Extended Irreversible Thermodynamics of Chemically Reacting Systems

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A phenomenological model for the thermodynamics of nonequilibrium chemically reacting systems is proposed. It is based on the assumption that the specific entropy of the system is a function of the net reaction rate, as well as of the classical variables. This assumption is confirmed by the kinetic theory of reacting dilute gas mixtures.

1. Introduction

Classical irreversible thermodynamics (CIT) is a very successful and general theory (see, e.g., ref 1). However, its range of validity is restricted to near-equilibrium systems, which excludes some relevant situations, such as fast phenomena or systems characterized by long relaxation times. Extended irreversible thermodynamics (EIT) deals with such more general situations by taking for granted that the specific entropy may depend on additional variables (see, e.g., refs 2 and 3). From this assumption, one obtains, e.g., the following expression for the specific entropy s of a system subject to a heat flux,

$$s = s_{le} - \frac{\tau}{2\rho\lambda T^2}(\vec{q})^2 \tag{1}$$

where s_{le} is the local equilibrium (or CIT) entropy per unit mass, τ is the relaxation time, $\vec{q}$ is the heat flux, ρ is the density, λ is the thermal conductivity, and T is the absolute temperature.

Many expressions of the type of eq 1 have been confirmed by microscopic derivations of the specific entropy for a wide range of phenomena (including heat conduction, convection and radiation, diffusion, and electrical conduction) and have been applied to a wide variety of physical systems (e.g., ideal and nonideal gases, polymer solutions, elastic solids, electronic devices, and nuclear matter). Does a similar result hold for chemically reacting systems? Opposite answers to this question have been proposed.[4,5] They have in common that they are based on phenomenological approaches. It seems therefore convenient to look for some microscopic approach that may shed some light on the dependence or not of the specific entropy on additional fluxes linked to the chemical reactions proceeding in the system. It is worth noting that whereas Grad's thirteen-moment kinetic theory method is very useful in the context of EIT, because it confirms the main points of this theory,[2] such a microscopic approach to chemically reacting systems[6,7] has not so far been applied with inclusion of backward reactions. In cases where only forward reactions are assumed, the calculations are simpler but the affinity diverges and this seems to make a sensible thermodynamical description impossible. In contrast, a detailed and well-established Chapman−Enskog theory exists with inclusion of the reverse reactions.[8,9] It its true that EIT of transport processes is based on the assumption that dissipative fluxes (such as the heat flux, the diffusion flux, etc.) enter as additional independent variables, and it is this point that makes EIT fully derivable from the Grad moment method, in which the same variables appear. In spite of this, in our opinion, the thermodynamical consequences of the Chapman−Enskog approach to chemical kinetics have not been analyzed in full detail, and we would like to show here that this approach may provide at least a first step towards the resolution of the question posed. In fact, in such a simple situation as that corresponding to heat conduction, one may also derive interesting properties of the nonequilibrium entropy purely from the Chapman−Enskog theory. Within this approach, one finds that the first-order correction to the Maxwell−Boltzmann distribution function is “proportional” to the temperature gradient. This means that in the nonequilibrium expansion for the distribution function

$$f = f^{(0)}\,(1 + \phi^{(1)} + ...) \tag{2}$$

where $f^{(0)}$ is the Maxwell−Boltzmann distribution function, the first-order correction is of the form $\phi^{(1)} \propto \nabla\vec{T}\cdot\vec{\mathbf{c}}$, where $\vec{\mathbf{c}}$ stands for the molecular velocity. Its explicit form is[10,11]

$$\phi^{(1)} = -\frac{2m}{5nk^2T}\left(\frac{2k}{mT}\right)^{1/2}\lambda\left(\xi^2 - \frac{5}{2}\right)\nabla\vec{T}\cdot\vec{\xi} \tag{3}$$

with $\vec{\xi} = (m/(2kT))^{1/2}\vec{\mathbf{c}}$, m the molecular mass, $n = \rho/m$ the molecular number density, and k the Boltzmann constant. Use of this expression for $\phi^{(1)}$ in the microscopic formula for the second-order specific entropy, namely[2]

$$s = s^{(0)} - \frac{k}{\rho}\int d\vec{\mathbf{c}}\, f^{(0)}\frac{\phi^{(1)^2}}{2} \tag{4}$$

yields the result

$$s = s^{(0)} - \frac{\lambda^2}{5k^2n^2T^3}(\nabla\vec{T})^2 \tag{5}$$

so that the nonequilibrium correction is of the form $s - s^{(0)} \propto (\nabla\vec{T})^2$. As it is well known, within the first-order Chapman−

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Enskog approximation (i.e., retaining only the first two terms in the expansion (2)), one obtains the Fourier law, which states that the heat flux is proportional to the temperature gradient,

$$\vec{q} = -\lambda \vec{\nabla T} \tag{6}$$

Therefore eq 5 may also be written

$$s = s^{(0)} - \frac{1}{5k^2 n^2 T^3} (\vec{\boldsymbol{q}})^2 \tag{7}$$

which shows that the nonequilibrium perturbation on the entropy is proportional to the square of the heat flux,

$$s - s^{(0)} \propto (\vec{\boldsymbol{q}})^2$$

and this is also a prediction of the result (1) of EIT (in contrast, CIT of transport processes corresponds to neglecting the second-order term in eq 7 or 1, i.e., to the first-order approximation for the entropy, namely $s \approx s^{(0)}$,[1,12] so that $s_{\mathrm{le}} = s^{(0)}$). As it has been stressed[13] and applied[14] recently, the previous results show that flux dependences of the specific entropy are not restricted to a particular kinetic or statistical model but ubiquitously arise in different microscopic and phenomenological approaches, and this is not inconsistent with the well-known fact that different evolution equations follow from the Chapman−Enskog kinetic approach and from Grad's theory (or from EIT). In view of this and of the difficulties we have summed up, it would be of importance to know if a result somehow similar to (7) can be derived for the Chapman−Enskog approach for chemically reacting systems. This is the problem we will tackle in the present paper. If a relation similar to (5) or (7) holds in the presence of chemical reactions, then there is a basis for expecting that the thermodynamics of chemically reacting systems can be described by means of EIT.

