Exergy Loss, Dissipation and Entropy Production. Towards a Rational Thermodynamics. II

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It is shown by application of Brønstedian energetics that the loss of mechanical work (dissipation) by a reversible "cinematographic" reproduction of an irreversible process is equal to the absolute temperature of the standard thermal reservoir from which the compensation entropy is taken times the entropy production during the irreversible process.

Furthermore it is shown that the loss in absolute exergy during an irreversible process in an isolated thermodynamic system is equal to the absolute temperature of the energetic zero-point times the entropy produced.

Examples are given and the difference between energetic zero points and "heat death points" is discussed. The relative exergy for open, stationary flow systems, previously discussed in literature is found to obey similar relations, but the energetic zero points are here arbitrarily chosen and not endogeneously determined by the capacities of the systems, as the case is for the absolute exergy.

In previous publications [1-3] I have tried to reconcile Brønstedian and Gibbsian thermodynamics and have shown that Gibbsian thermodynamics may be considered a sub-class within the more general framework of Brønstedian thermodynamics. In order to be in closest possible analogy with the procedures of analytical mechanics, Brønsted's energetics was extended to encompass an *exergy function* being the thermodynamic equivalent of potential energy in mechanics rather than the internal energy. Whereas internal energy is conserved during irreversible transformations in isolated systems, the exergy decreases. Furthermore, the exergy was shown to have an interesting non-additive property, when subsystems were combined into larger systems, whereas the internal energy has to be additive, if the law

of conservation of energy in nature should not be violated.

In the present paper the connection between loss in exergy and entropy production during irreversible processes will be described, and illustrated by simple examples as an introduction to the systematic treatment of multicomponent transport processes in forthcoming papers.

LOSS OF MECHANICAL WORK IN A REVERSIBLE REPRODUCTION OF AN IRREVERSIBLE PROCESS

In Fig. 1 we have depicted an *isolated* thermodynamic system (an energetic universe) which we have subdivided into a *closed* system described by the vectors of potentials and quantities (**P**, **K**), a mechanical reservoir (*e.g.* a weight in a gravity field) and a thermal standard reservoir with the fixed absolute temperature T_{st}. We now perform an infinitesimal irreversible process
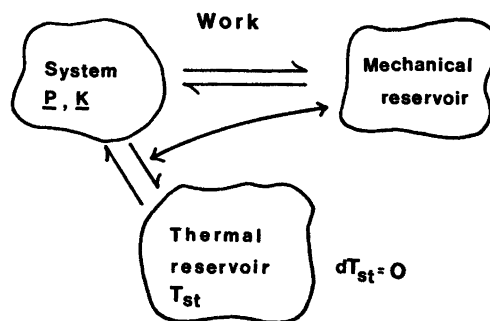

Fig. 1. Closed thermodynamic system in communication with mechanical and thermal reservoir.

$$\mathbf{P}, \quad \mathbf{K} \to \mathbf{P} + d\mathbf{P}, \quad \mathbf{K} + d\mathbf{K} \tag{1}$$

in the system. According to Brønstedian energetics we have

$$\sum T_i \, dS^i_{prod} + \sum_{K \,\neq\, S_{prod}} PdK + dE_{mech}(irr) +$$

$$T_{st}dS_{st}(irr) = 0 \tag{2}$$

The ϕdM terms (ϕ = gravity potential) in the mechanical reservoir have been lumped together in the mechanical potential energy term dE_{mech} and the terms due to produced entropy have been separated out from the PdK-sum for the system. We consider general *polythermal* systems, where the entropy may be produced at many different temperatures (*e.g.* heat conduction).

