WHAT IS DIFFUSION?

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ABSTRACT

In earlier publications, heat $Q^{\leftarrow}$ is defined as an interaction that is entirely distinguishable from work $W^{\rightarrow}$. The energy exchanged $Q^{\leftarrow}$ is T_Q times the entropy exchanged $S^{\leftarrow}$, where T_Q is the almost common temperature of the interacting systems.

Here, we define diffusion as another interaction that is entirely distinguishable from both work and heat, and that involves exchanges of energy, entropy, and amount of a constituent. It is an interaction between two systems A and B that pass through stable equilibrium states while their respective parameters remain fixed, and that have almost equal temperatures $T^A \approx T^B \approx T_D$ and almost equal total potentials $\mu^A \approx \mu^B \approx \mu_D$ of the diffusing constituent. The exchanges of entropy $S^{\rightarrow}$, energy $E^{\rightarrow}$, and amount of constituent $n^{\rightarrow}$ out of one system satisfy the relation

$$S^{\rightarrow} = \frac{E^{\rightarrow} - \mu_D n^{\rightarrow}}{T_D}$$

In the limit of $n^{\rightarrow} = 0$, a diffusion interaction becomes heat.

NOMENCLATURE

A	system
A_i	state i of system A
B	system
B_i	state i of system B
dE^A	infinitesimal change of energy of A
DE^X	change of energy of system X
dn^A	infinitesimal change of amount of constituent of A
Dn^X	change of amount of constituent of system X
DS^X	change of entropy of system X
$E^{\rightarrow}$	flow of energy out of a system
E_i^X	energy of system X in state i
$E^{X\leftarrow}$	flow of energy, positive if into system X
$E^{X\rightarrow}$	flow of energy, positive if out of system X
g	gravity acceleration
h	specific enthalpy
$n^{\leftarrow}$	flow of amount of constituent, positive if into a system
$n^{\rightarrow}$	flow of amount of constituent, positive if out of a system
$n^{X\leftarrow}$	flow of constituent, positive if into system X
$n^{X\rightarrow}$	flow of constituent, positive if out of system X
n_i^X	amount of constituent of system X in state i
$Q^{\leftarrow}$	heat, positive if into a system
s	specific entropy
$S^{\leftarrow}$	flow of entropy, positive if into a system
$S^{\rightarrow}$	flow of entropy, positive if out of a system

S^{X-}	flow of entropy, positive if into system X
S^{X-}	flow of entropy, positive if out of system X
S_i^X	entropy of system X in state i
$S^X(E^X,n^X)$	fundamental relation of system X
T_D	almost common value of temperatures of systems experiencing a diffusion interaction
T_Q	almost common temperature of systems experiencing a heat interaction
T^X	temperature of system X
T_i^X	temperature of system X in state i
W^{-}	work, positive if done by a system
X_i	cyclic engine i

Greek symbols

μ_D	almost common value of total potentials of systems experiencing a diffusion interaction
μ_{iD}	almost common value of total potentials of i-th constituent of systems experiencing a diffusion interaction
μ_i^X	total potential of system X in state i
μ^X	total potential of system X
ξ	speed of a bulk flow state

1. INTRODUCTION

In some expositions of thermodynamics, the concept of diffusion is assumed self-evident and not defined explicitly [1,2]. In other expositions, diffusion in the widest sense is "the macroscopically perceptible relative motion of individual particles" [3,4], or "the transport of matter caused by concentration gradients" [5]. From these definitions, it is not clear whether diffusion should be viewed as an interaction at a boundary of a system or as a property of a system.

Consistent with our earlier discussions of work, heat, and bulk-flow interactions [6], in this paper we define diffusion as an interaction occurring at a boundary of a system that is entirely distinguishable from work, and that involves exchanges of energy, entropy, and amounts of constituents between which exists a specified relation.

The paper is organized as follows. Nonwork interactions are discussed in Section 2, diffusion is defined in Section 3, and conclusions are presented in Section 4.

2. A NONWORK INTERACTION

An interaction that cannot be classified as work is called nonwork [7]. An example of a nonwork interaction is heat [8,9].

