.

Appendix IX. Statistical entropy difference in disequilibrium chemical processes

Abstract

The recently formulated concept of statistical entropy difference is applied to microscopic chemical processes. The entropy difference between the two states of a single microscopic reaction is defined. These results are generalized to the evolution of chemical reactions with many particles and are presented in several versions with different boundary conditions and different degrees of approximation. The entropy of the general formula for macroscopic chemical systems is proven to be extensive and the result is illustrated by an empirically based example.

1 Introduction

Since the entropy concept was introduced in the nineteenth century, physicists have aimed to describe the entropy evolution in disequilibrium processes. A major advance in this respect was made by Ludwig Boltzmann when he defined statistical entropy as[1]

$$S = k_B \cdot \ln W \ . \tag{1}$$

However, Boltzmann's entropy concept is most straightforwardly applicable to systems where the volume in phase space of the state in question can be expressed in terms of the number of possible configurations. In chemical and radioactive systems this is not easily done, and therefore Boltzmann's entropy is not immediately applicable in these cases.

In the present article, the problem will be solved by means of the formula for *statistical entropy difference*, which is derived in Skoruppa (2022b). If two states, A and B, in an isolated process can evolve to each other in an arbitrary time interval, $[t, t + \Delta t]$ (Δt here is, as well is the rest of the article, positive), statistical entropy difference is defined by the formula

$$S_A - S_B = k_B \cdot \ln \frac{p(A[t' + \Delta t]|B[t'])}{p(B[t'' + \Delta t]|A[t''])} = \lim_{t \to \infty} k_B \cdot \ln \frac{p(A[t])}{p(B[t])} \ , \tag{2}$$

---

[1] Actually, Boltzmann never wrote down this formula, even though it is engraved in his tombstone (Uffink, 2007).

where k_B denotes Boltzmann's constant and where t' and t'' denote arbitrary points in time. This expression is a measure of the entropy difference between two states in an isolated process in terms of probabilities and is assumed to be applicable to a range of different phenomena. In essence, statistical entropy difference is an extension of Boltzmann's statistical entropy. The statistical entropy difference concept is built on the assumption that every thermodynamic process can be correctly described as a stochastic process, where the *future-directed* transition probabilities (i.e. conditional probabilities where the conditional state precedes the outcome state) are time translation invariant. This assumption, in its turn, follows from the *law of statistical time asymmetry*, which is formulated recently in Skoruppa (2022a).

A noteworthy characteristic of the statistical entropy difference formula is that the quotient of the transition probabilities is independent of the length of the time interval, Δt, between the two states, as long as this interval is positive. This has been proven in Skoruppa (2022b) given certain assumptions, among them that *detailed balance* characterizes the processes when it is in equilibrium.

Many chemical processes display a time asymmetric evolution from disequilibrium to equilibrium when kept in isolation. Since evolutions in these systems are determined by the transition probabilities rather than the number of configurations that characterize each state, chemical processes are reasonable objects for the application of statistical entropy difference. Such an application is the aim of the present work.

The outline of the article is as follows. In Section 2, the statistical entropy difference of a single microscopic process is derived. In Section 3, this result is generalized to many-particle chemical processes, and the resulting expression is proven to be extensive in Section 4. Two simplified versions of entropy difference in chemical processes are derived in Section 5. In Section 6, the resulting formulas are applied to a specific chemical process. Finally, in Section 7, these results are discussed.

2 Application of statistical entropy difference to microscopic chemical processes

In the introduction it was established that the conventional statistical entropy expression $S = k \cdot \ln W$ is limited in several respects, since it is not applicable to disequilibrium chemical processes, radioactive decay, gravitation and to non-equilibrium processes in general. The statistical entropy difference concept does not have these limitations, which will be partly demonstrated by applying it to chemical processes.

Consider a chemical processes

$$\alpha_1 A_1 + \alpha_2 A_2 + ... + \alpha_q A_q \rightleftarrows \beta_1 B_1 + \beta_2 B_2 + ... + \beta_r B_r \ ,$$

where $\alpha_1, \alpha_2, ..., \alpha_q$ and $\beta_1, \beta_2, ..., \beta_r$ are stoichiometric coefficients. If all molecules are in either liquid or gas phase and the temperature is constant, there exists an equilibrium constant, K_c, such that [2]

$$K_c = \lim_{t\to\infty} \frac{\prod_{j=1}^{r}[B_j(t)]^{\beta_j}}{\prod_{i=1}^{q}[A_i(t)]^{\alpha_i}} = \{\text{for short}\} = \lim_{t\to\infty} \frac{\prod_{j}[B_j(t)]^{\beta_j}}{\prod_{i}[A_i(t)]^{\alpha_i}}\ , \tag{3}$$

where the square brackets denote the concentration measured as mole per litre in the isolated system.

