Generalized Non-equilibrium Heat and Work and the Fate of the Clausius Inequality

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Abstract

By generalizing the traditional concept of heat \( dq \) and work \( dw \) to also include their time-dependent irreversible components \( dq_i \) and \( dw_i \) allows us to express them in terms of the instantaneous internal temperature \( T(t) \) and pressure \( P(t) \), whereas the conventional form uses the constant values \( T_0 \) and \( P_0 \) of the medium. This results in an extremely useful formulation of non-equilibrium thermodynamics so that the first law turns into the Gibbs fundamental relation and the Clausius inequality becomes an equality \( \frac{dQ}{T} = dW \) in all cases, a quite remarkable but unexpected result. We determine the irreversible components \( dq_i = dw_i \) and discuss how they can be determined to obtain the generalized \( dw(t) \) and \( dQ(t) \).

Gislason and Craig \[1\] recently remarked that the definition of work in non-equilibrium "...thermodynamics processes remains a contentious topic," a rather surprising statement, as the field of thermodynamics is an old discipline. However, there is some truth to their critique, which was motivated by an earlier paper by Bertrand \[2\], who revisited the confusion first noted by Bauman \[3\] about different formulation of work \( dw = P_0 dV \) or \( dw = P dV \) in terms of internal (\( P \)) and external (\( P_0 \)) pressures \[4\], see Fig. \ref{fig:1} and discussed by many others \[5–10\] since then. Different formulation of work from the first law obviously results in different heat. We refer the reader to these papers for an interesting history of the confusion. Gislason and Craig \[1\] list twenty-six representative textbooks including \[11, 12\] where the pressure-volume work and heat are defined so differently that they are not equivalent in the presence of irreversibility, and there appears to be no consensus about their right formulation so far \[12\ p.181, Vol. 1\]. There is obviously no problem for reversible processes.

The first law of thermodynamics, see for example, Landau and Lifshitz \[14\] or Kondepudi and Prigogine \[15\], relates the change \( dE \) in the internal energy to heat \( dq \) added to and the work \( dw \) done by the system

\[
dE = dq - dw. \tag{1}
\]

It is a very general statement and is supposed to be valid for all processes. We mostly consider mechanical work, but the arguments are valid for all kinds of work; see near the end. Zemansky \[12, p.73\] defines heat as energy exchange "...by virtue of a temperature difference only." Unfortunately, this rules out any isothermal (reversible) heat exchange and cannot be considered general. Kirkwood and Oppenheim define heat as energy exchange resulting in "...the temperature increment..." (which rules out phase changes requiring latent heat) and later note that the work may be converted to heat due to frictional dissipation \[11\ pp.16,17\] as was first observed by Count Rumford in 1798 during the boring of cannon \[13\]. Therefore, it is natural to account for such viscous dissipation in work and heat when dealing with non-equilibrium systems. The fact that literature is not very clear on how to incorporate viscous dissipation has motivated this work; see however \[8, 10\], but the authors do not take the discussion far enough to obtain the results derived here. Our approach to incorporate viscous dissipation results in expressing the first law in terms of internal fields and provides an elegant formulation of non-equilibrium thermodynamics in which the Clausius inequality turns into an equality in all cases, which is a remarkable result in its own right. It has been recently suggested \[9\] that use of internal fields is not always consistent with the second law. We find no such problem in our approach.

We consider our system \( \Sigma \) (see Fig. \ref{fig:1}) surrounded by a very large medium \( \tilde{\Sigma} \) so large that its fields such as its temperature \( T_0 \), pressure \( P_0 \), etc. are not affected by the system. They form an isolated system \( \Sigma_0 \). In the following, all extensive quantities pertaining to \( \Sigma \) and \( \Sigma_0 \) carry an annotation tilde or a suffix 0, respectively, and those pertaining to \( \Sigma \) carry no suffix. Following modern notation \[13, 15\], exchanges with the medium and changes within the system carry the suffix e and i, respectively.