Consider now a reversible "cinematographic" reproduction of the irreversible process. That means the following: We move around all the quantities inside the closed system in exactly the same way as they move during the irreversible process. We also produce or destroy quantities inside the system (moles of chemical components, interfacial area, but *not* entropy) exactly as in the irreversible process, and make the same supplies from outside ($-dS_{st}(irr)$) from T_{st}, volume from external volume). But since we make the transformation (1) in a reversible manner, we have no production of entropy, and we have to compensate for that by supplying the *additional* entropy-quantities dS^i_{ex} to the temperature T_i from the standard reservoir by means of reversible Carnot-cycles. We therefore have

$$dS^i_{prod}(irr) = dS^i_{ex}(rev) \tag{3}$$

Brønsted's work principle applied to the reversible reproduction requires that

$$\sum T_i dS^i_{ex} + \sum_{K \,\neq\, S_{ex}} PdK + dE_{mech}(rev) +$$

$$T_{st}dS_{st}(rev) = 0 \tag{4}$$

When we speak about a reversible reproduction of the irreversible process we must have

$$\sum_{K \,\neq\, S_{ex}} PdK(rev) = \sum_{K \,\neq\, S_{prod}} PdK(irr) \tag{5}$$

and by subtraction of (2) from (4) we obtain

$$dE_{mech}(rev) - dE_{mech}(irr) = T_{st}(dS^{irr}_{st} - dS^{rev}_{st}) \tag{6}$$

The following eqn. must apply

$$dS^{irr}_{st} - dS^{rev}_{st} = \sum dS^i_{ex} = dS^{tot}_{prod} \tag{7}$$

From (6) and (7) we obtain for the loss of mechanical work by performing the same process irreversibly instead of reversibly

$$dE_{mech}(rev) - dE_{mech}(irr) = T_{st} \, dS^{tot}_{prod} \tag{8}$$

Only if T_{st} is equal to the temperature in the system (in case of monothermal systems), is the left hand side of (8) equal to the so-called "loss of work" in Brønsted's terminology. When T_{st} decreases, an increasing amount of the work gained by reversible performance is used again to "elevate" entropy from T_{st} to T_{system}. In the terminology of my previous paper,[3] the sum $\sum T_i \, dS^i_{prod}$ is equal to the loss of a very special *conditioned exergy*, defined by connecting the T_i-positions in the system with large thermostats of the same temperatures allowing the entropy to flow neutrally between system and thermostats.

A special situation arises when T_{st} tends to zero. As seen by eqn. (8) we will not get additional mechanical work out of the system by reversible performance. This is not so strange, as it might appear in the first place. Formally one cannot see the difference between using a certain amount of mechanical work to elevate entropy reversibly from $T_{st} \to 0$ to the local temperature T_i or dissipation of the mechanical work by friction processes at the temperature T_i. The entropy produced at T_i in the latter case is equivalent to the entropy supplied to T_i in the former. A certain manner of mimicking an irreversible process would be to make a reversible reproduction of the process supplying the compensating entropy by dissipating locally the additional mechanical work gained. There will be no difference between the original process and the mimicking process and the work difference (8) has to be zero.

As an example we may consider "simple" heat conduction, which is energetically not so simple as it is usually described in literature.[4] Consider stationary heat conduction in a rod between the temperatures T_2 and T_1 ($T_2 > T_1$). If we move the amount of entropy δS_{trans} reversibly from T to $T + dT$ (dT may be negative) by means of a Carnot cycle, the mechanical work thus locally gained is $- \delta S_{trans} \, dT$. We

now dissipate the work gained at the temperature T (making, e.g., like Count Rumford some canon-boring at the position in question). The produced entropy becomes $\delta S_{\text{prod}} = -\delta S_{\text{trans}}\ dT/T$. In case of stationary heat conduction the produced entropy joins the entropy transported so we get the differential eqn. for the transported entropy through the rod

$$d\delta S_{\text{trans}} = -\delta S_{\text{trans}}\ dT/T \qquad (9)$$

Separating the variables and solving we obtain

$$T_2\delta S_{\text{trans}}(2) = T\delta S_{\text{trans}}(T) = T_1\delta S_{\text{trans}}(1) \qquad (10)$$

A "quantity" named heat $= T\delta S_{\text{trans}}$ seems to flow in a conserved manner from T_2 to T_1. This superficial simplicity has made most thermodynamicists regard "heat" to be the primitive thermal quantity instead of entropy. Heat is, however, in our thermodynamics regarded as a pseudo-quantity. It is only defined in flow systems. Concentration of heat or heat content cannot be defined, whereas entropy is defined both as a stationary and a flowing entity.