The plan of the paper is as follows. In the next section, we propose a phenomenological model along the lines of EIT. In section 3, we make some deductions concerning the properties of the nonequilibrium entropy of chemically reacting systems from the Chapman−Enskog approach presented in refs 8, 9, and 15. In section 4, we compare both approaches and include some concluding remarks.

2. Thermodynamical Approach

Classical irreversible thermodynamics (CIT) of multicomponent systems is formulated upon the assumption of local thermodynamic equilibrium (LTE), which sates that the (local equilibrium) entropy per unit mass of the mixture depends on the total specific internal energy, u, the specific volume $v = 1/\rho$, and the mass fractions $\mathbf{c}_\gamma = \rho_\gamma/\rho$ (ρ_γ is the density of component γ), i.e., $s_{\mathrm{le}}(u, v, \mathbf{c}_\gamma)$. From this assumption and the thermodynamical definitions for the temperature, T, pressure, p, and chemical potentials, μ_γ, namely,[1,2]

$$\frac{1}{T} = \left(\frac{\partial s_{\mathrm{le}}}{\partial u}\right)_{v,\mathbf{c}_\gamma}, \quad \frac{p}{T} = \left(\frac{\partial s_{\mathrm{le}}}{\partial v}\right)_{u,\mathbf{c}_\gamma}, \quad \frac{\mu_\gamma}{T} = -\left(\frac{\partial s_{\mathrm{le}}}{\partial \mathbf{c}_\gamma}\right)_{u,v}$$

the local Gibbs equation immediately follows,

$$\mathrm{d}s_{\mathrm{le}} = \frac{1}{T}\,\mathrm{d}u + \frac{p}{T}\,\mathrm{d}v - \sum_\gamma \frac{\mu_\gamma}{T}\,\mathrm{d}\mathbf{c}_\gamma \tag{8}$$

Extended irreversible thermodynamics (EIT) deals with systems not necessarily in local thermodynamic equilibrium and is based on the assumption that additional macroscopic quantities (e.g., the heat flux in conductive systems) play the role of independent variables. This means that the whole set of space variables describing the system is formed by the classical (conserved) variables plus the (nonconserved) fluxes present in the system. Let us follow this perspective[2] and assume that the specific entropy of a nonlocal equilibrium system in which one single chemical reaction proceeds may depend on the reaction rate J, as well as on the classical variables, i.e., $s(u, v, \mathbf{c}_\gamma, J)$. We have for the entropy differential

$$\mathrm{d}s = \left(\frac{\partial s}{\partial u}\right)_{v,\mathbf{c}_\gamma,J} \mathrm{d}u + \left(\frac{\partial s}{\partial v}\right)_{u,\mathbf{c}_\gamma,J} \mathrm{d}v + \sum_\gamma \left(\frac{\partial s}{\partial \mathbf{c}_\gamma}\right)_{u,v,J} \mathrm{d}\mathbf{c}_\gamma + \left(\frac{\partial s}{\partial J}\right)_{u,v,\mathbf{c}_\gamma} \mathrm{d}J$$

and define, in the usual way, a generalized temperature θ, a generalized pressure Π, and the generalized chemical potentials η_γ as follows

$$\frac{1}{\theta} = \left(\frac{\partial s}{\partial u}\right)_{v,\mathbf{c}_\gamma,J} \quad \frac{\Pi}{\theta} = \left(\frac{\partial s}{\partial v}\right)_{u,\mathbf{c}_\gamma,J} \quad \frac{\eta_\gamma}{\theta} = -\left(\frac{\partial s}{\partial \mathbf{c}_\gamma}\right)_{u,v,J}$$

In the rest of this section, we shall briefly discuss the consequences of these extended expressions by following a procedure that consists of nothing but the usual steps in EIT.[2] Such an approach has been considered for chemically reacting systems by García-Colín and de la Selva,[4] as well as Nettleton.[16,17] The original approach[4] aims to a wider scope than the one we will present in this section, not only because of the inclusion of transport fluxes but also because higher-order terms were taken into account. It is worth mentioning that such an analysis led, in particular, to very interesting results and discussions on the relationship between the kinetic mass action law and thermodynamics.[5] Nevertheless, our main purpose here is to look for a microscopic basis of an EIT approach to chemically reacting systems. We will therefore consider the simplest possible case such that it makes possible to perform a comparison between extended thermodynamical and microscopical results (the latter will be presented in the next section). With this aim, and since the generalized entropy s must reduce to the classical entropy s_{le} in systems with vanishing reaction rate, in near-equilibrium states we may introduce a function $\alpha(u,v,\mathbf{c}_\gamma)$ that depends only on the classical variables and such that

$$\left(\frac{\partial s}{\partial J}\right)_{u,v,\mathbf{c}_\gamma} = -\frac{\alpha}{T} J$$

Therefore, the local Gibbs eq 8 is generalized into

$$\mathrm{d}s = \frac{1}{\theta}\,\mathrm{d}u + \frac{\Pi}{\theta}\,\mathrm{d}v - \sum_\gamma \frac{\eta_\gamma}{\theta}\,\mathrm{d}\mathbf{c}_\gamma - \frac{\alpha}{T} J\,\mathrm{d}J \tag{9}$$

Since this must be an exact differential in order for the specific entropy to be a state function, we can require that

$$\frac{\partial}{\partial J}\left(\frac{1}{\theta}\right) = -J \frac{\partial}{\partial u}\left(\frac{\alpha}{T}\right), \quad \frac{\partial}{\partial J}\left(\frac{\Pi}{\theta}\right) = -J \frac{\partial}{\partial v}\left(\frac{\alpha}{T}\right), \quad \frac{\partial}{\partial J}\left(\frac{\eta_\gamma}{\theta}\right) = J \frac{\partial}{\partial \mathbf{c}_\gamma}\left(\frac{\alpha}{T}\right)$$