![FIG. 1: Schematic representation of \( \Sigma, \tilde{\Sigma} \) and \( \Sigma_0 \). We assume that \( \Sigma \) and \( \tilde{\Sigma} \) are homogeneous and in internal equilibrium, but not in equilibrium with each other. The internal fields \( T(t), P(t), \cdots \) for \( \Sigma \) and \( T_0, P_0, \cdots \) of \( \tilde{\Sigma} \) are not the same unless they are in equilibrium with each other. There will be viscous dissipation in \( \Sigma \) when not in equilibrium with \( \tilde{\Sigma} \).](image)

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Traditional Formulation of the First Law To truly appreciate our contribution, it is useful to consider how the first law is traditionally expressed. While the change \( dE \) is uniquely defined for any infinitesimal process, the value of \( dQ \) is determined by \( dW \). If \( dW \) cannot be uniquely determined in irreversible processes because of the ambiguity noted above, then \( dQ \) will be ill-defined. Traditionally, \( dQ \) represents the amount of heat exchange done by the system to the surrounding medium, so that \(-dW = d\tilde{V} = P_0 dV\) by the medium to the system, giving \( d_eW = P_0 dV \) since \( d\tilde{V} = -dV \). This is true even if the instantaneous pressure \( P \) of the system is different from \( P_0 \). As the net heat exchange \( d_eQ + d\tilde{Q} = 0 \), we have \( d_eQ = -d\tilde{Q} = -T_0 d\tilde{S} = T_0 d_eS \) in terms of the entropy change \( d_eS \) of the system. In other words,

\[
dE = d_eQ - d_eW = T_0 d_eS - P_0 dV \tag{2}
\]

expressed in terms of either exchange quantities or external fields of \( \Sigma \). This is Protocol 3 of Bertrand \[2\].

However, the situation is not always clear. Kondepudi and Prigogine introduce the work by equating it to \( P dV \), where \( P \), “...is the pressure at the moving surface,” but they do not mention whether the form is applicable to all processes. Landau and Lifshitz are explicit and state that \( dW = P dV \) for reversible and irreversible processes \[14, 57\]. They require for this the existence of mechanical equilibrium (and do so \[11, 12\]) within \( \Sigma \) so that at each instant during the process \( P \) must be uniform throughout the body; its equality with \( P_0 \) is not required. However, they do not discuss \( dQ \) when they consider \( \Sigma \) and \( \tilde{\Sigma} \) out of equilibrium \[11, 57\]. If we use \( dW = P dV \) for the work done by \( \Sigma \) in terms of \( P \) of the system (this is similar to Protocol 4 of Bertrand \[2\]), then this will alter the heat \( dQ \) added to \( \Sigma \) in Eq. \[1\] for \( dE \) must be invariant to the choice of internal or external fields.

To the best of our knowledge, this issue of the actual forms of \( dQ \) in the two protocols and what is the correct form of \( dQ \) for non-equilibrium systems has not been discussed in the literature, even though Kestin \[13\], Sect. 5.12 clearly states that distinguishing heat and work in non-equilibrium states is not unambiguous.

General Consideration and Clausius Relation The first law is not useful for any computation unless we can ascribe temperatures, pressures, etc. to \( \Sigma \) and \( \tilde{\Sigma} \). This is done by taking them to be in internal equilibrium \[14, 17\] so that their instantaneous entropies are state functions \( S(t) = S(E(t), V(t), \cdots) \) and \( \tilde{S}(t) = \tilde{S}(\tilde{E}(t), \tilde{V}(t), \cdots) \) of (time-dependent) state variables. They change as respective state variables \( E(t), V(t), \cdots \) or \( \tilde{E}(t), \tilde{V}(t), \cdots \) change with time. We first only consider energy and volume. The temperatures and pressures are given by appropriate standard derivatives of the entropies; see Eq. \[3\]. It now follows that the Gibbs fundamental relations are given by \[14\]

\[
dE = TdS - PdV, \quad d\tilde{E} = T_0 d\tilde{S} - P_0 d\tilde{V}; \tag{3}
\]

quantities without the suffix 0 normally depend on time. The validity of Eq. \[3\] requires \( \Sigma \) and \( \tilde{\Sigma} \) to be independently homogeneous \[1, 14, 16, 17\]. We have \( dE_0 = dV_0 = 0 \) for \( \Sigma_0 \). The application of the first law gives

\[
dE = dQ - dW, \quad d\tilde{E} = d\tilde{Q} - d\tilde{W}, \quad dE_0 = dQ_0 - dW_0 = 0.
\]

