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Boltzmann and gas constant – ambiguities between energy and force

Erich Gnaiger

Oroboros Instruments, Innsbruck, Austria
Correspondence: erich.gnaiger@oroboros.at

Theoretical Communication

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$$\begin{tikzcd}
 & kT\left[\frac{\mathrm{J}}{\mathrm{x}}\right] & \\
\left[\frac{\mathrm{J}}{\mathrm{mol}}\right]RT \arrow[ur, leftrightarrow, "N_\mathrm{A}"] \arrow[rr, leftrightarrow, "z_\mathrm{Y}", "eN_\mathrm{A}"'] & & fT\cdot\frac{1}{z_\mathrm{Y}}\left[\frac{\mathrm{J}}{\mathrm{C}}\right] \arrow[ul, leftrightarrow, "e"', "z_\mathrm{Y}"]
\end{tikzcd}$$

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Faraday constant F
force
gas constant R
ion
motive force

Summary

Energy and force are distinct fundamental quantities, differing in both their physical meaning and units. In the International System of Units (SI), the Boltzmann constant is one of the seven defining constants. The Bureau International des Poids et Mesures explains the Boltzmann constant k as "a proportionality constant between the quantities temperature (with the unit kelvin) and energy (with the unit joule)" [1]. Consequently, "one kelvin is equal to the change of thermodynamic temperature that results in a change of thermal energy kT by $1.380\,649 \times 10^{-23}$ J" [1]. It should be noted that this groundbreaking definition concerns a physical constant, not the concept of energy itself. But a clear distinction is warranted: Energy in any form and expressed in the unit joule ('thermal energy', kinetic and potential energy, work and heat, Helmholtz and internal energy, Gibbs energy and enthalpy) is an *extensive* quantity that scales in direct proportion to the size of a system, whereas *intensive* quantities such as temperature and force are independent of system size. The concept that a fixed temperature change results in a proportional change of thermal energy kT lacks specification of the entity to which energy is attributed. By relating energy to the individual particle, kT accounts for the quantum structure of nature. The present analysis aims at resolving ambiguities of the term 'thermal energy kT' by a focus on SI units and corresponding symbols to describe adequately and clearly the full meaning of any form of energy related to fundamental physical or thermodynamic forces.

1. Introduction

On 20 May 2019 new definitions of several constants defining the SI units entered 'into force' [1]. Notably, while we say that legal or scientific definitions 'enter into force', it would be linguistically and conceptually inappropriate to state they 'enter into energy'. In everyday language, we tend to discriminate intuitively between energy and force. Scientific terminology, however, has historically blurred the two. For two centuries following Newton's *Principia* (1687), which formalized mechanical and gravitational force, the conceptual boundary between force and energy remained imprecise. Indeed, what is now recognized as the first law of thermodynamics — conservation of internal energy — was originally formulated as the principle of conservation of *force* [4; 11]. The fundamental forces of physics are the gravitational, electroweak (combining electromagnetic and weak nuclear) and strong nuclear forces. These forces are vectors, directed parallel to a spatial gradient, and are effective at a distance. In contrast, the electromotive force emF defined by the Nernst equation is a difference of electrochemical potentials. Direction of a gradient in space of physical forces is replaced in the emF by a potential difference between separate electrodes or compartments (the anode and cathode). Energy per distance l (per metre) of physical forces, with unit newton $[\mathrm{N} = \mathrm{J/m}]$, is replaced in the emF by energy per charge Q_{el} (per coulomb), with unit volt $[\mathrm{V} = \mathrm{J/C}]$. Both units N and V express ratios of 'free' energy (related to work) to a 'motive' quantity, making the fundamental physical and electromotive forces comparable as isomorphic *motive forces* [8]. These are known as generalized forces in the thermodynamics of irreversible processes [7; 12; 16; 17]. The present perspective considers the fundamental difference between 'thermal energy kT' and thermodynamic motive forces.

2. The units of the Boltzmann constant and the gas constant

The Boltzmann constant k, Avogadro constant N_{A}, and elementary charge e are among the seven SI constants redefined in 2019 as numerically fixed values [1]. These three constants share a common connection: each is fundamentally related to "the quantity number of elementary entities (with the unit one, symbol 1)" [1]. However, in the SI definitions, the symbol 1 is typically omitted — obscuring the fact that k and e are quantities expressed *per entity* whereas N_{A} is the number *of entities* per amount.

