The Open Chemical Engineering Journal, **2011**, *5*, **1-6**

Entropy of Irreversible Processes Across a Boundary

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Abstract: A novel method for determining the entropy associated with irreversible processes has been provided, differing from the conventional theory of irreversible thermodynamics. It permits the direct relation of heat and work transfers in irreversible processes to those in reversible changes, in terms of measurable properties. The same technique is applied to the construction of thermodynamic state functions that are no longer limited to reversible phenomena. The results are then used to construct line integrals for the contribution of irreversible processes to the entropy associated with the flow of heat, work, and matter across a junction. Specific examples are provided to illustrate the procedure; they relate to changes of temperature and volume and to cycling of systems interacting with a reservoir *via* a thin barrier.

Keywords: Irreversible process/phenomenon, irreversible function of state, quasistatic irreversible processes.

INTRODUCTION

The proper formulation of entropy changes during irreversible processes has been the subject of numerous investigations ever since the formulation of entropy as a function of state. It nevertheless seems appropriate to introduce an unconventional methodology through detailed calculations involving the irreversible exchange of heat and work for a system interacting with a reservoir through a thin intervening barrier. This problem is also of intrinsic interest. For this purpose we first derive fundamental information that is somewhat scattered in the literature, in which the commonly used inequalities in the second law are replaced with equalities. We then apply these concepts to determine the increase in entropy during the irreversible processes in the above-mentioned compound system. Several conclusions of interest are drawn. The present article represents an extension of earlier work in this area [1-5].

At the outset we introduce two basic assumptions. The object under study is an isolated compound unit consisting of a system anchored to its surroundings as sketched in Fig. (**1**), which shows the temperature profile in both parts of the unit. Corresponding profiles exist for the pressure and the chemical potentials. Processes in both sections are presumed to occur sufficiently slowly that one may assign uniform values T_0, P_0, μ_0 to the temperature, pressure, and chemical potential over almost all the region in the surroundings, and corresponding values T, P, μ over most of the region within the system. The changeover between the two sets of intensive variables is thus limited to a thin boundary region consisting of a poor thermal conductor imbedded in a slowly moving piston that also permits a slow diffusion of matter across its interface. The present situation is thus the exact opposite of the irreversible processes considered in the standard theory of irreversible thermodynamics, where T, P, and μ are locally functions of position within the system, and thereby relate to the flow of heat, work, and matter through the system as a whole. By contrast, in the present case attention is directed to the transfer of these entities across an interface.

The second restriction involves the commonly employed assumption that all processes in the surroundings (reservoirs) take place reversibly, whether the processes in the system occur reversibly or not. In the absence of this assumption the analysis becomes far more complex. Procedures carried out subject to the above qualifications are termed *Quasistatic Irreversible Processes* (QSIPs).

BASICS

To set up the fundamental expressions, consider an infinitesimal step in an interactive process - involving the system and the reservoir - that is carried out reversibly (r) and irreversibly (i). Since the entropy, S, is a function of state, the infinitesimal change dS of the system is the same for both processes. However, the entropy change of the reservoir differs in the two cases, which we designate as $dS_0^{(a)}$ and $dS_0^{(b)}$, respectively. Since entropy is conserved in the reversible operation, we set

$$dS + dS_0^{(a)} = 0 \tag{1a}$$

On the other hand, when executing the same process irreversibly, the entropy of the compound system can only increase, so that

$$dS + dS_0^{(b)} > 0 \tag{1b}$$

It is now apposite to introduce an *entropy deficit function* $\text{đ}\theta > 0$ which converts Eq. (1b) into an equality:

$$dS + dS_0^{(b)} - \text{đ}\theta = 0 \tag{1c}$$

While this may appear to be simply a bookkeeping operation it has important implications: a trivial rearrangement of the above equation leads to

$$dS_u \equiv dS + dS_0^{(b)} = \text{đ}\theta \tag{1d}$$

where S_u represents the entropy of the universe, here the compound system. Eq. (1d) shows that the deficit function is equivalent to the entropy increase of the universe resulting from the execution of any (infinitesimal) irreversible proc-

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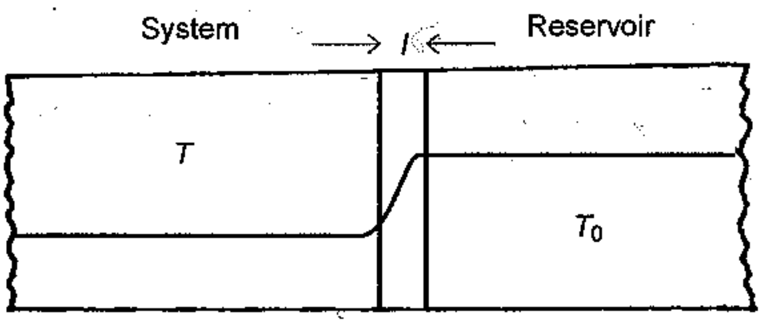

