Irreversible Exchange of Heat and Mass across Narrow Boundaries Under Specified Conditions

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Abstract

We extend here a set of earlier articles that deal with irreversible processes across a thin boundary separating a system from its surroundings. We consider the transfer of heat and material when the system and reservoir are held at constant volume, and the temperatures (T) and chemical potentials (μ) differ by arbitrary amounts in the two parts of the compound system. Three distinct time variations for changing temperature and composition in the system are adopted. Although for any specified change of state the entropies associated with the transfer of heat and matter are quite different in the three cases, the overall entropy change remains the same, as is consistent with entropy being a function of state. The relation of the present approach to standard methodology is discussed.

Keywords: irreversible thermodynamics, transfer of heat and material across a thin boundary, entropy changes, time-dependent transfer mechanisms

1. Background Information

The extension of thermostatic to irreversible processes, nowadays termed extended thermodynamics, has been the subject of intensive research over roughly one century. A recurrent problem in the theoretical treatment has been the specification of temperature, as well as pressure, and entropy, under nonequilibrium conditions – a subject area that has been accorded a review on its own (Jou, Casas-Vázquez, & Lebon, 1999). We merely draw attention to several discussions of the subject (Kaufmann, Muschik, & Schirrmeister, 1996; Lebon, Jou, & Casas-Vázquez, 1996; Jou, Casas-Vázquez, & Lebon, 2001) which indicate the complexities involved in such a task. Among other matters, there is no unique formulation for the specification of temperature under nonequilibrium conditions which depends on the particular irreversible phenomenon under investigation. Nevertheless, a study of several special cases (Evans 1989; Jou & Casas-Vázquez, 1992; Fort, 1997; Jou, Casas-Vázquez, & Lebon, 2010) indicates that the difference between the equilibration temperature and its dynamical analog, at least as it pertains to the flow of heat, tends to be small, generally much less than 10 %.

In these circumstances it seemed appropriate to ignore the difference between static and dynamic temperatures and to concentrate on the investigation of the transfer of heat, work, and matter across a boundary separating a system from its surroundings under conditions where the two portions are at different temperatures, volumes, and chemical potentials. The situation is depicted in Figure 1 by a temperature (T) profile that remains constant in the two parts of the system, but changes abruptly across the thin intervening boundary; a similar profile obtains for the pressure (P), and chemical potential (μ).

Figure 1. Sketch of a temperature profile for the combined system and reservoir at different temperatures T and T_0. The temperature develops over only a small region l at the interface

The standard analysis of the problem involves setting up linear phenomenological equations that relate fluxes and generalized forces, and imposing steady state conditions to identify the phenomenological coefficients. Here we proceed along different lines, based on a didactic article (Honig, 2011), that generalizes the standard thermodynamic functions of state, by including the contribution to the entropy arising from the irreversible transfers of heat, work, and material under the conditions represented in Figure 1. The processes occurring across the boundaries are characterized by specifying how the relevant control variables vary with time (t), and then integrating to find the total entropy change over the entire time interval. The principal drawback of this procedure is the assumption that changes in T, P, and μ occur uniformly within the system except very close to the boundary. By convention, all processes within the reservoir will take place reversibly, and in such a manner that its intensive variables remain constant. For such a situation to be approximated experimentally one could work with a system that is either very tiny, and/or by assuming that all processes within the system are subject to a very fast relaxation rate. Alternatively, one may conceive of many reservoirs surrounding the system and acting in concert.

