Definition of Heat
in Open Systems

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Abstract

Existing definitions of heat in open systems are considered with the aim of providing acceptable physical motivation in restricted circumstances. The extent to which these definitions are independent of the usual concept of heat in closed systems is clarified: they all have the feature that internal energy may be transferred by convection in workless adiabatic processes. The global definitions are compared with various definitions of heat flux in irreversible thermodynamics. As the domain of applicability of these definitions is wider than that of equilibrium thermodynamics, it is suggested that a minimal check for any definition of heat flux be that it agree with the global definition of heat flow between equilibrium states in as wide a range of circumstances as possible.

1. Introduction

The question of how best to define heat transfer in open systems is not yet settled, although it was first raised many years ago. That a real generalization of closed-system thermodynamics is required has been emphasized by Münster (1970): thus it is possible to increase the internal energy of an open system without doing work and without heat flow simply by adding more mass at the same temperature and pressure under adiabatic conditions. It is therefore expected that the usual version of the first law of thermodynamics for closed systems, namely $dU = dQ + dW$, will not be valid for open systems. Despite this, it is true that open systems can often be analysed by considering the motion of a fixed mass of the working fluid, as is done in engineering texts. However, this reduction to closed system thermodynamics can only be made after agreement has been reached on a suitable definition of heat.

For one-component systems, an agreed definition of heat is used by engineers for flow problems (see e.g. Rogers and Mayhew 1967). For multicomponent systems, Gillespie and Coe (1933) proposed, and partially motivated, a definition which reduces to the engineering version when the number of components is unity. In Sections 2 and 3 below we attempt to provide physical motivation for these definitions. In doing this, a convention is established that the heat flow into an open system is zero when the system, its supply tank and discharge tank are all surrounded by an adiabatic enclosure. This convention is partly a consequence of conventional notions of heat and partly an arbitrary device, depending on the physical conditions. For simplicity, all systems considered here are assumed to consist of one phase only.

In irreversible thermodynamics, which is usually formulated as a local rather than a global theory, there exist several definitions of heat flux. That due to Prigogine (1947; see also Glansdorff and Prigogine 1971) is most widely used, although many

authors employ several non-equivalent definitions (see e.g. de Groot and Mazur 1962), while Haase (1953, 1969) uses a different definition, the so-called reduced heat flux, exclusively. The Prigogine definition of heat flux is usually justified by showing that the balance equation for internal energy per unit mass, following the centre of mass motion, agrees with the second law of thermodynamics for *closed* systems. But the balance equations of irreversible thermodynamics apply to open systems also. When comparisons with the global definition of heat are made for *open* systems, it is found that Prigogine's heat flux is consistent with the global definition only for systems of one component, but Haase's reduced heat flux is consistent in all cases.
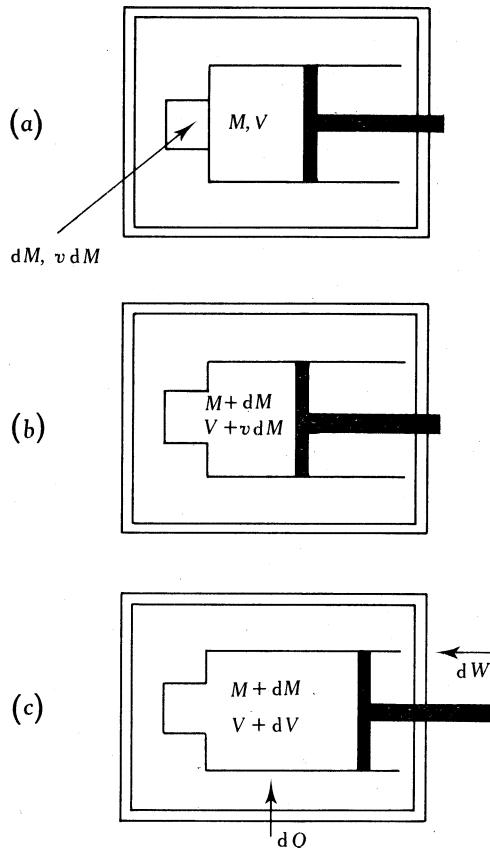

Fig. 1. Thermodynamic process for a one-component fluid involving mass addition: (*a*) To the system, which is the fluid of the main chamber, (*b*) fluid is added by removing the common wall between the two chambers, and then (*c*) work and heat are supplied to the resulting closed system.