Fig. (1). Sketch of a temperature profile for the combined system and resererervoir at different temperatures T and T_0. The temperature in each phase remains essentially constant over almost the entire region; the gradient in temperature develops over only a small region l at the interface.

ess. Note that dS represents the differential entropy change for the system characterized by intensive variables which differ from those which relate to the surroundings.

We now set $dS = \text{đ}_r Q/T$ and $dS_0^{(b)} = \text{đ}_r Q_0/T_0 = -\,\text{đ}_i Q/T_0$, where Q signifies the heat transfer into the system and T is its operating temperature. The second relation applies because of heat conservation in the isolated compound system. When these expressions are entered in (1c) one obtains the fundamental result

$$\text{đ}_i Q = (T_0/T)\,\text{đ}_r Q - T_0\,\text{đ}\theta < (T_0/T)\,\text{đ}_r Q \qquad (2a)$$

The central equality duplicates the expression derived by a different method in Ref. [6].

The constraint on the right may be tightened by noting that the inequality must be satisfied for any value of $T \geq T_0$ ($T \leq T_0$) when heat flows from the system (reservoir) into the reservoir (system). In particular, it must apply to the limiting case $T \to T_0$. We thereby obtain the string of inequalities

$$\text{đ}_i Q < \text{đ}_r Q < (T_0/T)\,\text{đ}_r Q \qquad (2b)$$

which are self evident for positive values of $\text{đ}_r Q$, where $T_0/T > 1$. Note that in the limiting case discussed above, the quantity $\text{đ}\theta$ in Eq. (2a) does not necessarily vanish [7]. For example, the reversible heating of a sample may trigger chemical processes totally within the system that cannot be controlled from the outside. However, in the absence of such processes, $\text{đ}_r Q$, is the sole applicable variable.

For heat outflows, with $T_0/T < 1$, the inequalities (2b) still hold; the quantities become progressively less negative from left to right. One should observe that the statement $\text{đ}_i Q < \text{đ}_r Q$ is a reformulation of the well-known Clausius inequality.

Eq. (2a) may also be recast in the familiar form as

$$dS = \text{đ}_i Q/T_0 + \text{đ}\theta > \text{đ}_i Q/T_0 \qquad (2c)$$

Note that it is the experimentally well established temperature of the reservoir that enters the above relations. Eq. (2a) may be rewritten as

$$\text{đ}_i Q = \text{đ}_r Q + (T_0/T - 1)\,\text{đ}_r Q - T_0\text{đ}\theta \qquad (2d)$$

which directly relates the two types of heat exchange processes.

LOWER BOUNDS ON THE DEFICIT FUNCTION

In the introduction of the deficit function we had originally set $\text{đ}\theta > 0$. A greater positive lower bound may be imposed by employing the condition $\text{đ}_i Q < \text{đ}_r Q$. Thus, the sum of the last two terms in Eq. (2d) must be negative. This imposes the requirement:

$$\text{đ}\theta > [(T_0 - T)/T_0 T]\,\text{đ}_r Q = [(T_0 - T)/T_0]dS \qquad (3)$$

The right hand side is always positive. For if $T_0 > T$ ($T_0 < T$), heat flows from the surroundings (system) into the system (surroundings), so that $\text{đ}_r Q$ and dS are both positive (negative). In either case the right hand side is positive, thus establishing a positive lower bound that involves experimentally accessible operating conditions.

INEQUALITIES RELATING TO WORK PERFORMANCE

Information relating to work becomes available *via* the First Law in the form

$$dE = \text{đ}_r Q + \text{đ}_r W = \text{đ}_i Q + \text{đ}_i W \qquad (4)$$

where E is the energy of the system and $\text{đ}_i W$ is the element of work performed in an infinitesimal step of an irreversible process. Eq. (4) holds because E is a function of state. Now introduce Eq. (2d) and solve for

$$\text{đ}_i W = \text{đ}_r W - (T_0/T - 1)\,\text{đ}_r Q + T_0\text{đ}\theta = \text{đ}_r W - (T_0 - T)\,dS + T_0\text{đ}\theta \qquad (5)$$

where the last two terms differ in sign from those of Eq. (2d), so that $\text{đ}_i W > \text{đ}_r W$. The irreversible performance of work always exceeds that which is required when the same step is executed reversibly, in accord with intuitive reasoning. The above equation is a reformulation of the *Gouy-Stodola* theorem.

