

A thermodynamical framework for chemically reacting systems

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Abstract. In this paper, we develop a thermodynamic framework that is capable of describing the response of viscoelastic materials that are undergoing chemical reactions that takes into account stoichiometry. Of course, as a special sub-case, we can also describe the response of elastic materials that undergo chemical reactions. The study generalizes the framework developed by Rajagopal and co-workers to study the response of a disparate class of bodies undergoing entropy producing processes. One of the quintessential feature of this framework is that the second law of thermodynamics is formulated by introducing Gibbs' potential, which is the natural way to study problems involving chemical reactions. The Gibbs potential-based formulation also naturally leads to implicit constitutive equations for the stress tensor. Another feature of the framework is that the constraints due to stoichiometry can also be taken into account in a consistent manner. The assumption of maximization of the rate of entropy production due to dissipation, heat conduction, and chemical reactions is invoked to determine an equation for the evolution of the natural configuration $\kappa_{p(t)}(B)$, the heat flux vector and a novel set of equations for the evolution of the concentration of the chemical constituents. To determine the efficacy of the framework with regard to chemical reactions, those occurring during vulcanization, a challenging set of chemical reactions, are chosen. More than one type of reaction mechanism is considered and the theoretically predicted distribution of mono, di and polysulfidic cross-links agree reasonably well with available experimental data.

Mathematics Subject Classification (2000). Primary 74F25 · 74F05.

Keywords. Gibbs potential · Chemical reactions · Rubber chemistry · Entropy production · Thermodynamics.

1. Introduction

A general thermodynamic framework has been put together, that builds upon, and extends significantly the work of numerous investigators (see Onsager [26], Eckart [10], Ziegler [41], Ziegler and Wehrli [42], and others) by Rajagopal and co-workers (see Rajagopal and Srinivasa [28–31], Rao and Rajagopal [34], Kannan and Rajagopal [18], Prasad and Rajagopal [27]) within which one can explain disparate responses such as the viscoelasticity of fluids and solids, traditional 'plasticity', super-plasticity, twinning and phase transitions undergone by solids, response of single crystal superalloys, the mechanics of mixtures, and crystallization of polymer melts, to name a few. The quintessential idea of the framework is that bodies respond to external stimuli in such a manner that the rate at which entropy is produced in a thermodynamic process is maximized. That is, constitutive relations that are appropriate from among a class of competing constitutive relations are those which assume the rate of entropy production to be maximal. In many bodies, the production of entropy leads to a change in the underlying 'natural configuration' of the body reflecting microstructural changes which take place in the body as the material symmetry associated with the underlying 'natural configuration' can evolve. The 'natural configuration' is a configuration, associated with the current configuration, that a body takes when all the external stimuli in its current configuration are removed. Which 'natural configuration' the body assumes might depend on how the external stimuli are removed. It is the ability to model the symmetry changes that can take place in

the natural configuration during a thermodynamic process that allows one to describe phase transitions within the construct of such a theory.

Recently, Malek and Rajagopal [21] used the framework to discuss the response of mixtures. However, they did not take into account the possibility of reactions between the constituents of the mixture. Chemical reactions play a vital role in the response of living matter, the most fecund and worthy area for research, as well as many other technological applications such as polymerization, oxidation of bodies, degradation, etc. This would require the integration of the stoichiometry that governs the chemical reactions, an aspect that has not been probed within the confines of the framework. It seems imperative that we should investigate whether the general framework that has been put into place could be used to study processes involving chemical and biochemical reactions. In this paper, we investigate this question and show that we can indeed use the framework to study chemical and biochemical reactions.

There are several fundamental questions concerning the thermodynamics of living matter that are far from well understood despite several attempts that have been made in the past. To date, there is no general thermodynamic framework within which the response of the thermodynamics of living matter can be explained satisfactorily. For instance, how living matter generates entropy while growing and atrophying is a case in point. The attempts at providing a thermodynamic basis for living matter is highly unsatisfactory, despite the efforts of giants like Schrodinger [35]. We shall not attempt to provide a basis for the thermodynamics of living matter. Our aim in this paper is much more modest, and it is a very small step in the direction of trying to understand the thermodynamics associated with biochemical reactions. We shall study simple chemical reactions within the context of the theoretical framework that is available, appealing to the fact that the rate of entropy production is maximized during the reaction.

There are several interesting and difficult questions concerning chemical and biochemical reactions that need to be answered. For instance, given a number of chemical constituents or species, we can ask several questions concerning their ability to react. We can use techniques in graph theory wherein we consider the chemicals to be nodes and the reactions between chemicals as edges. One question that naturally comes to mind is the following: given a number of chemicals that are capable of reacting which reactions ought to be enhanced or made possible and how, and which reactions retarded or eliminated, and how, in order to achieve a desired end? That is, given an input to a complicated cascade of reactions how do we modify them to ensure that we have a desired output? With regard to the graph, the corresponding question is which edge is to be cut or which new edge is to be brought into play? Our ability to cut an edge might require the introduction of one or more chemicals (one or more nodes) that prevents the reaction between pre-existing chemicals (nodes) and our capability to add an edge might imply, for instance, the introduction of a catalyst (a node). A related important problem is the design of a set of reactions based on appropriate chemicals in order to produce a desired cascade of reactions. Yet another question is whether the rate at which entropy is maximized dictates which cascade of reactions are possible and how they proceed? In a recent paper, Malik et al. [22] consider a much simpler mechanical problem consisting in masses (represented as nodes) and springs (represented as edges) to answer the corresponding questions for a purely mechanical system. Their analysis shows that even the much simpler mechanical problem that involves no reactions but each edge being associated with an ordinary differential equation is an exceedingly challenging problem.

We consider the chemical reactions by modeling them within the context of simple stoichiometric equations. We introduce a constitutive relation for the rate of entropy production that is due to chemical reactions, and we shall study the implications of the requirement of the maximization of the rate of entropy production. We also consider the effect of deformation of the mixture of chemicals and a thermal process, i.e., heat conduction, on the chemical reactions, and the effect of chemical reactions on the thermo-mechanical behavior of the mixture. Further, we assume that there is no relative motion among the chemical constituents (no diffusion), i.e., we shall assume that the body is a constrained mixture. We shall not consider biochemical reactions but merely restrict ourselves to simpler chemical reactions because, in addition to considering the effect of thermal and mechanical stimuli on chemical reactions,

one needs to consider the effect of diffusion of the chemical constituents, pH, electric potential, and so forth, on the chemical reactions. However, the ideas presented in this framework are an important first step in understanding the thermodynamics associated with biochemical reactions.

Let us consider a chemically reacting system with M reactions involving N chemical species, i.e.,

$$\begin{aligned}\nu_{11}S_1 + \nu_{12}S_2 + \cdots + \nu_{1N}S_N &= 0 \\ \nu_{21}S_1 + \nu_{22}S_2 + \cdots + \nu_{2N}S_N &= 0 \\ &\vdots \\ \nu_{M1}S_1 + \nu_{M2}S_2 + \cdots + \nu_{MN}S_N &= 0,\end{aligned}\tag{1.1}$$

where $S_i, i = 1, 2 \dots N$ represent the chemical species and $\nu_{ij}, i = 1, 2 \dots M$ and $j = 1, 2 \dots N$ are integers and represent the ‘stoichiometric’ co-efficients. In the above equation, i.e., Eq. (1.1), reactants and the products are grouped in the left-hand side of the equality symbol. Notice that the word stoichiometric is within quotation marks. This terminology is different from the usual sense in which the word is used, in that, the coefficients must only satisfy the mass balance individually for each reaction, unlike the set of atom-balance equations that must be satisfied for determining stoichiometric co-efficients corresponding to each reaction.

2. Kinematics

Let us consider a mixture containing N chemical species deforming, and chemically reacting with each other according to Eq. (1.1). Further, we shall assume that the N species coexist at a point and move together with the same velocity without relative motion among them (i.e., no diffusion), i.e., we are considering a constrained mixture. We shall assume that the deforming body is viscoelastic in nature. Kinematics that is provided below is sufficient to study the deformation of a constrained mixture, which behaves like a viscoelastic material.