There are additional tests that can be used to discriminate between the various definitions. Both the Prigogine and the Haase definitions of heat flux are invariant under Galilean transformations. However, Haase's definition is also superior in that it is invariant under changes of standard values for the partial internal energies and entropies (Tolhoek and de Groot 1952).

2. Open One-component Systems

We will take the global definition of heat to refer only to a process connecting equilibrium states. No progress can be made until we have some notion of adiabatic processes for these systems. We choose to define adiabatic processes in these systems by requiring that the process for the original system plus its infinitesimal added mass, which together form a closed system, is adiabatic in the usual sense. With this definition it is possible to have workless adiabatic processes which increase the internal energy (see Fig. 1). Hence for open systems the first law of thermodynamics must be of the form

$$dU = dW + dQ + dR, \qquad (1)$$

where dW is work done on the system, dQ is heat added according to the above convention and dR accounts for changes by addition of mass. Before dR can be specified we need to know the thermodynamic states of the original system and the added mass. Each state can be specified by two intrinsic variables, namely temperature and pressure, with values T and P for the system and T' and P' for the added mass. Furthermore, the initial state in each system is in equilibrium and therefore homogeneous, so the internal energies are $U(T, P)$ and $u(T', P')dM$ for the original system and the added mass respectively.

Three kinds of processes may be distinguished. In decreasing order of generality, they are:

(A) completely irreversible;

(B) mass-reversible, i.e. addition of mass takes place reversibly but the subsequent change is irreversible;

(C) completely reversible.

Even in the general case A, a simple expression for dR follows by treating the original system plus added mass as a closed system, as suggested by Gillespie and Coe (1933). The internal energy change of this closed system in the process of Fig. 1 is $(U + dU) - U - u'dM$, so

$$dU - u'dM = dW + dQ \qquad \text{(case A)} \qquad (2)$$

is the normal statement of the first law for this closed system. This is of the form (1) with $dR = u'dM$. For mass-reversible processes, the temperatures and pressures of the two systems before addition must be equal. This is the case with continuous flow systems, although the conventional analysis of such systems is more general in that the initial and final states are not equilibrium states. Thus the added mass has the same intrinsic variables as the original system; in particular $u' = u$, so

$$dU = dW + dQ + u\,dM \qquad \text{(case B)}. \qquad (3)$$

The technique of changing the boundary shows that no extra generality in the theory is required for open one-component systems. This can be verified explicitly for mass-reversible systems, where the total system (original system plus added mass) is initially homogeneous. We then expect that the work done and the heat entering per unit mass, namely

$$dw = dW/M \quad \text{and} \quad dq = dQ/M, \qquad (4)$$

obey the relation

$$du = dw + dq, \qquad (5)$$

which is the first law for a closed system. This result follows immediately from equation (3).

For completely reversible processes, the work done can be expressed in terms of state variables. As the volume change is $(V + dV) - V - v\,dM$, we have

$$dW = -P(dV - v\,dM) = -PM\,dv, \tag{6}$$

showing that any work done necessarily changes the specific volume v. Addition of mass at the same density is a workless process. Substitution in equation (3) gives

$$dU = -P\,dV + dQ + h\,dM \qquad \text{(case C)}, \tag{7}$$

where h is the enthalpy per unit mass, that is, $h = u + Pv$.

