



IRREVERSIBLE TRANSFER OF HEAT, WORK, AND MATTER ACROSS THIN BOUNDARIES

Elizabeth Duselis^[a] and Jurgen Honig^{[a]*}

Keywords: Irreversible Processes, Transfer Across Boundaries, Entropy of Irreversible Transfers, Quasistatic Irreversible Processes

Here we extend a set of earlier articles that dealt with time-dependent irreversible processes across a thin boundary separating a system from its surroundings. The entropy change for irreversible transfers of heat, work, and matter in this compound system is examined for a one component condensed phase for which temperature, pressure, and mole numbers are the control variables. The required fundamental relations are collected and evaluated to generate an expression for the entropy change in terms of experimentally determinable variables. Contributions to the entropy change from heat exchange, work performance, and material transfer are evaluated for two distinct time-dependent paths. While contributions from each element differ for the two cases, the sum of all three elements remains identical for both time variations, as is consistent with entropy being a function of state. The net entropy change upon irreversibly cycling is also assessed.

Corresponding Author
Tel: + 765 494 5279
Fax: +765 494 0239
E-Mail: jmh@purdue.edu
[a] Department of Chemistry
Purdue University
560 Oval Drive
West Lafayette, IN
47907-2084

Introduction

The study of irreversible processes in terms of thermodynamic variables¹⁻⁷ generally involves identifying the relevant fluxes and forces, setting up the corresponding linear phenomenological equations, and imposing steady state conditions to identify the transport coefficient. This method has been broadened over the last 25 years via the so-called extended thermodynamics approach⁸⁻¹¹ that permit handling greater departures from equilibrium. One of the problems in this latter treatment is the definition under nonequilibrium conditions of intensive variables such as temperature, pressure, or chemical potential, and the specification of the ordinary functions of state, such as energy and entropy, well away from equilibrium.

We base the present paper on earlier work¹²⁻¹⁹ in which we attempt to treat the contribution of heat exchange, work performance, and material transfers to entropy changes in irreversible processes relative to those executed reversibly. In setting up the requisite theory we note that in the extended thermodynamics method so far investigated²⁰⁻²⁴ the temperature θ appropriate for characterizing irreversible processes differed from the equilibrium temperature T by no more than 10%, and that the difference was frequently considerably smaller.

Accordingly, in the present approach we introduce the use of intensive variables appropriate to equilibrium configurations, while investigating significant departures

from equilibrium. Here that method is applied to a one-component system in the condensed state.

The system under study consists of a system at temperature T , pressure P , and chemical potential μ which is connected via a thin, porous, moveable boundary layer to an enormous reservoir – also called surroundings – whose intensive variables are specified by T_0 , P_0 , and μ_0 . The setup is shown in Fig. 1 with a superimposed temperature profile, which is uniform over virtually the entire extension of both the system and the reservoir, and which changes abruptly over the length of the junction. A similar profile obtains for pressure and chemical potential. For this situation to be applicable, our study is restricted to *quasistatic irreversible processes* (QSIPs): these are assumed to occur at a rate that permits the use of intensive variables which change *uniformly* with time t . In accord with standard convention, all processes within the reservoir are assumed to take place reversibly, while T_0 , P_0 , and μ_0 remain constant. To approach such conditions experimentally, the reservoir must be huge in extension, and one must deal with systems that are very thin in extension and/or for which the relaxation time for establishing equilibrium is exceedingly short; alternatively, one must surround small, separated regions of the entire system by their own reservoirs acting in concert.