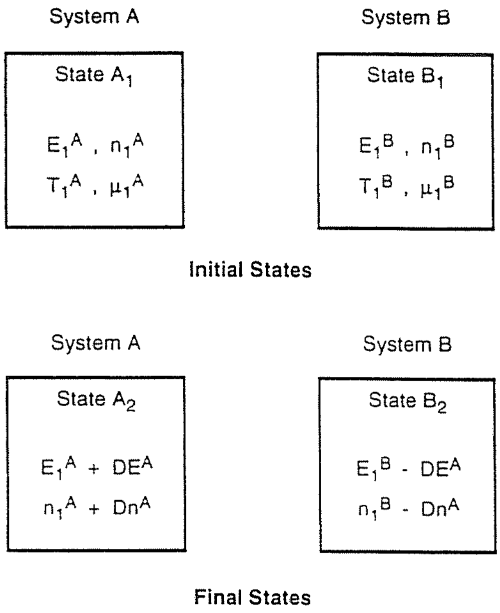

Figure 1

Another is the interaction between two systems A and B that experience a process under the following specifications (Figure 1). Each system consists of at least one common constituent and, initially, is in a stable equilibrium state but not in mutual stable equilibrium with the other because the initial temperature T_1^A at state A_1 differs from the initial temperature T_1^B at state B_1, and for the common constituent the initial total potential μ_I^A differs from the initial total potential μ_I^B. At the end of the process, the states A_2 and B_2 are not necessarily stable equilibrium, the energy and amount of constituent of system A are changed, the changes in energy and amount of constituent of system B are respectively equal and opposite to those of A, no net effects are left on the parameters and other constituents of either A or B, and no net effects are left on any system in the environment of the composite of systems A and B. Under these specifications, the interaction between A and B is nonwork because it involves exchanges of both energy and amount of the common constituent. In general, however, this interaction can be regarded as partly nonwork and partly work. To see this clearly, we reproduce the process just cited in two steps.

In the first step, we interpose between A and B a cyclic engine X_1 that produces shaft work without any entropy generation by irreversibility (Figure 2a). The cyclic engine can do work because the composite of systems A and B is not in a stable equilibrium state ($T_1^A \neq T_1^B$ and $\mu_I^A \neq \mu_I^B$) and, therefore, its

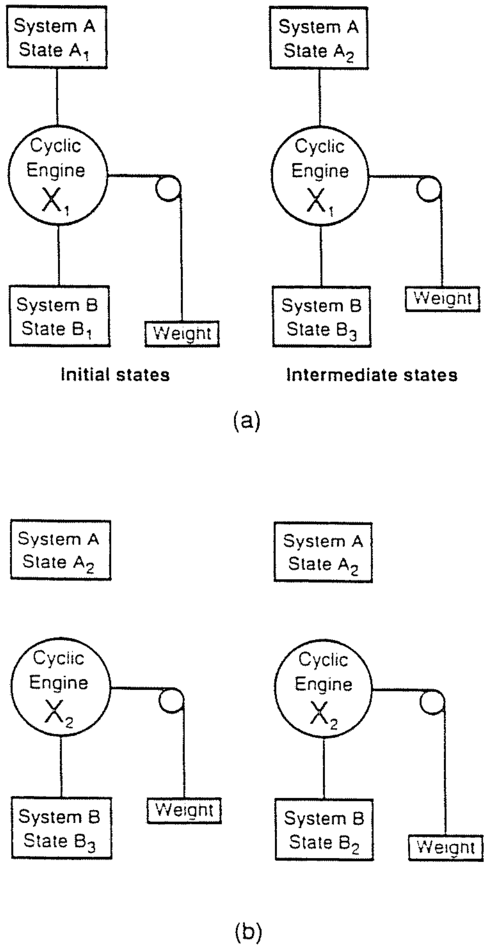

Figure 2

adiabatic availability is different from zero. The changes involved in the first step are as follows.

(a) Transfers of energy, amount of the common constituent, and perhaps entropy out of system A and into the cyclic engine X_1 equal to the respective transfers experienced in the course of the original nonwork interaction. As a result of these transfers and possibly internal effects, system A changes from state A_1 to its final state A_2, the state reached in the original nonwork process.

(b) Transfer of some of the energy received by X_1 to a weight — shaft work done to raise the weight.

(c) Transfer of the remaining energy received by X_1, and transfers of all the amount of constituent and entropy received by X_1 to system B. As a result of these transfers only, system B reaches an intermediate state B_3 different from the final state B_2 reached in the course of the original process because less energy is exchanged between X_1 and B than between A and B. Moreover, here the interaction between X_1 and B must be viewed as nonwork because it involves both energy and an amount of the constituent.

In the second step, we disconnect systems A and X_1, and connect the raised weight to a cyclic engine X_2 that can do work on system B while the weight is lowered to its initial elevation (Figure 2b), and do so without generating any entropy by irreversibility. As a result of the shaft work done on B and possibly internal effects, system B is carried from state B_3 to the final state B_2 reached by system B in the course of the original nonwork process.