Integration yields the following equations of state

$$\frac{1}{\theta} = \frac{1}{T} - \frac{J^2}{2}\frac{\partial}{\partial u}\left(\frac{\alpha}{T}\right) \tag{10}$$

$$\frac{\Pi}{\theta} = \frac{p}{T} - \frac{J^2}{2}\frac{\partial}{\partial v}\left(\frac{\alpha}{T}\right) \tag{11}$$

$$\frac{\eta_\gamma}{\theta} = \frac{\mu_\gamma}{T} + \frac{J^2}{2}\frac{\partial}{\partial \mathbf{c}_\gamma}\left(\frac{\alpha}{T}\right) \tag{12}$$

When our analysis is restricted to an incompressible, multicomponent fluid in which diffusion and other transport processes are absent and assuming for simplicity that the heat of reaction may be neglected, the evolution equation for the specific entropy in nonequilibrium processes may be written, up to second order in J, as

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t} = J\left(\frac{A}{T} - \frac{\alpha\rho}{T}\frac{\mathrm{d}J}{\mathrm{d}t}\right) \tag{13}$$

where we have taken into account that the absence of heat conduction and of heat of reaction implies an isothermal process; we have also applied the mass fraction balance equation for the case considered here, namely $\mathrm{d}c_\gamma/\mathrm{d}t = (\nu_\gamma/\rho)J$, and introduced the affinity of the chemical reaction as

$$A = -\sum_\gamma \nu_\gamma \mu_\gamma \tag{14}$$

Here ν_γ is the molecular mass, m_γ, times the stoichiometric coefficient with which component γ appears in the reaction (counted positive (negative) if γ appears in the second (first) member of the reaction equation). From the general law of balance of entropy, namely $\rho(\mathrm{d}s/\mathrm{d}t) = -\vec{\nabla}\cdot\vec{J}^s + \sigma^s$ ($\vec{J}^s$ is the entropy flux), it follows that the rate of production of entropy (per unit volume) is

$$\sigma^s = J\left(\frac{A}{T} - \frac{\alpha\rho}{T}\frac{\mathrm{d}J}{\mathrm{d}t}\right)$$

Note that eq 13 is a balance equation without the term containing the divergence of a flux. This stems from our assumption of the absence of transport processes. In fact, the unique flux in eq 13 is the reaction rate J, which does not appear as a true flux in the balance equation of mass fraction $\mathbf{c}_\gamma$ but as a source term. This distinct origin of fluxes prevents one from describing chemical reactions in the framework of EIT following its standard procedure.[5]

The second law of thermodynamics requires $\sigma^s \geq 0$. The simplest way to assure this is to assume an evolution equation of the form

$$\frac{A}{T} - \frac{\alpha\rho}{T}\frac{\mathrm{d}J}{\mathrm{d}t} = \beta J$$

with $\beta \geq 0$. This equation is an analogue to the Maxwell−Cattaneo equations for transport processes, and such an equation for the heat flux is assumed in the EIT derivation of the generalized entropy (1). In a more familiar notation,

$$\tau\frac{\mathrm{d}J}{\mathrm{d}t} + J = l\frac{A}{T} \tag{15}$$

where we have introduced τ (which plays the role of a relaxation time) and l through $\beta = 1/l$ and $\alpha = (\tau T)/(pl)$. It is very interesting that a special equation of this type has been derived and applied by King in order to obtain an expression for the relaxation time with which a reacting system slightly perturbed from equilibrium and then isolated attains the equilibrium state again and that his result coincides with that derived by other methods.[18] Equations of the form of (15), as well as more general ones, also follow from an action functional of Hamilton's type.[19]

With use of the expression for α derived above, the generalized Gibbs equation (9) may be written, up to second order in the fluxes, as

$$\mathrm{d}s = \frac{1}{T}\mathrm{d}u + \frac{p}{T}\mathrm{d}v - \sum_\gamma \frac{\mu_\gamma}{T}\mathrm{d}\mathbf{c}_\gamma - \frac{\tau}{\rho l}J\,\mathrm{d}J \tag{16}$$

Finally, we integrate eq 16 and obtain for the generalized nonequilibrium specific entropy

$$s(u,v,\boldsymbol{c}_\gamma,J) = s(u,v,\boldsymbol{c}_\gamma) - \frac{\tau}{2pl}J^2 \tag{17}$$

It is worth stressing that classical irreversible thermodynamics (as presented, e.g., in ref 1) cannot yield a result such as eq 17, simply because this theory relies on the local equilibrium hypothesis (which is nothing but the approximation $s \approx s_{\mathrm{le}}$). For the purposes of the present paper, the important point in eq 17 is precisely that it includes a nonequilibrium correction to the specific entropy, and that this correction is quadratic in the reaction rate, $s - s_{\mathrm{le}} \propto J^2$, just as the nonequilibrium correction in eq 1 is quadratic in the heat flux. However, the applicability of eq 17 to non-LTE chemically reacting systems would be reinforced if it could be backed by a microscopic approach, just as eq 6, which follows form the Chapman−Enskog theory, yields eq 7, which is in agreement with the EIT result (1). It is true that eq 6 is not a Maxwell−Cattaneo equation for the heat flux (such an equation would generalize eq 6 and can be derived microscopically from the Grad thirteen-moment method, whereas (6) follows from the Chapman−Enskog approach). However, eq 6 does lead to the conclusion that the nonequilibrium entropy of conductive systems must include an additional term in the heat flux. Such a derivation is valid in situations such that the term in the Maxwell−Cattaneo equation that contains the derivative of the heat flux is negligible, i.e., it is not valid for very fast processes. This important point, which has been already mentioned in the introduction and elsewhere,[13] is due to the fact that the second-order specific entropy (4) depends only on the *first-order* correction $\phi^{(1)}$ to the distribution function but not on higher-order corrections, $\phi^{(2)}$, $\phi^{(3)}$, etc. A microscopic, analogous approach to chemically reacting systems would certainly back the concept of a rate-dependent nonequilibrium entropy, and such an approach is discussed in the next section.