The subsequent analysis hinges on the differential of the path-dependent entropy change $đ\theta$ that tracks the difference in entropy S when the same element of a given process in the system is carried out irreversibly as opposed to reversibly. The corresponding entropy changes of the reservoir are designated by d_bS_0 and by d_aS_0 respectively; thus,

$$d_bS_0 \ - \ d_aS_0 = \ đ\theta, \tag{1}$$

Here we may set $d_aS_0 = - dS(T,V,n)$, so that Eq. (1) reads

$$dS(T,V,n) \ + \ dS_0(T_0,V_0,n_0) = \ đ\theta. \tag{2}$$

We now set up the differential equations for energy for the system and surroundings, as applicable to reversible processes; variables for the surroundings carry the subscript 0.

$$dE(S,V,n) = TdS - PdV + \mu dn; \quad dE_0(S_0,V_0,n_0) = T_0dS_0 - P_0dV_0 + \mu_0dn_0. \tag{3}$$

However, since E and E_0 are functions of state we may reconstitute the above so as to apply to irreversible processes, by substituting for dS_0 from Eq. (2). We next invoke energy conservation for the compound system by setting $dE + dE_0 = 0$, impose volume conservation by setting $dV + dV_0 = 0$, and conservation of material by setting $dn + dn_0 = 0$. Lastly, we introduce the functional dependence of the entropy of the system by setting $dS = (\partial S / \partial T)dT + (\partial S / \partial V)dV + (\partial S / \partial n)dn$. This leads to the fundamental relation derived earlier by using a different approach (Honig, 2011) :

$$T_0đ\theta \ = \ (T_0 - T)\left[(C_V/T)dT + (\partial P/\partial T) \, dV + \ \hat{S} \, dn\right] \ - \ (P_0 - P)dV \ + (\mu_0 - \mu)dn, \tag{4}$$

where C_V is the heat capacity at constant volume, the appropriate Maxwell relation has been invoked, $\hat{S}_i \equiv (\partial S / \partial n)_{T,V}$ is the differential entropy, and all other symbols retain their conventional significance.

In what follows we now assume special operating conditions in which the individual volumes are held fixed, leaving

$$đ\theta \ = \ (1 - T/T_0)\left[(C_V/T)dT\right] + \ \left[\ (1 - T/T_0)\,\hat{S} \ + (\mu_0/T_0)\,(1 - \mu/\mu_0)\right]dn. \tag{5}$$

With T, V, and n as control variables, the relevant function of state is the Helmholtz free energy, for which $\hat{A} \equiv \mu = \hat{E} - T\hat{S}$. Eq. (5) may then be rewritten in the form

$$đ\theta \ = đ\theta_T + đ\theta_n = \ (1 - T/T_0)\left[(C_V/T)dT\right] + \left[\ \hat{S} + \mu_0/T_0 \ - \ \hat{E}/T_0\right]dn, \tag{6}$$

where $\hat{E} \equiv (\partial E / \partial n)_{T,V}$ is the differential energy.

For definiteness we adopt the Berthetelot gas as a working substance in both parts of the compound unit; the equation of state for the system is specified by

$$P(T,V,n) = nRT/V + n^2RTb/V^2 - n^2a/V^2T, \tag{7}$$

where a and b are materials-specific parameters. The energy derivative with respect to volume is then found from the caloric equation of state as

$$(\partial E/\partial V) \ = \ T(\partial P/\partial T) - P = 2n^2a/V^2T, \tag{8}$$

which may be integrated to yield

$$E(T,V,n) = E(T_i,V,n_i) + 3nRT/2 - 2n^2a/VT; \quad C_V = 3nR/2 + 2n^2a/VT^2;$$
$$\hat{E} = \hat{E}(T_i,V,n_i) + 3RT/2 - 4na/VT. \tag{9}$$

The entropy of the system (at constant volume) at temperature T relative to the initial temperature T_i is specified via

$$S(T,V,n) = \int (C_V/T)dT = (3nR/2)\ln(T/T_i) - (n^2a/V)(1/T^2 - 1/T_i^2) + S(T_i,V,n_i), \tag{10}$$

where $E(T_i,V,n_i)$, $S(T_i,V,n_i)$ are the energy and entropy at initial temperature T_i and mole number n_i, while the energy and entropy are to be evaluated at a temperature T and mole number n. Then

$$\hat{S}(T,V,n) = (3R/2)\ln(T/T_i) - (2na/V)(1/T^2 - 1/T_i^2) + \hat{S}(T_i,V,n_i)). \tag{11}$$