Motion is a one to one mapping that assigns to each point $\mathbf{X}_{\kappa_R} \in \kappa_R(B)$, where $\kappa_R(B)$ is the reference configuration, a point $\mathbf{x} \in \kappa_t(B)$, where $\kappa_t(B)$ is the current configuration, B being the abstract body, for each $t \in \mathfrak{R}$, i.e.,

$$\mathbf{x} = \chi_{\kappa_R}(\mathbf{X}_{\kappa_R}, t).\tag{2.1}$$

The motion is assumed to be sufficiently smooth to make all the following derivatives meaningful. Velocity and acceleration of a particle \mathbf{X} at time t are given through

$$\mathbf{v} = \frac{\partial \chi_{\kappa_R}}{\partial t}\tag{2.2}$$

and

$$\mathbf{a} = \frac{\partial^2 \chi_{\kappa_R}}{\partial t^2}\tag{2.3}$$

The deformation gradient is defined through

$$\mathbf{F}_{\kappa_R} = \frac{\partial \chi_{\kappa_R}}{\partial \mathbf{X}_{\kappa_R}}\tag{2.4}$$

and multiplicatively decomposed as follows:

$$\mathbf{F}_{\kappa_R} = \mathbf{F}_{\kappa_p(t)}(\mathbf{X}_{\kappa_R}, t)\mathbf{G}(\mathbf{X}_{\kappa_R}, t),\tag{2.5}$$

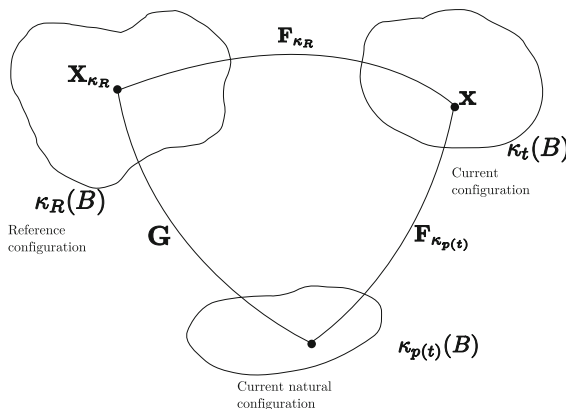


FIG. 1. Configurations associated with a deforming viscoelastic body

where \mathbf{G} is a mapping from the reference configuration to current natural configuration¹ (see Fig. (1)), i.e., $\kappa_{p(t)}(B)$ and $\mathbf{F}_{\kappa_{p(t)}}$ is a mapping from configuration $\kappa_{p(t)}(B)$ to the current configuration.

The velocity gradient is defined through

$$\mathbf{L} = \dot{\mathbf{F}}_{\kappa_R} \mathbf{F}_{\kappa_R}^{-1}, \tag{2.6}$$

where the dot signifies the material time derivative. Similarly, one can define a tensor $\mathbf{L}_{\kappa_{p(t)}}$ associated with the evolution of natural configuration $\kappa_{p(t)}(B)$, i.e.,

$$\mathbf{L}_{\kappa_{p(t)}} = \dot{\mathbf{G}} \mathbf{G}^{-1}. \tag{2.7}$$

The velocity gradient tensor \mathbf{L} and tensor $\mathbf{L}_{\kappa_{p(t)}}$ can be uniquely decomposed into a symmetric and an anti-symmetric part, i.e.,

$$\mathbf{L} = \frac{1}{2}(\mathbf{L} + \mathbf{L}^T) + \frac{1}{2}(\mathbf{L} - \mathbf{L}^T) = \mathbf{D} + \mathbf{W} \tag{2.8}$$

and

$$\mathbf{L}_{\kappa_{p(t)}} = \frac{1}{2}(\mathbf{L}_{\kappa_{p(t)}} + \mathbf{L}_{\kappa_{p(t)}}^T) + \frac{1}{2}(\mathbf{L}_{\kappa_{p(t)}} - \mathbf{L}_{\kappa_{p(t)}}^T) = \mathbf{D}_{\kappa_{p(t)}} + \mathbf{W}_{\kappa_{p(t)}}. \tag{2.9}$$

The left and right Cauchy-Green stretch tensors are defined through

$$\mathbf{B}_{\kappa_R} = \mathbf{F}_{\kappa_R} \mathbf{F}_{\kappa_R}^T \tag{2.10}$$

and

$$\mathbf{C}_{\kappa_R} = \mathbf{F}_{\kappa_R}^T \mathbf{F}_{\kappa_R}, \tag{2.11}$$

respectively. Similarly, one can define the left and the right Cauchy-Green stretch tensors associated with the tensor $\mathbf{F}_{\kappa_{p(t)}}$ as

$$\mathbf{B}_{\kappa_{p(t)}} = \mathbf{F}_{\kappa_{p(t)}} \mathbf{F}_{\kappa_{p(t)}}^T \tag{2.12}$$

¹We will be interested in viscoelastic bodies that have an instantaneous elastic response, the general response of the body being capable of description as a one-parameter family of responses from an evolving natural configuration. It is however possible that the response of a body cannot be described within such a concept and one may require to approach the modeling the response of such bodies differently. One such approach is the Gibbs potential formulation that is considered by Rajagopal and Srinivasa [31]. The preferred natural configuration is the configuration that the body takes, based on the allowable process class, when the external stimuli are removed. A detailed discussion of the notion of natural configuration can be found in Rajagopal and Srinivasa [29].

and

$$\mathbf{C}_{\kappa_p(t)} = \mathbf{F}_{\kappa_p(t)}^T \mathbf{F}_{\kappa_p(t)}, \tag{2.13}$$

respectively.

By taking the material time derivative of Eqs. (2.12) and (2.13), and on using Eqs. (2.5)–(2.9), one arrives at

$$\overset{\nabla}{\mathbf{B}}_{\kappa_p(t)} = \dot{\mathbf{B}}_{\kappa_p(t)} - \mathbf{L}\mathbf{B}_{\kappa_p(t)} - \mathbf{B}_{\kappa_p(t)}\mathbf{L}^T = -2\mathbf{F}_{\kappa_p(t)}\mathbf{D}_{\kappa_p(t)}\mathbf{F}_{\kappa_p(t)}^T \tag{2.14}$$

and

$$\dot{\mathbf{C}}_{\kappa_p(t)} + \mathbf{L}_{\kappa_p(t)}^T \mathbf{C}_{\kappa_p(t)} + \mathbf{C}_{\kappa_p(t)} \mathbf{L}_{\kappa_p(t)} = 2\mathbf{F}_{\kappa_p(t)}^T \mathbf{D}\mathbf{F}_{\kappa_p(t)}, \tag{2.15}$$

respectively. In Eq. (2.14), the tensor $\overset{\nabla}{\mathbf{B}}_{\kappa_p(t)}$ represents the upper convected derivative of tensor $\mathbf{B}_{\kappa_p(t)}$. Similarly, using Eq. (2.14), one can show that

$$\begin{aligned} \overset{\Delta}{\mathbf{B}}_{\kappa_p(t)}^{-1} &= \overset{\cdot}{\mathbf{B}}_{\kappa_p(t)}^{-1} + \mathbf{B}_{\kappa_p(t)}^{-1} \mathbf{L} + \mathbf{L}^T \mathbf{B}_{\kappa_p(t)}^{-1} = 2\mathbf{F}_{\kappa_p(t)}^{-T} \mathbf{D}_{\kappa_p(t)} \mathbf{F}_{\kappa_p(t)}^{-1} \\ &= -\mathbf{B}_{\kappa_p(t)}^{-1} \overset{\nabla}{\mathbf{B}}_{\kappa_p(t)} \mathbf{B}_{\kappa_p(t)}^{-1}, \end{aligned} \tag{2.16}$$

where $\overset{\Delta}{\mathbf{B}}_{\kappa_p(t)}^{-1}$ represents lower convected derivative of the tensor $\mathbf{B}_{\kappa_p(t)}^{-1}$.

The principal invariants of any second-order tensor \mathbf{A} are given through

$$\text{I}_{\mathbf{A}} = \text{tr}(\mathbf{A}), \quad \text{II}_{\mathbf{A}} = \frac{1}{2} \left\{ [\text{tr}(\mathbf{A})]^2 - \text{tr}(\mathbf{A}^2) \right\}, \quad \text{and}, \quad \text{III}_{\mathbf{A}} = \det(\mathbf{A}). \tag{2.17}$$

If a material is assumed to be incompressible, then

$$\text{tr}(\mathbf{L}) = \text{div}(\mathbf{v}) = 0 \quad (\text{or } \det(\mathbf{B}_{\kappa_R}) = 1). \tag{2.18}$$

In addition to the above constraint, one may assume that the natural configuration evolves in such a way that

$$\text{tr}(\mathbf{D}_{\kappa_p(t)}) = \text{tr}(\mathbf{L}_{\kappa_p(t)}) = 0. \tag{2.19}$$

We shall assume that the mixture is compressible, and therefore, we shall not enforce the constraints (2.18) and (2.19).

3. Balance equations

3.1. Balance of chemical constituents

For the systems in which there is interconversion of one species to another, the balance of mass in the local form can be shown as (see Rajagopal and Tao [32])

$$\frac{\partial \rho_{\kappa_t}^i}{\partial t} + \text{div}(\rho_{\kappa_t}^i \mathbf{v}) = \frac{D\rho_{\kappa_t}^i}{Dt} + \rho_{\kappa_t}^i \text{div}(\mathbf{v}) = m^i, \tag{3.1}$$

where m_i is the rate of production of mass of the i^{th} constituent per unit volume of mixture in the current configuration $\kappa_t(B)$ and $\rho_{\kappa_t}^i$ is the mass of the i^{th} species per unit volume of the mixture in the current configuration. In deriving the Eq. (3.1), we have invoked the assumption that at any material point corresponding to the mixture, there is no relative velocity among various species. Since we do not allow for relative motion between the constituents, we do not need to differentiate among $\mathbf{X}_{\kappa_R}^i$ as $\mathbf{X}_{\kappa_R}^i = \mathbf{X}_{\kappa_R}$, $i = 1, 2, \dots, N$, and therefore, there is only one material derivative represented by $D()/Dt$. Recall that a material point \mathbf{X}_{κ_R} consist in all the species as a result of the assumption of co-occupancy.