At the completion of the two steps: (1) both cyclic engines X_1 and X_2, and the weight are restored to their respective initial states; (2) systems A and B experience the same changes of states — exchange the same amounts of energy, constituent, and perhaps entropy as in the original process, and generate the same amounts of entropy; and (3) we conclude that the interaction between the two systems initially at different temperatures and different total potentials can be regarded partly as nonwork (step 1), and partly as work (step 2). The question now arises "Is this conclusion always valid?" We examine the answer to this question in the next section.

3. DIFFUSION

Here we discuss a special nonwork interaction that involves at least exchanges of both energy and amount of a constituent and yet is entirely distinguishable from work in that no fraction of any such interaction can be regarded as work. To proceed, we first evaluate the work done by the cyclic engine X_1 and the systems in Figure 2a in a reversible weight process for the composite of systems A, B, and cyclic engine X_1. In this process, the initial states A_1 and B_1 are stable equilibrium, the final states A_2 and B_3 are not necessarily stable equilibrium, and there are no net changes in parameters and other constituents of either system A or system B.

Under these conditions, and for given changes DE^A, DS^A, and Dn^A respectively in the energy, entropy, and amount of constituent of system A, or flows E^{A-}, S^{A-}, and n^{A-} out of system A, the corresponding energies E_2^A and E_3^B, entropies S_2^A and S_3^B, and amounts of constituents n_2^A and n_3^B of states A_2 and B_3, respectively, and the energies E_1^A and E_1^B, entropies

S_1^A and S_1^B, and amounts of constituents n_1^A and n_1^B of the initial states A_1 and B_1, respectively, satisfy the relations

$$E_2^A = E_1^A + DE^A = E_1^A - E^{A\rightarrow} \qquad E_3^B = E_1^B + DE^B = E_1^B + E^{B\leftarrow} \tag{1}$$

$$S_2^A = S_1^A + DS^A = S_1^A - S^{A\rightarrow} \qquad S_3^B = S_1^B + DS^B = S_1^B + S^{B\leftarrow} \tag{2}$$

$$n_2^A = n_1^A + Dn^A = n_1^A - n^{A\rightarrow} \qquad n_3^B = n_1^B + Dn^B = n_1^B + n^{B\leftarrow} \tag{3}$$

where, in writing the second of equations (3), we use the fact that no amount of constituent flows to the weight, DE^B and DS^B are, respectively, the changes in energy and entropy between states B_3 and B_1, and a superscript with an arrow pointing to the right indicates positive flow out of the system denoted by the superscript. If the arrow points to the left, then positive flow is into the system denoted by the superscript.

By virtue of the highest-entropy principle [10], the entropy S_2^A cannot be larger than the entropy of the stable equilibrium state corresponding to the same values of energy and amount of the common constituent as those of state A_2. Similarly, S_3^B cannot be larger than the entropy of the stable equilibrium state corresponding to the same values of energy and amount of the common constituent as those of state B_3. Moreover, by virtue of the state principle [11], the two highest entropies are functions of the forms $S^A(E^A,n^A)$ and $S^B(E^B,n^B)$, respectively, where we omit the dependences on parameters and other constituents because here the values of the parameters and the amounts of the other constituents experience no changes. So, we have the relations

$$S_2^A \le S^A(E_2^A,n_2^A) \quad \text{and} \quad S_3^B \le S^B(E_3^B,n_3^B) \tag{4}$$

where the equal sign in the first or second relation holds only if the final state A_2 or B_3 is stable equilibrium, respectively.

To find the work, in addition to relations (1) to (4), we consider the energy and entropy balances for the reversible process of the composite of systems A, B, and X_1, that is,

$$DE^A + DE^B = E_2^A - E_1^A + E_3^B - E_1^B = -W^{\leftarrow} \tag{5}$$

$$DS^A + DS^B = S_2^A - S_1^A + S_3^B - S_1^B = 0 \tag{6}$$

where $W^{\leftarrow}$ is the work done on the weight.