LOSS IN ABSOLUTE EXERGY AND ENTROPY PRODUCTION

In Fig. 2 is shown a trajectory in a *thermodynamic phase space* described by an infinitesimal, irreversible process in an *isolated* thermodynamic system from state I (P, K) to state II (P + dP, K + dK). The thermodynamic phase space is here macroscopically defined (in contrast to the one used in statistical thermodynamics). We may imagine a space
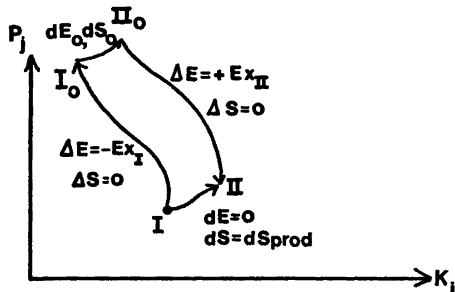

Fig. 2. Trajectory in thermodynamic phase space of an infinitesimal irreversible process and the corresponding energetic zero points.

spanned by orthogonal P- and K-axes for the different localities in our system. When the constraints of the system are known (the constitutive relations) they will not all be necessary, and any sufficient set of P's and K's may be selected to span the phase space. Since the process I→II happens in an isolated system the change in internal energy $dE = 0$ and $dS = dS_{\text{prod}}$.

We now open our system for interaction with an external mechanical reservoir, and extract the exergy from system I, until it reaches its energetic zero point I_0. It should be emphasized that volume in our energetics is a quantity and a definite volume V_{max} should be allocated to the system, and should be included as regions of vacuum from the beginning, if matter is not spread throughout the system. Due to the definition of exergy in the previous paper we have for the change in internal energy and entropy of the system along the path I→I_0: $\Delta E = -Ex_I$ and $\Delta S = 0$. Precisely the same can be said of the path II→II_0, but it is important to notice, that the two energetic zero-points differ infinitesimally, because of the presence of the extra produced entropy in system II. To close the cycle we have therefore to perform the process $I_0 \to II_0$ with $dE = dE_0$ and the entropy change $dS = dS_0$ which has to be supplied by an external thermal reservoir.

Since E and S are functions of state of the system, we get by considering the closed cycle in Fig. 2

$$dS_0 = dS_{\text{prod}} \qquad (11)$$

and

$$Ex_1 - Ex_2 = -dEx = dE_0 \qquad (12)$$

At the energetic zero-point the system occupies its maximum volume V_{max}, and the temperature is everywhere the same (T_0) as are all the transport-complex potentials, such as gravi-electrochemical potentials $\tilde{\mu}_i$. Pressure is not necessarily equalised, for example it varies in a gravity field even at equilibrium. The equalisation of potentials or composed potentials is the case both in I_0, in II_0, and in any point of the curve $I_0 \to II_0$, which may be regarded as intermediary energetic zero-points. The only quantity supplied from outside is entropy, and all the internal quantity transfers, creations

or destructions will be energetically neutral due to the equalisation of potentials or composed potentials. Therefore we have

$$dE_0 = \sum P_0 dK = T_0 dS_0 = T_0 dS_{prod} \qquad (13)$$

Introducing eqn. (13) into eqn. (12) we get the simple, but most important relation for the loss of absolute exergy (for the difference between absolute and relative exergies, see the next section)

$$-dEx = T_0 dS_{prod} \qquad (14)$$

The temperature of the energetic zero-point hides the information on the restricted capacities of the system, which is included in every exergy calculation. The relative nature of the exergy loss is hereby made clear: The lower the temperature of the energetic zero-point the lower the loss of exergy for a given entropy production. In the extreme case, where T_0 approaches zero, no exergy would ever be lost, since the $T dS_{prod}$ may be fully retransformated to mechanical work by reversible transfer of entropy from T to the very small absolute temperature. Also, T_0 depends on what is inside our system, and thus reflects again the non-additivity of exergy discussed in the previous paper.