Assume that $\Sigma A = \alpha_1 A_1 + \alpha_2 A_2 + ... + \alpha_q A_q$ and $\Sigma B = \beta_1 B_1 + \beta_2 B_2 + ... + \beta_r B_r$ are arbitrary macroscopic individual sets of A and B molecules, respectively. Let $n_e(\Sigma A[t])$ and $n_e(\Sigma B[t])$ be the statistically expected number of unique combinations of ΣA and ΣB, respectively, at the point in time t. Moreover, let $n_e(A_i[t])$ and $n_e(B_j[t])$ denote the statistically expected number of A_i and B_j, respectively, at the point in time t. This implies

$$n_e(\Sigma A[t]) = \prod_i \binom{n_e(A_i[t])}{\alpha_i} \approx \prod_i \frac{[n_e(A_i[t])]^{\alpha_i}}{\alpha_i!}\ , \tag{4}$$

according to Stirling's formula, since $n_e(A_i[t]) \gg \alpha_i$ in a macroscopic system. In a corresponding way,

$$n_e(\Sigma B[t]) \approx \prod_j \frac{[n_e(B_j[t])]^{\beta_j}}{\beta_j!}\ . \tag{5}$$

Let V_L denote the volume of the isolated system measured in litres and let N_A denote the Avogrado constant. Furthermore, let $\Sigma\alpha = \Sigma_{i=1}^{q}\alpha_i$ and $\Sigma\beta = \Sigma_{j=1}^{r}\beta_j$ denote the sums of the stoichiometric coef-

---

[2] In its general version, the equilibrium constant is be expressed in terms of *activity*, but in many cases the concentration is sufficient.

ficients on each side of the reaction. Then, according to equation (3),

$$\begin{aligned}
K_c &= \lim_{t\to\infty} \frac{\prod\limits_j [B_j(t)]^{\beta_j}}{\prod\limits_i [A_i(t)]^{\alpha_i}} = \{\text{concentrations in mole per litre}\} \\
&= \lim_{t\to\infty} \frac{\prod\limits_j \left[\dfrac{n_e(B_j[t])}{N_A \cdot V_L}\right]^{\beta_j}}{\prod\limits_i \left[\dfrac{n_e(A_i[t])}{N_A \cdot V_L}\right]^{\alpha_i}} \\
&= \lim_{t\to\infty} \frac{(N_A \cdot V_L)^{\Sigma\alpha} \cdot \prod\limits_j [n_e(B_j[t])]^{\beta_j}}{(N_A \cdot V_L)^{\Sigma\beta} \cdot \prod\limits_i [n_e(A_i[t])]^{\alpha_i}} = \{(4), (5)\} \\
&= \lim_{t\to\infty} (N_A \cdot V_L)^{\Sigma\alpha - \Sigma\beta} \cdot \frac{n_e(\Sigma B[t])}{n_e(\Sigma A[t])} \cdot \frac{\prod\limits_j \beta_j!}{\prod\limits_i \alpha_i!} \,, \qquad (6)
\end{aligned}$$

where n_e again denotes a statistically expected value.

The relation is written as an equivalence and not as an approximation, since K_c is typically obtained from macroscopic experiments with a huge amount of particles for which Stirling's formula gives negligible deviation from the correct result. This expression can be further developed by means of the frequency interpretation of probability. Let Ω denote an arbitrary combination of matter in the system that, without by-products, can develop to ΣA and therefore also to ΣB. Consequently, $n(\Omega[t])$ denotes all possible combinations that can react to form either ΣA or ΣB. Then, since the original state at t_0 has no significance for the probability of the equilibrium state,

$$\begin{aligned}
\lim_{t\to\infty} p(\Sigma A[t_0 + t] | \Sigma B[t_0]) &= \lim_{t\to\infty} p(\Sigma A[t_0 + t] | \Omega[t_0]) \\
&= \{\text{frequency interpretation}\} \\
&= \lim_{t\to\infty} \frac{n_e(\Sigma A[t_0 + t] \wedge \Omega[t_0])}{n(\Omega[t_0])} \\
&= \lim_{t\to\infty} \frac{n_e(\Sigma A[t])}{n(\Omega[t_0])} \,, \qquad (7)
\end{aligned}$$

and in a similar way,

$$\lim_{t\to\infty} p(\Sigma B[t_0 + t] | \Sigma A[t_0]) = \lim_{t\to\infty} \frac{n_e(\Sigma B[t])}{n(\Omega[t_0])} \,. \qquad (8)$$

Together with equation (6), equations (7) and (8) imply

$$\lim_{t\to\infty}\frac{p(\Sigma B[t_0+t]|\Sigma A[t_0])}{p(\Sigma A[t_0+t]|\Sigma B[t_0])}=\lim_{t\to\infty}\frac{n_e(\Sigma B[t])}{n_e(\Sigma A[t])}$$
$$=K_c\cdot(N_A\cdot V_L)^{\Sigma\beta-\Sigma\alpha}\cdot\frac{\prod\limits_i \alpha_i!}{\prod\limits_j \beta_j!}\,. \tag{9}$$