The rate of production of mass of the i th constituent is non-zero as there is interconversion of one species into another as a result of chemical reactions.

One can define the concentration (in terms of the volume) of the i th species in the current configuration, denoted by \bar{n}_i , as $\bar{n}_i := \rho_{\kappa_t}^i / \mathcal{M}_i$, where \mathcal{M}_i is the molar mass of the i th species, a constant. By rewriting the Eq. (3.1) in terms of \bar{n}_i , one arrives at

$$\frac{\partial \bar{n}_i}{\partial t} + \operatorname{div}(\bar{n}_i \mathbf{v}) = \dot{\bar{n}}_i + \bar{n}_i \operatorname{div}(\mathbf{v}) = \frac{m_i}{\mathcal{M}_i}, \quad i = 1, 2, \dots, N, \quad i \text{ no sum}, \quad (3.2)$$

where the dot in Eq. (3.2) signifies the rate of change of concentration of the i th species with respect to time for a fixed \mathbf{X}_{κ_R} . The total rate of change of concentration of i th constituent, i.e., $\dot{\bar{n}}_i$, is given through the sum of contributions due to rate of change of volume and rate of change of production of the same species. Since there cannot be net production of mass,

$$\sum_{i=1}^N m_i = 0. \quad (3.3)$$

One can rewrite Eq. (3.2) by introducing the concentration in terms of moles per unit mass of the mixture, i.e., $\rho_{\kappa_t} n_i = \bar{n}_i$, $i = 1, 2, \dots, N$, where n_i is number of moles of i th species per unit mass of mixture. Then, on appealing to the conservation of mass for the mixture, Eq. (3.2) can be rewritten as

$$\rho_{\kappa_t} \dot{n}_i = \frac{m_i}{\mathcal{M}_i}, \quad i = 1, 2, \dots, N, \quad (3.4)$$

where \dot{n}_i 's denote the material rate of change of concentration with respect to time, corresponding to each of the chemical species $S_1, S_2 \dots S_N$, respectively. Note that when concentration is expressed in terms of moles per unit volume, the rate of change of concentration of any species has contributions due to volume change and that due to chemical reactions. However, when concentration is expressed in terms of the mass, the rate of change of the same is only due to chemical reactions. Now, we shall arrive at an expression for mass production in terms of stoichiometric co-efficients.

Let $\mathcal{M}_1, \mathcal{M}_2 \dots \mathcal{M}_N$ represent the masses of one mole of species S_1, S_2, \dots, S_N , respectively. Then, each of the reactions (1.1) must satisfy the mass balance equation, i.e.,

$$\nu_{i1} \mathcal{M}_1 + \nu_{i2} \mathcal{M}_2 + \dots + \nu_{iN} \mathcal{M}_N = 0, \quad i = 1, 2, \dots, M. \quad (3.5)$$

One can rewrite the above equations in the following form:

$$\sum_{j=1}^N \nu_{ij} \mathcal{M}_j = 0, \quad i = 1, 2, \dots, M, \quad (3.6)$$

where ν_{ij} , $j = 1, 2, \dots, N$ represents the stoichiometric coefficients corresponding to the i th reaction. Unless stated otherwise, the first index i represents the i th reaction and the last index j represents the j th chemical constituent. Each ν_{ij} is determined, using Eq. (3.6), such that they are integers.

It is quite clear from Eq. (1.1) that for the k th reaction, at some fixed conditions such as temperature, stress, etc., ν_{k1} moles of S_1 , ν_{k2} moles of S_2 , and so forth are consumed in some time interval, which implies that the rate of change of concentration per unit mass of the mixture is not the same for each of the species. For a fixed reaction, it is customary to introduce a quantity called the extent of reaction in such a way that the change in the concentration of each chemical species normalized with respect to its respective stoichiometric co-efficient remains the same for that reaction, i.e.,

$$\xi_k = \frac{n_1^k(t) - n_1^k(0)}{\nu_{k1}} = \frac{n_2^k(t) - n_2^k(0)}{\nu_{k2}} = \dots = \frac{n_N^k(t) - n_N^k(0)}{\nu_{kN}}, \quad k = 1, 2, \dots, M, \quad (3.7)$$

where ξ_k , $k = 1, 2, \dots, M$ represent the extent of the reaction (or a point on the reaction co-ordinate) corresponding to reactions $1, 2 \dots M$, respectively, and $\frac{dn_i^k}{dt}$ represents the k th reaction contributions to the total rate of change of concentration with respect to time corresponding to species S_l . It is important

that one does not define the extent of chemical reaction in terms of change in concentration expressed in terms of the volume because the change in concentration, as seen earlier, can be brought forth by volume changes and not just the chemical reactions. The extent of reaction depends on the concentration of chemical constituents, temperature, stress, etc. However, at any given time, Eq. (3.7) is always satisfied.

By taking the material time derivative of Eq. (3.7), one arrives at the following equation:

$$\frac{1}{\nu_{k1}} \frac{dn_1^k}{dt} = \frac{1}{\nu_{k2}} \frac{dn_2^k}{dt} = \dots = \frac{1}{\nu_{kN}} \frac{dn_N^k}{dt} = \dot{\xi}_k, \quad k = 1, 2, \dots, M. \quad (3.8)$$

The total rate of change of concentration per unit mass of the mixture, associated with S_l^{th} species is given through:

$$\dot{n}_l = \frac{dn_l}{dt} = \sum_{k=1}^M \frac{dn_l^k}{dt}, \quad l = 1, 2, \dots, N. \quad (3.9)$$

From Eqs. (3.8) and (3.9), it is clear that

$$\dot{n}_j = \sum_{i=1}^M \nu_{ij} \dot{\xi}_i, \quad j = 1, 2, \dots, N. \quad (3.10)$$

By substituting Eqs. (3.4) and (3.10) into Eq. (3.2), one can arrive at an equation for concentration in terms of the volume, i.e.,

$$\dot{\bar{n}}_j + \bar{n}_j \operatorname{div}(\mathbf{v}) = \rho_{\kappa_t} \sum_{i=1}^M \nu_{ij} \dot{\xi}_i, \quad j = 1, 2, \dots, N. \quad (3.11)$$

By substituting Eq. (3.6) in Eq. (3.10), one arrives at

$$\sum_{j=1}^N \dot{n}_j \mathcal{M}_j = 0. \quad (3.12)$$

3.2. Balance of mass for the mixture as a whole

Using the definition $\bar{n}_i := \rho_{\kappa_t}^i / \mathcal{M}_i$, the fact that $\sum_{i=1}^N \rho_{\kappa_t}^i = \rho_{\kappa_t}$, the assumption that there is no relative motion among the N chemical constituents and the Eq. (3.3), and summing the Eq. (3.2) over all the species, one arrives at the balance of mass for the mixture as a whole, i.e.,

$$\dot{\rho}_{\kappa_t} + \rho_{\kappa_t} \operatorname{div}(\mathbf{v}) = 0, \quad (3.13)$$

where ρ_{κ_t} is the density of the mixture in the current configuration. Upon integrating over time, Eq. (3.13) becomes

$$\rho_{\kappa_R} = \rho_{\kappa_t} \det(\mathbf{F}_{\kappa_R}), \quad (3.14)$$

where ρ_{κ_R} is the density of the mixture in the reference configuration \mathbf{F}_{κ_R} . Further, since the mechanical response of the mixture is described with respect to the evolving configuration $\kappa_{p(t)}(B)$, one may define the density with respect to $\kappa_{p(t)}(B)$, i.e.,

$$\rho_{\kappa_R} = \rho_{\kappa_{p(t)}} \det(\mathbf{G}), \quad (3.15)$$

where $\rho_{\kappa_{p(t)}}$ is density of mixture in the natural configuration $\kappa_{p(t)}(B)$.

By operating by the material time derivative on both sides of Eqs. (3.14) and (3.15), one can rewrite both the equations as and

$$\dot{\rho}_{\kappa_{p(t)}} + \rho_{\kappa_{p(t)}} \operatorname{tr}(\mathbf{L}_{\kappa_{p(t)}}) = 0, \quad (3.16)$$

respectively.

3.3. Balance of linear momentum for the mixture as a whole

Since all the interaction forces amongst the various chemical species add up to zero, it is sufficient to consider the balance of linear momentum for the mixture as a whole, i.e.,

$$\operatorname{div}(\mathbf{T}^T) + \rho_{\kappa_t} \mathbf{b} = \rho_{\kappa_t} \dot{\mathbf{v}}, \quad (3.17)$$

where \mathbf{T} is Cauchy stress tensor and \mathbf{b} is specific body force. If relative motion between the various species were to be considered, then the balance of linear momentum for every species is required. Further, one should also consider interaction terms arising as a result due to the interplay between the various constituents due to the relative velocity, relative accelerations, relative spins, relative deformation histories, relative gradients of temperature and density, etc., as well as the conversion of one species to another. However, these internal interaction terms are assumed to vanish when one averages the equation for a mixture as a whole. For details, refer to Rajagopal and Tao [32].