We take \( dQ = d_eQ + d\tilde{Q} \) as a generalization of \( dQ = d_eQ \) in Eq. \[2\]: it denotes the heat added to the system either through exchange with its exterior \( (d_eQ) \) or by dissipative internal forces within \( (d\tilde{Q}) \). Similarly, \( dW = d_eW + d\tilde{W} = P dV \) is the work done by the system on its exterior \( (d_eW) \) and by dissipative internal forces \( (d\tilde{W}) \). A somewhat similar looking approach, but different in spirit, is taken in \[18\].

To make our approach computationally useful, we need to determine \( dQ \) and \( dW \); see later. With our generalization, \( dQ_0 \equiv d_eQ_0 \) and \( dW_0 \equiv d_eW_0 \) and \( dQ_0 \equiv d\tilde{Q}_0 \) and \( dW_0 \equiv d\tilde{W}_0 \) for \( \Sigma_0 \). Let us assume that \( P > P_0 \). The (internal) work done by the pressure difference \( \Delta P = P - P_0 > 0 \) is \( dW_0 = \Delta P dV > 0 \), since \( dV > 0 \). This results in raising the kinetic energy \( dK_S \) of the center-of-mass of the surface separating \( \Sigma \) and \( \tilde{\Sigma} \) and overcoming work \( dW_i \) done by all sorts of viscous or frictional drag. Thus,

\[
dW_0 = d\tilde{W}_0 \equiv dK_S + dW_i.
\]

Because of the stochasticity associated with any statistical system, both energies on the right side dissipate among the particles so as to increase the entropy and appear in the form of heat \( (= d_iQ_0 > 0) \) within the isolated system. This is the generalized heat \( dQ_0 > 0 \), since \( d_iQ_0 = 0 \) for \( \Sigma_0 \). It is normal to associate all irreversible components in \( \Sigma_0 \) with \( \Sigma \) \( (d_iQ \equiv d_iQ_0, d_iW \equiv d_iW_0) \) and not with the (extensively large) medium \( \tilde{\Sigma} \), which always remain in internal equilibrium \[17\]; compare with the situation of finite surroundings considered by Bizarro \[8\]. Thus, when there are irreversible processes going on, it is natural to generalize heat from \( d_iQ \) in Eq. \[2\] to include the irreversible heat \( d_iQ \) and identify \( dQ \) as the heat added to the system. Similarly, we need to generalize work from \( d_iW = P_0 dV \) to \( dW = P dV \) and identify it as work done by the system. Remarkably, we find that

\[
d_iQ \equiv d_iW. \tag{4}
\]

The generalization does not change \( dE \) and we have

\[
dE = d_eQ - d_eW \equiv dQ - dW = dQ - P dV. \tag{5}
\]

However, the most important result is that \[17\]

\[
dQ = TdS, \tag{6}
\]