This can be used as a part of an expression for *microscopic* entropy difference if equation (9) is combined with the *statistical entropy difference* expression (2):

$$S_{\Sigma B}-S_{\Sigma A}=\lim_{t\to\infty}k_B\cdot\ln\frac{p(\Sigma B[t_0+t]|\Sigma A[t])}{p(\Sigma A[t_0+t]|\Sigma B[t])}=\{(9)\}$$
$$=k_B\cdot\ln\left(K_c\cdot[N_A\cdot V_L]^{\Sigma\beta-\Sigma\alpha}\cdot\frac{\prod\limits_i \alpha_i!}{\prod\limits_j \beta_j!}\right)\,. \tag{10}$$

As an example, consider a N_2O_4 molecule, which alters its state in a 1 litre vessel at 25° according to the reaction N_2O_4 (g) $\rightleftarrows$ $2NO_2$ (g). Since

$$K_c=\frac{[NO_2]^2}{[N_2O_4]}=\frac{K_p}{(RT)^{\Delta n_{gas}}}=\frac{0.3160}{(0.08206\cdot 298)^1}\ \mathrm{dm}^{-3}\,, \tag{11}$$

the entropy difference between a N_2O_4 and two NO_2 molecules is, according to equation (10),

$$S_{2NO_2}-S_{N_2O_4}$$
$$=1.381\cdot 10^{-23}\cdot ln\left(\frac{0.3160}{0.08206\cdot 298}\cdot[6.02\cdot 10^{23}\cdot 1.00]^1\cdot\frac{1}{2}\right)\ \mathrm{J/K}$$
$$=6.87\cdot 10^{-22}\ \mathrm{J/K}\,.$$

This is a remarkable result, since it displays the entropy difference between *a single molecule* and its chemical products in a given volume, no matter how many other molecules of the same kinds that are contained in the volume. It should also be noted that a crucial parameter in the expression (10) is the difference $\Sigma\beta-\Sigma\alpha$, since it determines the sign of the entropy difference if the volume V is not extremely small.[3]. Therefore, in descriptions of processes with macroscopic volumes, the

---

[3] It can easily be shown that the microscopic entropy difference between the two states is zero, when the alteration between a single N_2O_4 and two NO_2 molecules takes place in a volume of $0.08206\cdot 298\cdot 2/(0.3160\cdot 6.02\cdot 10^{23})$ litre $\approx 2.57\cdot 10^{-22}$

side of the reaction formula with the greatest number of constituents normally has the greatest microscopic entropy.

Another notable fact is that both K_c and the equations (4) and (5) bring approximations into the calculations. However, since the leftmost quotient in equation (9) is independent of the number of particles involved, and since the mentioned approximations are very good for a large number of particles, the resulting formula (10) can be expected to be just as reliable as K_c.

3 Derivation of statistical entropy difference in disequilibrium chemical processes

Now it is possible to express the evolution of a macroscopic number, N, of transitions in a chemical reaction as the joint probability of all the microscopic transitions probabilities, expressed by equation (9), that constitutes the macroscopic evolution. In order to do so, once again consider a chemical reaction

$$\Sigma A \rightleftarrows \Sigma B$$

in an isolated system, where the constituents of a single reaction, $\Sigma A = \alpha_1 A_1 + \alpha_2 A_2 + ... + \alpha_q A_q$ and $\Sigma B = \beta_1 B_1 + \beta_2 B_2 + ... + \beta_r B_r$, are molecules in either liquid or gas phase. Let $(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}[t])$ denote the macroscopic state of the system with a given number, n, of particles of every sort, $A_1, A_2, \ldots, A_q$ and $B_1, B_2, \ldots, B_r$, at a given point of time, where

$$\{\mathbf{n}_{A_i}\} = \{n_{A_1}, n_{A_2}, \ldots, n_{A_q}\} \text{ and } \{\mathbf{n}_{B_j}\} = \{n_{B_1}, n_{B_2}, \ldots, n_{B_r}\} .$$

First, we consider the probability relations between two states that differ with respect to one single transition $\Sigma A \to \Sigma B$. This means that $\{\mathbf{n}_{A_i}\} = \{n_{A_1}, n_{A_2}, \ldots, n_{A_q}\}$ develops to $\{\mathbf{n}_{A_i} - \alpha_i\} = \{n_{A_1} - \alpha_1, n_{A_2} - \alpha_2, \ldots, n_{A_q} - \alpha_q\}$ and in a corresponding way that $\{\mathbf{n}_{B_j}\}$ develops to $\{\mathbf{n}_{B_j} + \beta_j\}$. According to equation (2), the following holds in an isolated system (the introduction of the limit $\lim_{\Delta t \to 0}$ in the third line below is justified by the fact that *statistical entropy difference* is valid for an