The value of the work depends on the types of the final states A_2 and B_3. Indeed, upon combining relations (4) and equation (6), we find

$$\begin{aligned} S_1^A + S_1^B = S_2^A + S_3^B &\le S_2^A + S^B(E_3^B,n_3^B) \\ &\le S^A(E_2^A,n_2^A) + S^B(E_3^B,n_3^B) \end{aligned} \tag{7}$$

where the first inequality becomes an equality only if state B_3 is stable equilibrium, and the second only if state A_2 is stable equilibrium. From relations (7), we conclude further that

$$S_1^A + S_1^B - S^A(E_2^A,n_2^A) \le S_1^A + S_1^B - S_2^A \le S^B(E_3^B,n_3^B) \tag{8}$$

where the first inequality becomes an equality only if state A_2 is stable equilibrium, and the second only if state B_3 is stable equilibrium. Moreover, using equations (1) and (5) in relations (8), we find

$$\begin{aligned} S_1^A + S_1^B - S^A(E_1^A + DE^A, n_1^A + Dn^A) &\le S_1^A + S_1^B - S_2^A \\ &\le S^B(E_1^B - DE^A - W^{\leftarrow}, n_1^B - Dn^A) \end{aligned} \tag{9}$$

For given initial states A_1 and B_1, and given changes in energy, DE^A, and in amount of constituent, Dn^A, we observe that the left-hand side of relations (9) has a fixed value. This is the smallest value that can be achieved by $S_1^A + S_1^B - S_2^A$, and can be assumed by $S^B(E_1^B - DE^A - W^{\leftarrow}, n_1^B - Dn^A)$ only if both states A_2 and B_3 are stable equilibrium. Next, we recall that the fundamental relation $S^B(E^B,n^B)$ is monotonically increasing with E^B. It follows that $S^B(E_1^B - DE^A - W^{\leftarrow}, n_1^B - Dn^A)$ is monotonically decreasing with $W^{\leftarrow}$ and, therefore, that $W^{\leftarrow}$ is the largest only if $S^B(E_1^B - DE^A - W^{\leftarrow}, n_1^B - Dn^A)$ is the smallest, that is, only if both states A_2 and B_3 are stable equilibrium.

For infinitesimal changes in energy, dE^A, and amount of constituent, dn^A, we can find an explicit expression for the largest work $(W^{\leftarrow})_{\mathrm{largest}}$. Indeed, upon expanding S^A in the first relation (9) into a Taylor series around E_1^A and n_1^A, and upon expanding S^B in the second relation (9) into a Taylor series around E_1^B and n_1^B, and retaining only first order terms in these expansions, we find

$$S^A(E_1^A + dE^A, n_1^A + dn^A) = S_1^A + \frac{1}{T_1^A}dE^A - \frac{\mu_I^A}{T_1^A}dn^A \tag{10}$$

and

$$\begin{aligned} &S^B(E_1^B - dE^A - W^{\leftarrow}, n_1^B - dn^A) \\ &\qquad = S_1^B + \frac{1}{T_1^B}(-dE^A - W^{\leftarrow}) + \frac{\mu_I^B}{T_1^B}dn^A \end{aligned} \tag{11}$$

where $1/T = \partial S/\partial E$, and $\mu/T = -\partial S/\partial n$. Upon substituting equations (10) and (11) into relations (9), and rearranging terms, we find

$$\frac{1}{T_1^B} W^{\leftarrow} \leq \left(\frac{1}{T_1^B} - \frac{1}{T_1^A}\right)(-dE^A) + \left(\frac{\mu_I^B}{T_1^B} - \frac{\mu_I^A}{T_1^A}\right) dn^A \qquad (12)$$

Clearly, the largest work is done only if the equal sign applies, that is, only if the final states A_2 and B_3 are stable equilibrium, so that

$$\frac{1}{T_1^B}(W^{\leftarrow})_{largest} = \left(\frac{1}{T_1^B} - \frac{1}{T_1^A}\right) E^{A\leftarrow} - \left(\frac{\mu_I^B}{T_1^B} - \frac{\mu_I^A}{T_1^A}\right) n^{A\leftarrow} \qquad (13)$$

where in writing the right-hand side of equation (13) we use the notation introduced in equations (1) to (3).

Equation (13) indicates that if the initial temperature T_1^A and the initial ratio μ_I^A/T_1^A of system A differ from the initial temperature T_1^B and the initial ratio μ_I^B/T_1^B of system B, respectively, a fraction of the energy $E^{A\leftarrow}$ plus an energy-equivalent fraction of the amount of constituent $n^{A\leftarrow}$ transferred out of system A can always be transferred to a weight, while the remainders of these fractions are transferred to system B. The energy stored in the weight can always be returned to B by means of a weight process. Thus system B appears to experience an interaction which is partly nonwork and partly work.

But if the two initial temperatures are almost equal, and the two initial total potentials are almost equal, $(W^{\leftarrow})_{largest}$ approaches zero faster than both $E^{A\leftarrow}$ and $n^{A\leftarrow}$, and the interaction between A and B is entirely distinguishable from work in that no fraction of such an interaction can be regarded as work, even if we interpose a cyclic engine between the two interacting systems.