Since the mixture is assumed to exist in more than one natural configuration, it is natural to describe the stress response with respect to the evolving natural configurations. Accordingly, one can define the second Piola Kirchhoff stress tensor as follows:

$$\mathbf{S} = \det(\mathbf{F}_{\kappa_{p(t)}}) \mathbf{F}_{\kappa_{p(t)}}^{-1} \mathbf{T} \mathbf{F}_{\kappa_{p(t)}}^{-T}. \quad (3.18)$$

3.4. Consequence of balance of angular momentum

In addition to the moment produced by external forces, we shall assume that the only source of internal angular momentum is due to production of mass, which upon summing over all the species vanishes. Accordingly, in the absence of internal body couples, one can show that for a mixture as a whole (see Rajagopal and Tao [32])

$$\mathbf{T} = \mathbf{T}^T. \quad (3.19)$$

3.5. Balance of energy for the mixture as a whole

Balance of energy for the mixture under consideration, in the local form, is given through

$$\rho_{\kappa_t} \dot{\epsilon} = \mathbf{T} \cdot \mathbf{D} - \operatorname{div}(\mathbf{q}) + \rho_{\kappa_t} r, \quad (3.20)$$

where ϵ is specific internal energy for the mixture as a whole, \mathbf{q} is heat flux and r is specific radiant heating. The above form for the energy equation is a consequence of the fact that we have a constrained mixture. In general mixtures, the term for the heat flux vector and the radiant heating will be defined in terms of the terms associated with the individual components. Refer to Rajagopal and Tao [32] for details.

4. Restrictions on constitutive equations

4.1. Second law of thermodynamics

We shall formulate a mathematical statement of second law of thermodynamics that is amenable to developing constitutive equations. To that end, we introduce an entropy equation in the form (see Green and Naghdi [16])

$$\rho_{\kappa_t} \dot{\eta} - \rho_{\kappa_t} \frac{r}{\theta} + \operatorname{div} \left(\frac{\mathbf{q}}{\theta} \right) = \rho_{\kappa_t} \zeta, \quad (4.1)$$

where θ , \mathbf{q} , r , η and ζ are absolute temperature, heat flux, specific radiant heating, specific entropy and total rate of entropy production per unit mass, respectively, associated with the mixture. We shall assume that every constituent coexists at a point and undergoes the same motion, and that the only source of entropy supply to a sub-part of a body is through conduction (no radiant heating), and neglect entropy supply, which could be facilitated through relative motion among chemical constituents. It is important to note that chemical reactions do not occur without collision of chemical constituents with sufficient energy (molecular motion), and thus, relative motion is important. However, the motion we are neglecting is large-scale diffusion of chemical constituents. Thus, the entropy equation as expressed by Eq. (4.1) is sufficient for the problem under consideration.

Using the equation for energy balance and entropy equation in the local form, eliminating the specific radiant heating term between the two equations, one arrives at the following equation:

$$\mathbf{T} \cdot \mathbf{D} - \rho_{\kappa_t} \dot{\epsilon}(\eta, n_1, n_2, \dots, n_N, \mathbf{C}_{\kappa_p(t)}) + \rho_{\kappa_t} \dot{\eta} \theta - \frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) = \rho_{\kappa_t} \theta \zeta. \quad (4.2)$$

In general, when one considers radiant heating, it is essential to obtain constitutive restrictions on the radiant heating, and second law of thermodynamics expressed in the form of Eq. (4.2) is insufficient because specific radiant heating does not show up explicitly (see §1 of Rajagopal and Tao [33]).

Now, we will assume the existence of sufficiently smooth, specific Gibbs potential, which is introduced through the Legendre transform:²

$$G(\theta, n_1, n_2, \dots, n_N, \mathbf{S}) = \epsilon - \eta \theta - \frac{1}{2\rho_{\kappa_p(t)}} \mathbf{S} \cdot \mathbf{C}_{\kappa_p(t)}. \quad (4.3)$$

Notice that the conjugate variables $\frac{1}{2\rho_{\kappa_p(t)}} \mathbf{C}_{\kappa_p(t)}$ and \mathbf{S} are present in the definition for the Gibbs potential rather than the specific volume and pressure, which can be recovered by setting the constitutive equation for stress of an ideal gas, i.e., $\mathbf{T} = -p\mathbf{I}$, where p is pressure, thereby reducing Eq. (4.3) to $G = \epsilon - \eta \theta + \frac{3}{2}pv$, where v is specific volume. Equation (4.3) is required to describe the thermo-mechanical response of a viscoelastic material using the idea of evolving natural configurations.

By substituting Eq. (4.3) into Eq. (4.2), and on using Eq. (2.15), one arrives at

$$\begin{aligned} & -\rho_{\kappa_t} \dot{G}(\theta, n_1, n_2, \dots, n_N, \mathbf{S}) - \rho_{\kappa_t} \eta \dot{\theta} - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \dot{\mathbf{S}} \cdot \mathbf{C}_{\kappa_p(t)} \\ & + \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \mathbf{S} \cdot (\mathbf{L}_{\kappa_p(t)}^T \mathbf{C}_{\kappa_p(t)} + \mathbf{C}_{\kappa_p(t)} \mathbf{L}_{\kappa_p(t)}) \\ & - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \text{tr}(\mathbf{D}_{\kappa_p(t)}) \mathbf{S} \cdot \mathbf{C}_{\kappa_p(t)} - \frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) = \rho_{\kappa_t} \theta \zeta \geq 0. \end{aligned} \quad (4.4)$$

The above equation is the form of second law of thermodynamics that is suitable for what follows. It can be rewritten as:

$$\begin{aligned} & -\rho_{\kappa_t} \left(\frac{\partial G}{\partial \theta} + \eta \right) \dot{\theta} - \rho_{\kappa_t} \left(\frac{\partial G}{\partial \mathbf{S}} + \frac{1}{2\rho_{\kappa_p(t)}} \mathbf{C}_{\kappa_p(t)} \right) \cdot \dot{\mathbf{S}} \\ & - \rho_{\kappa_t} \sum_{i=1}^N \mu_i \dot{n}_i + \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \mathbf{S} \cdot (\mathbf{L}_{\kappa_p(t)}^T \mathbf{C}_{\kappa_p(t)} + \mathbf{C}_{\kappa_p(t)} \mathbf{L}_{\kappa_p(t)}) \\ & - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \text{tr}(\mathbf{D}_{\kappa_p(t)}) \mathbf{S} \cdot \mathbf{C}_{\kappa_p(t)} - \frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) = \rho_{\kappa_t} \theta \zeta \geq 0, \end{aligned} \quad (4.5)$$

²One cannot always use a Legendre transform to obtain a Gibbs potential formulation from a Helmholtz potential formulation as shown by Rajagopal and Srinivasa [31]. In fact, for some systems, one cannot even define a Helmholtz potential. Similarly, there are systems for which one cannot define a Gibbs potential. Here, we are making the assumption that one can define a Helmholtz potential and a Gibbs potential for the system under consideration in a meaningful manner.

where $\mu_i := \frac{\partial G}{\partial n_i}$, $i = 1, 2, \dots, N$ is the chemical potential associated with chemical constituents S_1, S_2, \dots, S_N , respectively.

One way to satisfy the above equation is by setting

$$\eta = -\frac{\partial G}{\partial \theta} \quad (4.6a)$$

and

$$\frac{1}{2\rho_{\kappa_p(t)}} \mathbf{C}_{\kappa_p(t)} = -\frac{\partial G}{\partial \mathbf{S}}. \quad (4.6b)$$

The Eqs. (4.6a) and (4.6b) represent the relation between the conjugate pairs η and θ , and $\frac{1}{2\rho_{\kappa_p(t)}} \mathbf{C}_{\kappa_p(t)}$ and \mathbf{S} . If the Gibbs potential is smooth, the Eqs. (4.6a) and (4.6b) are meaningful, and hence the Legendre transform can be defined. Thus, the Eq. (4.5) assumes a reduced form:

$$\begin{aligned} -\rho_{\kappa_t} \sum_{i=1}^N \mu_i \dot{n}_i + \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \mathbf{S} \cdot (\mathbf{L}_{\kappa_p(t)}^T \mathbf{C}_{\kappa_p(t)} + \mathbf{C}_{\kappa_p(t)} \mathbf{L}_{\kappa_p(t)}) \\ - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_p(t)}} \text{tr}(\mathbf{D}_{\kappa_p(t)}) \mathbf{S} \cdot \mathbf{C}_{\kappa_p(t)} - \frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) = \rho_{\kappa_t} \theta \zeta = \xi. \end{aligned} \quad (4.6c)$$

We need to ensure that Eq. (4.6c) is satisfied for all possible thermo-mechanical and chemical processes undergone by a viscoelastic material.