---

litre. Under these circumstances, the process satisfies, according to (10),

$$S_{\Sigma A} = S_{\Sigma B} \Rightarrow p(\Sigma B[t_0 + t]|A[t]) = p(\Sigma A[t_0 + t]|B[t]) ,$$

i.e. what Holster (2003) terms *the orthodox criterion for reversal symmetry.* See also Skoruppa (2022c).

arbitrary time interval, Δt):

$$\begin{aligned}
&\lim_{t\to\infty} \frac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])} = \{(2)\} \\
&= \frac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t+\Delta t]|\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t+\Delta t]|\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])} \\
&= \lim_{\Delta t\to 0} \frac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t+\Delta t]|\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t+\Delta t]|\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])} \,. \qquad (12)
\end{aligned}$$

Next, the possibility that more than one transition will take place during the infinitesimal time interval Δt, given the condition $\lim_{\Delta t\to 0}$, is assumed to be negligible and, moreover, the probability for a transition in either direction $\Sigma A \rightleftarrows \Sigma B$ is assumed to be proportional to the number of possible transitions $\prod_i \binom{n_{A_i}-\alpha_i}{\alpha_i}$ and $\prod_j \binom{n_{B_j}+\beta_j}{\beta_j}$ in each direction.[4] Hence,

$$\begin{aligned}
&\lim_{\Delta t\to 0} p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t+\Delta t]|\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t]) \\
&= \lim_{\Delta t\to 0} p(\Sigma A[t+\Delta t]|\Sigma B[t]) \cdot \prod_j \binom{\mathbf{n}_{B_j}+\beta_j}{\beta_j} \\
&= \lim_{\Delta t\to 0} p(\Sigma A[t+\Delta t]|\Sigma B[t]) \cdot \prod_j \frac{(n_{B_j}+\beta_j)!}{n_{B_j}!\cdot\beta_j!} \,. \qquad (13)
\end{aligned}$$

In a corresponding way,

$$\begin{aligned}
&\lim_{\Delta t\to 0} p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t+\Delta t]|\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t]) \\
&= \lim_{\Delta t\to 0} p(\Sigma B[t+\Delta t]|\Sigma A[t]) \cdot \prod_i \frac{n_{A_i}!}{(n_{A_i}-\alpha_i)!\cdot\alpha_i!} \,. \qquad (14)
\end{aligned}$$

Starting with equation (12) and then using the results from equations (13) and (14) gives

$$\begin{aligned}
&\lim_{t\to\infty} \frac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])} \\
&= \lim_{\Delta t\to 0} \frac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t+\Delta t]|\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t+\Delta t]|\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])} \\
&= \{(13),(14)\} \\
&= \lim_{\Delta t\to 0} \frac{p(\Sigma A[t+\Delta t]|\Sigma B[t])}{p(\Sigma B[t+\Delta t]|\Sigma A[t])} \cdot \prod_i \frac{(n_{A_i}-\alpha_i)!\cdot\alpha_i!}{n_{A_i}!} \cdot \prod_j \frac{(n_{B_j}+\beta_j)!}{n_{B_j}!\cdot\beta_j!} \\
&= \{\text{equation (2) is valid for arbitrary time intervals}\} \\
&= \lim_{t\to\infty} \frac{p(\Sigma A[t_0+t]|\Sigma B[t_0])}{p(\Sigma B[t_0+t]|\Sigma A[t_0])} \cdot \prod_i \frac{(n_{A_i}-\alpha_i)!\cdot\alpha_i!}{n_{A_i}!} \cdot \prod_j \frac{(n_{B_j}+\beta_j)!}{n_{B_j}!\cdot\beta_j!} \,. \qquad (15)
\end{aligned}$$

---

[4] These assumptions ought to be put on a firmer theoretical ground, which the present author is not able to do.

The many-particle evolution $\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\} \to \{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}$ is constituted by a series of N single transitions $\Sigma B \to \Sigma A$ with probabilities that can be assumed to be independent, and their joint probability therefore has to be the product of the single transition probabilities. Thus, it follows, if $0 \leq \alpha_i \cdot N \leq n_{A_i}$ for all i, that