3. Microscopic Approach

We consider a system composed of ideal gases in which a chemical reaction proceeds. The entropy per unit volume of the system is

$$\tilde{s} = \rho s = -k\sum_\gamma \int \mathrm{d}\vec{\mathbf{c}}_\gamma f_\gamma(\ln f_\gamma - 1) \tag{18}$$

with $\vec{\mathbf{c}}_\gamma$ and f_γ the molecular velocity and distribution function of component γ, respectively. For the case in which a chemical reaction characterized by an activation energy proceeds, fast molecules of some species disappear and transform into products. Only in equilibrium is this temporal evolution cancelled out by the reverse reaction. Thus, even in the absence of transport processes, the Maxwell−Boltzmann form for the distribution functions of the mixture, namely[1]

$$f_\gamma^{(0)} = n_\gamma \left(\frac{m_\gamma}{2\pi kT}\right)^{3/2} \mathrm{e}^{-m_\gamma \mathbf{c}_\gamma^2/2kT} = \mathrm{e}^{m_\gamma(\mu_\gamma - \mathbf{c}_\gamma^2/2)/kT} \tag{19}$$

with μ_γ the chemical potential per unit mass of a component γ of an ideal gas mixture, cannot lead to exact results for nonequilibrium reacting systems. In eq 19, we have assumed for simplicity that the system is macroscopically at rest so that the barycentric velocity vanishes. The quantities n_γ and m_γ are the molecular number density and molecular mass of component γ, respectively.

Let us first consider a very simple case, namely that in which the system is very near to equilibrium. This will allow us to introduce our notation and procedure, check its consistency with well-known results for the thermodynamics of chemically reacting systems, and then consider more general situations.

In the case of small nonequilibrium effects, the distribution functions of the components may be approximated by Maxwellians,

$$f_\gamma \approx f_\gamma^{(0)} \tag{20}$$

and eq 18 may be written

$$\tilde{s} \approx \tilde{s}^{(0)} = -k\sum_\gamma \int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)}(\ln f_\gamma^{(0)} - 1) \tag{21}$$

so that the entropy density differential $\delta\tilde{s}$ is given, within this approximation, by

$$\delta\tilde{s}^{(0)} = -k\sum_\gamma \int \mathrm{d}\vec{\mathbf{c}}_\gamma \ln\, f_\gamma^{(0)}\, \delta f_\gamma^{(0)}$$

($\delta\tilde{s}$ is the entropy difference between two closely thermodynamic states of the system; as in ref 20 we prefer the notation $\delta\tilde{s}$, instead of $\mathrm{d}\tilde{s}$, in order to avoid confusion in all equations in which additional differentials appear). Making use of eq 19,

$$\delta\tilde{s}^{(0)} = -\sum_\gamma \frac{m_\gamma\mu_\gamma}{T}\int \mathrm{d}\vec{\mathbf{c}}_\gamma\, \delta f_\gamma^{(0)} + \frac{1}{T}\sum_\gamma \int \mathrm{d}\vec{\mathbf{c}}_\gamma\, \frac{m_\gamma \mathbf{c}_\gamma^{2}}{2}\, \delta f_\gamma^{(0)}$$

From the microscopic expressions for the number densities and internal energies, namely,

$$n_\gamma = \int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma \tag{22}$$

$$\tilde{u}_\gamma = \int \mathrm{d}\vec{\mathbf{c}}_\gamma \frac{m_\gamma \mathbf{c}_\gamma^{2}}{2} f_\gamma \tag{23}$$

introducing the energy density of the system,

$$\tilde{u} = \sum_\gamma \tilde{u}_\gamma$$

and using eq 20, we obtain the macroscopic expression for the rate of change of the entropy density,

$$\begin{aligned}\frac{\mathrm{d}\tilde{s}^{(0)}}{\mathrm{d}t} &= -\frac{1}{T}\sum_\gamma \mu_\gamma \frac{\mathrm{d}n_\gamma}{\mathrm{d}t} + \frac{1}{T}\frac{\mathrm{d}\tilde{u}}{\mathrm{d}t} \qquad (24)\\ &= -\frac{1}{T}\sum_\gamma \mp m_\gamma n_\gamma\, J^{(0)} + \frac{1}{T}\frac{\mathrm{d}\tilde{u}}{\mathrm{d}t}\end{aligned}$$

where we have made use of the law of balance of mass for each component, which assuming a simple reaction of the type

$$\mathrm{A + B \rightleftarrows C + D}$$

reads[1] $\mathrm{d}n_\gamma/\mathrm{d}t = \mp J(\mathrm{d}n_\gamma/\mathrm{d}t = -J$ for γ = A, B; for C, D), with the rate of reaction J being given, within the approximation (20), by[21]

$$\begin{aligned}J \approx J^{(0)} = J_f^{(0)} - J_b^{(0)} \equiv k_f^{(0)}\, n_\mathrm{A} n_\mathrm{B} - k_r^{(0)}\, n_\mathrm{C} n_\mathrm{D} = \\ \int\int\int \mathrm{d}\Omega\, \mathrm{d}\vec{\mathbf{c}}_\mathrm{A}\, \mathrm{d}\vec{\mathbf{c}}_\mathrm{B}\, f_\mathrm{A}^{(0)}\, f_\mathrm{B}^{(0)} \sigma_f^*\, \mathbf{c}_{\mathrm{rel\ AB}} - \\ \int\int\int \mathrm{d}\Omega\, \mathrm{d}\vec{\mathbf{c}}_\mathrm{C}\, \mathrm{d}\vec{\mathbf{c}}_\mathrm{D}\, f_\mathrm{C}^{(0)} f_\mathrm{D}^{(0)} \sigma_b^*\, \mathbf{c}_{\mathrm{relCD}}\end{aligned} \tag{25}$$