Fundamentals

In the current study the control variables are temperature T , pressure P , and mole number n . Consider now an infinitesimal step in a process involving these variables. Let $d\theta$ represent the path-dependent differential change in entropy S when this step is carried out irreversibly (designated as $d_b S_0$) as compared to reversibly (designate as $d_a S_0$). Then

$$d\theta = d_b S_0 - d_a S_0. \quad (1)$$

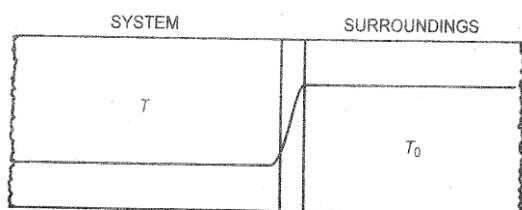


Fig. 1. Temperature Profile Across a Thin Junction Separating a System from its Surroundings in the QSIP Mode of Operation

For the reversible operation we may set $d_a S_0 = -dS(T, P, n)$, so that Eq. (1) reads

$$dS(T, P, n) + dS_0(T_0, P_0, n_0) = d\theta \quad (2)$$

We now set up the differential equations for the energy of the system and surroundings, as applicable to reversible processes:

$$dE(S, V, n) = TdS - PdV + \mu dn \quad (3a)$$

$$T_0 d\theta = (T - T_0) \left[\frac{C_P}{T} dT - \alpha V dP + \tilde{S} dn \right] - (P_0 - P) [\alpha V dT - \beta P dP + \tilde{V} dn] + (\mu_0 - \mu) dn \quad (5)$$

where quantities with the tilde represent the partial molal entropy and volume. Eq. (5) is the fundamental relation derived earlier by a different approach¹⁶.

We now introduce the requisite equation of state for condensed matter, in which higher order terms are omitted:

$$\tilde{V} = \tilde{V}(T, P) = \tilde{V}_a \left[1 + \alpha(T - T_i) - \beta(P - P_i) \right] \quad (6)$$

where $\tilde{V}_a \equiv \tilde{V}(T_i, P_i)$. Here \tilde{V}_a is the molar volume at some specified initial pressure P_i and temperature T_i common to the system and the reservoir. However, to simplify the subsequent operations we adopt the truncated form

$$\tilde{V}(T_i, P_i) = \tilde{V}_a (1 + \alpha T - \beta P), \quad (7)$$

which is permissible since we will show that only the first order terms in $\alpha \tilde{V}_a$ and $\beta \tilde{V}_a$ are encountered in the final results. When Eq. (7) is used in Eq. (5) we may specify $d\theta$ as a sum of three terms:

$$d\theta = d\theta_T + d\theta_P + d\theta_n, \quad (8)$$

where

$$d\theta_T = \left[\left(1 - \frac{T}{T_0} \right) \frac{n \tilde{C}_P}{T} - \frac{P_0}{T_0} \left(1 - \frac{P}{P_0} \right) \alpha n \tilde{V}_a \right] dT \quad (9)$$

$$d\theta_P = \left[\frac{P_0}{T_0} \left(1 - \frac{P}{P_0} \right) \beta n \tilde{V}_a - \left(1 - \frac{T}{T_0} \right) \alpha n \tilde{V}_a \right] dP \quad (10)$$

$$d\theta_n = \frac{1}{T_0} \left[\tilde{T}_0 (\tilde{S} - \tilde{S}_0) + (\tilde{H}_0 - \tilde{H}) - (P_0 - P) \tilde{V} \right] dn \quad (11)$$

$$dE_0(S_0, V_0, n_0) = T_0 dS_0 - P_0 dV_0 + \mu_0 dn_0 \quad (3b)$$

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 $dn + dn_0 = 0$. Then for a sequence of elementary steps we write

$$dS = (\partial S / \partial T) dT + (\partial S / \partial P) dP + (\partial S / \partial n) dn \quad (4a)$$

$$dV = (\partial V / \partial T) dT + (\partial V / \partial P) dP + (\partial V / \partial n) dn, \quad (4b)$$

and introduce the standard Maxwell relation, the heat capacity under constant pressure, C_P , the isobaric coefficient of expansion α , and isothermal coefficient of compression β of the material to obtain by addition of the two energy differentials in Eq. (2) the result

The last equation requires elaboration. We need to determine the molar entropy and enthalpy for the system on the assumption that they are independent of mole number n . Integration of Eq. (4a) from the initial temperature and pressure to any intermediate temperature and pressure yields:

$$\tilde{S}(T, P) = \tilde{S}(T_i, P_i) + \int_{T_i, P_i}^{T, P} \frac{\tilde{C}_P}{T} dT - \int_{T_i, P_i}^{T, P} \alpha \tilde{V}_a dP \quad (12a)$$

$$\tilde{S}(T, P) = \tilde{S}(T_i, P_i) + \tilde{C}_P \ln \frac{T}{T_i} - \alpha \tilde{V}_a (P - P_i) \quad (12b)$$

The same relations obtain for the molar entropy of the reservoir, by replacing T and P with T_0 and P_0 respectively.