SPECIFICATION OF THE DEFICIT FUNCTION

To be of use the deficit function must be specified in terms of experimentally accessible quantities. This may be achieved in two ways. The first method involves solving Eq. (5) for $\text{đ}\theta$:

$$\text{đ}\theta = (\text{đ}_i W - \text{đ}_r W)/T_0 + (1 - T/T_0)dS \qquad (6a)$$

The total performance of work, based on an integration of $\text{đ}_i W$, may be determined experimentally and the integrated value of $\text{đ}_r W$ may be obtained by calculation. The determination of entropy through calorimetric measurements is also well established. Thus, in principle, θ may be found by performing the required integrations. Details concerning this methodology are left to a future publication. We briefly note that in the absence of work Eq. (6a) reduces to

$$\text{đ}\theta = (1/T - 1/T_0)\, \text{đ}_r Q \qquad (6b)$$

which is derived by different means in Ref. [8]. If work is processed without heat transfer one obtains the relation obtained by a different approach in Ref. [9] below Eq. (3.53), namely

$$\text{đ}\theta = (\text{đ}_i W - \text{đ}_r W)/T_0 \qquad (6c)$$

FUNCTIONS OF STATE FOR IRREVERSIBLE PROCESSES

For future use we now set up the differential form for the energy, E_0, of the *surroundings*, as appropriate to processes that take place reversibly

$$dE_0 = T_0 dS_0 - P_0 dV_0 + \textstyle\sum_i \mu_{0i} dn_{0i} \qquad (7a)$$

where P_0 is the pressure, V_0 the volume, μ_{0i} the chemical potential of species i, and n_{0i} its mole number, all referred to the surroundings. For the closed entity (system + surroundings) energy and material is conserved, whence $dE = -dE_0$ and $dn_{0i} = -dn_i$, where the nonsubscripted quantities refer to the system. If the volume of the compound unit is held fixed as well, we may set $dV_0 = -dV$. Lastly, we use Eq. (1d) and replace dS_0 in Eq. (7a) with $dS_0^{(b)} = -dS + \text{đ}\theta$, which is appropriate to irreversible processes in the system. This leads to the expression for the energy of the *system* in the form

$$dE = T_0 dS - P_0 dV + \textstyle\sum_i \mu_{0i} dn_i - T_0 \text{đ}\theta \qquad (7b)$$

This relation, involving different arguments, was derived by Kestin [8]. Note that it is the intensive variables of the reservoir, different from those of the system, which appear in the above relationship, which applies even to irreversible phenomena. All extensive variables also remain well defined. Conditions of the type introduced here were termed QSIPs.

It is expedient to rewrite the above in the equivalent form

$$\begin{aligned} dE &= (T_0 - T)dS - (P_0 - P)dV + \textstyle\sum_i (\mu_{0i} - \mu_i) dn_i \\ &\quad + TdS - PdV + \textstyle\sum_i \mu_i dn_i - T_0 \text{đ}\theta \qquad (7c) \end{aligned}$$

which explicitly introduces the intensive variables of the system proper. The irreversibilities are subsumed in the last term on the right. The reversible execution of the same step, while retaining the same intensive variables of the system, leads to the customary expression for the same differential energy:

$$dE = TdS - PdV + \textstyle\sum_i \mu_i dn_i \qquad (7d)$$

Since E is a function of state we may subtract (7d) from (7c) to obtain

$$\text{đ}\theta = (1/T_0)\,(T_0 - T)dS - (P_0 - P)dV + \textstyle\sum_i (\mu_{0i} - \mu_i) dn_i \qquad (7e)$$

which determines the incremental deficit function in terms of independent variables that are experimentally accessible, namely: S, V, and n_i. Eq. (7e) is consistent with Eq. (1d); when integrated, it relates the entropy increase in the universe to the transfer of entropy (heat), mechanical work, and matter across the interface that connects the system to its surroundings when QSI processes take place. While correct, the above formulation involves S as the independent variable, which is not readily controlled experimentally. An alternate approach is thus desirable.