With Eqs. (6) and (9) the entropy contribution associated with the temperature variation is given by

$$\theta_T = \int (3nR/2T)dT - \int (3nR/2T_0)dT + \int (2n^2a/VT^3)dT - \int (2n^2a/VT^2T_0)dT. \tag{12}$$

The contribution associated with the transfer of matter is specified via the second bracketed term in Eq. (6) as

$$\Theta_n = \int \left[\frac{3R}{2} \ln \frac{T}{T_i} - \frac{3RT}{2T_0} - \frac{2na}{V}\left(\frac{1}{T^2} - \frac{1}{T_i^2} - \frac{2}{TT_0} \right) + \frac{\mu_0}{T_0} - \frac{\hat{E}}{T_0}(T_i,V,n_i) + \hat{S}(T_i,V,n_i) \right] dn. \tag{13}$$

This completes the specification of the fundamentals. In what follows we shall temporarily ignore the contributions arising from $\mu_0/T_0 - \hat{E}(T_i,V,n_i)/T_0 + \hat{S}(T_i,V,n_i)$, which remain unchanged in the operations outlined in the next section.

2. Specification of Entropy

To determine the contributions of irreversible processes to the entropy of the combined unit we selected three different paths, by introducing time t ($0 \le t \le \tau$) as a parameter and adopting three types of time dependence. We assume that $T_i \le T \le T_f \le T_0$; $n_i \le n \le n_f \le n_0$.

2.1 Case 1

We set $T = T_i \exp(k_T t)$, $T_f/T_i = \exp(k_T \tau)$, $n = n_i \exp(k_n t)$, $n_f/n_i = \exp(k_n \tau)$, $k_T/k_n = \ln(T_f/T_i)/\ln(n_f/n_i)$.

Insertion of these relations into Eq. (12) and carrying out the required integrations is a tedious but straightforward process and leads to the following contribution to the entropy arising from the transfer of heat associated with the temperature change:

$$\theta_{1T} = \theta_{1Ta} + \theta_{1Tb} + \theta_{1Tc} + \theta_{1Td}, \tag{14}$$

where the first two terms on the right apply to the ideal gas case (via the first two terms in Eq. (12)), and the second set involves the additional corrections arising from the Berthelot equation of state. We find that

$$\theta_{1Ta} \equiv \frac{3R}{2}\frac{k_T}{k_n}\left(n_f - n_i\right); \quad \theta_{1Tb} \equiv -\frac{3R}{2T_o}\frac{k_T/k_n}{1+k_T/k_n}\left(n_f T_f - n_i T_i\right);$$
$$\theta_{1Tc} \equiv \frac{a}{V}\frac{k_T/k_n}{1-k_T/k_n}\left[\frac{n_f^2}{T_f^2} - \frac{n_i^2}{T_i^2}\right]; \quad \theta_{1Td} \equiv -\frac{2a}{VT_0}\frac{k_T/k_n}{2-k_T/k_n}\left[\frac{n_f^2}{T_f} - \frac{n_i^2}{T_i}\right]. \tag{15}$$

Similarly, on applying this case to Eq. (13), corresponding to the transfer of matter, we obtain

$$\theta_{1n} = \theta_{1na} + \theta_{1nb} + \theta_{1nc} + \theta_{1nd}, \tag{16}$$

where the first two terms relate to the contribution involving terms in $1/T_0$ (excepting $\hat{E}/T_0$), as specified by

$$\theta_{1na} = -\frac{3R}{2T_0}\frac{1}{1+k_T/k_n}\left(T_f n_f - T_i n_i\right); \quad \theta_{1nb} = \frac{4a}{VT_0}\frac{1}{2-k_T/k_n}\left(\frac{n_f^{\,2}}{T_f} - \frac{n_i^{\,2}}{T_i}\right), \tag{17}$$

and the remaining terms read

$$\theta_{1nc} = \frac{3R}{2}\frac{k_T}{k_n}\left(n_f\ln\frac{n_f}{n_i} + (n_i - n_f)\right); \quad \theta_{1nd} = -\frac{a}{V}\left[\left(\frac{k_T/k_n}{1-k_t/k_n}\right)\left(\frac{n_f^2}{T_f^2} - \frac{n_i^2}{T_i^2}\right) + \frac{n_f^2}{T_i^2} - \frac{n_i^2}{T_i^2}\right]. \tag{18}$$