Another way of expressing equation (7) is to write $dq = T\,ds$, which follows by using equations (4). This is a generalization of the Carnot–Clausius equality, and has the attractive feature that heat flow necessarily increases the entropy density. Thus in homogeneous one-component systems the mass is almost an irrelevant variable; all changes can be described by using the laws of closed-system thermo-dynamics on thermodynamic densities. This situation does not persist for multi-component systems.

The order of operations detailed in Fig. 1 is not important for an infinitesimal process. The system can suffer an infinitesimal closed change *before* mass is added rather than afterwards, the difference being of second order in infinitesimal quantities. The same equations can also be shown to apply to the case of mass loss if dM is negative.

3. Open Multicomponent Systems

For simplicity we consider multicomponent systems without external forces and chemical reactions, although the extensions required to include these are trivial.

For the completely irreversible case A, the addition of mass dM of a fluid with intrinsic variables T', P', x' (where the $x = x_1, ..., x_n$ are the mass fractions of the n components) to a fluid of mass M in state T, P, x leads to a first law of form (1) with

$$dR = \sum_i u_i'\,dM_i, \tag{8}$$

where u_i' is the partial internal energy per unit mass of component i, dM_i is the added mass of that component, and the convention for defining heat is as proposed in Section 2. The usual definition of partial quantities is used, namely

$$u_i = (\partial U / \partial M_i)_{T,P,M'} \qquad (M' = \{M_j; j \neq i\}).$$

For a mass-reversible process (case B), each component must be added reversibly, with additional irreversible changes on the closed systems formed after each addition. Again, the order of operations is not important if the processes are infinitesimal. There are various physical arrangements for adding components reversibly, but the most convenient for our purposes is shown in Fig. 2. The added masses in each of the vertical cylinders are all at the same temperature, pressure and chemical composition as the main system, but each cylinder i ($i = 1, ..., n$) is fitted with a membrane permeable only to species i. Each vertical piston is used to displace an infinitesimal

mass dM_i into the main chamber. Subsequent changes of a closed-system variety can be carried out by clamping these pistons and using the piston of the main chamber. Thus $u_i' = u_i$ and $v_i' = v_i$, where u_i and v_i are values for the main chamber, and so

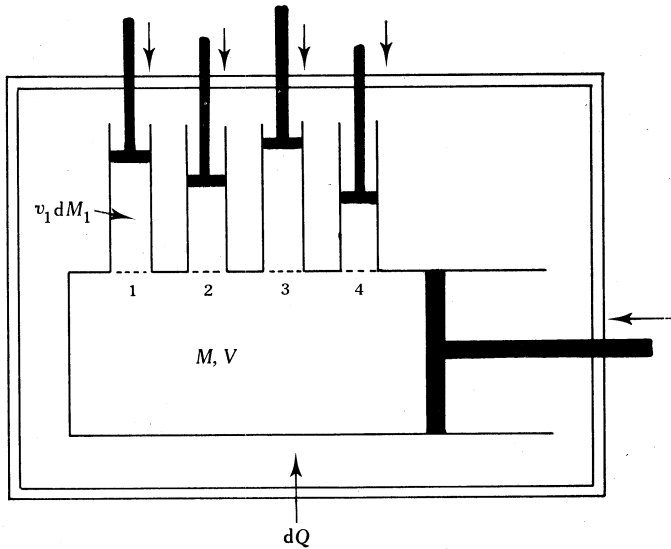$$dU = dQ + dW + \sum_i u_i dM_i \quad \text{(case B)}. \tag{9}$$

Fig. 2. Process for a general change of state in a multicomponent fluid. Masses $dM_1, dM_2, \dots$ of fluid at the same temperature, pressure and composition as the fluid of the main chamber are added through semipermeable membranes $1, 2, \dots$. The net work done by all pistons is dW, and heat dQ enters through the surrounding wall.