$$\begin{aligned}
&\lim_{t\to\infty} \frac{p(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}[t])}{p(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}[t])} \\
&= \lim_{t\to\infty} \tfrac{p(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])} \\
&\quad \cdot \tfrac{p(\{\mathbf{n}_{A_i}-\alpha_i\},\{\mathbf{n}_{B_j}+\beta_j\}[t])}{p(\{\mathbf{n}_{A_i}-2\alpha_i\},\{\mathbf{n}_{B_j}+2\beta_j\}[t])} \cdot \ldots \\
&\quad \ldots \cdot \tfrac{p(\{\mathbf{n}_{A_i}-\alpha_i(N-1)\},\{\mathbf{n}_{B_j}+\beta_j(N-1)\}[t])}{p(\{\mathbf{n}_{A_i}-\alpha_i N\},\{\mathbf{n}_{B_j}+\beta_j N\}[t])} = \{(15)\} \\
&= \lim_{t\to\infty} \tfrac{p(\Sigma A[t_0+t]|\Sigma B[t_0])}{p(\Sigma B[t_0+t]|\Sigma A[t_0])} \cdot \prod_i \tfrac{(n_{A_i}-\alpha_i)!\cdot\alpha_i!}{n_{A_i}!} \cdot \prod_j \tfrac{(n_{B_j}+\beta_j)!}{n_{B_j}!\cdot\beta_j!} \\
&\quad \cdot \tfrac{p(\Sigma A[t_0+t]|\Sigma B[t_0])}{p(\Sigma B[t_0+t]|\Sigma A[t_0])} \cdot \prod_i \tfrac{(n_{A_i}-2\alpha_i)!\cdot\alpha_i!}{(n_{A_i}-\alpha_i)!} \cdot \prod_j \tfrac{(n_{B_j}+2\beta_j)!}{(n_{B_j}+\beta_j)!\cdot\beta_j!} \cdot \ldots \\
&\quad \ldots \cdot \tfrac{p(\Sigma A[t_0+t]|\Sigma B[t_0])}{p(\Sigma B[t_0+t]|\Sigma A[t_0])} \cdot \prod_i \tfrac{(n_{A_i}-N\cdot\alpha_i)!\cdot\alpha_i!}{(n_{A_i}-[N-1]\cdot\alpha_i)!} \cdot \prod_j \tfrac{(n_{B_j}+N\cdot\beta_j)!}{(n_{B_j}+[N-1]\cdot\beta_j)!\cdot\beta_j!} \\
&= \lim_{t\to\infty} \left[\tfrac{p(\Sigma A[t_0+t]|\Sigma B[t_0])}{p(\Sigma B[t_0+t]|\Sigma A[t_0])}\right]^N \cdot \prod_i \tfrac{(n_{A_i}-\alpha_i N)!\cdot(\alpha_i!)^N}{n_{A_i}!} \cdot \prod_j \tfrac{(n_{B_j}+\beta_j N)!}{n_{B_j}!\cdot(\beta_j!)^N} = \{(9)\} \\
&= \left[K_c^{-1}\cdot(N_A\cdot V_L)^{\Sigma\alpha-\Sigma\beta}\cdot\tfrac{\prod_j \beta_j!}{\prod_i \alpha_i!}\right]^N \cdot \prod_i \tfrac{(n_{A_i}-\alpha_i N)!\cdot(\alpha_i!)^N}{n_{A_i}!} \cdot \prod_j \tfrac{(n_{B_j}+\beta_j N)!}{n_{B_j}!\cdot(\beta_j!)^N} \\
&= K_c^{-N} \cdot [N_A \cdot V_L]^{(\Sigma\alpha-\Sigma\beta)\cdot N} \cdot \prod_i \tfrac{(n_{A_i}-\alpha_i N)!}{n_{A_i}!} \cdot \prod_j \tfrac{(n_{B_j}+\beta_j N)!}{n_{B_j}!} \,. \qquad (16)
\end{aligned}$$

.

This result can be combined with equation (2) to express the entropy difference between the states $(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\})$ and $(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\})$:

$$\begin{aligned}
&S(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}) - S(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}) \\
&= \lim_{t\to\infty} k_B \cdot \ln \frac{p(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}[t])}{p(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}[t])} = \{(16)\} \\
&= k_B \cdot \ln\left(K_c^{-N} \cdot [N_A \cdot V_L]^{(\Sigma\alpha-\Sigma\beta)\cdot N} \cdot \prod_i \frac{(n_{A_i} - \alpha_i N)!}{n_{A_i}!} \cdot \prod_j \frac{(n_{B_j} + \beta_j N)!}{n_{B_j}!}\right) . \qquad (17)
\end{aligned}$$

Thereby, the entropy difference between two states in a chemical process is expressed as a function of the volume and the numbers of molecules of the two states beside the equilibrium constant and the stoichiometric coefficients $\{\alpha_i\}$ and $\{\beta_i\}$, which are specific for the reaction.

An advantage of this formula is that it is applicable to systems with only a few particles, since no further approximations are made in addition to what is included in the derivation of *microscopic entropy difference* in Section 2. Thus, when the formula (17) is applied to the transformation of a single set of $\Sigma A \rightleftarrows \Sigma B$, i.e. $n_{A_i} = \alpha_i$, $n_{B_j} = 0$ and $N = 1$, it is identical to equation (10).