2.2. Case 2

We set $T = T_i\exp(k_T t)$, $\quad T_f/T_i = \exp(k_T\tau)$, $\quad n = n_i(1+k_n t)$, $\quad n_f/n_i = 1+k_n\tau$, $\quad k_T/k_n = \ln(T_f/T_i)/(n_f/n_i - 1)$.

Proceeding as before, for the contribution to the entropy from the temperature difference we write

$$\theta_{2T} = \theta_{2Ta} + \theta_{2Tb} + \theta_{2Tc} + \theta_{2Td}, \tag{19}$$

where the first two terms involve the ideal gas contribution, and the others, the Berthelot portion. We obtain from Eq. (12)

$$\theta_{2Ta} \equiv \frac{3R}{4}\ln\frac{T_f}{T_i}\left[n_f + n_i\right]; \quad \theta_{2Tb} = -\frac{3RT_i}{2T_0}n_i\left\{\left(1-\frac{k_n}{k_T}\right)\left(\frac{T_f}{T_i}-1\right) + \frac{k_n}{k_T}\left(\frac{T_f}{T_i}\ln\frac{T_f}{T_i}\right)\right\};$$

$$\theta_{2Tc} \equiv \frac{a}{V}n_i^2\left\{\begin{array}{l}-\left(\dfrac{1}{T_f^{\,2}} - \dfrac{1}{T_i^{\,2}}\right) + \left(\dfrac{k_n}{k_T}\right)\left[\dfrac{1}{T_f^{\,2}}\ln\dfrac{T_i^2}{T_f^2} - \left(\dfrac{1}{T_f^{\,2}} - \dfrac{1}{T_i^{\,2}}\right)\right] \\[12pt] -\left[\left(\dfrac{n_f}{n_i}-1\right)^2\dfrac{1}{T_f^{\,2}} - \dfrac{1}{2}\left(\dfrac{k_n}{k_T}\right)^2\left[\dfrac{1}{T_f^{\,2}}\ln\dfrac{T_i^2}{T_f^2} - \left(\dfrac{1}{T_f^{\,2}} - \dfrac{1}{T_i^{\,2}}\right)\right]\right]\end{array}\right\}. \tag{20}$$

$$\theta_{2Td} \equiv \frac{2a}{VT_0}n_i^2\left\{\begin{array}{l}-\left(\dfrac{1}{T_f} - \dfrac{1}{T_i}\right) + 2\left(\dfrac{k_n}{k_T}\right)\left[\dfrac{1}{T_f}\ln\dfrac{T_i}{T_f} - \left(\dfrac{1}{T_f} - \dfrac{1}{T_i}\right)\right] \\[12pt] +\left(\dfrac{n_f}{n_i}-1\right)^2\ln\dfrac{T_i^2}{T_f^2} - 2\left(\dfrac{k_n}{k_T}\right)^2\left[\dfrac{1}{T_f}\ln\dfrac{T_i}{T_f} - \left(\dfrac{1}{T_f} - \dfrac{1}{T_i}\right)\right]\end{array}\right\}.$$