with $\vec{\mathbf{c}}_{\mathrm{rel}\ ij} = \vec{\mathbf{c}}_i - \vec{\mathbf{c}}_j$ and σ_f^* (σ_b^*) the differential cross section of the reaction A + B → C + D (A + B ← C + D). In nonequilibrium states $J^{(0)}$ does not vanish because the number densities n_γ do not satisfy the equilibrium relationship $(n_\mathrm{A} n_\mathrm{B})/(n_\mathrm{C} n_\mathrm{D}) = k_r^{(0)}/k_f^{(0)}$. Assuming for simplicity that the heat of reaction is negligible, comparison of eq 24 with the balance equation of entropy allows us (taking into account that $\mathrm{d}\tilde{u}/\mathrm{d}t = 0$ in the absence of fluxes other than J and of heat of reaction) to identify the entropy production rate due to the proceeding of the chemical reaction, within this approximation, as

$$\sigma^{s(0)} = -\frac{1}{T}\sum_\gamma \mp m_\gamma \mu_\gamma J^{(0)}$$

Making use of the definition (14) for the affinity, i.e., $A = m_\mathrm{A}\mu_\mathrm{A} + m_\mathrm{B}\mu_\mathrm{B} - m_\mathrm{C}\mu_\mathrm{C} - m_\mathrm{D}\mu_\mathrm{D}$, we obtain

$$\mathrm{s}^{s(0)} = \frac{AJ^{(0)}}{T} \tag{26}$$

which is the result first derived microscopically by Prigogine.[12] It is not difficult to derive the local Gibbs equation (8) from the previous results in this section. Moreover, the second law requires that $\sigma^s \geq 0$. This will hold provided that

$$J^{(0)} = L^{(0)}A \tag{27}$$

with $L^{(0)} \geq 0$. It is true that this linear law is unrealistic except very close to equilibrium,[22,23] but it is an adequate starting point in order to try to extend the classical theory.

We now consider states further away from equilibrium. This implies that the approximation (20) no longer holds. We write the distribution functions as

$$f_\gamma = f_\gamma^{(0)}(1 + \phi_\gamma^{(1)} + ...) \tag{28}$$

which are analogous to eq 2, with the difference that the nonequilibrium corrections are now due to the proceeding of the chemical reaction. The number of necessary terms for this expansion to yield a reasonable description will increase as further away from equilibrium states are considered. As it is shown in Appendix A that from the theory due to Shizgal and collaborators a simple expression for the first-order correction can be obtained,

$$\phi_\gamma^{(1)} = F_\gamma\,(q,\epsilon^*,T,\{m_\gamma\})A\left(\frac{3}{2} - \xi_\gamma^{2}\right) \tag{29}$$

where q and ϵ^* are parameters for the reaction. In order to find out the entropy density, we expand eq 18 up to second order:

$$\tilde{s} = \tilde{s}(0) - k\sum_\gamma \int d\vec{\mathbf{c}}_\gamma\ f_\gamma^{(0)} \ln f_\gamma^{(0)}\phi_\gamma^{(1)} - k\sum_\gamma \int d\vec{\mathbf{c}}_\gamma\ f_\gamma^{(0)} \ln f_\gamma^{(0)}\phi_\gamma^{(2)} - k\sum_\gamma \int d\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)}\frac{\phi_\gamma^{(1)2}}{2} \tag{30}$$

with $\tilde{s}^{(0)}$ given by (21). From eq 19, we see that both the second and third terms in the former expression for $\tilde{s}$ are of the form

$$k\sum_\gamma \int d\vec{\mathbf{c}}_\gamma\ f_\gamma^{(0)} \ln f_\gamma^{(0)}\phi_\gamma^{(i)} = \sum_\gamma \frac{\mu_\gamma}{T}\int d\vec{\mathbf{c}}_\gamma\ f_\gamma^{(0)}\phi_\gamma^{(i)} - \frac{1}{T}\sum_\gamma \int d\vec{\mathbf{c}}_\gamma \frac{m_\gamma \mathbf{c}_\gamma^2}{2} f_\gamma^{(0)}\phi_\gamma^{(i)}$$

with $i = 1, 2$, respectively. However, in the kinetic theory, it follows from the microscopic expressions for the molecular number densities and the internal energy density that $\int d\vec{\mathbf{c}}_\gamma f_\gamma^{(0)}\phi_\gamma^{(i)} = 0$ for any values of i and γ, and that the $\sum_\gamma \int d\vec{\mathbf{c}}_\gamma ((m_\gamma \mathbf{c}_\gamma^2)/2) f_\gamma^{(0)}\phi_\gamma^{(i)} = 0$, respectively.[10] Therefore, the second and third terms in eq 30 vanish. This is analogous to the vanishing of similar integrals in the microscopic expression for the entropy density of systems under matter[1,2] and radiation[24] transport processes. Equation 30 reduces to

$$\tilde{s} = \tilde{s}^{(0)} - k\sum_\gamma \int d\vec{\mathbf{c}}_\gamma\ f_\gamma^{(0)}\frac{\phi_\gamma^{(1)2}}{2} \tag{31}$$

which is the analogue to eq 4 for chemically reacting dilute mixtures instead of transport processes in a single-component ideal gas.