For a completely reversible process (case C), the work done is

$$dW = -P\left(dV - \sum_i v_i dM_i\right) \tag{10}$$

and hence

$$dU = -P dV + dQ + \sum_i h_i dM_i \quad \text{(case C)}, \tag{11}$$

where $h_i = u_i + Pv_i$ is a partial enthalpy. This is the definition suggested by Gillespie and Coe (1933). There is an alternative form, namely

$$dQ = T \sum_i M_i ds_i.$$

Note that the result (11) is different from what one gets by using the process of Fig. 1 with a multicomponent fluid. This would lead to equation (11) with the last term replaced by $\bar{h} dM$, where

$$\bar{h} = M^{-1} \sum_i h_i M_i \tag{12}$$

is the mean enthalpy per unit mass. The difference between the two terms is just the quantity $h_i(dM_i - M_i dM/M)$ summed over each component. In fact both results are correct in the context of Fig. 1, because that process merely adds more fluid of

the same composition, that is, $dM_i/dM = M_i/M$. This illustrates an important point, namely that the processes considered must be sufficiently general to include all possible changes of state. To include composition changes and to carry them out reversibly requires the use of semipermeable membranes, as was realized by van't Hoff.

Other physical arrangements may be used to change composition, either reversibly or not. However, equation (8) remains true whatever apparatus is used. For mass-reversible processes, an alternative arrangement is to fill the vertical cylinders of Fig. 2 with infinitesimal amounts $dM_1, dM_2, ...$ of pure components of types $1, 2, ...$ and adjust the pressures in those cylinders to the membrane pressures $P_1, P_2, ...$ of the corresponding components in the main chamber. The temperatures in all chambers are to be equal. With the pure fluids prepared in this way, they will be in thermal, mechanical and chemical equilibrium with the main fluid mixture, and by pushing each vertical piston down to zero volume the mixing is again carried out reversibly. However, the work done, in general, is not given by equation (10). The work of mixing is formally equal to

$$\sum_i P_i v_i^\phi(T, P_i) \, dM \,, \tag{13}$$

where v_i^ϕ is the specific volume of the pure component i. This should be compared with the result $P v_i(T, P, x) \, dM_i$ appearing in equation (10). Formally, the membrane pressures are determined from the condition of chemical equilibrium, which for component i is

$$\mu_i(T, P, x) = \mu_i^\phi(T, P_i) \tag{14}$$

in terms of the chemical potentials (μ_i^ϕ is actually the Gibbs energy per unit mass for pure i). The specific volumes are also related through the expressions

$$v_i = (\partial \mu_i/\partial P)_{T,x}, \qquad v_i^\phi = (\partial \mu_i/\partial P_i)_T, \tag{15}$$

so that equations (14) and (15) determine P_i and v_i^ϕ in terms of the state variables of the mixture. For a perfect gas mixture one can show that $P v_i = P_i v_i^\phi$, but in general this is not true and the two arrangements lead to different expressions for the heat increment.

We are thus confronted with the unsatisfactory situation that, even with the convention of Section 2 for adiabatic processes, the expression for heat in open multi-component systems depends on the process chosen, even in the purely reversible case. To introduce some order into this situation, it is useful to distinguish the following two types of processes.

(1) Processes of the first kind: the added fluid is at the same temperature, pressure and composition as the original fluid.

(2) Processes of the second kind: the added fluid is in a different state.

Those of the first kind imply that the thermodynamic variables are continuous across the boundary of the original system. Thus it is these processes that can be compared with those of irreversible thermodynamics, where the existence of local equilibrium at each point of the fluid is assumed. Local equilibrium implies that the intrinsic thermodynamic variables are continuous functions of position.

If one is prepared to accept the restriction to processes of the first kind, then it appears likely that the arrangement of Fig. 2 is unique, at least for mass-reversible

processes. If this were so, then equations (9) and (11) would constitute unique definitions of heat in open multicomponent systems, for the mass-reversible (B) and completely reversible (C) cases respectively.