even when the system is not in equilibrium with the medium. This is easily seen by comparing Eq. \[5\] with...
the Gibbs fundamental relation in Eq. (3). This makes \( dQ/T \) an exact differential \( dS \) so that
\[
\int dQ/T \equiv 0 \quad \text{for any cyclic process.} \tag{7}
\]
This leads to
\[
\oint dQ/T = -\oint d_s Q/T \geq 0, \tag{8}
\]
which is consistent with the traditional Clausius inequality \( \oint dQ/T \leq 0 \). Thus, the Clausius equality in Eq. (7) should not be interpreted as the absence of irreversibility, as it is clear from the above inequality. It is only because of the use of the generalized heat \( dQ \) that this inequality has become an equality. The second integral with its sign in Eq. (8) can be thought of as the uncompensated transformation \( N \) \([3]\). Our formulation has allowed us to identify it with the first integral
\[
N \equiv \oint dQ/T = \oint d_s W_0/T, \tag{9}
\]
which provides a way of computing \( N \) using equations of state of \( \Sigma \) and \( \Sigma \). From \( d_s S = dS - d_e S \), we find that
\[
\oint d_s S = -\oint d_e Q/T_0 \geq 0,
\]
which is the second law for a cyclic process and represents the irreversible entropy generated in a cycle; recall that \( d_s Q \) is the traditional \( dQ \) in Eq. (2).

**General Form of Work** Let us follow the consequences of this particular extension a bit further and prove that only \( dW = PdV \) is consistent with the second law. Since \( dQ_0 = dQ + d\tilde{Q} = dW_0 = dW + d\tilde{W} \geq 0 \), we find that the net heat \( dQ_0 \) in the medium and the system need not vanish, in contrast to what happens in equilibrium:
\[
dQ + d\tilde{Q} = dW_0 \geq 0 \tag{10}\]
because of viscous dissipation \( d_s Q_0 \equiv d_s W_0 \), and is related to the irreversible entropy generation within \( \Sigma_0 \) or \( \Sigma \), as we will see later. For frictional forces only \((P = P_0)\) which are included in our approach \([19]\), the above relation reduces to Eq. (7) of Bizarro \([8]\). From
\[
dW + d\tilde{W} = PdV + P_0d\tilde{V}
\]
valid for any arbitrary \( dV \), it follows that
\[
dW = PdV, \quad \tilde{W} = P_0d\tilde{V}, \tag{11}
\]
which proves the above assertion. The alternate choice \( dW = P_0dV \) and \( d\tilde{W} = Pd\tilde{V} \) employed in the traditional formulation, see Eq. (2), will violate the second law as the choice will lead to negative heat dissipation \( dQ_0 = dW_0 = (P_0 - P)dV < 0 \), a physical impossibility. Thus, we must write the first law for the system and the medium, respectively, as
\[
dE = dQ - PdV, \quad \tilde{E} = d\tilde{Q} - P_0d\tilde{V}. \tag{12}
\]

The above demonstration establishes that the work is given by Eq. (11) in terms of the instantaneous pressure in all cases contrary to the traditional wisdom, see Eq. (2), that it is given by \( P_0dV \). The generalized formulation brings out a symmetry in the form of \( dW \) and \( d\tilde{W} \) under the interchange system\( \leftrightarrow \)medium: the work for any body is always uses its own internal pressure. This symmetry is absent in the traditional formalism in which both terms are given by the external pressure \( P_0 \).

**Benefits of the Generalized Formulation** The new formulation has many other desirable properties. For example, the entire thermodynamics and stability considerations for any body can be expressed in terms of the variables associated with the body alone at each instant. We can use the equations of state of the body alone for thermodynamic computation. The first law is no longer different from the Gibbs fundamental relation so we only deal with equalities and not inequalities. The generalized heat \( dQ \) and work \( dW \) differ from \( d_s Q \) and \( d_s W \), respectively, by the same contribution \( d_s W \equiv d_s W_0 \); the latter is the term \( dS_\Sigma \) in Eq. (19) of Eq. (20), which can be absorbed in his work term \((= -d_s W \) in our notation) to reduce this equation to the above form for \( dE \). The determination of \( d_s W_0 \) is straightforward by measuring \( P \) and \( P_0 \). Adding this to \( dQ \) then allows us to determine \( dQ \). Consider, as an example, the case when the medium pressure \( P_0 = 0 \) such as when a gas expands in vacuum. In this case, \( d_s W = 0 \); \( dW \) is the irreversible work, which cannot be less than zero, as it is given by the irreversible entropy generation as shown below.