As a very simple example, consider irreversible "heat" conduction between two identical objects with entropy capacities c independent of temperature. In the previous paper we found the exergy to be

$$Ex = \frac{c}{4}(T_2 - T_1)^2 \qquad (15)$$

We consider $T_2 > T_1$ and connect the two objects with a thin heat conducting rod, in which (quasi) stationarity can be assumed at any time. By eqn. (10) we can express the "degree of advancement" of the irreversible process through the integral quantity $S_{trans}(2)$, which has left the highest temperature. The produced entropy is given by

$$dS_{prod} = dS_{trans}(1) - dS_{trans}(2) =$$
$$\left(\frac{T_2}{T_1} - 1\right) dS_{trans}(2) \qquad (16)$$

The loss of exergy is given by differentiation of (15) and application of the constitutive relations

$$-dEx/dS_{trans}(2) =$$
$$-\frac{c}{2}(T_2 - T_1)\left(\frac{dT_2}{dS_{trans}(2)} - \frac{dT_1}{dS_{trans}(1)}\right)$$
$$\frac{dS_{trans}(1)}{dS_{trans}(2)} = \frac{1}{2}\frac{(T_1 + T_2)}{2}\left(\frac{T_2}{T_1} - 1\right) \qquad (17)$$

Since the temperature of the energetic zero-point is seen to be the arithmetic mean of T_1 and T_2 by symmetry considerations, we have in (16) and (17) a verification of the relation (14). It should be stressed, that T_0 is *not* equal to the end temperature of the irreversible heat conduction process, which will be in the interval $(T_0|T_2)$ due to the greater amount of entropy delivered to the temperature T_1 than removed from the temperature T_2.

As a somewhat more realistic example take two bodies with *heat* capacities C_1 and C_2 independent of the temperatures T_1 and T_2. For the exergy in that case we have by the general method given in the previous paper

$$Ex(T_2, T_1) = C_1 T_1 + C_2 T_2 - T_0 \sum C_i \qquad (18)$$

with the energetic zero-point

$$T_0 = T_1^{C_1/\Sigma C_i} T_2^{C_2/\Sigma C_i} \qquad (19)$$

Doing the analogous differentiation to the one performed in (17) we obtain

$$-dEx/dS_{trans}(2) = T_2\left[\left(\frac{T_2}{T_1}\right)^{C_1/\Sigma C_i} - \left(\frac{T_1}{T_2}\right)^{C_1/\Sigma C_i}\right] \qquad (20)$$

For $dS_{prod}/dS_{trans}(2)$ we still have eqn. (16), and eqn. (14) is now easily seen to be obeyed. The temperature reached in the end by the irreversible process — which we shall call the "heat death point" of the system — is given by

$$T_{Heat\ death} = T_1 + \frac{C_2}{\sum C_i}(T_2 - T_1) =$$
$$T_2 - \frac{C_1}{\sum C_i}(T_2 - T_1) \qquad (21)$$