In this limit, equations (10) and (11) yield

$$\begin{aligned} S^{A\leftarrow} &= S_1^A - S^A(E^A + dE^A, n_1^A + dn^A) \\ &= -\frac{dE^A - \mu_D dn^A}{T_D} = \frac{E^{A\leftarrow} - \mu_D n^{A\leftarrow}}{T_D} \end{aligned} \qquad (14)$$

$$\begin{aligned} S^{B\leftarrow} &= S^B(E_1^B - dE^A, n_1^B - dn^A) - S_1^B \\ &= -\frac{dE^A - \mu_D dn^A}{T_D} = S^{A\leftarrow} \end{aligned} \qquad (15)$$

where T_D is the almost common value of the initial temperatures T_1^A and T_1^B, and μ_D the almost common value of the initial total potentials μ_I^A and μ_I^B of the interacting systems A and B.

An interaction resulting in net exchanges of entropy, energy, and amount of a constituent between two systems A and B that are in stable equilibrium states at almost equal temperatures, and almost equal total potentials, and such that the flows of entropy $S^{A\leftarrow}$, energy $E^{A\leftarrow}$, and amount of constituent $n^{A\leftarrow}$ out of system A are related by the last of equations (14), that is,

$$S^{A\leftarrow} = \frac{E^{A\leftarrow} - \mu_D n^{A\leftarrow}}{T_D} \qquad (16)$$

is called *diffusion*. Thus, diffusion is not a property of a system, nor is it contained in a system. It is a mode of transfers of energy, entropy, and amount of a constituent that are related by equation (16), and that characterize an interaction entirely distinguishable from work.

For comparison, the exchanges of energy, entropy, and amount of constituent in work, heat, bulk flow, and diffusion interactions are listed in Table 1.

TABLE 1
EXCHANGES IN FOUR DIFFERENT INTERACTIONS

EXCHANGE	INTERACTION			
	WORK	HEAT	BULK FLOW[(a)]	DIFFUSION
ENERGY	$W^{\leftarrow}$	$Q^{\leftarrow}$	$(h + \frac{\xi^2}{2} + gz) n^{\leftarrow}$	$E^{\leftarrow}$
ENTROPY	0	$\frac{Q^{\leftarrow}}{T_Q}$	$sn^{\leftarrow}$	$\frac{E^{\leftarrow} - \mu_D n^{\leftarrow}}{T_D}$
CONSTITUENT	0	0	$n^{\leftarrow}$	$n^{\leftarrow}$

(a) The specific enthalpy h and specific entropy s refer to the stable equilibrium state part of the bulk flow state [6]. The speed ξ, and elevation z in the gravity field g refer to the mechanical features of the bulk flow state. Flow of the constituent is into the system if $n^{\leftarrow}$ is positive.

In the limit of $n^{\leftarrow} = 0$, a diffusion interaction becomes a heat interaction.

A diffusion interaction can be generalized to more than one constituent. If two systems A and B, each consisting of r constituents denoted by subscripts $1, 2, \ldots, r$, are in stable equilibrium states at almost the same temperature T_D, and at almost the same total potentials $\mu_{1D}, \mu_{2D}, \ldots, \mu_{rD}$, and such that the flows of entropy $S^{A\leftarrow}$, energy $E^{A\leftarrow}$, and amounts of constituents $n_1^{A\leftarrow}, n_2^{A\leftarrow}, \ldots, n_r^{A\leftarrow}$ out of system A satisfy the relation

$$S^{A\leftarrow} = \frac{E^{A\leftarrow} - \sum_{i=1}^{r} \mu_{iD} n_i^{A\leftarrow}}{T_D} \qquad (17)$$

then the interaction is called *multiconstituent diffusion* or, simply, *diffusion*.

It can be readily shown that two or more diffusion interactions are very useful in discussions of heat conduction, flow of neutral particles through a medium, such as neutrons in nuclear reactors, flow of electrons in an electric circuit, and thermoelectricity, that is, in discussions of transport phenomena.

4. CONCLUSIONS

Diffusion is another ingenious thermodynamic concept that allows the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions. By itself or combined with work, heat, and bulk-flow interactions in writing the energy, entropy, and mass balances, diffusion provides us with practical means for identifying opportunities to reduce the entropy generated by irreversibility and, hence, to improve the performance of a system. These opportunities could be missed if the definition of diffusion were ambiguous.

The proposed definition is consistent with the requirements of the phenomenological equations discussed under the headings of either irreversible thermodynamics or transport phenomena.

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