Toward this end we introduce the Helmholtz free energy $A = E - TS$, with the differential form $dA = dE - TdS - SdT$. When Eq. (7c) is inserted we obtain.

$$\begin{aligned} dA &= (T_0 - T)dS - (P_0 - P)dV + \textstyle\sum_i (\mu_{0i} - \mu_i) dn_i - SdT - PdV \\ &\quad + \textstyle\sum_i \mu_i dn_i - T_0 \text{đ}\theta \qquad (8a) \end{aligned}$$

However, the appropriate control variables for the function, $A = A(T, V, \{n_i\})$, should be temperature, volume, and composition. Accordingly, we reexpress the entropy in terms of these independent variables as $S = S(T, V, \{n_i\})$, with

$$dS = (\partial S/\partial T)_{V,\, n_i}\, dT + (\partial S/\partial V)_{T,\, n_i}\, dV + \textstyle\sum_i (\partial S/\partial n_i)_{T, V,\, n_{i \neq j}}\, dn_i \qquad (8b)$$

We next set $(\partial S/\partial T)_V = C_{V,.n_i}/T$, where C_{V,n_i} is the heat capacity at constant volume and composition, introduce the relevant Maxwell relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, and set $\hat{S}_i \equiv (\partial S/\partial n_i)_{T,V,n_{j \neq i}}$. Eq. (8a) then reads

$$\begin{aligned} dA &= (T_0 - T)[(C_{V,\, n_i}/T)\, dT + (\partial P/\partial T)_{V,\, n_i}\, dV + \textstyle\sum_i \hat{S}_i\, dn_i] \\ &\quad - (P_0 - P)\, dV + \Sigma_i (\mu_{0i} - \mu_i)\, dn_i - SdT - PdV + \textstyle\sum_i \mu_i dn_i - T_0 \text{đ}\theta \qquad (8c) \end{aligned}$$

which is the desired expression for an infinitesimal change in Helmholtz free energy in QSIPs.

Since A is a function of state, we now subtract from the above the standard expression for operations under reversible conditions,

$$dA = -SdT - PdV + \textstyle\sum_i \mu_i dn_i \qquad (8d)$$

to obtain

$$\begin{aligned} T_0 \text{đ}\theta &= (T_0 - T)[(C_{V,\, n_i}/T)dT + (\partial P/\partial T)_{V,\, n_i}\, dV + \textstyle\sum_i \hat{S}_i\, dn_i] \\ &\quad - (P_0 - P)dV + \textstyle\sum_i (\mu_{0i} - \mu_i) dn_i \qquad (8e) \end{aligned}$$

which relates the differential of the deficit function to temperature, volume, and composition of the system as the appropriate control variables.

The integral formulation requires that we specify how each of the variables changes with time t. We assume that the reservoir is so huge and well mixed that all of its intensive variables remain fixed, so that we set

$$\theta = \int \left[\left(1 - \frac{T(t)}{T_0}\right)\right]\left[\frac{C_{V,n}[T(t), V(t), n_i(t)]}{T(t)} \frac{dT}{dt} + \frac{\partial P}{\partial T}\frac{dV}{dt} + \sum\nolimits_i \hat{S}_i \frac{dn_i}{dt}\right] dt$$

$$- \int \frac{P_0}{T_0}\left(1 - \frac{P(t)}{P_0}\right)\frac{dV}{dt} dt + \sum\nolimits_i \int \frac{\mu_{0i}}{T_0}\left(1 - \frac{\mu_i(t)}{\mu_{0i}}\right)\frac{dn_i}{dt} dt \qquad (9)$$

where the integrals are taken between the initial time, $t_i = 0$, and the final time, $t_f = \tau$, as lower and upper limits respectively.

SPECIAL CASES

To illustrate how Eq. (9) is used we now introduce several simplifying, but reasonable, qualifications. First, we already assumed that the reservoir is so huge that none of its intensive properties is significantly altered in any interchange with the system; then T_0, P_0, and μ_{0i} remain essentially constant. Second, we restrict consideration to a one - component system of fixed composition, which eliminates the third and fifth integrals in (9). Third, for definiteness assume that the system is initially in a state with $T_i < T_0$ and

$P_i < P_0$. Then as the interaction between the system and its surroundings is turned on, T and P both increase. The latter requirement is satisfied by fulfilling the sufficient condition that the volume of the system should diminish during the interaction. Thus, T and V become the control variables, while P adjusts in accordance with the relevant equation of state of the system. The volume is subject to direct control by the experimenter. Then, during the interaction, the temperature of the system is allowed to increase by heat conduction from its initial value T_i to its final value $T_f < T_0$, and its volume is manipulated to decrease from V_i to V_f, such at the end of the process the prevailing pressure has increased from P_i to $P_f < P_0$. As will be seen, in the approximation used below, we do not need to specify the path by which T and V are altered; what is important are the specifications of the initial and final states. Fourth, this process also requires forcing an increase in volume of the reservoir to keep the total volume of the compound system constant, as required in setting up Eq. (7b). Fifth, for illustrative purposes, let the system and reservoir consist of a gas which satisfies the Berthelot equation of state [9],

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{TV^2} \approx \frac{nRT}{V}\left(1+nb/V\right) - \frac{n^2a}{TV^2} \tag{10}$$

where a and b are both constants and all other symbols retain their conventional significance; the expansion applies as long as $nb << V$.