4 Extensivity

The formula (17) has the drawback of being only approximately extensive. However, extensivity is a quality that is expected to characterize entropy and it will here be shown that extensivity with a high degree of exactness is accomplished if the number of involved particles is assumed to be large. This can be proven since a large number of particles justifies the application of Stirling's formula to equation (17):

$$\begin{aligned}
&S(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\}) - S(\{\mathbf{n}_{A_i} - \alpha_i N\},\{\mathbf{n}_{B_j} + \beta_j N\}) \\
&\approx k_B \cdot \ln \Bigg(K_c^{-N} \cdot [N_A \cdot V_L]^{(\Sigma\alpha - \Sigma\beta)\cdot N} \\
&\qquad \cdot \prod_i \frac{(n_{A_i} - \alpha_i N)^{n_{A_i} - \alpha_i N + \frac{1}{2}} \cdot e^{\alpha_i N}}{(n_{A_i})^{n_{A_i} + \frac{1}{2}}} \cdot \prod_j \frac{(n_{B_j} + \beta_j N)^{n_{B_j} + \beta_j N + \frac{1}{2}}}{(n_{B_j})^{n_{B_j} + \frac{1}{2}} \cdot e^{\beta_j N}} \Bigg) \\
&\approx \{\text{removal of negligible terms}\} \\
&\approx k_B \cdot \ln \Bigg(K_c^{-N} \cdot [e \cdot N_A \cdot V_L]^{(\Sigma\alpha - \Sigma\beta)\cdot N} \\
&\qquad \cdot \prod_i \frac{(n_{A_i} - \alpha_i N)^{n_{A_i} - \alpha_i N}}{(n_{A_i})^{n_{A_i}}} \cdot \prod_j \frac{(n_{B_j} + \beta_j N)^{n_{B_j} + \beta_j N}}{(n_{B_j})^{n_{B_j}}} \Bigg) . \qquad (18)
\end{aligned}$$

Extensivity is proven by converting the first line of the expression (18) to a function where also V_L is a parameter, and in that connection multiplying the extensive parameters (i.e. volume and quantities) with a constant c:

$$
\begin{aligned}
&S(\{c\cdot\mathbf{n}_{A_i}\},\{c\cdot\mathbf{n}_{B_j}\},c\cdot V_L)-S(\{c\cdot\mathbf{n}_{A_i}-c\cdot\alpha_i N\},\{c\cdot\mathbf{n}_{B_j}+c\cdot\beta_j N\},c\cdot V_L)\\
&=k_B\cdot\ln\Bigg(K_c^{-c\cdot N}\cdot[e\cdot N_A\cdot c\cdot V_L]^{c\cdot(\Sigma\alpha-\Sigma\beta)\cdot N}\\
&\qquad\cdot\prod_i\frac{(c\cdot n_{A_i}-c\cdot\alpha_i N)^{c\cdot n_{A_i}-c\cdot\alpha_i N}}{(c\cdot n_{A_i})^{c\cdot n_{A_i}}}\\
&\qquad\cdot\prod_j\frac{(c\cdot n_{B_j}+c\cdot\beta_j N)^{c\cdot n_{B_j}+c\cdot\beta_j N}}{(c\cdot n_{B_j})^{c\cdot n_{B_j}}}\Bigg)\\
&=k_B\cdot\ln\Bigg(c^{c\cdot(\Sigma\alpha-\Sigma\beta)\cdot N}\cdot K_c^{-c\cdot N}\cdot[e\cdot N_A\cdot V_L]^{c\cdot(\Sigma\alpha-\Sigma\beta)\cdot N}\\
&\qquad\cdot\prod_i\frac{c^{c\cdot n_{A_i}-c\cdot\alpha_i N}}{c^{c\cdot n_{A_i}}}\cdot\frac{(n_{A_i}-\alpha_i N)^{c\cdot n_{A_i}-c\cdot\alpha_i N}}{(n_{A_i})^{c\cdot n_{A_i}}}\\
&\qquad\cdot\prod_j\frac{c^{c\cdot n_{B_j}+c\cdot\beta_j N}}{c^{c\cdot n_{B_j}}}\cdot\frac{(n_{B_j}+\beta_j N)^{c\cdot n_{B_j}+c\cdot\beta_j N}}{(n_{B_j})^{c\cdot n_{B_j}}}\Bigg)\\
&=k_B\cdot\ln\Bigg(c^{c\cdot(\Sigma\alpha-\Sigma\beta)\cdot N}\cdot\prod_i\frac{1}{c^{c\cdot\alpha_i N}}\cdot\prod_j c^{c\cdot\beta_j N}\Bigg)\\
&\qquad+k_B\cdot\ln\Bigg(K_c^{-c\cdot N}\cdot[e\cdot N_A\cdot V_L]^{c\cdot(\Sigma\alpha-\Sigma\beta)\cdot N}\\
&\qquad\cdot\prod_i\frac{(n_{A_i}-\alpha_i N)^{c\cdot n_{A_i}-c\cdot\alpha_i N}}{(n_{A_i})^{c\cdot n_{A_i}}}\cdot\prod_j\frac{(n_{B_j}+\beta_j N)^{c\cdot n_{B_j}+c\cdot\beta_j N}}{(n_{B_j})^{c\cdot n_{B_j}}}\Bigg)\\
&=k_B\cdot\ln(1)+c\cdot k_B\cdot\ln\Bigg(K_c^{-N}\cdot[e\cdot N_A\cdot V_L]^{(\Sigma\alpha-\Sigma\beta)\cdot N}\\
&\qquad\cdot\prod_i\frac{(n_{A_i}-\alpha_i N)^{n_{A_i}-\alpha_i N}}{(n_{A_i})^{n_{A_i}}}\cdot\prod_j\frac{(n_{B_j}+\beta_j N)^{n_{B_j}+\beta_j N}}{(n_{B_j})^{n_{B_j}}}\Bigg)\\
&=c\cdot\big[S(\{\mathbf{n}_{A_i}\},\{\mathbf{n}_{B_j}\},V_L)-S(\{\mathbf{n}_{A_i}-\alpha_i N\},\{\mathbf{n}_{B_j}+\beta_j N\},V_L)\big]\ .
\end{aligned}
$$