4.2. Galilean invariance

Two frames $\{\mathbf{x}, t\}$ and $\{\mathbf{x}^*, t^*\}$, each being associated with an observer, are said to be related by a Galilean transformation, if

$$\boldsymbol{\chi}^*(X, t^*) = \mathbf{c}_0 + \mathbf{c}_1 t + \mathbf{Q}(\boldsymbol{\chi}(X, t) - \mathbf{x}_0), \quad X \in \mathcal{B}, \quad (4.7a)$$

and

$$t^* = t + a, \quad (4.7b)$$

where $\mathbf{x}^* = \boldsymbol{\chi}^*(X, t^*)$, $\mathbf{x} = \boldsymbol{\chi}(X, t)$, \mathcal{B} is the abstract body, \mathbf{Q} is a constant, but an arbitrary orthogonal tensor,³ and \mathbf{c}_0 , \mathbf{c}_1 , \mathbf{x}_0 and a are arbitrary constants.

Usually, one requires that the constitutive relations be frame indifferent. However, there is some controversy concerning the status of frame-indifference. For the development of some theories such as elasticity, Galilean invariance is sufficient to obtain the theory in its entirety. For our purposes also, Galilean Invariance is sufficient.

The mappings, i.e., Eqs. (4.7), apart from preserving distance between two material points as viewed from both frames, time intervals between any two events and direction of time, also ensure that the acceleration vector \mathbf{a} associated with any material point as calculated with reference to both frames are related through $\mathbf{a}^* = \mathbf{Q}\mathbf{a}$.

A scalar ϕ , vector \mathbf{v} , and a tensor \mathbf{A} are said to be Galilean invariant if

$$\phi^* = \phi, \quad (4.8a)$$

$$\mathbf{v}^* = \mathbf{Q}\mathbf{v} \quad (4.8b)$$

³If one requires agreement on orientation of directed line segments, then one needs to restrict \mathbf{Q} to be a proper orthogonal transformations.

and

$$\mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T, \quad (4.8c)$$

where ϕ^* , \mathbf{v}^* and \mathbf{A}^* are corresponding quantities relative to an observer in the frame $\{\mathbf{x}^*, t^*\}$. Using the definitions (4.8) for invariant quantities together with Eq. (4.7), one can determine whether the kinematical quantities defined in Sect. (2) are Galilean invariant or not. For example

$$\mathbf{F}^* = \frac{\partial \chi^*}{\partial X} = \mathbf{Q} \frac{\partial \chi}{\partial X} = \mathbf{Q}\mathbf{F} \quad (4.9)$$

shows that the tensor \mathbf{F} is not Galilean invariant.⁴ We will assume that $\mathbf{F}_{\kappa_R}^* = \mathbf{Q}\mathbf{F}_{\kappa_R}$. Similarly, we shall assume that the tensor $\mathbf{F}_{\kappa_p}^* = \mathbf{Q}\mathbf{F}_{\kappa_p}$. Accordingly, using Eq. (2.5), tensor $\mathbf{G}^* = \mathbf{G}$, and consequently, using Eqs. (2.7) and (4.7b), $\mathbf{L}_{\kappa_p}^* = \mathbf{L}_{\kappa_p}$. It is easy to check that $\mathbf{C}_{\kappa_p}^* = \mathbf{C}_{\kappa_p}$.

If one requires the Cauchy stress tensor \mathbf{T} to be Galilean invariant, then $\mathbf{S}^* = \mathbf{S}$ implying that \mathbf{S} is not Galilean invariant. However, the Gibbs potential G , which is a function of \mathbf{S} , is Galilean invariant, i.e.,

$$G(\theta^*, n_1^*, n_2^*, \dots, n_N^*, \mathbf{S}^*) = G(\theta, n_1, n_2, \dots, n_N, \mathbf{S}). \quad (4.10)$$

One requires that the functional form of the Gibbs potential to be the same with respect to both the observers. In Eq. (4.10), $n_i^* = n_i$, $i = 1, 2, \dots, N$ because n_i 's represent the concentration of the chemical constituents in terms of the mass. Next, we will assume that the total rate of entropy production per unit mass, i.e., ζ , or equivalently, ξ is a function of $\theta, \rho, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{S}, \mathbf{D}_{\kappa_p}$ and $\text{grad}(\theta)$. We shall require that the functional form of ξ be Galilean invariant with respect to change of observer, i.e.,

$$\begin{aligned} \xi(\theta^*, \rho^*, \dot{n}_1^*, \dot{n}_2^*, \dots, \dot{n}_N^*, \mathbf{S}^*, \mathbf{D}_{\kappa_p}^*, \text{grad}^*(\theta^*)) \\ = \xi(\theta, \rho, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{S}, \mathbf{D}_{\kappa_p}, \text{grad}(\theta)) \\ = \xi(\theta, \rho, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{S}, \mathbf{D}_{\kappa_p}, \mathbf{Q}\text{grad}(\theta)), \quad \forall \mathbf{Q} \in \mathcal{O}, \end{aligned} \quad (4.11)$$

where \mathcal{O} is the set of orthogonal tensors. The Eq. (4.11) must be satisfied for any set of arbitrarily fixed variables $\theta, \rho, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{S}$ and \mathbf{D}_{κ_p} .

4.3. Material symmetry

We shall require that

$$G(\theta, n_1, n_2, \dots, n_N, \mathbf{S}) = G(\theta, n_1, n_2, \dots, n_N, \mathbf{H}\mathbf{S}\mathbf{H}^T), \quad \mathbf{H} \in \mathcal{O}_{\text{sub}}, \quad (4.12)$$

where \mathbf{H} is an orthogonal tensor and \mathcal{O}_{sub} is the set of all constant orthogonal tensors such that Eq. (4.12) is satisfied. If \mathcal{O}_{sub} is the full orthogonal group, then the material is said to be isotropic,⁵ and if \mathcal{O}_{sub} is a proper subgroup of the orthogonal group, then the material is said to be anisotropic.

Mathematically, if \mathcal{O}_{sub} is the full orthogonal group, the Gibbs potential is an isotropic scalar-valued function. Recall that the Gibbs potential is Galilean invariant, and thus, we will have to ensure that Eq. (4.12) is satisfied. By invoking the representation theorem for isotropic scalar-valued functions (see Spencer and Rivlin [37]), one arrives at $G = G(\theta, n_1, n_2, \dots, n_N, \mathbf{I}_S, \mathbf{II}_S, \mathbf{III}_S)$.

⁴In obtaining Eq. (4.9), one assumes that $\kappa_R(B)$ is a surrogate for the abstract body and that $\kappa_R(B)$ is not a specific observable configuration of the body, and thus in both frames, the particle $\mathbf{X}_{\kappa_R} \in \kappa_R(B)$ is the same, and there is nothing like a $\mathbf{X}_{\kappa_R}^*$ that is observable in the $*$ frame (see Tao and Rajagopal [38] for a discussion of the ramifications of this issue).

⁵There are some that would not define isotropy through invariance with respect to the full orthogonal group but would insist only on the group of proper orthogonal transformations as isotropy is defined only through rotational invariance.

We will require that

$$\xi(\theta, \rho_{\kappa_t}, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{D}_{\kappa_p(t)}, \text{grad}(\theta)) = \xi(\theta, \rho_{\kappa_t}, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{H} \mathbf{D}_{\kappa_p(t)} \mathbf{H}^T, \mathbf{H} \text{grad}(\theta)), \quad \mathbf{H} \in \mathcal{O}_{\text{sub}}. \quad (4.13)$$

If \mathcal{O}_{sub} is the full orthogonal group, then the above equations implies that ξ is an isotropic scalar-valued function. Accordingly, using the representation theorem for such functions (see Smith [36] and Truesdell and Noll [39]), one arrives at

$$\begin{aligned} \xi = & \xi(\theta, \rho_{\kappa_t}, \dot{n}_1, \dot{n}_2, \dots, \dot{n}_N, \mathbf{I}_{\mathbf{D}_{\kappa_p(t)}}, \mathbf{II}_{\mathbf{D}_{\kappa_p(t)}}, \mathbf{III}_{\mathbf{D}_{\kappa_p(t)}}, \text{grad}(\theta) \cdot \text{grad}(\theta), \\ & \mathbf{D}_{\kappa_p(t)} \text{grad}(\theta) \cdot \text{grad}(\theta), \mathbf{D}_{\kappa_p(t)}^2 \text{grad}(\theta) \cdot \text{grad}(\theta)). \end{aligned} \quad (4.14)$$

4.4. Stoichiometric equations

Now, we shall determine the number of independent \dot{n}_i 's. To that end, we shall follow a proof similar to that employed by Brinkley [3] and Bjornbom [2].

Definition 4.1. The set of chemical reactions, i.e., Eq. (1.1) are said to be independent if the rows of ν_{ij} are linearly independent.

Theorem 4.2. *If N chemical species undergo M reactions according to Eq. (1.1), then, there are $\text{Rank}(\nu_{ij})$ independent rates of change of concentration per unit mass of mixture, and the $\text{Rank}(\nu_{ij})$ is at most $N - 1$.*

Proof: Referring to Eq. (3.6), notice that each row of $\nu_{ij} \in \text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)$.⁶ Since $\text{Rank}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N) = 1$, using rank-nullity theorem, $\dim(\text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)) = N - 1$, where 'dim' represents the word 'dimension'. Therefore, one can have a maximum of $N - 1$ linearly independent vectors belonging to $\text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)$, i.e., a maximum of $N - 1$ linearly independent rows of ν_{ij} , which implies that $\text{Rank}(\nu_{ij})$ is at most $N - 1$.