To make this dimension explicit, the symbol x is introduced to represent the unit of countable entities [8; 10]. Instead of the SI symbol 1, the explicit symbol x for the count serves a conceptual purpose: it highlights the distinction between energy and thermodynamic force — namely, presenting energy per *count* $[\mathrm{x}]$ analogous to energy per *amount* $[\mathrm{mol}]$ or per *charge* $[\mathrm{C}]$. Expressing the Boltzmann constant in the unit $[\mathrm{J{\cdot}K^{-1}/x}]$ clarifies that kT represents energy per entity, whereas omitting the symbol 1 (as in $\mathrm{J{\cdot}K^{-1}}$) conceals this interpretation.

Notably, the symbol x is not part of the SI, but is proposed as a notational aid to explicitly represent the abstract unit 'one' [2] associated with the quantity count — the number of elementary entities [10]. While the SI permits omission of the symbol 1, its explicit inclusion can be problematic. For instance, stating the number of defining SI constants (SIC) as $N_{\mathrm{SIC}} = 7\ 1$ is formally correct but visually confusing. Neither '$7{\cdot}1$' nor '7 times 1' resolve the issue without introducing formal inconsistency, analogous to writing '25 times °C'. In contrast, the format $N_{\mathrm{SIC}} = 7\ \mathrm{x}$ is consistent with SI unit structure and allows seamless integration with derived units. While omitting the symbol 1 (the numeral representing the number one) does not affect the mathematical validity of equations involving multiplication or division by 1, it obscures the conceptual distinction between energy [J] and force [J/x]. This distinction becomes evident in the ideal gas law, where the energy associated with pressure-volume work can be expressed in two distinct but representationally isomorphic formats: one referring to energy per amount of substance n_{B} (amount of ideal gas B; Eq. 1a), the other per elementary entity N_{B} (the corresponding count, Eq. 1b):

$$\text{molar format:} \qquad RT = \frac{pV}{n_{\mathrm{B}}} \qquad [\mathrm{J/mol}] \tag{1a}$$

$$\text{molecular format:} \qquad kT = \frac{pV}{N_{\mathrm{B}}} \qquad [\mathrm{J/x}] \tag{1b}$$

These expressions are structurally identical in form and meaning, yet differ in their referential framework: In both cases, pressure-volume work pV [J] is divided by an extensive quantity — amount or count — to yield a motive force. Expressing kT in the explicit unit [J/x] helps clarify that it is not energy, but energy *per elementary entity* — a thermodynamic driving force or, more precisely, a motive force quantum accounting for the quantum structure of nature (Figure 1) [8].

3. Gibbs force

In physical chemistry, it is conventionally accepted to divide in a particular context all extensive quantities by amount of substance and then use identical names and symbols for the corresponding intensive and extensive quantities [3]. This generates fertile ground of confusion when intensive quantities are then referred to out of context. An example is the 'reaction Gibbs energy' $\Delta_{\mathrm{r}}G$ with the unit [J/mol], as defined by the International Union of Pure and Applied Chemistry (IUPAC) [3]. Importantly, this is the driving force of chemical reactions and should be considered as Gibbs *force* of reaction $\Delta_{\mathrm{r}}F$ [J/mol], different from the extensive quantity Gibbs energy change $\Delta_{\mathrm{r}}G$ [J] [7; 8]. Comparable to the molar reaction Gibbs energy, the SI term 'thermal energy' [1] refers to an intensive quantity in relation to the Boltzmann constant, which is ambiguous when kT is presented in the unit of energy [J] (Figure 1). Clarifying this distinction is essential to prevent misconceptions about energy and driving forces of chemical reactions — and lends conceptual force to the growing role of quantum chemistry and quantum biology in advancing our understanding of thermodynamic processes at the atomic and molecular level.

Figure 1. Motive force quantum in three formats: kT (per count), RT (per amount), and fT/z_Y (per charge of Y) corresponding to the Boltzmann constant, gas constant, and electromotive constant, respectively (Table 1). The three isomorphic units are shown in brackets. The unit of the quantity count is represented by the symbol x. Modified from [8].