We may mention that if one wishes to evaluate the entropy density *up to first-order*, the last term in (31) is negligible. It is therefore clear that the first equality in eq 24 still holds and we have

$$\frac{d\tilde{s}}{dt} = -\frac{1}{T}\sum_\gamma \mp m_\gamma \mu_\gamma J + \frac{1}{T}\frac{d\tilde{u}}{dt}$$

We may proceed as in the zeroth-order approximation and, after comparison with the law of balance of entropy, find that the entropy production for the case considered may be written as $\sigma^s = AJ/T$, which generalizes eq 26, holds *in the first-order approximation*, and is in agreement with the results by Ross and Mazur.[21]

After inserting eq 29 into eq 31 and performing the integrations, we obtain for the second-order entropy,

$$\tilde{s} = \tilde{s}^{(0)} - \frac{3k}{4}\sum_\gamma n_\gamma [F_\gamma(q,\epsilon^*,T,\{m_\gamma\})]^2 A^2 \tag{32}$$

as it is shown in Appendix B.

4. Discussion

Equation 32 is a chemical analogue to (5). Both of them have been derived from the Chapman−Enskog theory. We now recall that in the well-established approach to heat conduction, eq 5, transforms into the flux-dependent entropy (7) by use of eq 6, which holds in the first-order approximation (2). In the same level of approximation for chemically reactive systems, the reaction rate is given by

$$J = J^{(0)} + J^{(1)} \tag{33}$$

where

$$J^{(1)} = \int\int\int d\Omega\ d\vec{\mathbf{c}}_A\, d\vec{\mathbf{c}}_B\, f_A^{(0)} f_B^{(0)}(\phi_A^{(1)} + \phi_B^{(1)})\sigma_f^*\, \mathbf{c}_{\text{rel AB}} - \int\int\int d\Omega\, d\vec{\mathbf{c}}_C\, d\vec{\mathbf{c}}_D\, f_C^{(0)} f_D^{(0)}(\phi_C^{(1)} + \phi_D^{(1)})\sigma_b^*\, \mathbf{c}_{\text{relCD}} \tag{34}$$

Insertion of eq 29 into eq 34 and integration will yield a result of the form

$$J^{(1)} = L^{(1)}A \tag{35}$$

where the explicit form of $L^{(1)}$ can be derived only if a specific reaction mechanism is assumed so that eq 34 can be integrated (the same happens for $L^{(0)}$, see eqs 27 and 25. Such an expression for $L^{(1)}$, together with that for the affinity in terms of concentrations, are necessary in studies of nonequilibrium effects on the reaction rate but not in the context of a thermodynamical analysis of the system, which is the main purpose of the present paper. The conclusion that $J^{(1)}$ is proportional to the affinity A is consistent with the results in ref 15, where the contribution to $J^{(1)}$ stemming from the forward reaction was found to be proportional to the affinity in the case of near-equilibrium systems. According to eqs 33, 27, and 35, in the first-order approximation (28) we have

$$J = (L^{(0)} + L^{(1)})A \tag{36}$$

so that eq 32 yields for the specific entropy $s = \tilde{s}/\rho$,

$$s = s^{(0)} - \frac{3k}{4\rho}\sum_\gamma n_\gamma \left(\frac{F_\gamma(q,\epsilon^*,T,\{m_\gamma\})}{L^{(0)} + L^{(1)}}\right)^2 J^2 \tag{37}$$

with $\rho = \sum_\gamma \rho_\gamma$. The fact that $s < s^{(0)}$ was to be expected, since the entropy maximum corresponds to the equilibrium state and in this case the forward and backward reactions balance each other ($J = 0$). According to eq 37, the nonequilibrium correction to the entropy of the reacting system is proportional to J^2 in near-equilibrium states. This is in agreement with the EIT result (17). Thus, a reaction rate entropy dependence is predicted, just as a heat flux dependence is predicted by the Chapman−Enskog theory in the case of heat conduction (eq 7), and both results are consistent with EIT (eqs 17 and 1, respectively).[25] Therefore, and in spite of the fact that we have considered situations very close to equilibrium, we conclude that EIT seems to be an adequate framework for the thermodynamical description of chemically reacting systems. Before closing this paper, we would like to mention that, in some way, this result is not surprising because the same conclusion has recently been reached for radiative transfer,[24] which is nothing but a transformation of one species of matter into another by the interchange of photons; that is, it may be viewed as an special case of a chemically reacting system. The reason why, in contrast to what was done in refs 20 and 24, we have not made use of statistical mechanics but of kinetic theory is that the radiative transfer equation is much simpler mathematically than the Boltzmann equation and, within information statistical theory, the use of the chemical rate of reaction as an additional constraint leads to extremely complicated equations except for some simple systems for which one may not consistently evaluate the entropy density of the overall system.[26]

Just to summarize, the reaction rate is not a flux in the usual sense because it does not appear as a true flux in the balance equations of mass fractions; instead, it appears as a source term there. In spite of this, we have shown how chemical reactions can be included in the much broader framework of extended irreversible thermodynamics (EIT). Such a conclusion has been reached here under the assumptions that diffusion and other transport processes, as well as the heats of reaction, are negligible. These assumptions simplify the problem since they imply that the internal energy and temperature are constant and that there is no entropy flux. We have shown that, close to equilibrium, the nonequilibrium entropy contains a term in the square of the reaction rate and that our conclusion is comforted by comparison to the kinetic theoretical results of Shizgal and co-workers for the case in which linearity between the reaction rate and the chemical affinity holds (eq 36). We stress again that this linearity is unrealistic unless when dealing with states very close to equilibrium. In the future, it would therefore be of importance to try to extend the approach here presented to situations including a nonlinear mass action law instead of eq 15.

Note Added in Proof: In the microscopic approach, presented in section 3 and Appendix A, we have made use of the assumptions that the first Sonine term yields a reasonable approximation and that Present's line-of-centers model can be applied. Such assumptions have allowed us to perform explicit microscopic calculations (see the explicit expressions for $F_\gamma(q,\epsilon^*,T,\{m_\gamma\})$ at the end of Appendix A). It is worth stressing, however, that according to Shizgal's microscopic approach (see Appendix A to ref 15), the nonequilibrium corrections $\phi_\gamma^{(1)}$ are proportional to the affinity even without need to consider such assumptions so that eq 37 is still valid. This is in agreement with the reaction flux quadratic dependance in the EIT result (17), which does not rely on those assumptions either.

