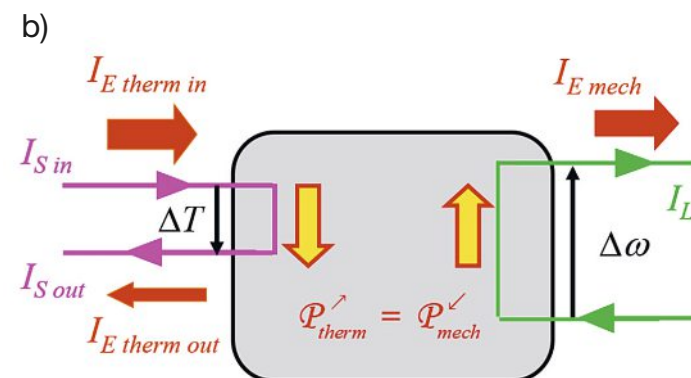\end{aligned} \tag{14}
$$

Fig. 2. Ideal thermal engine: a) representation of the flows; b) process diagram. Notice that Fig. 2a) allows us to obtain Eqn. (7) in a purely geometrical way.
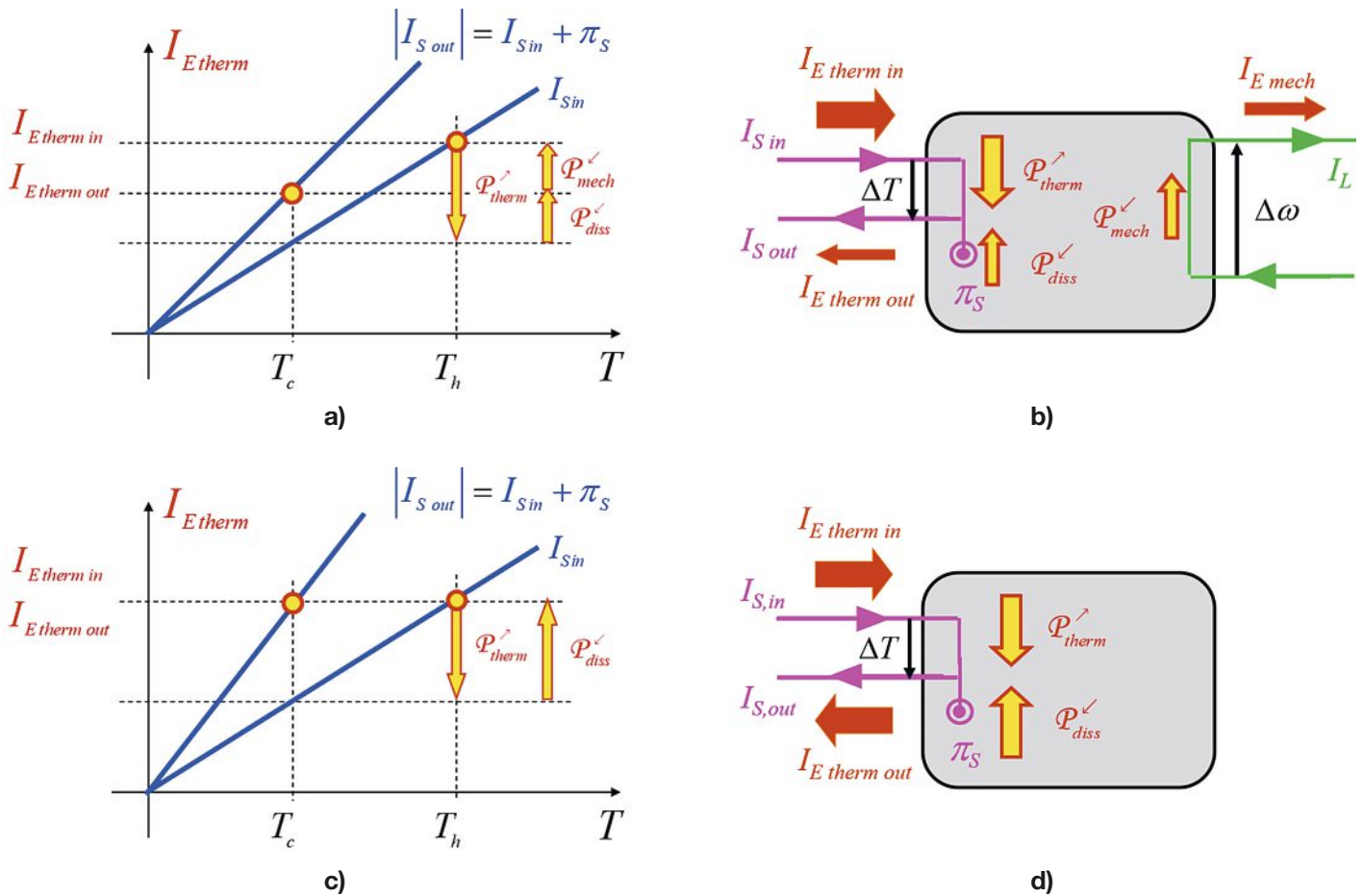
a)