As an illustration we consider equal amounts of the same substance at 0 and 100 °C with the heat capacity taken to be independent of temperature. In Fig. 3 we have shown the irreversible path in a $T_1 - T_2$ phase space when the two substances are connected by a thin conductor. The trajectory of energetic zero-points is also shown. The two trajectories have to meet in the heat death point of the system.
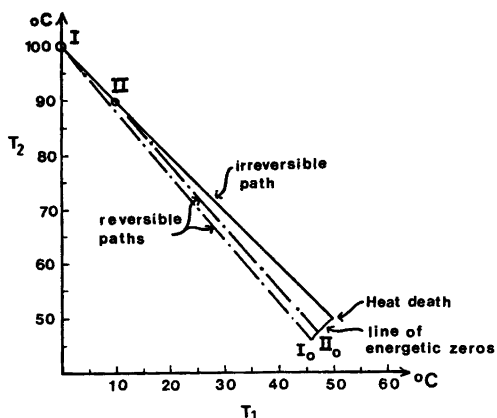
Fig. 3. Heat conduction between equal amounts of the same substance at initial temperatures 0 and 100 °C.

As our last example let us take the irreversible Joule expansion of an ideal gas. Our system consists of an insulated cylinder with piston and volume $V_{max} = 2V$. The n mol of ideal gas are confined in the volume V with the pressure p and the temperature T. We perform an irreversible expansion δV, whereby (experimentally) the temperature remains constant. We have

$$T\delta S_{prod} = p\delta V \tag{22}$$

The absolute exergy before the expansion is found by making a reversible, adiabatic expansion of the gas from V to $V_{max} = 2V$. We obtain

$$T_0(\text{before}) = T \cdot 2^{-R/C_v} \tag{23}$$

and

$$Ex(\text{before}) = nC_v \{T - T_0(\text{before})\} \tag{24}$$

After the expansion δV we have for the energetic zero-point

$$T_0(\text{after}) = T\left(\frac{2V}{(V+\delta V)}\right)^{-R/C_v} =$$
$$T \cdot 2^{-R/C_v}\left[1 + \frac{R}{C_v}\frac{\delta V}{V}\right] \tag{25}$$

The last equation is obtained by Taylor-expansion of the first. Subtracting the exergy after the expansion (given by the analogous equation to (24) for the exergy before, we obtain for the loss of exergy

$$-dEx = nC_v[T_0(\text{after}) - T_0(\text{before})] =$$
$$nRT\frac{\delta V}{V}2^{-R/C_v} = p\delta V \cdot 2^{-R/C_v} \tag{26}$$

and by comparison with (22) and (23) we observe, that eqn. (14) is verified once more. We might have taken our system to include a big thermostat surrounding the cylinder with a temperature T. From the point of view of the irreversible expansion δV, we cannot see any difference, since — as shown by Joule — no entropy is exchanged with the thermostat. The energetic zero-points are very different, however, since they are $(2V,\ T,\ p/2)$ before as well as after the infinitesimal expansion. Eqn. (14) holds for that system as well, and the increase in internal energy of the energetic zero-point of the gas cylinder *plus* the thermostat is exactly $T\delta S_{prod}$ as required by eqn. (13)

RELATIVE EXERGY FOR STATIONARY FLOW SYSTEMS

To join the exergy concept developed here and in the previous paper with the exergy concept already in use in power and refrigeration technology [5] and in irreversible thermodynamics,[6] we consider the stationary flow system visualized in Fig. 4. We shall denote specific quantities (quantities per kg mass) by lower case letters. Thus, w is the useful work (*e.g.* electric power) exported from the system to the surroundings per kg mass passed through the flow system. The corresponding "heat" from the surroundings to the system is denoted q and is given by

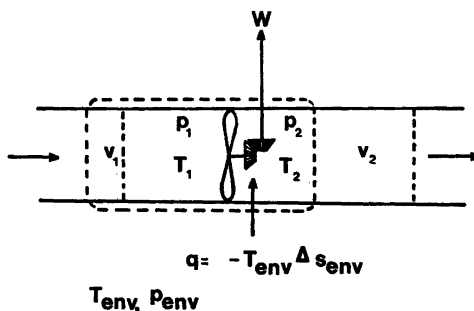$$q = -T_{env}\Delta s_{env} \tag{27}$$

Fig. 4. Generalised Joule-Thomson experiment.

where "env" stands for environment. The system in Fig. 4 is subdivided into three systems: (I) The flowing mass of incoming and outgoing streams + the more or less complex machinery encircled by the broken line. This system follows a specific amount of mass of "fuel" and "smoke" during passage. (II) The surrounding flowing mass. (III) The environments.