The molar enthalpy is found by utilizing Eq. (7) and the caloric equation of state:

$$\left(\frac{\partial \tilde{H}}{\partial P} \right)_T = \tilde{V} - T \left(\frac{\partial \tilde{V}}{\partial T} \right)_P = \tilde{V}_a (1 - \beta P) \quad (13)$$

which yields the integrated form:

$$\tilde{H}(T, P) = \tilde{H}(T_i, P_i) + \tilde{V}_a P - \frac{1}{2} \beta \tilde{V}_a P^2 + F(T) \quad (14)$$

where $F(T)$ is an arbitrary function of temperature, which is found by setting $\tilde{H}(0, T) = 3RT$ for a monatomic solid with no internal degrees of freedom, which is maintained at intermediate temperatures. When this approximation is inserted back into (14), we obtain:

$$\tilde{H}(T, P) = \tilde{H}(T_i, P_i) + \tilde{V}_a P - \frac{1}{2} \beta \tilde{V}_a P^2 + 3RT \quad (15)$$

The same relation can be used for \tilde{H}_0 by replacing P and T with P_0 and T_0 , respectively. Clearly, for later use, the above approximation restricts us to a rather narrow temperature range. When we insert $S(T, P)$, $S_0(T_0, P_0)$, $\tilde{H}(T, P)$, and $\tilde{H}_0(T_0, P_0)$ into (11), we obtain:

$$d\theta_n = \left[3R \left(1 + \ln \frac{T}{T_0} - \frac{T}{T_0} \right) + \alpha \tilde{V}_a (P_0 - P) \left(1 - \frac{T}{T_0} \right) - \frac{\beta \tilde{V}_a}{2T_0} (P_0 - P)^2 \right] dn \quad (16)$$

Eqs. (9), (10), and (16) form the basis of all subsequent operations.

Special cases

To obtain the entropy associated with the above approach we must integrate Eq. (8). For this purpose, we specify two distinct irreversible processes that involve: heat exchange

while the temperature of the system evolves, execution of work during changes in pressure exerted on the system, and the transfer of matter across the boundary. To that end we introduce the time t as a parameter and set $T = T(t)$, $P = P(t)$, and $n = n(t)$, while keeping the corresponding intensive variables of the reservoir fixed. We then integrate Eqs. (9), (10), and (16) for a time interval $0 \leq t \leq \tau$ within which the system goes from initial temperature T_i , pressure P_i , and mole number n_i to final values T_f , P_f , and n_f . For definiteness we assume that $T < T_0$, $P < P_0$, and $n < n_0$, and we also set $dT = (dT/dt)dt$, $dP = (dP/dt)dt$, and $dn = (dn/dt)dt$. The resulting integrations are straightforward but tedious.

Case 1

Let $T(t) = T_i e^{k_T t}$, $P(t) = P_i e^{k_P t}$, and $n(t) = n_i e^{k_n t}$,

$T_f = T_i e^{k_T \tau}$, $P_f = P_i e^{k_P \tau}$, $n_f = n_i e^{k_n \tau}$, where k_T , k_P , and k_n are constants such that $(k_P/k_n) = \ln(P_f/P_i)/\ln(n_f/n_i)$, and $(k_P/k_T) = \ln(P_f/P_i)/\ln(T_f/T_i)$, and $(k_T/k_n) = \ln(T_f/T_i)/\ln(n_f/n_i)$. Integration of (9), (10), and (16) yields, respectively:

$$\theta_T = 3R \left[\frac{k_T}{k_n} (n_f - n_i) - \frac{1}{T_0} \left(\frac{1}{1 + k_n/k_T} \right) (n_f T_f - n_i T_i) \right] - \alpha \tilde{V}_a \left[\frac{P_0}{T_0} \left(\frac{1}{1 + k_n/k_T} \right) (n_f T_f - n_i T_i) - \frac{1}{T_0} \left(\frac{1}{1 + (k_n + k_P)/k_T} \right) (n_f T_f P_f - n_i T_i P_i) \right] \quad (17)$$

$$\theta_P = \beta \tilde{V}_a \left[\frac{P_0}{T_0} \left(\frac{1}{1 + k_n/k_P} \right) (n_f P_f - n_i P_i) - \frac{1}{T_0} \left(\frac{1}{2 + k_n/k_P} \right) (n_f P_f^2 - n_i P_i^2) \right] + \alpha \tilde{V}_a \left[\frac{1}{T_0} \left(\frac{1}{1 + (k_n + k_T)/k_P} \right) (n_f T_f P_f - n_i T_i P_i) - \left(\frac{1}{1 + k_n/k_P} \right) (n_f P_f - n_i P_i) \right] \quad (18)$$

Case 2

Case 2 differs from case 1 by the pressure and mole number dependence on time. Let $T(t) = T_i e^{k_T t}$, as before,

$P(t) = P_i(1 + k_P t)$, and $n(t) = n_i(1 + k_n t)$, so that $(k_T/k_n) = \ln(T_f/T_i)/(n_f/n_i - 1)$, $(k_T/k_P) = \ln(T_f/T_i)/(P_f/P_i - 1)$, $(k_T/k_n) = (P_f/P_i - 1)/(n_f/n_i - 1)$. Eqs. (20), (21), and (22) are found in the same manner as for case 1:

$$\begin{aligned} \theta_n = & 3R \left[(n_f - n_i) \left(\ln \frac{T_i}{T_0} + 1 \right) + \frac{k_T}{k_n} \left(n_f \ln \frac{n_f}{n_i} - (n_f - n_i) \right) - \frac{1}{T_0} \left(\frac{1}{1 + k_T/k_n} \right) (n_f T_f - n_i T_i) \right] \\ & + \beta \tilde{V}_a \left[\frac{P_0}{T_0} \left(\frac{1}{1 + k_P/k_n} \right) (n_f P_f - n_i P_i) - \frac{2}{T_0} \left(\frac{1}{2k_P/k_n + 1} \right) (n_f P_f^2 - n_i P_i^2) - \frac{P_0^2}{2T_0} (n_f - n_i) \right] \\ & - \alpha \tilde{V}_a \left[\left(\frac{1}{1 + k_P/k_n} \right) (n_f P_f - n_i P_i) + \frac{P_0}{T_0} \left(\frac{1}{1 + k_T/k_n} \right) (n_f T_f - n_i T_i) - \frac{1}{T_0} \left(\frac{1}{1 + (k_n + k_P)/k_T} \right) (n_f T_f P_f - n_i T_i P_i) + P_0 (n_f - n_i) \right] \end{aligned} \quad (19)$$

$$\begin{aligned} \theta_T = & \frac{3R}{2} \left\{ \ln \frac{T_f}{T_i} (n_f + n_i) - \frac{2}{T_0} n_i \left[(T_f - T_i) + \frac{k_n}{k_T} \left(T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \right] \right\} \\ & - \alpha \tilde{V}_a \left\{ \frac{P_0}{T_0} n_i \left[(T_f - T_i) + \frac{k_n}{k_T} \left(T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \right] \right. \\ & \left. - \frac{1}{T_0} n_i P_i \left[\left(T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \left(\frac{k_P + k_n}{k_T} \right) + (T_f - T_i) + \frac{2k_P k_n}{k_T^2} \left(\frac{1}{2} T_f \ln^2 \frac{T_f}{T_i} - T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \right] \right\} \end{aligned} \quad (20)$$