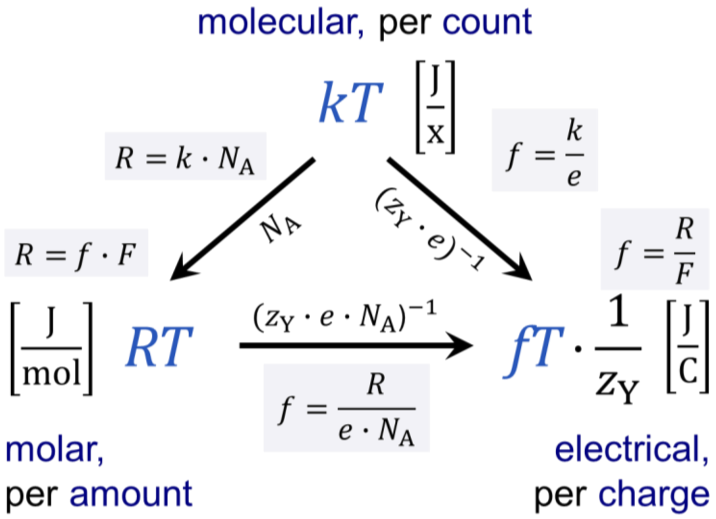

Table 1. Motive force quantum defined by SI constants (k, N_A, and e) and expressed in different formats of the Boltzmann constant k, gas constant R, and electromotive constant f. Values of these quantum effects are shown for the standard temperature of 25 °C ($T° = 298.15$ K). The motive force quantum at any temperature T is obtained by multiplication by $T/T°$. Multiplication factors for 0 °C and 37 °C are 0.916 and 1.040, respectively; $\ln(10) \approx 2.3026$.

Format	**Relation**	**Motive force quantum** times $\ln(10)$	**Unit**
particle	$kT = RT \cdot \frac{1}{N_A} = fT \cdot e$	$kT° \cdot \ln(10) = 9.4784 \cdot 10^{-21}$	J/x
chemical	$RT = kT \cdot N_A = fT \cdot F$	$RT° \cdot \ln(10) = 5.7080 \cdot 10^{3}$	J/mol
electrical	$fT = kT \cdot \frac{1}{e} = RT \cdot \frac{1}{F}$	$fT° \cdot \ln(10) = 59.159 \cdot 10^{-3}$	J/C

4. The electromotive constant in electrochemistry

> ‘The phenomena associated with electrolysis were studied by M. Faraday (1832-33), and the nomenclature which he used, and which is still employed, was devised for him by W. Whewell. .. Faraday assumed the flow of electricity to be associated with the movement of charged particles ..; these were called *ions* (Greek: wanderer).’ – Samuel Glasstone (1948) [6]

Charged motive particles are properly called ions — a term introduced through the collaboration of Faraday and Whewell to describe entities that *wander* under the influence of an electric potential difference. This etymology resonates with the concept of *motive force*, which drives ion translocation across membranes or electrode systems. The Nernst equation quantifies the resulting electromotive force (emF) for a one-component system, $emF \overset{\text{def}}{=} \Delta\Psi_Y$ as:

$$emF = emF^\circ + \frac{RT}{F}\cdot\frac{1}{z_\mathrm{Y}}\cdot\ln\left(\frac{a_{\mathrm{Y}_b}}{a_{\mathrm{Y}_a}}\right) \qquad [\mathrm{J/C}] \qquad (2)$$

where z_Y is the charge number of ion Y, and a_{Y_a} and a_{Y_b} are its activities in compartments a and b ($a \rightarrow b$). The standard electromotive force is $emF^\circ = 0\ \mathrm{V}$ at identical activities in both compartments ($a_{\mathrm{Y}_a}{}^\circ = a_{\mathrm{Y}_b}{}^\circ$). $F = e \cdot N_\mathrm{A}$ $[\mathrm{C/mol}]$ is the Faraday constant. In this context, the *electromotive constant* f is introduced as $f = R/F$, combining the Boltzmann constant and elementary charge ($f = k/e$), analogous to the combination of the Boltzmann constant and Avogadro constant in the gas constant ($R = k \cdot N_\mathrm{A}$; Table 2).