We now proceed to use Eq. (9) as follows: Introduce the caloric equation of state for the energy E and Eq. (10) to determine

$$\partial E/\partial V = T\left(\partial P/\partial T\right) - P = 2n^2a/V^2T \tag{11}$$

and integrate. The arbitrary function of temperature is specified by $3nRT/2$, so that

$$\begin{aligned} &\mathrm{E} = 3\mathrm{nRT}/2 - 2\mathrm{n}^2\mathrm{a}/\mathrm{VT};\ \mathrm{C}_{\mathrm{V},\imath} \\ &= 3\mathrm{nR}/2 + 2\mathrm{n}^2\mathrm{a}/\mathrm{VT}^2 \quad \ldots \end{aligned} \tag{12}$$

where $C_{V,n}$ is the heat capacity at constant volume and composition. Now substitute Eqs. (10) – (12) in (8e). At constant composition, changes in temperature and volume of the system produce an infinitesimal change in entropy given by:

$$\begin{aligned} d\theta &= \left(1-\frac{T}{T_0}\right)\left[\frac{3nR}{2T}+\frac{2n^2a}{VT^3}\right]dT + \left\{\left(\frac{nR}{V-nb}+\frac{n^2a}{V^2T^2}\right)\right. \\ &\left. -\frac{\mathrm{P_0}}{\mathrm{T_0}} - \frac{2}{\mathrm{T_0}}\left(\frac{\mathrm{n^2a}}{\mathrm{V^2T}}\right)\right\}\mathrm{dV} \end{aligned} \tag{13}$$

For subsequent ease of handling we next set up contributions under separate headings. (i) We first consider integrals that involve either T or V as the sole integration variable for transitioning the system from its initial state (T_i,V_i) to its final state (T_f,V_f). The corresponding contribution to the entropy is specified by:

$$\theta_{0i} = \frac{3nR}{2}\ln\frac{T_f}{T_i} - \frac{3nR}{2T_0}(T_f - T_i) - nR\ln\left[\frac{V_i-nb}{V_f-nb}\right] + \frac{P_0}{T_0}(V_i - V_f) \tag{14a}$$

(ii) For possible later use we separately study the entropy increase of the reservoir whose volume increases reversibly from V_0 to $V_0 + (V_i - V_f)$ at fixed T_0, P_0, which matches the volume change of the system, thereby preserving the overall volume. For this purpose we adopt the basic relation $dS_0 = (1/T_0)(dE_0 + P_0dV_0)$, with $dE_0 = (dE_0/dV_0)dV_0$ for fixed T_0. On introducing (11) and integrating we find that

$$\begin{aligned} S_{0,f} - S_{0,i} &= \frac{2n_0{}^2a}{T_0{}^2}\left(\frac{1}{V_{0,i}} - \frac{1}{V_{0,f}}\right) + \frac{P_0}{T_0}(V_{0,f} - V_{0,i}) \qquad \ldots \\ &\approx \frac{2n_0{}^2a}{T_0{}^2}\left(\frac{V_i - V_f}{V_{0,i}^2}\right) + \frac{P_0}{T_0}(V_i - V_f) = \frac{2a}{T_0{}^2}c_0^2(V_i - V_f) + \frac{P_0}{T_0}(V_i - V_f) \end{aligned} \tag{14b}$$

where we had expanded the denominator for small values of $V_i - V_f$ relative to $V_{0,i}$; also we set $c_0 \equiv n_0/V_0$ as the concentration variable for the reservoir.