b)

c)

d)

Fig. 3. Energy flows and process diagram for a real thermal engine (a and b) and for a pure thermal conduction process (c and d).

where we have used $\Delta\mu_R^o = \left\{ \mu_{Zn^{2+}}^o + 2\,\mu_{Ag}^o \right\} - \left\{ \mu_{Zn}^o + 2\,\mu_{Ag^+}^o \right\}$. It is worth noting that inserting Eqn. (14) in Eqn. (13) an expression totally equivalent to the well-known *Nernst equation* is obtained. Once again the proposed approach provides us with an explanation for a relationship otherwise often received by students as unrelated to the overall context. It also allows to determine the voltage drop across the cell. With concentrations of 1.0 M we find:

$$\Delta\varphi = \frac{-\Delta\mu_R^o}{z\,\mathcal{F}} = \frac{301,28 \text{ kJ mol}^{-1}}{2 \cdot 9,65 \times 10^4 \text{ C mol}^{-1}} = 1,56 \text{ V} \qquad (15)$$

in good agreement with experimental results.
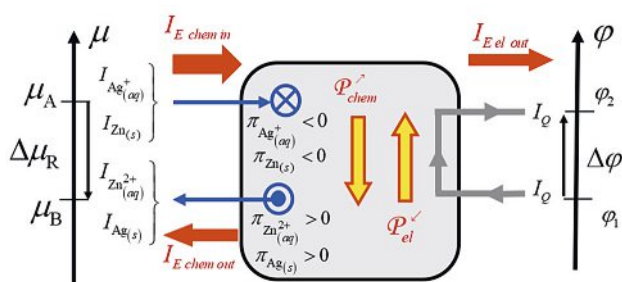
Fig. 4. Process diagram for the ideal electrochemical cell. Notice in particular how the process that leads to the manifestation of an electrical potential difference is supported by the process that is generated by the chemical potential difference.

Example 3: Osmosis

To conclude we would like to at least mention an example that opens up to biology: osmosis. Again, the basic goal is to show how van 't Hoff's law law can be derived through simple considerations based on chemical potential, in this case that of water. To do this, we will use:[7]

1) the relationship that gives the pressure dependence of the chemical potential of a fluid, which in the linear approximation and neglecting the solute's own volume takes the form:

$\mu_l(p) = \mu_l(p^o) + \hat{V}\left[p - p^o\right]$

where $\hat{V}$ is the molar volume of the fluid and $p = p^o + p_{hydr}$ is the total pressure at the point under consideration, *i.e.* atmospheric pressure added to the corresponding hydrostatic pressure;

2) the relationship:

$\mu_l(x_B) = \mu_l^o - R\,T\,x_B$

which indicates how the chemical potential of the solvent varies in the presence of a solute B at low concentration (*i.e.* $x_B \ll 1$).

Fig. 5 shows a typical situation: the two compartments shown are separated by a membrane that is permeable for water, but through which the solute cannot diffuse. Initially (Fig. 5a) in the two compartments the water reaches the same level, and at points A_1 and A_2 located near the membrane the water chemical potential is the same. Assuming that the external atmospheric pressure equals the reference pressure, the pressure difference is given by the hydrostatic pressure, and we will have an equilibrium situation with:

$\mu_l(A_1) = \mu_l^o + \hat{V}\,\rho_l\,g\,h_1 = \mu_l^o + \hat{V}\,\rho_l\,g\,h_2 = \mu_l(A_2)$.