In summary, three constants multiplied by T express the motive force quantum in their respective units: kT per elementary unit $[\mathrm{x}]$, RT per mole $[\mathrm{mol}]$, and fT per coulomb $[\mathrm{C}]$ (Tables 1 and 2; Figure 1). Notably, the ratio RT/F appears in 59 equations in the chapter *Electrochemistry* (Glasstone 1948; [6]). More recently, the terms RT/F or kT/e occur in 24 equations across five chapters of *Biothermodynamics* [18]. Avoiding the detour through these ratios by introducing the electromotive constant f simplifies both the presentation and interpretation of equations (see Eq. 3 and Eq. 5 below).

Table 2. Three defining SI constants (k, N_A, and e) [1] with units containing the explicit symbol x [8]. The elementary unit x cancels in the derived constants F, R, and f.

Constant	Relation			Numerical value	Unit	
Boltzmann constant	k	$= f \cdot e$	$= R/N_\mathrm{A}$	$= 1.380\,649 \cdot 10^{-23}$	$\mathrm{J \cdot K^{-1}}$	$/\mathrm{x}$
Avogadro constant	N_A	$= R/k$	$= F/e$	$= 6.022\,140\,76 \cdot 10^{23}$	x	$/\mathrm{mol}$
elementary charge	e	$= k/f$	$= F/N_\mathrm{A}$	$= 1.602\,176\,634 \cdot 10^{-19}$	C	$/\mathrm{x}$
Faraday constant	F	$= e \cdot N_\mathrm{A}$	$= R/f$	$= 96\,485.332\,12$	C	$/\mathrm{mol}$
gas constant	R	$= k \cdot N_\mathrm{A}$	$= f \cdot F$	$= 8.314\,462\,618$	$\mathrm{J \cdot K^{-1}}$	$/\mathrm{mol}$
electromotive constant	f	$= k/e$	$= R/F$	$= 8.617\,333\,262 \cdot 10^{-5}$	$\mathrm{J \cdot K^{-1}}$	$/\mathrm{C}$

To align Eq.(2) with logarithmic activity measures of ion-selective electrodes commonly used in chemistry and biology (e.g., pH), the natural logarithm is replaced with a base-10 logarithm, yielding Eq.(3) as a base-10 version of Eq.(2):

$$emF = -fT \cdot \frac{1}{z_\mathrm{Y}} \cdot \ln(10) \cdot \Delta\mathrm{pY} \qquad [\mathrm{J/C}] \qquad (3)$$

where $\mathrm{pY} = -\log_{10}(a_\mathrm{Y})$, such that $-\Delta\mathrm{pY}$ corresponds to the compartmental direction of ion flow ($a \rightarrow b$). It is practical, therefore, to multiply the motive force quantum by $\ln(10)$ (Table 1).

Ultimately, using the symbol x for the SI unit one makes explicit the physical meaning of energy per elementary entity. It helps differentiating between the extensive thermodynamic quantity energy $[\mathrm{J}]$ and intensive motive force $[\mathrm{J/x}]$, improving conceptual clarity in the interpretation of fundamental thermodynamic equations such as the ideal gas law and the Nernst equation.

A motive force of fundamental importance in bioenergetics is the protonmotive force pmF which drives ATP synthesis in mitochondria, bacteria, and chloroplasts by a chemiosmotic process [14; 15]. This force is generated in mitochondria by the action of molecular proton pumps that translocate protons (H^+) from the negatively charged matrix (cathodic compartment) across the mitochondrial inner membrane to the positively charged intermembrane space (anodic compartment). The pmF is the sum of two partial motive forces: (*1*) The electromotive contribution pmF_{el} results from the distribution of all ions generating an electric potential difference according to Eq.(2). (*2*) Irrespective of charge, the partial diffusional contribution pmF_{d} is related to the pH difference $\Delta\mathrm{pH}$ across the semipermeable inner membrane. The diffusional pmF_{d} is the partial Gibbs energy change [J] per advancement of proton translocation, where advancement [17] can be expressed per amount of H^+ $[\mathrm{mol}]$ pumped out of the cathodic compartment, with unit $[\mathrm{J/mol}]$ (Eq. 4a). Alternatively, the diffusional pmF_{d} can be expressed in electrical units of volts $[\mathrm{J/C}]$ (Eq. 4b). Unlike Eq.(3), Eq.(4) omits the charge number $z_{\mathrm{H^+}}$ because the diffusional component pmF_{d} reflects a statistical (entropic) force arising from particle distribution. It is additive to the electric component pmF_{el}, yet independent of the ion's charge [8; 9; 15].