Using Eqs. (3.3) and (3.4), it is clear that $\sum_{j=1}^N \mathcal{M}_j \dot{n}_j = 0$, i.e., $(\dot{n}_1 \dot{n}_2 \dots \dot{n}_N) \in \text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)$. However, since every realizable $(\dot{n}_1 \dot{n}_2 \dots \dot{n}_N)$ is brought forth by the chemical reactions represented by Eq. (3.10), $(\dot{n}_1 \dot{n}_2 \dots \dot{n}_N)$ only spans a sub-space of $\text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)$ because the rows of ν_{ij} spans a sub-space of $\text{Null}(\mathcal{M}_1 \mathcal{M}_2 \dots \mathcal{M}_N)$, which is at most of dimension $N - 1$. If all the rows of ν_{ij} are not linearly independent, then, some rows of ν_{ij} can be written as a linear combination of linearly independent rows of ν_{ij} , i.e., Eq. (3.10) can be rewritten as $\dot{n}_j = \sum_{i=1}^{M'} \nu_{ij} \alpha_i$, $j = 1, 2, \dots, N$, $\alpha_i \in \mathfrak{R}$, $M' \leq N - 1$, where \mathfrak{R} is the set of real numbers and M' is the dimension of the space spanned by the rows of ν_{ij} , which is same as that of $\text{Rank}(\nu_{ij})$. Thus, there are M' independent α_i , which implies that there are M' independent \dot{n}_i 's. \square

Remark 4.3. Since \dot{n}_j , $j = 1, 2, \dots, N$ represent the rate of change of concentration with respect to time, unlike ν_{ij} , which are non-negative integers, \dot{n}_j 's are real numbers. Therefore, $\alpha_i \in \mathfrak{R}$ is meaningful. Physically, different values for α_i 's (rate of extent of reactions) can be realized, for example, by changing the concentration of the various chemical species, temperature, etc.

Remark 4.4. One may invoke a more restrictive conservation of atoms instead of the mass balance expressed through Eq. (3.6). In such a case, every row of ν_{ij} is chosen such that the conservation of atoms is satisfied, which would imply that the balance of mass, i.e., Eq. (3.6), is automatically satisfied. If the rank of the formula matrix⁷ is R , then, one can apply Brinkley's criterion, i.e., there can be a maximum of

⁶We are referring to a $1 \times N$ matrix, which is a fixed quantity for a given chemical system and do not change with the choice of basis vectors.

⁷A matrix with each row/column containing information about the number of like atoms in each of the species. Every type of atom that make up the N species is included in each row/column.

$N - R$ independent chemical reactions (see Brinkley [3] and Bjornbom [2]). In other words, $M' \leq N - R$. Thus, the upper bound for M' gets revised to $N - R$, and the rest of the theory discussed in this paper is not affected by invoking the conservation of atoms.

Remark 4.5. Sometimes, the various chemical compounds that make up the chemically reacting system can be lumped into several species such that the conservation of atoms is automatically satisfied, whenever the balance of mass is satisfied (for example, see Sect. 5.4.4). In such cases, ensuring balance of mass is sufficient.

As a result of the above theorem, there are M' independent \dot{n}_i . Therefore, there must be $N - M'$ relationships among $\dot{n}_i, i = 1, 2, \dots, N$. To determine these relationships, we shall rewrite Eq. (3.10) as

$$\begin{Bmatrix} \dot{n}_1 \\ \dot{n}_2 \\ \vdots \\ \dot{n}_N \end{Bmatrix} = \begin{Bmatrix} \nu_{11} & \nu_{21} & \cdots & \nu_{M1} \\ \nu_{12} & \nu_{22} & \cdots & \nu_{M2} \\ \vdots & \vdots & & \vdots \\ \nu_{1N} & \nu_{2N} & \cdots & \nu_{MN} \end{Bmatrix} \begin{Bmatrix} \dot{\xi}_1 \\ \dot{\xi}_2 \\ \vdots \\ \dot{\xi}_M \end{Bmatrix}. \quad (4.15)$$

In the above equation, the j th row of the matrix ν_{ij} represents stoichiometric coefficients associated with the j th chemical species, corresponding to each of the M chemical reactions. Without loss of generality, let us assume that the first M' rows of Eq. (4.15) are linearly independent. Then, $M' + 1$ th and the subsequent rows can be written as a linear combination of the first M' rows, i.e., there exists non-trivial, real, $(\beta_{(j-M')1} \beta_{(j-M')2} \cdots \beta_{(j-M')M'})$, $j = M' + 1, M' + 2, \dots, M' + N - M'$ such that

$$\begin{aligned} \sum_{i=1}^{M'} \beta_{(j-M')i} (\nu_{1i} \nu_{2i} \cdots \nu_{Mi}) &= (\nu_{1j} \nu_{2j} \cdots \nu_{Mj}), \quad j = M' + 1, \\ &M' + 2, \dots, M' + N - M', \end{aligned} \quad (4.16)$$

respectively. It immediately follows, after rewriting the indices, that

$$\sum_{i=1}^{M'} \beta_{ji} \dot{n}_i = \dot{n}_{M'+j}, \quad j = 1, 2, \dots, N - M', \quad (4.17)$$

which provide the $N - M'$ linear constraints on $\dot{n}_i, i = 1, 2, \dots, N$.

5. Special constitutive equations

Balance equations described in the above section are not sufficient to fully describe a chemically reacting system. One should augment balance equations with additional constitutive equations. In this section, we describe how to obtain constitutive equations for the stress tensor, specific entropy, specific internal energy, heat flux and equations that govern the conversion of one species to another.

5.1. Constitutive assumptions on total rate of entropy production and the second law of thermodynamics

If one assumes that $\zeta = \zeta_{\text{cond}} + \zeta_{\text{diss}} + \zeta_{\text{chem}}$, where ζ_{cond} , ζ_{diss} and ζ_{chem} are the rates of entropy production due to conduction, dissipation and chemical reactions, respectively. We shall require that $\zeta_{\text{cond}} \geq 0$, $\zeta_{\text{diss}} \geq 0$ and $\zeta_{\text{chem}} \geq 0$. Thus, we are requiring more than what the second law requires. Not only do we assume an additive decomposition for the rate of entropy production, we also require that each of these

terms be individually non-negative. Such an assumption is not overly restrictive as we could restrict the processes to correspond to just one in which we have conduction, etc., and in such processes the rate of entropy production will be non-negative. However, we are in fact assuming that the fact that all the various basic mechanisms for producing entropy do not in some sense interact and create additional means of producing entropy. The first term of Eq. (4.6c) is associated with chemical reactions because this term vanishes if \dot{n}_i 's are zero. Similarly, it is easy to recognize that the second term and the third term are associated with evolution of configuration $\kappa_{p(t)}(B)$, i.e., these terms are associated with dissipation. The fourth term is associated with thermal conduction. As a result, the Eq. (4.6c) reduces to

$$-\frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) = \rho_{\kappa_t} \theta \zeta_{\text{cond}} \geq 0, \quad (5.1a)$$

$$\frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \mathbf{S} \cdot (\mathbf{L}_{\kappa_{p(t)}}^T \mathbf{C}_{\kappa_{p(t)}} + \mathbf{C}_{\kappa_{p(t)}} \mathbf{L}_{\kappa_{p(t)}}) - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \text{tr}(\mathbf{D}_{\kappa_{p(t)}}) \mathbf{S} \cdot \mathbf{C}_{\kappa_{p(t)}} = \rho_{\kappa_t} \theta \zeta_{\text{diss}} \geq 0 \quad (5.1b)$$

and

$$-\rho_{\kappa_t} \sum_{i=1}^N \mu_i \dot{n}_i = \rho_{\kappa_t} \theta \zeta_{\text{chem}} \geq 0. \quad (5.1c)$$

5.2. Heat conduction

Heat flux vector \mathbf{q} should be chosen such that Eq. (5.1a) is satisfied. Alternatively, one can prescribe a constitutive equation for $\rho\theta\zeta_{\text{cond}}$, i.e., $\frac{K}{\theta} \text{grad}(\theta) \cdot \text{grad}(\theta)$, $K > 0$, where K is the thermal conductivity. The constitutive assumption made for $\rho\theta\zeta_{\text{cond}}$ is that it is non-negative and is equal to zero if and only if $\text{grad}(\theta) = \mathbf{0}$, and its mathematical structure is consistent with that of an isotropic material with respect to heat conduction. Further, the expression $\frac{K}{\theta} \text{grad}(\theta) \cdot \text{grad}(\theta)$ is also Galilean invariant. Equation (5.1a) imposes a constraint on the components of the heat flux vector, in that one can pick two components independently and the third is determined using Eq. (5.1a). To determine the constitutive equation for the heat flux vector, we shall assume that the expression $\frac{K}{\theta} \text{grad}(\theta) \cdot \text{grad}(\theta)$ is maximized with respect to $\text{grad}(\theta)$ with Eq. (5.1a) as constraint. We are thus requiring a much more stringent requirement than that the total entropy production be maximized. We are requiring that the rate of entropy production due to mechanical working being transformed to heat, due to conduction, due to chemical reaction, each be individually maximized. Accordingly, we shall define the augmented function Π through

$$\Pi(\theta, \text{grad}(\theta), \mathbf{q}, \tilde{\lambda}) = \frac{K}{\theta} \text{grad}(\theta) \cdot \text{grad}(\theta) + \tilde{\lambda} \left(\frac{K}{\theta} \text{grad}(\theta) \cdot \text{grad}(\theta) + \frac{1}{\theta} \mathbf{q} \cdot \text{grad}(\theta) \right). \quad (5.2)$$