When solute (*e.g.* sugar) is dissolved in the left compartment, this equilibrium is perturbed: the chemical potential of the water
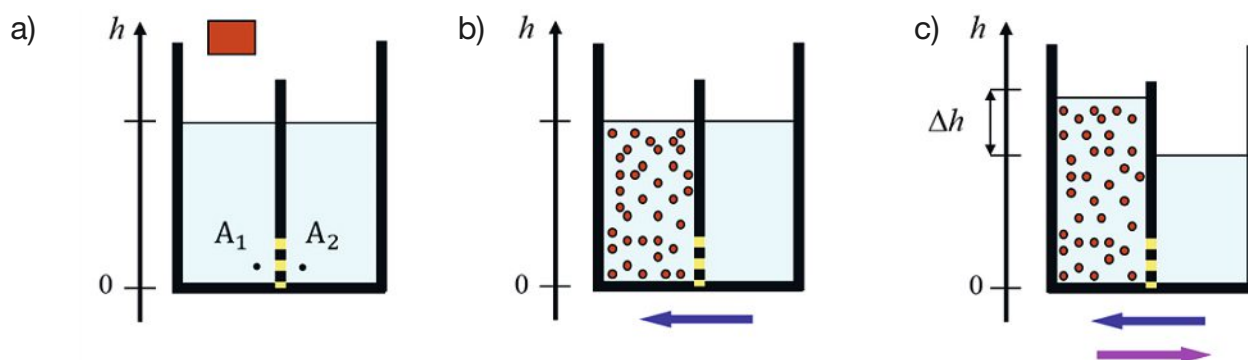
Fig. 5. Schematic diagram of the experimental situation for the study of osmosis: a) initial situation: the water level in the two compartments is the same; b) a certain amount of solute is dissolved in the left compartment; c) final equilibrium situation.

in the left compartment is lower than that of the water in the right compartment.

Therefore, this difference in the water's chemical potential acts as a driving force that causes the water to start flowing from the right to the left compartment (blue arrow, situation b). This displacement generates a level difference between the two compartments, which in turn results in the appearance of a second driving force, directed in the opposite direction to the previous one. When this second 'mechanical' driving force exactly counterbalances the 'chemical' one, equilibrium is reached (purple arrow, situation c): between points A_1 and A_2 there is no longer a potential difference: $\mu_l^{eq}(A_1) = \mu_l^{eq}(A_2)$.

Using the above relations explicitly, at equilibrium must therefore hold

$$\mu_l^o + \hat{V}\,\rho_l\,g\,h_1 - R\,T\,x_B = \mu_l^o + \hat{V}\,\rho_l\,g\,h_2 \qquad (16)$$

For the pressure difference Δp across the membrane (osmotic pressure) we get:

$$\Delta p = \rho_l\,g\,\Delta h = \rho_l\,g\,[h_1 - h_2] = \frac{R\,T}{\hat{V}}\,x_B \qquad (17)$$

That is, the well-known van 't Hoff equation.

Conclusion and Outlook

The tools provided to students outlined here enable them to reinvest basic approaches and ideas that are cross-cutting in multiple areas, such as in describing the attainment of equilibrium or determining an energy balance. This brings not only a saving of time in the classroom, but more importantly it provides students with the skills to move with some autonomy within a known and coherent conceptual framework, so that gradually their attention is less and less focused on the specific formalism but can be directed to the essence of the phenomenon under consideration.

From a cross-curricular sustainability education perspective, this approach also provides students with important conceptual tools, enabling them, for example, to distinguish clearly between *first law efficiency* η and *second law efficiency* ε of a given process (the former limited by laws of nature, the latter dependent on the state of technology). It is also important to notice that this approach can be extended not only by broadening it to the examination of a multitude of other experimental situations, but that, by providing the appropriate tools in a natural way, it can provide a solid basis both for the more formal introduction of coupled potentials (*e.g.* gravito-chemical or electro-chemical) and for introducing students to aspects more directly related to the time evolution of processes through dynamic modeling.[11]

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