$$\begin{aligned} \theta_P = & -\beta \tilde{V}_a \frac{(P_f - P_i)}{T_0} \left\{ -\frac{P_0}{2} (n_f - n_i) + \frac{1}{3} \left[n_i P_i + n_f P_f + \frac{1}{2} (n_i P_f + n_f P_i) \right] \right\} \\ & + \alpha \tilde{V}_a \left\{ \frac{1}{2} (P_f - P_i) (n_f - n_i) + \frac{1}{T_0} n_i P_i \frac{k_P}{k_T} \left[(T_f - T_i) + \frac{k_n}{k_T} \left(T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \right] \right\} \end{aligned} \quad (21)$$

$$\begin{aligned} \theta_n = & 3R \left\{ (n_f - n_i) \left[1 + \ln \frac{T_i}{T_0} + \frac{1}{2} \ln \frac{T_f}{T_i} \right] - \frac{1}{T_0} \frac{k_n}{k_T} n_i (T_f - T_i) \right\} + \beta \tilde{V}_a \left\{ \frac{(n_f - n_i)}{2T_0} \left[P_0 (P_f + P_i - P_0) - \frac{1}{3} (P_f^2 + P_f P_i + P_i^2) \right] \right\} \\ & - \alpha \tilde{V}_a \left\{ \frac{P_0}{T_0} \frac{k_n}{k_T} n_i (T_f - T_i) - \frac{1}{2} (P_f + P_i) (n_f - n_i) + \frac{1}{T_0} \frac{k_n}{k_T} n_i P_i \left[(T_f - T_i) + \frac{k_P}{k_T} \left(T_f \ln \frac{T_f}{T_i} - (T_f - T_i) \right) \right] + P_0 (n_f - n_i) \right\} \end{aligned} \quad (22)$$

Despite the considerable differences encountered in the two cases, the total entropy change associated with (8),

upon eliminating k_n/k_P , k_n/k_T , and k_P/k_T ratios, leads to exactly the same grand total result:

$$\begin{aligned} \theta = & 3R \left[n_f \ln \frac{T_f}{T_0} - n_i \ln \frac{T_0}{T_i} + (n_f - n_i) + \frac{1}{T_0} (n_f T_f - n_i T_i) \right] \\ & - \beta \tilde{V}_a \left[\frac{1}{2T_0} (n_f P_f^2 - n_i P_i^2) + \frac{P_0^2}{2T_0} (n_f - n_i) - \frac{P_0}{T_0} (n_f P_f - n_i P_i) \right] \\ & - \alpha \tilde{V}_a \left[\frac{P_0}{T_0} (n_f T_f - n_i T_i) + (n_f P_f - n_i P_i) - \frac{1}{T_0} (n_f T_f P_f - n_i T_i P_i) - P_0 (n_f - n_i) \right] \end{aligned} \quad (23)$$

The pathway in which the system went from initial to final configuration across the boundary was not specified in the approximation. Thus, when we initially defined the two cases, we set up ratios for T_f/T_i , P_f/P_i , and n_f/n_i , which required k_T , k_P , k_n , and τ to change to fit the specified ratios. What (17), (18), and (19) and (20), (21), and (22) do is to show the differences in the contributions to the overall entropy from the heat evolution, execution of work due to pressure changes, and matter transfers across the boundary.

However, the individual contributions in the two cases sum to the same final result; this is consistent with entropy being a function of state.

The Cyclic Process

So far we have considered variations of temperature, pressure, and chemical potential only in one direction.

Also of interest is a cyclic process in which the intensive variables of the system are changed in the order $T_i \rightarrow T_f \rightarrow T_i$, $P_i \rightarrow P_f \rightarrow P_i$, and $n_i \rightarrow n_f \rightarrow n_i$.