5. Appendix A

Derivation of Eq 29. The problem of how a chemical reaction affects the distribution functions of the components was solved, with inclusion of the back reaction and in near-equilibrium states, by Shizgal and Karplus[8] (see also ref 9). Therefore, their derivation will not be repeated here. They made use of the Chapman−Enskog method. This approach is valid provided that the elastic time scale is much less than the reactive time scale.[27] It means that reactive collisions are much less frequent than elastic ones and therefore the reaction causes a small perturbation on the system under consideration. In refs 8 and 9, this method has been applied to a variety of cross sections and levels of approximations. The authors were interested in the important problem of the nonequilibrium effects on the reaction rate. For this reason, they gave general expressions and performed many evaluations but did not include explicit expressions for the perturbations $\phi_\gamma^{(1)}$ in terms of thermodynamical quantities. Thus, in this appendix we show, for the sake of completeness, that the results in refs 8 and 9 lead to eq 29.

The general form for $\phi_\gamma^{(1)}$, within the Chapman−Enskog method, is an infinite series of Sonine polynomials. The first nonvanishing term is a reasonable approximation in some cases, but in general, additional terms are necessary. The number of necessary terms has been evaluated by comparison of several subaproximations in specific cases and depends on the mechanism and parameters of the reaction considered.[8,9,15] For the purposes of the present paper, it is sufficient to consider situations such that the first nonvanishing term dominates so that the corrections $\phi_\gamma^{(1)}$ are of the simple form[8]

$$\phi_\gamma^{(1)} = a_1^{(\gamma)}\left(\frac{3}{2} - \xi_\gamma^{\ 2}\right) \tag{38}$$

where

$$\xi_\gamma^{\ 2} = \frac{m_\gamma \mathbf{c}_\gamma^{\ 2}}{2kT} \tag{39}$$

and ξ_γ is the reduced speed of the γ-component molecules. In order to find out $a_1^{(\gamma)}$ explicitly, it is necessary to find out some additional quantities first. As in ref 9, for simplicity we consider the simple reaction

$$\mathrm{B} + \mathrm{B} \rightleftarrows \mathrm{C} + \mathrm{C} \tag{40}$$

so that the conservation of mass implies that $m_\mathrm{B} = m_\mathrm{C} \equiv m$.

We begin with the definitions[8,15]

$$K_0^{(\gamma)} = \frac{1}{\pi}\int_0^\infty \mathrm{e}^{-m\mathbf{c}_{\mathrm{rel}\gamma}^{\ 2}/4kT}\left(\frac{m}{4kT}\right)^2 \mathbf{c}_{\mathrm{rel}\gamma}^{\ 3}\ \sigma^*(\mathbf{c}_{\mathrm{rel}\gamma})\ \mathrm{d}\mathbf{c}_{\mathrm{rel}\gamma}$$

$$K_1^{(\gamma)} = \frac{1}{\pi}\int_0^\infty \mathrm{e}^{-m\mathbf{c}_{\mathrm{rel}\gamma}^{\ 2}/4kT}\left(\frac{m}{4kT}\right)^3 \mathbf{c}_{\mathrm{rel}\gamma}^{\ 5}\ \sigma^*(\mathbf{c}_{\mathrm{rel}\gamma})\ \mathrm{d}\mathbf{c}_{\mathrm{rel}\gamma}$$

where $\mathbf{c}_{\mathrm{rel}\gamma}$ is the relative velocity of the pair of reactively colliding molecules, and $\gamma = \mathrm{B}, \mathrm{C}$ denotes the component. We will make use of the Present line-of-centers cross section

$$\sigma^*(\mathbf{c}_{\mathrm{rel}\gamma}) = 0 \quad \mathbf{c}_{\mathrm{rel}\gamma} < \mathbf{c}_{\mathrm{rel}\gamma}^{\ *} \tag{41}$$

$$\frac{\pi^2}{4}qd^2\left(1 - \frac{\epsilon^*}{\epsilon}\right), \quad \mathbf{c}_{\mathrm{rel}\gamma} \geq \mathbf{c}_{\mathrm{rel}\gamma}^{\ *}$$

where $\epsilon = {}^m/_4\mathbf{c}_{\mathrm{rel}\gamma}^{\ 2}$ and we have assumed for simplicity the same threshold energy ϵ^* for the forward and backward reactions. This corresponds to assuming that the heat of reaction is negligible (in this way we are able to concentrate on the problem posed by making use of rather simple equations; if we considered exothermic or endothermic reactions, we would have a nonsteady system temperature and its effect on the nonequilibrium corrections could become very important[8,9]). Also for simplicity, we have assumed the steric factors and elastic collision diameters (q and d, respectively) to be the same for the forward and backward reactions (this does not affect the conclusions in the present paper and, again, makes equations simpler; in fact, according to microscopical reversibility the product qd^2 must be the same for both reactions[9]). After performing the integrations,

$$K_0^{(\gamma)} = \frac{qd^2}{2}\,\mathrm{e}^{-\epsilon^*/kT}$$

$$K_0^{(\gamma)} = \frac{qd^2}{2}\,\mathrm{e}^{-\epsilon^*/kT}\left(2 + \frac{\epsilon^*}{kT}\right)$$

We use a notation consistent with that in refs 8 and 9 by introducing

$$A_1^{(\gamma)} = 2n_\gamma^{\ 2}\left(\frac{\pi kT}{m}\right)^{1/2}\left(\frac{3}{2}K_0^{(\gamma)} - K_1^{(\gamma)}\right) = n_\gamma^{\ 2}qd^2\left(\frac{\pi kT}{m}\right)^{1/2}\mathrm{e}{-}^{\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