As regards the transfer of matter as specified by Eq. (13), we find that

$$\theta_{2n} = \theta_{2na} + \theta_{2nb} + \theta_{2nc} + \theta_{2nd}, \tag{21}$$

where the first two terms relate to the contribution involving terms in $1/T_0$ (excepting $\hat{E}/T_0$), as specified by

$$\theta_{2na} = -\frac{3R}{2T_0}n_i\frac{k_n}{k_T}(T_f - T_i); \quad \theta_{2nb} = \frac{4an_i^2}{V}\left[-\frac{k_n}{T_0 k_T}\left(\frac{1}{T_f} - \frac{1}{T_i}\right) + \frac{1}{T_i^2}\left(\frac{k_n}{k_T}\right)^2\left(\frac{T_f}{T_i}\ln\frac{T_f}{T_i} - \frac{T_f}{T_i} + 1\right)\right] \tag{22}$$

and the remaining terms read

$$\theta_{2nc} = \frac{3R}{4}\left(\ln\frac{T_f}{T_i}\right)(n_f - n_i) \tag{23}$$

$$\theta_{2nd} = \frac{an_i^2}{V}\left\{\left[\frac{k_n}{k_T}\left(\frac{1}{T_f^2} - \frac{1}{T_i^2}\right)\right] - \left[\frac{1}{2}\left(\frac{k_n}{k_T}\right)^2\left(\frac{1}{T_f^2}\ln\frac{T_i^2}{T_f^2} - \frac{1}{T_f^2} + \frac{1}{T_i^2}\right)\right] + \frac{1}{n_i^2}\left(\frac{n_f^2}{T_i^2} - \frac{n_i^2}{T_i^2}\right)\right\}.$$

2.3. Case 3

Set $T = T_i(1 + k_T t)$, $\quad T_f/T_i = (1 + k_T\tau)$, $\quad n = n_i(1 + k_n t)$, $\quad n_f/n_i = 1 + k_n\tau$, $\quad k_T/k_n = (T_f/T_i - 1)/(n_f/n_i - 1)$.

For this case the integrals associated with the Berthelot corrections become extremely unwieldy. We therefore opted to examine only the contributions associated with the ideal gas. Proceeding as before we find that

$$\theta_{3T}^{ig} = \frac{-3R}{4T_0}(n_f - n_i)(T_f - T_i) \ . \tag{24}$$

$$\theta_{3n}^{ig} = \frac{3R}{2}\left[n_i \frac{k_T}{k_n} \ln \frac{T_f}{T_i} + (n_f - n_i) \ln \frac{T_f}{T_i} - (n_f - n_i) \right]. \tag{25}$$

3. Discussion

We call attention to an important point that was also encountered in earlier treatments of other irreversible phenomena (Hoehn & Honig, 2011; Honig & Hoehn, 2011): Even though the θ_T and θ_n contributions to the total entropy are vastly different for the three cases treated above, the sum of these two terms is invariant, which is in consonance with the requirement that entropy be a function of state. We find that in all cases the entropy production for an ideal gas is given by

$$\theta^{ig} = \frac{3R}{2} n_f \ln \frac{T_f}{T_i} - \frac{3R}{2T_0}\left(n_f T_f - n_i T_i\right). \tag{26}$$

If we include the Berthelot corrections we obtain

$$\theta = \frac{3R}{2} n_f \ln \frac{T_f}{T_i} - \frac{3R}{2T_0}\left(n_f T_f - n_i T_i\right) + \frac{a}{V}n_f^2\left(\frac{1}{T_i^2} - \frac{1}{T_f^2}\right) + \frac{2a}{VT_0}\left(\frac{n_f^2}{T_f} - \frac{n_i^2}{T_i}\right). \tag{27}$$

One must, however, not forget to take account of the contributions that have been neglected, namely

$$\theta_n^0 = \left[\mu_0/T_0 - \frac{\hat{E}}{T_0}(T_i,V,n_i) + \hat{S}(T_i,V,n_i) \right](n_f - n_i). \tag{28}$$

On the right hand side we determined the chemical potential via $\mu_0 = \hat{E}_0 - T_0\hat{S}_0$, where $\hat{E}_0, T_0\hat{S}_0$ were specified by replacing T, V, n in Eqs. (9) and (11) with T_0, V_0, n_0 respectively; the terms in the initial configuration T_i, V, n_i cancel against identical terms contained in μ_0/T_0, because the material in the system and the reservoir is the same. Since the latter remains at constant temperature T_0 (and the volume remains fixed as well) only the change in mole number enters in the derivation. We obtain

$$\theta_n^0 = \left\{\left[\frac{3}{2}R - \frac{3}{2}R\ln\frac{T_0}{T_i}\right] - a(c_{0f} + c_{0i})\left[\frac{1}{T_0^2} + \frac{1}{T_i^2}\right]\right\}(n_f - n_i), \tag{29}$$

where $c_0 \equiv n_0/V_0$ is the concentration of gas in the reservoir.