Finally, we are now in a position to make more sense of the convention proposed for adiabatic processes in open systems in Section 2. Crudely speaking, this amounts to saying that only heat flows from the surroundings to the original system or the added mass will be counted as 'heat', whereas heat flows between the original system and the added mass (e.g. on mixing) will be ignored. If the process is of the first kind, then no heat exchange between the original system and added mass is expected anyway, at least for the mass-reversible case. In these circumstances, our convention loses all arbitrary aspects and becomes merely a consequence of the conventional concepts of heat.

4. Comparisons with Irreversible Thermodynamics

As noted in the Introduction, there exist two different definitions of the heat flux vector in irreversible thermodynamics, due essentially to Prigogine (1947; see also Glansdorff and Prigogine 1971) and Haase (1953, 1969) respectively. Tolhoek and de Groot (1952) have shown that these definitions correspond to the two global definitions of heat contained in equations (7) and (11) respectively. For completeness, we repeat their argument here, using an integral formulation which displays more clearly the restrictions required to deal with processes connecting equilibrium states. Only reversible processes will be considered.

In the absence of an external potential, the total energy in a non-equilibrium multicomponent fluid is the sum of kinetic and internal energies. The local form of the first law is a conservation equation for the total energy density. Let E denote total energy and $e(r, t)$ its mass density at position r and time t. The conservation law is

$$\partial(\rho e)/\partial t + \nabla \cdot j_E = 0, \tag{16}$$

where ρ is the mass density, and the energy flux j_E is the sum of some convective terms, a term describing the rate of working against internal stresses and a heat flux W. For fluids, we have two suggestions for j_E, namely

$$j_E = \rho e v + \mathbf{P} \cdot v + W \qquad \text{(Prigogine)}, \tag{17P}$$

$$j_E = \rho e v + \sum_i h_i j_i + \mathbf{P} \cdot v + W \qquad \text{(Haase)}, \tag{17H}$$

where v is the centre of mass velocity, $\mathbf{P}$ is the pressure tensor and $j_i = \rho_i(v_i - v)$ is the mass flux of component i in the centre of mass frame at the same position in space. Haase's definition (17H) has been used by other authors and is known as the reduced heat flux. The standard development of the subject follows by subtracting the balance equation for the kinetic energy of the centre of mass motion. When this is done, one finds the corresponding balance equations for internal energy

$$\rho \frac{Du}{Dt} + \nabla \cdot W = -\mathbf{P} : \nabla v, \tag{18P}$$

$$\rho \frac{\mathrm{D}u}{\mathrm{D}t} + \nabla \cdot \left(W + \sum_i h_i j_i \right) = -\mathbf{P}:\nabla v, \tag{18H}$$

where $\mathrm{D}/\mathrm{D}t = \partial/\partial t + \boldsymbol{v} \cdot \nabla$ is the material derivative.

To obtain global equivalents of equations (18), consider an open system with volume $V(t)$ at time t and surface velocity $v_s(r, t)$ at some point r on the surface. The physical form of the surface can be left unspecified: it may be permeable to all components, to some of them in some places, or to none. The nature of the surface will dictate appropriate boundary conditions on the various fluxes and, as generality is crucial, these boundary conditions need not be given. The internal energy of the system changes at a rate

$$\begin{aligned}
\frac{\mathrm{d}U}{\mathrm{d}t} &= \int \frac{\partial}{\partial t}\left(\rho u \right) \mathrm{d}V + \int \rho u v_s \cdot \mathrm{d}S \\
&= \int \rho \frac{\mathrm{D}u}{\mathrm{D}t} \mathrm{d}V - \int \rho u(v - v_s) \cdot \mathrm{d}S \\
&= -\int \mathbf{P}:\nabla v \, \mathrm{d}v - \int \left(W + \sum_i h_i j_i + \rho u(v - v_s) \right) \cdot \mathrm{d}S,
\end{aligned} \tag{19H}$$

using Haase's definition of heat flux.