$$\text{molecular format:} \quad pmF_{\mathrm{d}}(\mathrm{count}) = -kT\cdot\ln(10)\cdot\Delta\mathrm{pH} \quad [\mathrm{J/x}] \tag{4a}$$

$$\text{molar format:} \quad pmF_{\mathrm{d}}(\mathrm{amount}) = -RT\cdot\ln(10)\cdot\Delta\mathrm{pH} \quad [\mathrm{J/mol}] \tag{4b}$$

$$\text{electrical format:} \quad pmF_{\mathrm{d}}(\mathrm{charge}) = -fT\cdot\ln(10)\cdot\Delta\mathrm{pH} \quad [\mathrm{J/C}] \tag{4c}$$

Boltzmann, a pioneer of statistical thermodynamics, laid the foundation for describing diffusion at the level of individual particles. In particle physics and quantum biology, diffusion is analyzed in the molecular or particle format, as captured in Eq.(4a) [5]. In the chemical and electrical formats, the Boltzmann constant is replaced by the gas constant R (Eq. 4b) and the electromotive constant f (Eq. 4c), respectively.

Another example for the relevance of the electromotive constant f comes from electrostatics and the Debye-Hückel theory. The local charge density of a particular ion $[\mathrm{C/m^3}]$ at a given distance from the central ion is related to the local electric potential of the perturbed field $[\mathrm{V{=}J/C}]$ and ionic strength $[\mathrm{mol/m^3}]$, with a proportionality coefficient $\frac{N_{\mathrm{A}}e^2}{kT}$ (Eq. 4.31 in [13]). This term is difficult to grasp. Introducing $N_{\mathrm{A}}\cdot e = F$ and $k/e = f$ (Table 2), this proportionality coefficient is,

$$\frac{N_{\mathrm{A}}\cdot e^2}{kT} = \frac{F}{fT} \quad \left[\frac{\mathrm{C}^2}{\mathrm{J\cdot mol}}\right] \tag{5}$$

The Faraday constant F $[\mathrm{C/mol}]$ is required when the concentration term in ionic strength is expressed as amount concentration c_i $[\mathrm{mol/m^3}]$. However, when expressed as count concentration C_i $[\mathrm{x/m^3}]$, elementary charge e $[\mathrm{C/x}]$ replaces F. Consequently, the proportionality coefficient becomes e/fT. Moreover, when the local electric potential of the perturbed field is not expressed as a voltage but as energy per particle $[\mathrm{J/x}]$, the proportionality coefficient is reformulated as e/kT. Finally, if the local charge density of the ion is also expressed as a local count concentration $[\mathrm{x/m^3}]$, the unit conversion factor $N_\mathrm{A} \cdot e^2$ cancels from Eq.(5). The complex original proportionality coefficient in Eq.(5) can thus be decomposed into two conceptually distinguished steps: (*1*) expression of the motive force quantum in context-dependent units (Table 1). (*2*) unit conversion of the electrical potential and concentrations (Table 2). Taken together, the isomorphic proportionality coefficients unfold stepwise,

$$\frac{F}{fT}\left[\frac{\mathrm{C}^2}{\mathrm{J{\cdot}mol}}\right] \rightarrow \frac{e}{fT}\left[\frac{\mathrm{C/x}}{\mathrm{J/C}}\right] \rightarrow \frac{e}{kT}\left[\frac{\mathrm{C}}{\mathrm{J}}\right] \rightarrow \frac{1}{kT}\left[\frac{1}{\mathrm{J/x}}\right]$$

This illustrates the utility of introducing the electromotive constant f and unit symbol x in quantity calculus.