This completes the specification of the entropy change under the assumed condition for the exchange of heat and transfer of matter.

4. Relation to Standard Methodology

The present approach has its antecedent in early work (Bejan, 1997; Honig, 2008; Jarzynski, 1997; Kestin, 1996; Tolman & Fine, 1948), who dealt with special aspects, as reviewed by Honig (2011). Earlier work along the present line of approach may be found in Ben Amotz and Honig (2006a; 2006b), Honig and Ben Amotz (2005; 2008), Hoehn and Honig (2011) and Honig and Hoehn (2011).

It is also of interest to relate the above methodology to standard procedures (de Groot & Mazur, 1962; Gyarmati, 1970; Haase, 1990; Kondepudi & Prigogine, 1998; Meixner, 1954; Mueller & Ruggeri, 1993; Prigogine, 1967) for treating irreversible processes in discontinuous systems such as depicted in Figure 1. In this latter approach these authors focused attention on identifying the prevailing forces and fluxes for particular situations and then

invoking a linear response of the various forces or fluxes to their the conjugate variables. This engenders the standard linear phenomenological equations subject to the Onsager reciprocity conditions. These relations are then solved under a variety of assumed steady state conditions, so as to analyze thermomolecular and mechanocaloric effects. In the present procedure emphasis is placed on investigating irreversible processes in discontinuous system whose path is specified by a predetermined time variation, which precludes the establishment of steady state conditions. It is nevertheless possible to link the current approach to standard methodology. Toward that end we reformulate Eq. (4) under constant volume conditions as

$$T_0 \, d\theta = (-\Delta T)\cdot\left(\frac{\partial S}{\partial T}\right)_{V,n} dT - \Delta T \cdot \left(\frac{\partial S}{\partial n}\right)_{T,V} dn - \Delta\mu \cdot dn. \tag{30}$$

Now take derivatives with respect to time for an infinitesimal step, to write

$$T_0 \, d\theta = -\Delta T \cdot \left(\frac{\partial S}{\partial T}\right)_{V,n} \frac{dT}{dt} - \Delta T \cdot \left(\frac{\partial S}{\partial n}\right)_{T,V} \frac{dn}{dt} - \Delta\mu \cdot \frac{dn}{dt} = -(\Delta T)\left[\left(\frac{\partial S}{\partial t}\right)_{V,n} + \left(\frac{\partial S}{\partial t}\right)_{T,V}\right] - \Delta\mu \cdot \frac{dn}{dt}. \tag{31}$$

Now introduce the entropy density, ϑ, where for a junction of cross section A and length l

$$d\dot\vartheta = (1/T_0)\left[-\frac{\Delta T}{l}\cdot\frac{1}{A}\left\{\left(\frac{\partial S}{\partial t}\right)_{V,n} + \left(\frac{\partial S}{\partial t}\right)_{T,V}\right\} - \frac{\Delta\mu}{l}\cdot\frac{1}{A}\frac{dn}{dt}\right]. \tag{32}$$

In the limit of a very thin junction, and on adopting the standard formulation for entropy flux J_S and particle flux, J_n, we obtain (∇ is the gradient operator)

$$d\dot\vartheta = \frac{1}{T_0}\left[-\nabla T \cdot J_S - \nabla\mu \cdot J_n\right]. \tag{33}$$

This expression is the standard formulation for the entropy density flux in terms of the conjugate force-flux pairs. Thus, the present formulation is seen to be a variant of the ordinary treatment of irreversible thermodynamics procedure, and is therefore subject to the extremum and variational principles and Hamilton's principle, as discussed by Gyarmati (1970).

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