Discussion

$$\begin{aligned} \theta = 3R & \left[n_f \left(\ln \frac{T_f}{T_0} + \ln \frac{T_f}{T_1} \right) + n_i \left(\ln \frac{T_i}{T_0} + \ln \frac{T_i}{T_1} \right) - (n_i T_i - n_f T_f) \left(\frac{1}{T_0} - \frac{1}{T_1} \right) \right] \\ & + \frac{\beta \tilde{V}_a}{2} \left[(n_f P_f^2 - n_i P_i^2) \left(\frac{1}{T_0} - \frac{1}{T_1} \right) + 2(n_f P_f - n_i P_i) \left(\frac{P_0}{T_0} - \frac{P_1}{T_1} \right) + (n_f - n_i) \left(\frac{P_1^2}{T_1} - \frac{P_0^2}{T_0} \right) \right] \\ & + \alpha \tilde{V}_a \left[(n_i T_i - n_f T_f) \left(\frac{P_0}{T_0} - \frac{P_1}{T_1} \right) + (n_f T_f P_f - n_i T_i P_i) \left(\frac{1}{T_0} - \frac{1}{T_1} \right) + (n_f - n_i) (P_0 - P_1) \right] \end{aligned} \quad (24)$$

Close examination of Eq. (23) shows the following: In accord with past experience^{14,19} this end result is independent of the time protocol that had been selected. Mathematically this is related to the fact that the right hand side of Eq. (1) involves a difference in two functions of state. The present analysis shows, however, how the individual contributions θ_T , θ_P , and θ_n depend on the selected time dependence of the control variables.

One should note that the quantity \tilde{V}_a does not appear in the above relation; only the first order terms $\alpha \tilde{V}_a$ and $\beta \tilde{V}_a$ are encountered in Eqs. (23) and (24). Going back to Eq. (10), this implies that changes of pressure exert only a secondary effect on the properties of the system. Effectively, in zero order, the material is incompressible. It is for this reason that Eq. (7) rather than (6) could be used in the derivations.

The leading term in Eq. (23) is of the form

$$\theta = 3R \left\{ n_f \left[\ln \frac{T_f}{T_0} - \frac{T_f}{T_0} \right] - n_i \left[\ln \frac{T_i}{T_0} - \frac{T_i}{T_0} \right] + (n_f - n_i) \right\}$$

Eur. Chem. Bull. **2012**, (6), 175-180

DOI: 10.17628/ECB.2012.1.175

To accomplish this, we attach the system to another reservoir at temperature T_1 , pressure P_1 , and mole number n_1 , in which $T_1 < T_i$, $P_1 < P_i$, and $n_1 < n_i$.

While the system interacts with reservoir 0, reservoir 1 remains sealed off, and vice versa. The interaction with the reservoir for the return process is handled by reversing the indices i and f and replacing subscript 0 by subscript 1 in (23). When this newly generated expression is added to (23), one obtains for the cyclic process:

(25)

When there is no transfer of material, $n_f = n_i \equiv n$, the above reduces to

$$\theta = 3Rn \left(\ln \frac{T_f}{T_i} - \frac{T_f}{T_0} + \frac{T_i}{T_0} \right). \quad (26)$$

Numerical calculations reveal that for ratios $T_f/T_i \leq 2$ (with $T_i < T_f$) the above quantity is positive. If additionally there is no temperature difference between the reservoir and the system, $\theta = 0$.

This is reasonable, given the fact that when T and P are uniform throughout the compound system, the transfer of essentially incompressible material incurs no changes in entropy (in the approximation of Eq. (7)). In the range $T_f/T_i > 2$ the calculations involving (25) and (26) become increasingly unreliable, which indicates that the

approximation $\tilde{C}_p = 3R$, adopted earlier, has failed, as was is to be expected. One may extend the present approach by adopting the Debye theory for the heat capacity of monatomic solids to replace the current approximation.

It is instructive to note how Eqs. (23) and (24) differ. The cyclic process refers only to what goes on in the system. In actuality, heat, work, and material are transferred from the reservoir at temperature T_0 to the one at temperature T_1 . This is reflected in the difference between the leading terms in the two equations.

The first order terms may all be grouped into contributions $\alpha\tilde{V}_a$ and $\beta\tilde{V}_a$ associated with the thermal expansion and compressibility of the condensed phase respectively. These terms are small relative to the leading expressions that involve the gas constant R .

If desired, one may determine $d_b S_0 = -dS + d\theta$, using Eqs. (4), (9), (10), and (16) to determine the entropy change of the reservoir in response to the irreversible processes occurring in the system.