5. Conclusions

The isomorphic nature of the Boltzmann constant, gas constant, and electromotive constant provides a compelling argument for an unambiguous definition of k by conceiving kT not as thermal energy but linking kT to thermodynamic motive forces (Figure 1). The Boltzmann constant k is a proportionality constant between the quantities temperature $[\mathrm{K}]$ and thermodynamic force $[\mathrm{J/x}]$. This definition of the Boltzmann constant should come to the fore. A rigorous distinction between extensive and intensive quantities resolves existing ambiguities of energy and force in thermodynamics and statistical mechanics. Strengthening conceptual rigor is crucial for proper application of core thermodynamic principles in electrochemistry and quantum biology, helping to resolve persistent misunderstandings of the fundamental concept of the protonmotive force and linking thermodynamics and kinetics [8]. Clarifying the distinction between all forms of energy and motive forces will enhance interdisciplinary scientific communication and improve education.

Terms and symbols (see also Table 2)

a_B	activity of B
C_B	count concentration of B $[\mathrm{x/m^3}]$
c_B	amount concentration of B $[\mathrm{mol/m^3}]$
emF	electromotive force
N_B	count of B $[\mathrm{x}]$
n_B	amount of B $[\mathrm{mol}]$
p	pressure $[\mathrm{Pa}]$
pmF	protonmotive force
Q_{H^+}	charge of H^+ $[\mathrm{C}]$
V	volume $[\mathrm{m^3}]$
z_Y	charge number of ion Y

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References

1. Bureau International des Poids et Mesures (2019) The International System of Units (SI). 9th edition (V3.01 August 2024):117-216. ISBN 978-92-822-2272-0
2. Brown RJC (2021) A metrological approach to quantities that are counted and the unit one. https://doi.org/10.1088/1681-7575/abf7a4
3. Cohen ER, Cvitas T, Frey JG, Holmström B, Kuchitsu K, Marquardt R, Mills I, Pavese F, Quack M, Stohner J, Strauss HL, Takami M, Thor HL (2008) Quantities, Units and Symbols in Physical Chemistry. IUPAC Green Book 3rd Edition, 2nd Printing, IUPAC & RSC Publishing, Cambridge.
4. Coopersmith J (2010) Energy, the subtle concept. The discovery of Feynman’s blocks from Leibnitz to Einstein. Oxford Univ Press:400 pp.
5. Einstein A (1905) Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. Ann Physik 4, XVII:549-60.
6. Glasstone S (1948) Textbook of physical chemistry. 2nd ed, Macmillan and Co, London:1320 pp.
7. Gnaiger E (1993) Nonequilibrium thermodynamics of energy transformations. https://doi.org/10.1351/pac199365091983
8. Gnaiger E (2020) Mitochondrial pathways and respiratory control. An introduction to OXPHOS analysis. 5th ed. doi https://doi.org/10.26124/bec:2020-0002
9. Gnaiger E (2025) The protonmotive force – from motive protons to membrane potential. https://doi.org/10.26124/becprep.2025-0003
10. Gnaiger E (2025) The elementary unit — count and numbers in the International System of Units. https://doi.org/10.26124/becprep.2025-0004
11. Heimann PM (1974) Conversion of forces and the conservation of energy. https://doi.org/10.1111/j.1600-0498.1974.tb00562.x
12. Katchalsky A, Curran PF (1965) Nonequilibrium thermodynamics in biophysics. Harvard Univ Press:248 pp. ISBN 9780674494121
13. Maskow T, Haynes CA (2013) The thermodynamics of electrically charged molecules in solution. In: von Stockar U, ed (2013) Biothermodynamics. The role of thermodynamics in biochemical engineering. EPFL Press:33-61.
14. Mitchell P (1961) Coupling of phosphorylation to electron and hydrogen transfer by a chemi-osmotic type of mechanism. https://doi.org/10.1038/191144a0
15. Mitchell P (1966) Chemiosmotic coupling in oxidative and photosynthetic phosphorylation. https://doi.org/10.1016/j.bbabio.2011.09.018
16. Onsager L (1931) Reciprocal relations in irreversible processes. I. https://doi.org/10.1103/PhysRev.37.405
17. Prigogine I (1967) Introduction to thermodynamics of irreversible processes. Interscience, New York, 3rd ed:147pp.
18. von Stockar U, ed (2013) Biothermodynamics. The role of thermodynamics in biochemical engineering. EPFL Press:608 pp. ISBN 978-2-940222-61-2