(iii) It remains to work with two types of line integrals in Eq. (13) which simultaneously involve both T and V in the integrand. The first deals with temperature changes that accompany heat transfers

$$d\theta_T = \left(1-\frac{T}{T_0}\right)\left[\frac{2n^2a}{VT^3}\right]dT \tag{14c}$$

and the second relates to volume changes which are produced by work exchange,

$$d\theta_V = \left\{\frac{n^2a}{V^2T^2} - \frac{2}{T_0}\left(\frac{n^2a}{V^2T}\right)\right\}dV \tag{14d}$$

For their evaluation one must introduce time, t, as a parameter and specify the time dependence of both T and V. We consider two cases at random in conformity with the earlier discussion. Changes in volume and heat flows are adjusted to lead to the following time dependences:

Case 1. Let $V(t) = V_ie^{-k_Vt}$, $T(t) = T_ie^{k_Tt}$, $0 \le t \le \tau$, where k_V and k_T are time constants such that in the time interval $0 \le t \le \tau$ the volume (temperature) changes from the initial value V_i, (T_i) to the final value V_f, (T_f). Insert these two functions of time into (14c) and set $dT = (dT/dt)dt$ to carry out the integrations, which are lengthy though straightforward. One finds that

$$\begin{aligned} \theta_T = +\frac{2n^2a}{V_iT_i}&\left\{\frac{1}{T_i\,(k_V/k_T-2)}\left[\frac{V_i}{V_f}\left(\frac{T_i{}^2}{T_f{}^2}\right) - 1\right]\right. \\ &\left. - \frac{1}{T_0\,(k_V/k_T-1)}\left[\frac{V_i}{V_f}\left(\frac{T_i}{T_f}\right) - 1\right]\right\}; \qquad \frac{k_V}{k_T} = \frac{\ln(V_i/V_f)}{\ln(T_f/T_i)} \end{aligned} \tag{15a}$$

Proceeding similarly with (14d), using $dV = (dV/dt)dt$ one obtains

$$\begin{aligned} \theta_V = \frac{n^2a}{V_iT_i}&\left\{\frac{-1}{T_i(1-2k_T/k_V)}\left[\frac{V_i}{V_f}\frac{T_i^2}{T_f^2} - 1\right]\right. \\ &\left. + \frac{2}{T_0(1-k_T/k_V)}\left[\frac{V_i}{V_f}\frac{T_i}{T_f} - 1\right]\right\} \end{aligned} \tag{15b}$$

If the denominators such as $(k_V/k_T - 1)^{-1}$ or $(2k_T/k_V - 1)^{-1}$ approach zero their multipliers in square brackets do likewise since under these conditions $V_f \to V_i$, $T_f \to T_i$; l'Hôpital's rule then shows that the respective products approach zero, as anticipated.

If in its final state the system is equilibrated with its surroundings, then $T_f = T_0$; one then also requires that V_f satisfy Eq. (10) with $P_f = P_0$.

Case 2: We consider the time dependence of the volume $V = V_i/(1+k_V t)$, with the same temperature dependence as before. The upper limit for $k_V\tau$ is determined by the choice for the final volume, V_f. Eqs. (14a) and (14b) are the same as before. On substituting the assumed time dependence for temperature into Eq. (14c) one obtains

$$\theta_T = +\frac{n^2 a}{T_i^2 V_i}\left\{\left[1-\frac{T_i^2}{T_f^2}\right]+\frac{k_V}{2k_T}\left[1-\frac{T_i^2}{T_f^2}+2\frac{T_i^2}{T_f^2}\ln\frac{T_i}{T_f}\right]\right\}$$

$$-\frac{2n^2 a}{T_i T_0\ V_i}\left\{\left[1-\frac{T_i}{T_f}\right]+\frac{k_V}{k_T}\left[1-\frac{T_i}{T_f}+\frac{T_i}{T_f}\ln\frac{T_i}{T_f}\right]\right\},\quad \frac{k_V}{k_T}=\frac{V_i/V_f-1}{\ln(T_f/T_i)} \tag{16a}$$

Proceeding similarly with Eq. (14d) one finds

$$\theta_V=\frac{n^2 a}{V_i T_i}\frac{k_V}{k_T}\left\{\frac{-1}{2T_i}\left(1-\frac{T_i^2}{T_f^{\,2}}\right)+\frac{2}{T_0}\left(1-\frac{T_i}{T_f}\right)\right\} \tag{16b}$$

both of which clearly differ from Case 1.