As shown by Shizgal and collaborators,[8,9] from the Chapman–Enskog method it is found that the coefficients $a_1(\gamma)$ that appear in the single-Sonine approximation (38) are the solutions to the following set of two equations

$$\{\mathrm{BB}\}\, n_\mathrm{C} a_1^{(\mathrm{B})} + \{\mathrm{BC}\} n_\mathrm{C} a_1^{(\mathrm{C})} = n_\mathrm{B} \alpha_1^{(\mathrm{B})}$$

$$n_\mathrm{B} a_1^{(\mathrm{B})} + n_\mathrm{C} a_1^{(\mathrm{C})} = 0$$

where, for the case considered, $\alpha_1^{(\mathrm{B})}$ is given by[9]

$$\alpha_1^{(\mathrm{B})} = \frac{1 - \left(\frac{n_\mathrm{C}}{n_\mathrm{B}}\right)^2}{n_\mathrm{B}^2} A_1^{(\mathrm{B})} = -\left(1 - \frac{n_\mathrm{C}^2}{n_\mathrm{B}^2}\right) q d^2 \left(\frac{\pi kT}{m}\right)^{1/2} \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

and {BB} and {BC} are typical elastic collision integrals of Sonines[11] (in the notation in ref 8, $\{S_\mathrm{B}^{(1)}, S_\mathrm{B}^{(1)}\}$ and $\{S_\mathrm{B}^{(1)}, S_\mathrm{C}^{(1)}\}$, respectively, with $S_\gamma^{(1)} = (^3/_2 - \xi_\gamma^2)$, which have been performed for the hard-sphere cross section to yield (see Tables I and II in ref 8)

$$\{\mathrm{BB}\} = -\{\mathrm{BC}\} = -2\left(\frac{\pi kT}{m}\right)^{1/2} d^2 \qquad (42)$$

The system is easily solved and we find

$$a_1^{(\mathrm{B})} = \frac{1}{2}\left(1 - \frac{n_\mathrm{C}}{n_\mathrm{B}}\right) q \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right) \qquad (43)$$

$$a_1^{(\mathrm{C})} = \frac{1}{2}\left(1 - \frac{n_\mathrm{B}}{n_\mathrm{C}}\right) q \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right) \qquad (44)$$

In equilibrium ($J_f^{(0)} = J_b^{(0)}$), for the case considered in this appendix we have (from eqs 41, for both reactions, and 25) that $n_\mathrm{B} = n_\mathrm{C}$. This implies, according to eqs 43 and 44, that $a_1^{(\mathrm{B})} = 0$ and $a_1^{(\mathrm{C})} = 0$. Therefore, the corrections (38) vanish and the distribution functions are Maxwellians, as they should be.

In order to write down eqs 43 and 44 in terms of the affinity, namely (see eqs 14, 40, and 19)

$$A = 2(\mu_\mathrm{B} - \mu_\mathrm{C}) = -2kT \ln \frac{n_\mathrm{C}}{n_\mathrm{B}}$$

we note that near equilibrium

$$\frac{n_\mathrm{C}}{n_\mathrm{B}} = \mathrm{e}^{-A/2kT} \approx 1 - \frac{A}{2kT}$$

Within this approximation, eqs 43 and 44 become

$$a_1^{(\mathrm{B})} = \frac{A}{4kT} q \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

$$a_1^{(\mathrm{C})} = -\frac{A}{4kT} q \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

Obviously, in equilibrium $A = 0$ and the perturbations vanish, again as they should.

Insertion of the above results into eq 38 completes the derivation of eq 29. For the case considered, we also find that

$$F_\mathrm{B}(q,\epsilon^*,T,\{m_\gamma\}) = \frac{q}{4kT} \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

and

$$F_\mathrm{C}\,(q, \epsilon^*, T, \{m_\gamma\}) = -\frac{q}{4kT} \mathrm{e}^{-\epsilon^*/kT}\left(\frac{1}{2} + \frac{\epsilon^*}{kT}\right)$$

The results in the present appendix can also be obtained, in a lengthier way, from the kinetic–theoretical approach presented in ref 8, where use is made of the chemical affinity.

6. Appendix B

Derivation of Eq 32. From eqs 31 and 29, it follows that

$$\tilde{s} = \tilde{s}^{(0)} - \frac{kA^2}{2} \sum_\gamma [F_\gamma\,(q,\epsilon^*,T,\{m_\gamma\})]^2 \left[\frac{9}{4}\int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)} - 3\int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)} \xi_\gamma^{\,2} + \int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)} \epsilon_\gamma^{\,4}\right]$$

The first and second integrals are simply n_γ and $\tilde{u}_\gamma/(kT) = {}^3/_2 n_\gamma$, respectively (see eqs 22, 23, and 39). The third integral is easily performed by making use of the well-known formula

$$\int_0^\infty \mathrm{d}\mathbf{c}_\gamma\, \mathbf{c}_\gamma^{\,6}\, \mathrm{e}^{-a\mathbf{c}_\gamma^2} = \frac{15}{16}\frac{\sqrt{\pi}}{a^{7/2}}$$

and we immediately find eq 32. A second way to derive eq 32 is by making use of the tabulated value for the integral $\int \mathrm{d}\vec{\mathbf{c}}_\gamma\, f_\gamma^{(0)}\, (^3/_2 - \xi_\gamma^2)$ (see the tables in ref 15 or ref 8).

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(25) We would like to stress that, both in chemical reactions and heat conduction, there is no conflict between this conclusion and the specific form of evolution equations, which will in general depend on the microscopic (or phenomenological) approach used. We have mentioned in section 1 that the Grad method has not been yet applied to the explicit determination of the distribution functions in chemically reacting systems with inclusion of the reverse reactions. It is tempting to expect that such an analysis would lead to an evolution equation of the Maxwell−Cattaneo type. In such a case, the conclussion reached here that the nonequilibrium contribution to the specific entropy is quadratic in the reaction rate would be extended to systems for which the term containing the reaction rate time derivative in such a Maxwell−Cattaneo equation might be of importance.

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