We now pass on to energy and entropy balances for the three subsystems in various contexts. For the environment we have for the change in internal energy per kg mass passed

$$\Delta e_{env} = \Delta e_{III} = T_{env} \, \Delta s_{env} + w = -q + w \quad (28)$$

The corresponding change in the surrounding flowing mass is

$$\Delta e_{II} = (-p_1)v_1 - (-p_2)v_2 \quad (29)$$

since the only changes in quantities are the neutral transports of specific volumes between System I and System II. Due to the conservation of energy we have

$$\Delta e_I = e_2 - e_1 = -\Delta e_{II} - \Delta e_{III} = q - w - p_2 v_2 + p_1 v_1 \quad (30)$$

That is — with the usual definition of the enthalpy h — we have

$$w = q - h_2 + h_1 \quad (31)$$

It should be remarked, that in the classical Joule-Thomson experiment, where a real gas is forced through a porous plug, $q = w = 0$ and the process is going on at constant enthalpy.

We shall now carry on a calculation of the specific exergy ex_1 of the incoming stream *relative* to the surrounding temperature T_{env} and pressure p_{env}. We let all the internal processes, *e.g.* chemical reactions, come to equilibrium extracting the maximum work by reversible processes. If the temperature and the pressure in the final state are different from (T_{env}, p_{env}) we move entropy and volume reversibly between the system and the environment until temperature and pressure have been equalized. The outgoing stream is now reduced to a *relative exergy* $ex_2 = 0$ at $T_2 = T_{env}$ and $p_2 = p_{env}$ and the total work delivered $w = ex_1$. This kind of exergy is called relative, since it calls for an arbitrary point of reference

(T_{env}, p_{env}) and since it does not account for the additional exergy which could be extracted by equalizing the chemical potentials in the outgoing stream and in the environment by mass transfer (exergy of chemical pollution of the environment). We obtain (ref. means values taken at T_{env} and p_{env})

$$w = ex_1 = h_1 - h_{ref} + q = h_1 - h_{ref} - T_{env} \, \Delta s_{env} \quad (32)$$

Since

$$\Delta s_I = s_{ref} - s_1 \quad (33)$$

and

$$\Delta s_{II} = 0 \quad (34)$$

and entropy is conserved in reversible processes, we obtain

$$\Delta s_{env} = -(s_{ref} - s_1) \quad (35)$$

and

$$ex_1 = h_1 - h_{ref} + T_{env}(s_{ref} - s_1) \quad (36)$$

In a process where the maximum work is not extracted we have not $ex_2 = 0$ but ex_2 is given by a formula analogous to (36). Thus, generally, we have for the *change* in specific relative exergy

$$-\Delta ex_I = ex_1 - ex_2 = -\Delta h_I + T_{env}\Delta s_I \quad (37)$$

The *loss* of relative exergy is given by

$$\text{Loss of relative exergy} = -\Delta ex_I - w \quad (38)$$

Using (37) for the change in exergy and (31) for the work we obtain

$$\text{Exergy loss} = T_{env}(\Delta s_I + \Delta s_{env}) = T_{env}\Delta s_{prod} \quad (39)$$

This formula is the analogue of the expression (14) for the loss in absolute exergy. The difference is, that while the temperature T_0 in eqn. (14) is endogeneously determined by the finite capacities of the isolated energetic system, the environment reference temperature in (39) is just arbitrarily chosen, and the loss in relative exergy is not the complete loss in absolute exergy in the complete energetic universe, since the "pollution exergy" has not been accounted for.

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