**Irreversible entropy generation in an isothermal process** We now give an alternative derivation of Eq. (11) by computing the irreversible entropy gain so that the role of the latter can be clearly seen in an irreversible process. A brief discussion of this issue can be found in Kondepudi and Prigogine \([12]\, pp. 94-95\) where they discuss irreversible expansion of a gas; see also \([17]\). We will assume that the temperature of the system and the medium is constant during the process at \( T_0 \). The pressure difference gives rise to dissipation, which results in an irreversible heat generation \( d_s Q = T_0d_s S \) in addition to the heat \( d_e Q = -d\tilde{Q} = -T_0d\tilde{S} = T_0d_e S \) received from the medium; here, \( d_s S = d_s S^{(V)} \) is the irreversible entropy gain \([15, 17]\)
\[
d_s S^{(V)} = (P - P_0)dV/T_0 \geq 0.
\]
We see that \( dQ = T_0(d_e S + d_s S) = T_0dS \) in accordance with Eq. (10) so that by including \( d_s Q \) in \( dQ \) relates \( dQ \) to the entropy change \( dS \). The generalized first law for the medium in Eq. (12) reads \( dE = T_0d\tilde{S} - P_0d\tilde{V} \), in which we can replace \( d\tilde{V} \) by \(-dV \) and \( d\tilde{E} \) by \(-dE \) to obtain \( dE = -d\tilde{Q} - P_0dV \). We compare this with the right side of Eq. (11) for the system and use the fact that
\[
dQ + d\tilde{Q} = d_s Q_0 = d_s Q
\]
to determine the work \( dW \). Simple algebra immediately leads to \( dW = PdV \), as claimed above. We also note that we do not need Jarzynski result [9] to obtain \( d_i S^{(V)} \).

General Irreversible Process We now consider the same process as above, except that the temperature \( T \) of the system is also allowed to be different from that of the medium, which we take to be the constant \( T_0 \). The general relation in Eq. (4) is still valid. However, \( d_i S \) consists of \( d_i S^{(V)} \) and \( d_i S^{(Q)} \) or \( d_i S^{(S)} \); the former is given above and the latter contribution is given by

\[
d_i S^{(Q)} = \left( \frac{1}{T-1} - \frac{1}{T_0} \right) dQ = -(T-T_0) dS/T_0 = d_i S^{(S)} \geq 0.
\]

We immediately find that \( d_i S^{(Q)} \) and \( d_i S^{(V)} \) are formally of the same form; see [17]. To be convinced of the form of \( d_i S^{(Q)} \equiv d_i S^{(S)} \), we start with the identity

\[
d_i Q - P_0 dV \equiv T dS - P dV
\]

which can be transformed into

\[
d_0 dS = (T_0 - T) dS + (P_0 - P) dV.
\]

We can now identify the above two components of \( d_i S \). To obtain \( d_i S^{(Q)} \), we use Eq. (6) to replace \( dS \). Both irreversible components are non-negative as expected from the second law. We thus see that expressing the first law in terms of internal fields is consistent with irreversible entropy production, contrary to a recent claim [9].

Both irreversible entropy gains can be easily determined. The determination requires measuring the two temperatures and pressures, while the determination of \( dQ \) has already been explained. Thus, the generalized formulation creates no additional problem in experimentally determining various quantities.

Inclusion of other state variables Let us now extend the discussion to include other extensive quantities such as the flow of matter, the electric interactions, chemical reactions, etc. For specificity, we focus on chemical reactions, which we assume to be described by a single extent of reaction \( \xi \). The corresponding affinity for the system is given by \( A \), while that for the medium is given by \( A_0 = 0 \). We assume another observable \( X \) such as the number of solvent in a binary mixture. The corresponding chemical potential is \( \mu \) for the system and \( \mu_0 \) for the medium. The work is now

\[
dW = PdV - \mu dX + Ad\xi[21].
\]

The Gibbs fundamental relation for \( \Sigma \) is given by

\[
dE = T dS - P dV + \mu dX - Ad\xi,
\]

while the first law for it takes the form

\[
de = dQ - P dV + \mu dX - Ad\xi.
\]