Now consider the change δU in U over a small time interval δt in the quasistatic limit, where the process becomes reversible. This limit requires all velocity gradients, including the surface velocity gradient, to tend to zero. For a fixed change in U, the time interval required will diverge as this limit is taken, that is, δt cannot remain small. Hence the quasistatic limit will not be taken explicitly in what follows. We simply note that the system then passes through a succession of infinitesimally spaced equilibrium states, so that the pressure tensor can be replaced by the hydrostatic pressure P, and thermodynamic variables such as P, ρ and u are spatially uniform and can be taken outside integrals. On making the identifications

$$\delta Q = -\int W \cdot \mathrm{d}S \, \delta t, \qquad \delta V = \int v_s \cdot \mathrm{d}S \, \delta t, \tag{20a}$$

$$\delta M = -\int \rho(v - v_s) \cdot \mathrm{d}S \, \delta t, \qquad \delta M_i = -\int \rho_i(v_i - v_s) \cdot \mathrm{d}S \, \delta t, \tag{20b}$$

it is found that equation (19H) becomes equivalent to the Gillespie–Coe (1933) definition (11) of heat in equilibrium thermodynamics. If Prigogine's heat flux (17P) is used instead, the amended version of equation (19H) becomes equivalent to equation (7) with h interpreted as mean enthalpy.

5. Some Additional Tests

There are two simple tests to be satisfied by any definition of heat: (i) the heat flux in any local theory should be invariant under Galilean transformations, and (ii) heat transfer should be invariant under changes of reference values for thermodynamic potentials. We first consider (i).

If one accepts that internal energy can be transported by convection as well as by heat flow, then the heat flux should be invariant under a Galilean transformation, with the convective part of the internal energy flux transforming in the usual manner. The balance equations (18P) and (18H) for internal energy are both invariant under transformation if the heat fluxes are the same in both frames of reference; thus no distinction between them can be made on this basis. To see that this is so, introduce a new reference frame such that the position of a material point in the new frame is $r' = r - v_0 t$. Then $u' = u$, which is obvious from the meaning of internal energy, and $\mathbf{P'} = \mathbf{P}$ which follows from the transformation properties of the momentum balance equation (de Groot and Mazur 1962). The mass fluxes j_i are also invariant since they are defined in the centre of mass frame. Hence $W' = W$.

It has been shown by Tolhoek and de Groot (1952) that Haase's reduced heat flux is invariant under changes in reference values of the partial internal energies and entropies, whereas Prigogine's heat flux is not. This test is only relevant for multicomponent systems; for single-component systems all that need be done is to ensure that the arbitrary constants U_0 and S_0 in internal energy and entropy scale with the mass of the system. But for multicomponent systems each component has arbitrarily assigned reference values for energy and entropy, so that the partial mass quantities for each component of the mixture contain arbitrary additive constants. Let these constants be changed by $u_i^{(0)}$ and $s_i^{(0)}$ respectively, so that

$$u_i' = u_i + u_i^{(0)}, \qquad s_i' = s_i + s_i^{(0)} \qquad (i = 1, ..., n). \tag{21}$$

Note that the Gibbs–Duhem relation in the form $Ts_i = u_i + Pv_i - \mu_i$ is preserved only if the chemical potentials are allowed to shift, i.e.

$$\mu_i' - \mu_i = \mu_i^{(0)}(T) \equiv u_i^{(0)} - Ts_i^{(0)}, \tag{22}$$

the shift being temperature dependent. On applying these relations to the two contending global definitions of heat, namely equations (7) and (11), we have from these equations respectively

$$dQ' - dQ = \sum_i u_i^{(0)}(dM_i - M_i dM/M), \tag{23P}$$

$$dQ' - dQ = 0. \tag{23H}$$

6. Discussion

The consequences of using Haase's reduced heat flux in irreversible thermodynamics are quite well known, since even those authors who start with the Prigogine definition are apt to revert to the reduced heat flux for some applications of the theory, particularly diffusion problems. The interpretation given here of the reduced heat flux as 'pure' heat flow, unassociated with mass motions, should lend extra weight to this choice.