Thus,

$$\frac{\partial \Pi}{\partial \text{grad}(\theta)} = \mathbf{0} \Rightarrow \frac{1 + \tilde{\lambda}}{\tilde{\lambda}} \left(2 \frac{K}{\theta} \text{grad}(\theta) \right) + \frac{1}{\theta} \mathbf{q} = \mathbf{0}. \quad (5.3)$$

By taking inner product of Eq. (5.3) with $\text{grad}(\theta)$, and comparing it with the constraint, the expression $\frac{1+\tilde{\lambda}}{\tilde{\lambda}}$ is determined to be $\frac{1}{2}$. Accordingly, the above equation implies that

$$\mathbf{q} = -K \text{grad}(\theta). \quad (5.4)$$

The Eq. (5.4) is a constitutive equation for heat flux vector and is the same as that of Fourier's equation for heat flux. To determine whether $\text{grad}(\theta) = -\frac{\mathbf{q}}{K}$ is a maximum (see Chong and Zak [4]), which is a regular point, one has to determine the Hessian of the function Π with respect to $\text{grad}(\theta)$, and evaluate

the resultant expression at $\tilde{\lambda} = -2$ and $\text{grad}(\theta) = -\frac{q}{K}$, and show that it is negative definite. Accordingly, one arrives at

$$\frac{\partial^2 \Pi}{\partial \text{grad}(\theta)^2} \Big|_{\tilde{\lambda}=-2, \text{grad}(\theta)=-\frac{q}{K}} = -2 \frac{K}{\theta} \mathbf{I}, \tag{5.5}$$

which implies that Eq. (5.5) is negative definite. Thus, $\text{grad}(\theta) = -\frac{q}{K}$ maximizes the rate of entropy production due to heat conduction.

5.3. Thermo-mechanical behavior

In this section, we shall derive constitutive equations for specific entropy, specific internal energy, the expression relating the Cauchy stress tensor and the stretch tensor $\mathbf{B}_{\kappa_{p(t)}}$, and an evolution equation for the natural configuration $\kappa_{p(t)}(B)$.

We will assume that the Cauchy stress tensor associated with the mixture is given through the sum of partial Cauchy stress tensor associated with each of the chemical species (see [32]), i.e., $\mathbf{T} = \sum_{i=1}^N \mathbf{T}_i$. Recall that the assumption of a constrained mixture involves only balance equations for the mixture as a whole, and therefore, one needs to make assumptions on partial Cauchy stresses. We shall further assume that $\mathbf{T}_i = \chi_i \mathbf{T}$, $i = 1, 2, \dots, N$, where χ_i is the mole fraction, which is defined as $\chi_i = \frac{n_i}{\sum_{i=1}^N n_i}$. Accordingly, since the tensor $\mathbf{F}_{\kappa_{p(t)}}$ is assumed to be the same for all the species, using Eq. (3.18), it follows that $\mathbf{S}_i = \chi_i \mathbf{S}$, $i = 1, 2, \dots, N$, where \mathbf{S}_i is partial second Piola Kirchhoff stress tensor associated with the i th species. One begins the derivation of constitutive equations by prescribing constitutive equations for the specific Gibbs potential of the mixture and the rate of dissipation function, i.e.:

$$\begin{aligned} G(\theta, n_1, n_2, \dots, n_N, \mathbf{S}) &= \sum_{i=1}^N \left\{ \chi_i C_i \left(\theta - \theta_0 - \theta \ln \left(\frac{\theta}{\theta_0} \right) \right) - \frac{1}{2\rho_{\kappa_{p(t)}}} \text{tr}(\mathbf{S}_i) \right. \\ &\quad \left. - \frac{E_i^{(1)} \theta_0}{4\rho_{\kappa_{p(t)}} \theta} \text{tr}(\mathbf{S}_i^2) - \frac{E_i^{(2)} \theta_0^2}{6\rho_{\kappa_{p(t)}} \theta^2} \text{tr}(\mathbf{S}_i^3) \right\}, E_i^{(1)} \geq 0, E_i^{(2)} \geq 0. \\ &= \sum_{i=1}^N \left\{ \chi_i C_i \left(\theta - \theta_0 - \theta \ln \left(\frac{\theta}{\theta_0} \right) \right) - \chi_i \frac{1}{2\rho_{\kappa_{p(t)}}} \text{tr}(\mathbf{S}) \right. \\ &\quad \left. - (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{4\rho_{\kappa_{p(t)}} \theta} \text{tr}(\mathbf{S}^2) - (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{6\rho_{\kappa_{p(t)}} \theta^2} \text{tr}(\mathbf{S}^3) \right\}, \\ &\quad \sum_{i=1}^N (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} < 2 \sqrt{\sum_{i=1}^N (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2}}, \end{aligned} \tag{5.6a}$$

where $E_i^{(1)}$, $E_i^{(2)}$ and C_i , $i = 1, 2, \dots, N$ are assumed to be constants, and

$$\begin{aligned} \rho_{\kappa_t} \theta \zeta_{\text{diss}} &= \xi_{\text{diss}}(\theta, n_1, n_2, \dots, n_N, \mathbf{S}, \mathbf{D}_{\kappa_{p(t)}}) \\ &= \eta_1(\theta, n_1, n_2, \dots, n_N) \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{D}_{\kappa_{p(t)}} \\ &\quad + \eta_2(\theta, n_1, n_2, \dots, n_N) \mathbf{S} \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{S} \mathbf{D}_{\kappa_{p(t)}}, \\ &\quad \eta_1(\theta, n_1, n_2, \dots, n_N) > 0, \eta_2(\theta, \mathbf{n}) > 0, \end{aligned} \tag{5.6b}$$

respectively. The Eqs. (5.6a) and (5.6b) are consistent with the assumption that the body is isotropic. In general, the Gibbs potential will have additional terms corresponding to the chemical reactions, and the combined thermo-mechanical and chemical response could be studied. For the sake of simplicity, chemical reactions are not included in this subsection. However, in the next subsection, a separate example,

namely rubber chemistry is studied and special constitutive equations representing chemical reactions are derived. The chemical potential of the i^{th} species can be computed by determining $\frac{\partial G}{\partial n_i}$. Notice that Eq. (5.6b) is non-negative and the second term of the same equation accounts for the contribution of the stress with regard to the rate of dissipation, however, it does not differentiate between tensile and compressive loads. For example, the mechanical behavior of granular materials is different under tensile and compressive loads.

On substituting Eq. (5.6a) in Eqs. (4.6a) and (4.6b), one arrives at the constitutive equations for the specific entropy and the stretch tensor $\mathbf{C}_{\kappa_{p(t)}}$, i.e.:

$$\eta = \sum_{i=1}^N \left\{ \chi_i C_i \ln \left(\frac{\theta}{\theta_0} \right) - (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{4 \rho_{\kappa_{p(t)}} \theta^2} \text{tr}(\mathbf{S}^2) - (\chi_i)^3 \frac{2 E_i^{(2)} \theta_0^2}{6 \rho_{\kappa_{p(t)}} \theta^3} \text{tr}(\mathbf{S}^3) \right\} \quad (5.7a)$$

and

$$\mathbf{C}_{\kappa_{p(t)}} = \mathbf{I} + \sum_{i=1}^N \left\{ (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} \mathbf{S} + (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2} \mathbf{S}^2 \right\}. \quad (5.7b)$$

The expression for specific entropy in Eq. (5.7a) is consistent with that of a material, which upon tensile loading results in decrease in entropy, and vice versa. Since the stretch tensor $\mathbf{C}_{\kappa_{p(t)}}$ is positive definite, the right-hand side of Eq. (5.7b) must also be positive definite. Since the eigen values for the tensor \mathbf{S} can be negative, one has to place restrictions on the parameters associated with Eq. (5.7b).

To that end, the restriction $\sum_{i=1}^N (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} < 2 \sqrt{\sum_{i=1}^N (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2}}$ is sufficient to ensure that the right-hand side of Eq. (5.7b) is positive definite. Further, notice that when the tensor $\mathbf{S} = \mathbf{0}$, one recovers that $\mathbf{C}_{\kappa_{p(t)}} = \mathbf{I}$. By premultiplying Eq. (5.7b) by $\mathbf{F}_{\kappa_{p(t)}}$ and post-multiplying by $\mathbf{F}_{\kappa_{p(t)}}^T$, one arrives at

$$\frac{1}{\det(\mathbf{F}_{\kappa_{p(t)}})} \mathbf{B}_{\kappa_{p(t)}} (\mathbf{B}_{\kappa_{p(t)}} - \mathbf{I}) = \sum_{i=1}^N \left\{ (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} \mathbf{T} + \det(\mathbf{F}_{\kappa_{p(t)}}) (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2} \mathbf{T} \mathbf{B}_{\kappa_{p(t)}}^{-1} \mathbf{T} \right\}, \quad (5.8)$$

which is an implicit relation of the form $\mathbf{f}(n_1, n_2, \dots, n_N, \mathbf{B}_{\kappa_{p(t)}}, \mathbf{T}) = \mathbf{0}$. Using Eqs. (4.3), (5.7a) and (5.7b), the specific internal energy is given through

$$\epsilon = \sum_{i=1}^N \chi_i C_i (\theta - \theta_0). \quad (5.9)$$

The above equation implies that the internal energy is only a function of temperature. The Eqs. (5.7a) and (5.9) are consistent with a material exhibiting entropic behavior.