This result is in accordance with the extensivity criterion

$$f(c\cdot\mathbf{n}_{A_i},c\cdot\mathbf{n}_{B_j},c\cdot N,c\cdot V_L)=c\cdot f(\mathbf{n}_{A_i},\mathbf{n}_{B_j},N,V_L).$$

5 Simplified versions

The expression (18) for entropy difference between two states in a chemical process is generally applicable to arbitrary macroscopic states, given that the system is isolated. However, in many cases the formula can be simplified, particularly when one of the compared states of the process, i.e. $(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\})$, is an equilibrium state, which means, in accordance with equation (6),

$$K_c = \lim_{t\to\infty} \frac{\prod\limits_j [B_j(t)]^{\beta_j}}{\prod\limits_i [A_i(t)]^{\alpha_i}} = (N_A \cdot V_L)^{\Sigma\alpha - \Sigma\beta} \cdot \frac{\prod\limits_j (n_{B_j} + \beta_j N)^{\beta_j}}{\prod\limits_i (n_{A_i} - \alpha_i N)^{\alpha_i}} \,. \tag{19}$$

Combined with equation (18) this implies

$$\begin{gathered} S(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}) - S(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}) \\ = k_B \cdot \ln\left(e^{(\Sigma\beta - \Sigma\alpha)N} \cdot \prod_i \frac{(n_{A_i})^{n_{A_i}}}{(n_{A_i} - \alpha_i N)^{n_{A_i}}} \cdot \prod_j \frac{(n_{B_j})^{n_{B_j}}}{(n_{B_j} + \beta_j N)^{n_{B_j}}} \right) \,. \end{gathered} \tag{20}$$

This can also be expressed as a sum:

$$\begin{gathered} S(\{\mathbf{n}_{A_i} - \alpha_i N\}, \{\mathbf{n}_{B_j} + \beta_j N\}) - S(\{\mathbf{n}_{A_i}\}, \{\mathbf{n}_{B_j}\}) \\ = k_B \cdot \left([\Sigma\beta - \Sigma\alpha]N - \sum_i \left[n_{A_i} \cdot \ln\left(1 - \frac{\alpha_i N}{n_{A_i}}\right)\right] - \sum_j \left[n_{B_j} \cdot \ln\left(1 + \frac{\beta_j N}{n_{B_j}}\right)\right]\right) \,. \end{gathered} \tag{21}$$

An even simpler case occurs if the initial non-equilibrium state only consists of A-molecules, and if the number of A-molecules is in proportion to the stochastic coefficients, which means

$$\frac{n_{A_1}}{\alpha_1} = \frac{n_{A_2}}{\alpha_2} = \ldots = \frac{n_{A_q}}{\alpha_q} = n_A \,,$$

and

$$n_{B_1} = n_{B_2} = \ldots = n_{B_r} = 0 \,.$$

Then, according to equation (21)

$$\begin{gathered} S(\{\mathbf{n}_A - \alpha_i N\}, \{\beta_j N\}) - S(\{\mathbf{n}_A\}, \{0\}) \\ = k_B \cdot \left([\Sigma\beta - \Sigma\alpha] \cdot N - \Sigma\alpha \cdot n_A \cdot \ln\left[1 - \frac{\alpha_i N}{n_A}\right] \right) \,. \end{gathered} \tag{22}$$

6 Empirical application

As an example, assume that 1.00 mole N_2O_4 is contained in an isolated 1.00 litre vessel at 25° and reaches equilibrium through the reaction $N_2O_4\ (g) \rightleftarrows 2NO_2\ (g)$, which implies $\Sigma\alpha = 1$ and $\Sigma\beta = 2$ and with $K_c = \frac{0.3160}{0.08206 \cdot 298}\ \mathrm{dm}^{-3}$ according to equation (11). Thus, initially $n_{N_2O_4} =$