Comparing the two we find that Eq. (6) still holds so that the validity of Eq. (7) is not affected by the presence of other variables in the first law [19]. Rewriting

\[
dQ = dE + P dV - \mu dX + Ad\xi \quad dQ = dE + P dV - \mu_0 dX + (P - P_0) dV - (\mu - \mu_0) dX + Ad\xi,
\]

we can identify \( d_i Q \) with the first three terms in which \( d_i W = P dV - \mu dX \) for work of all types [21]. Similarly, \( d_i Q = d_i W \equiv dW_0 \) represents the last three terms \( (P - P_0) dV - (\mu - \mu_0) dX + Ad\xi \); see Eq. (4). We again obtain the general results in Eq. (6), as expected. According to the second law, each contribution in \( d_i W \) is non-negative. The extension to arbitrary number of observables and internal variables is trivial [19].

In summary, we have shown that the definition of the generalized heat \( dQ \), which includes its irreversible component \( d_i Q \), follows uniquely from the unique choice of \( dW \) resulting from the second law; see Eq. (11). It includes its irreversible component \( d_i W \equiv d_i Q \); see Eq. (4). Another remarkable consequence is that in terms of generalized \( dQ \), the Clausius equality (7) is always maintained, in contrast to the inequality (8) in the traditional approach. Our generalized formulation brings about a symmetry between the system and its surrounding medium, see Eq. (11), which is absent in the traditional approach using external fields. The first law becomes identical with the Gibbs fundamental relation so that we only deal with equalities that are easier to deal with than the inequalities in the traditional approach.

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[1] E.A. Gislason and N.C. Craig, J. Chem. Educ. 84, 499-508 (2007).
[2] G.L. Bertrand, J. Chem. Educ. 82, 874-877 (2005).
[3] R.P. Bauman, J. Chem. Educ. 41, 102-104, 675, 676-677 (1964).
[4] The internal fields such as internal pressure or internal temperature refer to the fields inside a homogeneous system. The internal pressure should not be confused with the concept of the internal pressure used in the theory of cohesive energy; see for example A.A. Smith and P.D. Gujrati, Eur. Polym. J., 43, 425 (2007).
[5] D. Kivelson and I Oppenheim, J. Chem. Educ. 43, 233-235 (1966).
[6] E.A. Gislason and N.C. Craig, J. Chem. Thermodynamics. 37, 954-966 (2005).
[7] D. Ben-Amotz and J.M. Honig, Phys. Rev. Lett. 96, 020602 (2006).
[8] J.P.S. Bizarro, J. Appl. Phys., 82, 054907 (2010).
[9] J. Anacleto, M.G. Pereira, and N. J. Gonçalves, Rev. Bras. Ensino Fís. 32, 2304 (2010).
[10] J. Anacleto, M.G. Pereira, and J.M. Ferreira, Eur. J. Phys. 32, 37 (2011).
[11] J.G. Kirkwood and I. Oppenheim, Chemical Thermodynamics, McGraw-Hill, New York, 1961.
[12] M.W. Zemansky, Heat and Thermodynamics, 5th edition, McGraw-Hill Book Company, New York (1979).
[13] J. Kestin, A e in Thermodynamics, McGraw-Hill Book Company, New York (1979).
[14] L.D. Landau, E.M. Lifshitz, Statistical Physics, Vol. 1, Third Edition, Pergamon Press, Oxford (1986).
[15] D. Kondepudi and I. Prigogine, Modern Thermodynamics, John Wiley and Sons, West Sussex (1998).
[16] S.R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics, First Edition, Dover, New York (1984).
[17] P.D. Gujrati, Phys. Rev. E 81, 051130 (2010).
[18] D. Ben-Amotz and J.M. Honig, J. Chem. Phys. 118, 5932 (2003).
[19] P.D. Gujrati, arXiv:1101.0438
[20] B.C. Eu, Chem. Phys. Lett. 143, 65 (1988).
[21] R.A. Alberty, Pure Appl. Chem. 73, 1349 (2001).