Nevertheless, despite the differences between the two cases, the *total* entropy change associated with step (iii) for the above integrals (on elimination of the k_T/k_V ratios, and summing Eqs. (15a) and (15b) or Eqs. (16a) and (16b)), is exactly the same, namely.

$$\theta_V+\theta_T=\frac{n^2 a}{V_i T_i}\left\{\frac{2}{T_0}\left[\frac{V_i T_i}{V_f T_f}-1\right]-\frac{1}{T_i}\left[\frac{V_i T_i^{\,2}}{V_f T_f^{\,2}}-1\right]\right\}$$

$$= n^2 a\left\{\frac{2}{T_0}\left[\frac{1}{V_f T_f}-\frac{1}{V_i T_i}\right]-\left[\frac{1}{V_f T_f^{\,2}}-\frac{1}{V_i T_i^{\,2}}\right]\right\} \tag{17}$$

This finding may be rationalized by noting that we had selected T_f/T_i and V_f/V_i at the outset for the two cases; in turn this required an adjustment of k_T, k_V, and τ to meet this particular choice. The processes were selected to occur at rates sufficiently slow that the uniformity of temperature and pressure was maintained over almost all the volume of the system. Thus, the final results involve only the initial and final temperatures and volumes of the system; the temperature of the reservoir; the amount of material in the system and reservoir; the parameters appropriate to the Berthelot equation of state; and fundamental constants. In the QSIP approximation, with the assumed uniformly changing properties, no reference is made to pathways by which the system changes from its initial to its final configuration. What Eqs. (15) and (16) do show is a difference in the contributions of heat and work to θ_T and θ_V respectively, but they sum to the same final result. Further, if $V_f = V_i$, $T_f = T_i$ the above equations show, as they should, that there is no entropy change in the system and surroundings. We have examined other changes of control variables with time and again obtain results fully in accordance with the above findings.

The total entropy change of the compound system under the assumed conditions is the sum of Eqs. (14a) and (17); the entropy change of the reservoir responding to the irreversible processes is given by (14b).

For an ideal gas as a working substance Eq. (17) drops out and Eq. (14a) simplifies to

$$\theta_{ig}=\frac{3nR}{2}\ln\frac{T_f}{T_i}-\frac{3nR}{2T_0}(T_f-T_i)-nR\ln\left[\frac{V_i}{V_f}\right]+\frac{P_0}{T_0}(V_i-V_f) \tag{18}$$

Here the first and third terms agree with the entropy change accruing to the system under reversible operations.

CYCLIC PROCESSES

So far we have considered only monotonic changes in T and V. Also of interest is the execution of a circular process in which the initial state of the system is restored. To explore this situation we attach to the system a second reservoir at temperature $T_1 < T_i$, pressure $P_1 < P_i$, that initially remains sealed off while the interaction between the system and the first reservoir proceeds as shown above. After the end point T_f and V_f has been reached the first reservoir is sealed off and the interaction between the system and the second reservoir is initiated and maintained until the initial state of the system has been restored.

Assume again that the reservoirs and system are comprised of a Berthelot gas; then, for the return path the subscripts f and i in Eqs. (14a) must be interchanged and the subscript 0 must be replaced by 1. On adding this modified equation to (14a) for the forward process, one obtains (in the approximation $nb << V$) the net contribution associated with (i) the path-independent integrals as:

$$\theta_1=\frac{3}{2}nR(T_f-T_i)\left(\frac{1}{T_1}-\frac{1}{T_0}\right)+R(V_i-V_f)[(c_0-c_1)+(c_1^{\,2}-c_0^{\,2})b] \tag{19a}$$

We proceed similarly (ii) with the same index alterations to Eq. (14b) to deal with the entropy contribution for the volume change of reservoir 1 in the reverse process. We also again expand P_1/T_1 and add the resultant to Eq. (14b) to obtain

$$\theta_2=a(V_i-V_f)\left(\frac{c_0^2}{T_0^2}-\frac{c_1^2}{T_1^2}\right)+R(V_i-V_f)\left[(c_0-c_1)+(c_0^{\,2}-c_1^{\,2})b\right] \tag{19b}$$

as the overall change in entropy of the two reservoirs.

(iii) Lastly, we must evaluate the line integrals. To handle the exchange between the system and reservoir 1 we must repeat the mathematical operations that led to Eqs. (15), but with $V(t)=V_i e^{+k_V t}$, $T(t)=T_i e^{-k_T t}$, $0 \le t \le \tau$. It turns out that we then recover Eq. (17) with the indices once more interchanged. When this resultant is added to (17) we obtain

$$\theta_3 = 2n^2 a\left[\frac{1}{V_f T_f} - \frac{1}{V_i T_i}\right]\left(\frac{1}{T_0} - \frac{1}{T_1}\right) \tag{19c}$$

The total entropy change during the cyclic process is the sum of (19a), and (19c).

The major contribution to the entropy changes in the cyclic process of the compound system is in the form

$$\theta = \frac{3}{2} nR\,(T_f - T_i)\left(\frac{1}{T_1} - \frac{1}{T_0}\right) \tag{19d}$$

In fact, if matters are arranged such that $c_0 = c_1$, Eq. (19d) is the only contribution. In a strictly reversible process the total entropy change would add up to zero.