$6.02 \cdot 10^{23}$, and $n_{NO_2} = 0$. In order to express the entropy difference between the original disequilibrium state and the equilibrium state, it is suitable first to calculate the change in the number of N_2O_4 and NO_2 molecules, N and $2N$ respectively, according to equation (19):

$$\begin{aligned} K_c &= (N_A \cdot V_L)^{\Sigma\alpha - \Sigma\beta} \cdot \frac{(\beta N)^{\Sigma\beta}}{(n_{N_2O_4} - \alpha N)^{\Sigma\alpha}} \\ \Rightarrow \frac{0.3160}{0.08206 \cdot 298} &= (6.02 \cdot 10^{23})^{-1} \cdot \frac{(2N)^2}{6.02 \cdot 10^{23} - N} \\ \Rightarrow N &\approx 3.33 \cdot 10^{22} \ . \end{aligned}$$

Then, according to equation (22),

$$\begin{aligned} & S(\{n_{N_2O_4} - N\}, \{n_{NO_2} + N\}) - S(\{n_{N_2O_4}\}, \{n_{NO_2}\}) \\ &= S(\{n_{N_2O_4} - N\}, \{N\}) - S(\{n_{N_2O_4}\}, \{0\}) \\ &\approx k_B \cdot \left((\Sigma\beta - \Sigma\alpha)N - q \cdot n_{N_2O_4} \cdot \ln \left[1 - \frac{\alpha_i N}{n_A} \right] \right) \\ &\approx 1.38 \cdot 10^{-23} \cdot \left([2-1] \cdot 3.33 \cdot 10^{22} - 6.02 \cdot 10^{23} \cdot \ln \left[1 - \frac{1 \cdot 3.33 \cdot 10^{22}}{6.02 \cdot 10^{23}} \right] \right) \text{ J/K} \\ &\approx 0.931 \text{ J/K} \ . \end{aligned}$$

Since this is an entropy difference in accordance with equation (2), it can be translated into a quotient of two future-directed probabilities, which can be constructed from the two states in question (where the subscripts *eq* and *dis* denotes equilibrium and extreme disequilibrium states, respectively):

$$\begin{aligned} \frac{p\Big((N_2O_4 \rightleftarrows 2NO_2)_{eq}[t + \Delta t] \big| (N_2O_4)_{dis}[t]\Big)}{p\Big((N_2O_4)_{dis}[t + \Delta t] \big| (N_2O_4 \rightleftarrows 2NO_2)_{eq}[t]\Big)} &\approx \exp\left(\frac{0.931}{1.38 \cdot 10^{-23}} \right) \\ &\approx 10^{10^{22.5}} \ . \end{aligned}$$

Expressed in another way, the future-directed probability of an evolution from one mole of N_2O_4 molecules in a one litre vessel to the corresponding equilibrium state of N_2O_4 and NO_2 molecules is $10^{10^{22.5}}$ times greater than the future-directed probability of the reversed evolution. Undeniably, this is an extreme figure, which is partly a consequence of the large number of particles involved, and which mirrors that the evolution from disequilibrium to equilibrium in practice is deterministic.

7 Discussion

The chemical disequilibrium entropy formulas (17) and (18), derived in the present article, seem to meet reasonable criteria for an entropy difference between two states. Especially, equation (18) implies that the described entropy difference is an extensive property.

It should be noted that when the *concentration quotient*, K_c, differs from the *equilibrium constant*, the *activity* must be used instead of the concentration, which gives a more complicated formula. Still, this can easily be derived from the formula given in the present work.

Further understanding of the entropy evolution of chemical reactions can be achieved by studying the rate of reactions. If combined with the rate equation, the time evolution of the entropy can also be calculated, and this is a possible subject of future studies.

In Section 2, other systems, for which Boltzmann's entropy formula is not applicable, is mentioned: radioactive decay, gravitation and non-equilibrium processes. In the present article it has been shown that the *statistical entropy difference* formula is applicable at least to non-equilibrium chemical processes. A natural further step would be to try to derive an expression for entropy differences in other non-equilibrium systems. For example, an isolated system with radioactive atoms and decay products seems like a suitable candidate for such a derivation, since it shares many crucial characteristics with a non-equilibrium chemical process. The only parameter in the central equation (18) that is not immediately given in a radioactive decay system is K_c, which, however, can be experimentally derived.

Admittedly, there is at least one salient weakness in the derivation in Section 3 , which is noted in Footnote 4. However, the connected assumptions seem, at least to the present author, as intuitively self-evident.

References

Holster, A. (2003). The criterion for time symmetry of probabilistic theories and the reversibility of quantum mechanics. *New Journal of Physics*, 5, 130.1–130.28.

Skoruppa, B. (2022a). A proposed law for statistical time asymmetry. Appendix II.

Skoruppa, B. (2022b). Statistical entropy difference. Appendix VIII.

Skoruppa, B. (2022c). Time reversal invariance and asymmetry in probability based laws. Appendix I.

Uffink, J. (2007). Compendium of the foundations of classical statistical physics. In I. J. Butterfield & J. Earman (Eds.), *Philosophy of Physics* (pp. 923–1074). Amsterdam: Elsevier.