It is enlightening to compare the expressions for entropy production that follow from the two equations (18). The entropy balance equation is obtained by making the usual assumption of local equilibrium in the centre of mass frame at each point in space, and is of the form

$$\partial(\rho s)/\partial t + \nabla \cdot \boldsymbol{j}_s = \sigma_s, \tag{24}$$

with the following forms for entropy flux j_s and source density σ_S (de Groot and Mazur 1962):

$$j_s = \rho s v + T^{-1}W - T^{-1}\sum_i j_i \mu_i, \qquad (25P)$$

$$j_s = \rho s v + T^{-1}W + \sum_i j_i s_i, \qquad (25H)$$

and

$$\sigma_S = -T^{-1}(\mathbf{P}-P\mathbf{1}):\nabla v + \left(W - \sum_i j_i h_i\right).\nabla(T^{-1}) - T^{-1}\sum_i j_i.(\nabla \mu_i)_T, \quad (26P)$$

$$\sigma_S = -T^{-1}(\mathbf{P}-P\mathbf{1}):\nabla v + W.\nabla(T^{-1}) - T^{-1}\sum_i j_i.(\nabla \mu_i)_T. \qquad (26H)$$

The division of terms between source density and divergence of flux is of course arbitrary, but it is made in the standard way and for the usual reasons. Note that the interpretation to come has been forced slightly by making a clean separation between gradients of temperature and chemical potential in the second and third terms of the equations (26). We assume that $\nabla(T^{-1})$ is the correct generalized force for heat flow and that the isothermal gradient $(\nabla \mu_i)_T = \nabla \mu_i + s_i \nabla T$ is the correct diffusion force. In many places this separation is not realized through allowing a diffusion force of the form $\nabla(\mu_i/T)$. Haase's definition of heat flux then seems preferable to Prigogine's, as the coefficient of the thermal force in equation (26H) is just the heat flux W whereas the same coefficient in equation (26P) is a mixture of the heat and diffusion fluxes. A bonus is that the entropy flux (25H) is a sum of heat and diffusion terms with an obvious form $j_i s_i$ for the diffusion flux of species i.

Similar results are found for the entropy production in discontinuous systems, e.g. two systems both in internal equilibrium but connected by a capillary tube (de Groot and Mazur 1962; Haase 1969). In fact de Groot and Mazur's discussion of discontinuous systems uses the reduced heat flux throughout. When discussing the heats of transfer introduced in this context by Eastman (1926) and Wagner (1929), it is useful to remember that they too refer to flows of pure heat, even though the transfer contributions are caused by mass or diffusion flows.

7. Conclusions

Heat transfer in open systems has been defined here so that internal energy inputs associated with addition of mass are not counted as heat. Simple expressions follow for thermodynamic processes of the first kind, where the added mass is at the same temperature, pressure and chemical composition as the original system. For multicomponent systems, a variety of definitions are possible depending on the experimental arrangement for adding fluid, but it is suggested here that, for mass-reversible processes which are of the first kind, the arrangement of Fig. 2 is essentially unique. Thus equations (9) and (11) would then constitute unique definitions of heat for mass-reversible and completely reversible processes of the first kind.

The restriction to processes of the first kind is not particularly severe; local processes described by continuum irreversible thermodynamics are of this kind, as the thermodynamic densities are taken to be continuous functions of position. Definitions of heat flux given by Prigogine (1947; Glansdorff and Prigogine 1971) and Haase (1953, 1969) have been tested against the global definition (11). For processes not allowing composition changes, both are consistent with equation (11)

but for the more general process of Fig. 2 only Haase's definition agrees. This is not to say that Haase's heat flux is consistent with equation (11) for all processes connecting equilibrium states, but if our previous supposition is correct, then this will be true for all reversible processes of the first kind.

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