Eqs. (19a) and (19c) specify the increase in entropy of the compound unit when the system is cycled through the changes $T_i \rightarrow T_f \rightarrow T_i$ and $V_i \rightarrow V_f \rightarrow V_i$. The results depend on the difference between the initial and final temperatures and volumes of the system, the temperatures of the hot and cold reservoir, the concentration of the gases in the reservoirs, the number of moles of gas in the system, and on the parameters of the Berthelot equation of state. Remarkably, the major contribution, Eq. (19d), is independent of the constitution of the gas phases, and depends only on the indicated temperatures.

CONCLUSIONS

By generalizing the standard thermodynamic theory pertaining to irreversible phenomena it is possible to determine changes in the state of a system during an irreversible transfer of heat or irreversible execution of work in terms of measurable quantities. The theory was extended to set up thermodynamic functions of state when irreversible changes take place, as shown by Eqs. (7c) and (8c). One can then specify the entropy associated with QSI processes across the boundary of a system attached to a reservoir, as shown by Eq. (9), in terms of changes in temperature, volume, and composition. The theory is applicable to QSIPs no matter how big the initial difference between the intensive properties of the reservoir and the system. Whenever two or more of the independent variables are simultaneously changed the relevant integrals require the specification of the time dependence of T, V and n. Specific examples have been provided to show how to determine the contributions of irreversible processes to the entropy when different kinds of changes in temperature and volume are maintained across a thin boundary between a system and its surroundings at fixed composition. As is verified by explicit calculations, or by general considerations, in the QSIP approximation the total entropy change associated with the irreversible processes does not depend on the chosen pathway. The entropy change in QSIPs, as specified by temperature and volume as independent variables, are specified by Eqs. (14a,b) and (17). Also investigated was the entropy change in the universe when the system executes a cyclic change, as specified by Eqs. (19a,b,c) .

This analysis should serve as a prototype study of irreversible phenomena under specified initial assumptions. It complements the standard theory of irreversible processes, in which emphasis is placed on the specification of fluxes, such as transport of entropy and matter, in response to external forces either within a system or across boundaries.

ACKNOWLEDGEMENTS

The authors are indebted to Professor Dor Ben Amotz of Purdue University for many insightful discussions. They also acknowledge contributions by Ms. Kasi Rubadue; both she and the junior author of this paper were undergraduate students at Purdue University. The research was supported by Award SI – 06 – 021 of the Dreyfus Foundation.

NOTES:

1. The notation is now somewhat confusing. What is meant by $\text{đ}_i Q$ in the limiting case is actually a reversible heat transfer while additional irreversible processes are triggered totally within the system; $\text{đ}_r Q$ represents the reversible transfer in the absence of such additional events.
2. Actually, it is only necessary to demand that the volume change of the surroundings be exactly the negative of that of the system. This allows the surroundings to assume other volume changes not associated with the irreversible process of the system.

REFERENCES

[1] J.M. Honig, and D.B. Amotz, "The analysis of spontaneous processes using equilibrium thermodynamics", *J. Chem. Ed.,* vol. 83, pp. 132-7, 2005.

[2] D.B. Amotz, and J.M. Honig, "Average entropy dissipation in irreversible mesoscopic processes", *Phys. Rev. Lett.,* vol. 96, pp. 1-4, 2006.

[3] D.B. Amotz, and J.M. Honig, "The rectified second law of thermodynamics", *J. Phys. Chem. B.,* vol. 110, pp. 10066-72, 2006.

[4] J.M. Honig, and D.B. Amotz, "Rectification of thermodynamic inequalities as a means of characterizing irreversible phenomena", *Chem. Educator.*, vol.13, pp. 220-6, 2008.

[5] J.M. Honig, "*Thermodynamics, principles characterizing chemical and physical processes*". 3rd ed. Academic Press: Amsterdam 2008.

[6] R.C. Tolman, and P.C. Fine, "On the irreversible production of entropy", *Rev. Mod. Phys.,* vol. 20: pp. 51-77, 1948.

[7] J. Kestin, "*A course in thermodynamics*", Blaisdell: Waltham MA 1966, Chap. 13.

[8] A. Bejan. "*Advanced engineering thermodynamics*". 2nd ed., Wiley: New York 1997, p. 135.

[9] R.S. Berry, S.A. Rice, and Ross J. "*Physical chemistry*" 2nd ed. Oxford University Press: New York 2000, p. 553.

Received: December 20, 2010 Revised: February 10, 2011 Accepted: March 03, 2011