# Brønstedian Energetics and the Basic Kinetic Process

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Reading the article entitled "Brønstedian Energetics, Classical Thermodynamics and the Exergy" by Torben Smith Sørensen in this journal [1] provided me with great pleasure and excited the old feeling of enthusiasm for this ingenious construction called energetics, with its substantial didactic value. It is my hope, that this article might work in the direction of promoting the Brønsted scheme of thermodynamics on levels of education within physical chemistry.

In the definition of the kinetic conjugated potential and quantity Sørensen suggests the couple $v^2/2$ and $M$, being the velocity raised to the second power and mass, respectively. This definition seems to me in bad agreement with the purely thermodynamic conjugated pairs $(S,T)$, $(V,-P)$ and $(n_i,\mu_i)$ as defined by Brønsted. Instead the pair $v$ and $p$ should be chosen, being velocity and momentum, which to my mind constitutes a consistent analogy to the Brønstedian pairs of conjugated potentials and quantities.

To see this, let us consider an example of a mechanical system of a simple but explanatory kind. Two bodies 1 and 2 interact with the mutual force $F$ and change their momenta $p_1$ and $p_2$ by $\mathrm{d}p_1$ and $\mathrm{d}p_2$ in the time elapse $\mathrm{d}t$. The $\mathrm{d}p$'s are governed by the equation:

$$\mathrm{d}p_1 + \mathrm{d}p_2 = 0 \qquad (1)$$

being the principle of conservation of momentum. This equation is suggestive of the choice of quantity (in the sense of Brønsted) consistent with the Brønsted scheme. If we define $\mathrm{d}p$ according to:

$$\mathrm{d}p = \mathrm{d}p_1 = -\mathrm{d}p_2 \qquad (2)$$

$\mathrm{d}p$ will constitute a small part of a quantity $p$, transported from body 2 to body 1. This is an important property of a Brønsted quantity, that it should be transportable in a basic process, conserving its magnitude.

The choice of potential should be such, that the work done by the system by the transport of the quantity, should be expressible in the form:

(Work done) = $\Delta$(potential) × (transported quantity)

Now the choice of potential is obvious from the other fundamental relation of mechanics:

$$v_1\mathrm{d}p_1 + v_2\mathrm{d}p_2 = F\mathrm{d}s \qquad (3)$$

stating the conservation of kinetic plus potential energy for this conservative system. $\mathrm{d}s$ is here the distance between the particles. Inserting (2) into (3) the analogy to the Brønsted scheme is apparent:

$$(v_1 - v_2)\mathrm{d}p = F\mathrm{d}s \qquad (4)$$

By treating the right hand side of (4) in analogy with the conjugated pairs $(V,-P)$ or $(A,\gamma)$, where $V$ is volume, $P$ pressure, $A$ interfacial area and $\gamma$ interfacial tension, the content of the whole equation can be interpreted in the terminology of Brønsted: The kinetic basic process coupled to the mechanical basic process communicates work, by transport of momentum between velocities $v_1$ and $v_2$ in the kinetic basic process, and transport of distance between $F$ and zero force in the mechanical basic process.

It is interesting to see, that the concept of mass takes the meaning of capacity in the presented formulation of the fundamental laws of mechanics. The kinetic capacity is derived from the expression:

$$C_{\mathrm{kin}} = \partial p/\partial v \qquad (5)$$

in analogy with the purely thermodynamic capacities. One might speculate whether the introduction of the concept mass in textbooks of mechanics as a capacity, would tend to ease the conceptual jump to relativistic mechanics, when leaning on this analogy to thermodynamical capacities, which are known to be functions of the potentials of the system.

The kinetic energy term for the single body will appear in analogy with the energetic scheme:

$$\mathrm{d}E = (\text{potential}) \times \mathrm{d}(\text{quantity}) \qquad (6)$$

as $\mathrm{d}E_{\mathrm{kin}} = vC_{\mathrm{kin}}\mathrm{d}v = \mathrm{d}(v^2/2)C_{\mathrm{kin}}$

It may be stated, that the coupling between the kinetic and the mechanical basis process described here constitutes the microscopical principle of the second law of thermodynamics. This particular coupling differs namely substantially from the coupling between purely thermodynamic basic processes. A thermal and a spatial basic process for instance can be brought in static equilibrium with each other, and a reversible communication of work between the two can be conceived as an indefinitely slow transport of quantities in their potentials, which can be stopped and reversed by principally no exertion of work from outside. In contrast to this stands any coupling in which the kinetic basic process is taking part. This kind of coupling can never be brought to static equilibrium, and will end up vibrating or be-

ing directional in the sense of given priority to kinetic energy at the expense of any form of potential energy. Time's arrow points in the direction of kinetic chaos.

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## Rational Thermodynamics and Mechanics

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In the short communication "Brønstedian Energetics and the Basic Kinetic Process" [1] Torben Knudsen criticises my choice of $v^2/2$ and $M$ as the potential and the quantity in the basic kinetic process in mechanics.[2] He argues that it would be better to choose momentum **p** as the conserved quantity and velocity as the conjugated potential. I perfectly agree with this objection, since I had already some qualms about it when I wrote that **p** and **v** is a more convenient bipartition of the kinetic energy than the pair chosen in Table 1, Ref. 2. This was written in connection with eqn. (20) in the paper No. III in the series "Towards a Rational Thermodynamics".[3]

It is not true – as states Knudsen – that conservation in itself is a fundamental property of a Brønsted quantity. Moles are not conserved in chemical reactions, interfacial area is not conserved in emulsification process and entropy not in irreversible processes, just to take some examples. Also, the heavy mass is just as conserved as momentum in classical mechanics. However, **p** and **v** is a better choice, since the analogy between momentum transport in velocity gradients in viscous processes, charge transport in electric fields, entropy transport in temperature gradients and so on is much more clearly put forward, as well as the differences: momentum transport is a tensorial process in contrast to the "normal" vectorial transport processes or scalar chemical processes. With respect to the transition to relativistic mechanics, I would like to point out the pages 95 to 110 in my Ph. D. dissertation [4] where I have sketched the outlines of a general thermodynamic systems theory. Similar attempts were at the same time and independently made by Oster, Perelson and Katchalsky [5] and by Karin Beyer.[6] Especially, one observes in Table 2, p. 98 in Ref. 4, that the basic difference between classical mechanics and relativistic mechanics is that the constitutive relation between momentum and velocity is nonlinear in the latter, and therefore there is a difference between kinetic energy and coenergy in relativistic mechanics, but not in classical mechanics. Whenever a difference, the coenergy turns out to be the fundamental energy-function to be used *e.g.*, in Hamilton's variational principle, see also Lanczos' monography.[7]

Finally, I do not quite agree with the statement of Knudsen, that any coupling in which the basic kinetic process is taking part stands in contrast to reversible couplings between other Brønstedian basic processes, since it can never be brought to any static equilibrium. Purely mechanical systems with no dissipative elements are just examples of static equilibrium between potential forces and inertial forces, as expressed in the principle of d'Alembert.[7] The earth revolving around the sun is a system in perfect thermodynamic equilibrium (tidal effects neglected): reversible coupling between the gravitational basic process and the kinetic basic process is taking place and the system is neutrally stable (in the Liapounov sense) to external disturbances. The fact that time explicitly enters the kinetic potential (velocity) should not obscure this fundamental analogy to other reversible couplings between Brønsted's basic processes.

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6. Beyer, K. *Entropi og Biologiske Økosystemer*, Prisopgave i Fysik, University of Copenhagen 1972.
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