Conclusions

In conclusion, we have considered the transfer of heat, work, and mass across a thin junction separating a system from the reservoir under conditions where the intensive variables in the two portions of the combined unit are different. The principal restriction of the study of the irreversible processes is the adoption of QSIPs, so that the intensive variables still retain their meaning even under nonequilibrium conditions. The resulting changes in state were studied by using time t as a parameter to characterize the processes. As anticipated, in the two cases studied, the entropy change is independent of the time protocol involved; the same should hold true for any other chosen time protocol. However, the individual contribution to the total entropy, i.e., the contributions due to heat flow, work exchange, and mass transfer do depend on the chosen path.

References

- ¹Bejan, A., *Advanced Engineering Thermodynamics*, 2nd edition, p.135, Wiley, New York, **1997**.
- ²de Groot, S. R., Mazur, P., *Non-Equilibrium Thermodynamics*. North Holland, Amsterdam, **1962**.
- ³Gyarmati, I., *Non-equilibrium Thermodynamics*, Field Theory, and Variational Principles, Springer Verlag, New York, **1970**.
- ⁴Haase, R., *Thermodynamics of Irreversible Processes*, Dover, New York, **1990**.

- ⁵Kondepudi, D., Prigogine, I., *Modern Thermodynamics, from Heat Engines to Dissipative Structures*, Chaps. 15-17, Wiley, Chichester, **1998**.
- ⁶Meixner, J., *Thermodynamik der Irreversiblen Prozesse*, Meixner, Aachen, Germany, **1954**.
- ⁷Prigogine, I., *Introduction to Thermodynamics of Irreversible Processes*, Wiley, New York, **1967**.
- ⁸Jou, D., Casas-Vázquez, J., Lebon, G., *Extended Irreversible Thermodynamics*, 4th edition, Chap. 3, Springer Verlag, Berlin, **2010**.
- ⁹Jou, D., Casas-Vázquez, J., Lebon, G. Extended thermodynamics revisited (1988-1998), *Rep. Progr. Phys.* **1999**, 62, 1052.
- ¹⁰Lebon, G., Jou, D., Casas-Vázquez, J., in *Entropy and Entropy Generation*, Shiner J. S., Ed., 37-45, Kluwer Academic, Dordrecht **1996**.
- ¹¹Mueller, I., Ruggeri, T., *Extended Thermodynamics*, Springer Verlag, New York, **1993**.
- ¹²Ben Amotz, D., Honig, J. M., *J. Phys. Chem. B*, **2006**, 110, 19966.
- ¹³Ben Amotz, D., Honig J. M., *Phys. Rev. Lett.*, **2006**, 96, 020602/1-4.
- ¹⁴Hoehn, R., Honig J. M. *Acta Phys. Polon. A*, **2011**, 119, 323.
- ¹⁵Honig, J. M. *Thermodynamics, Principles Characterizing Chemical and Physical Processes*, 3rd edition, Chapter 6, Academic Press, Amsterdam, **2008**.
- ¹⁶Honig, J. M., *Appl. Phys. Res.*, **2011**, 3, 3.
- ¹⁷Honig, J. M., Ben Amotz, D., *J. Chem. Educ.*, **2005**, 83, 132.
- ¹⁸Honig, J. M., Ben Amotz, D., *Chem. Educator*, **2008**, 13, 220.
- ¹⁹Honig, J. M., Hoehn, R., *Open J. Chem. Eng.*, **2011**, 5, 1.
- ²⁰Evans, D. J., *J. Stat. Phys.* **1989**, 57, 745.
- ²¹Fort, J., *Physica A*, 1997, 243, 275.
- ²²Jou, D., Casas-Vázquez, J., *Phys. Rev. A*, **1992**, 45, 8371.
- ²³Kaufmann, M., Muschik, W., Schirrmester, D., in *Entropy and Entropy Generation*, Shiner, J., S., Ed., Chap 1, Kluwer Academic, Dordrecht, **1996**.
- ²⁴Jou, D., Cimmelli, V. A., Sellitto, A., *J. Non-equil. Thermodyn.*, **2011**, 36, 373.

Received: 11.09.2012.

Accepted: 25.09.2012.