The specific heat capacity of the mixture at constant stress, i.e., C_S is given through

$$\frac{\partial \epsilon}{\partial \theta} = C_S = \sum_{i=1}^N \chi_i C_i. \quad (5.10)$$

Since the internal energy must increase with an increase in the temperature, it is necessary that $C_S > 0$.

Now, we will derive an equation to describe how the natural configuration evolves. First, note that the second law of thermodynamics, namely Eq. (5.1b), constraints how a natural configuration evolves, in that the tensor $\mathbf{L}_{\kappa_{p(t)}}$ related to evolution of natural configuration must be chosen such that Eq. (5.1b) is satisfied. Since Eq. (5.1b) is a scalar, for a fixed set of parameters $\theta, n_1, n_2, \dots, n_N, \mathbf{S}, \mathbf{C}_{\kappa_{p(t)}}, \rho$ and $\rho_{\kappa_{p(t)}}$, eight components of tensor $\mathbf{L}_{\kappa_{p(t)}}$ can be chosen independently, and the ninth component is chosen such that the second law of thermodynamics is satisfied, which implies that there are infinite number of choices for the tensor $\mathbf{L}_{\kappa_{p(t)}}$. As a constitutive restriction, we shall invoke the assumption of maximization of the rate of dissipation, in that, we shall assume that the natural configuration $\kappa_{p(t)}(B)$ evolves in such a way

that the rate of dissipation is maximized with Eq. (5.1b) as a constraint. Accordingly, the augmented function Γ is defined as

$$\begin{aligned} \Gamma = & \eta_1(\theta, n_1, n_2, \dots, n_N) \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{D}_{\kappa_{p(t)}} \\ & + \eta_2(\theta, n_1, n_2, \dots, n_N) \mathbf{S} \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{S} \mathbf{D}_{\kappa_{p(t)}} \\ & + \hat{\lambda} \left\{ \eta_1(\theta, n_1, n_2, \dots, n_N) \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{D}_{\kappa_{p(t)}} \right. \\ & + \eta_2(\theta, n_1, n_2, \dots, n_N) \mathbf{S} \mathbf{D}_{\kappa_{p(t)}} \cdot \mathbf{S} \mathbf{D}_{\kappa_{p(t)}} \\ & \left. - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \mathbf{S} \cdot (\mathbf{L}_{\kappa_{p(t)}}^T \mathbf{C}_{\kappa_{p(t)}} + \mathbf{C}_{\kappa_{p(t)}} \mathbf{L}_{\kappa_{p(t)}}) + \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \text{tr}(\mathbf{D}_{\kappa_{p(t)}}) \mathbf{S} \cdot \mathbf{C}_{\kappa_{p(t)}} \right\}, \end{aligned} \quad (5.11)$$

where $\hat{\lambda}$ is a Lagrange multiplier.

A necessary condition for existence of an extremum is given through

$$\begin{aligned} \frac{\partial \Gamma}{\partial \mathbf{D}_{\kappa_{p(t)}}} &= \mathbf{0} \\ \Rightarrow \frac{1 + \hat{\lambda}}{\hat{\lambda}} & \left\{ 2\eta_1(\theta, n_1, n_2, \dots, n_N) \mathbf{D}_{\kappa_{p(t)}} + \eta_2(\theta, n_1, n_2, \dots, n_N) (\mathbf{S}^2 \mathbf{D}_{\kappa_{p(t)}} + \mathbf{D}_{\kappa_{p(t)}} \mathbf{S}^2) \right\} \\ & + \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \mathbf{S} \cdot \mathbf{C}_{\kappa_{p(t)}} \mathbf{I} - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} 2\mathbf{C}_{\kappa_{p(t)}} \mathbf{S} = \mathbf{0}. \end{aligned} \quad (5.12)$$

It is clear from Eq. (5.7b) that the tensors $\mathbf{C}_{\kappa_{p(t)}}$ and \mathbf{S} have the same eigen vectors and therefore commute. Starting from Eq. (5.12), it can be shown that using the procedure described by Rajagopal and Srinivasa [28], that the tensors $\mathbf{D}_{\kappa_{p(t)}}$ and \mathbf{S} also have the same eigen vectors, i.e., the tensors $\mathbf{C}_{\kappa_{p(t)}}$, \mathbf{S} and $\mathbf{D}_{\kappa_{p(t)}}$ have the same eigen vectors. Since the rate of dissipation function is defined with respect to the tensor $\mathbf{D}_{\kappa_{p(t)}}$, the extremization is carried out with respect to tensor $\mathbf{D}_{\kappa_{p(t)}}$. The expression $\frac{1+\hat{\lambda}}{\hat{\lambda}}$ is determined by operating the inner product of Eq. (5.12) with the tensor $\mathbf{L}_{\kappa_{p(t)}}$, and using properties of the trace operator and comparing with the constraint, i.e., the expression within the curly braces of Eq. (5.11), yielding $\frac{1+\hat{\lambda}}{\hat{\lambda}} = \frac{1}{2}$.

The extremum $\mathbf{D}_{\kappa_{p(t)}}^o$ computed using Eq. (5.12) is

$$\mathbf{D}_{\kappa_{p(t)}}^o = -\frac{\hat{\lambda}}{1 + \hat{\lambda}} \left\{ 2\eta_1 \mathbf{I} + 2\eta_2 \mathbf{S}^2 \right\}^{-1} \left\{ \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} \mathbf{S} \cdot \mathbf{C}_{\kappa_{p(t)}} \mathbf{I} - \frac{\rho_{\kappa_t}}{2\rho_{\kappa_{p(t)}}} 2\mathbf{C}_{\kappa_{p(t)}} \mathbf{S} \right\}. \quad (5.13)$$

In obtaining the above equation, we have used the fact that the tensors $\mathbf{D}_{\kappa_{p(t)}}$ and \mathbf{S} commute, and the fact that the tensor $2\eta_1 \mathbf{I} + 2\eta_2 \mathbf{S}^2$ is invertible. Further, the above expression for the tensor $\mathbf{D}_{\kappa_{p(t)}}^o$ also implies that there is a unique extremum.

Note that since the tensors $\mathbf{C}_{\kappa_{p(t)}}$ and \mathbf{S} commute, it follows that the tensors $\mathbf{B}_{\kappa_{p(t)}}$ and \mathbf{T} commute, and hence the latter pair possess the same eigen vectors. By pre-multiplying Eq. (5.12) with the tensor $\mathbf{F}_{\kappa_{p(t)}}$ and post-multiplying it by the tensor $\mathbf{F}_{\kappa_{p(t)}}^T$, using the fact that the pairs $\mathbf{C}_{\kappa_{p(t)}}$ and \mathbf{S} , and $\mathbf{B}_{\kappa_{p(t)}}$ and \mathbf{T} commute, utilizing the Eqs. (2.14), (3.14) and (3.15), and by substituting Eq. (5.7b) in Eq. (5.12), one can show that the evolution equation for the natural configuration $\kappa_{p(t)}(B)$ is given through

$$\begin{aligned} \overset{\nabla}{\mathbf{B}}_{\kappa_{p(t)}} = & \left\{ \text{tr}(\mathbf{T}) \mathbf{B}_{\kappa_{p(t)}} - 2\mathbf{T} \left(\mathbf{I} + \det(\mathbf{F}_{\kappa_{p(t)}}) \sum_{i=1}^N (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} \mathbf{B}_{\kappa_{p(t)}}^{-1} \mathbf{T} \right. \right. \\ & \left. \left. + \det(\mathbf{B}_{\kappa_{p(t)}}) \sum_{i=1}^N (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2} \mathbf{B}_{\kappa_{p(t)}}^{-2} \mathbf{T}^2 \right) \right\} \left(\eta_1 \mathbf{I} + \eta_2 \det(\mathbf{B}_{\kappa_{p(t)}}) \mathbf{B}_{\kappa_{p(t)}}^{-2} \mathbf{T}^2 \right)^{-1}. \end{aligned} \quad (5.14)$$

In deriving the above equation, we have also used the fact that the tensor $\eta_1 \mathbf{I} + \eta_2 \det(\mathbf{B}_{\kappa_{p(t)}}) \mathbf{B}_{\kappa_{p(t)}}^{-2} \mathbf{T}^2$ is invertible. Note that using Eq. (2.16), one can also rewrite Eq. (5.14) in terms of the lower convected derivative of the tensor $\mathbf{B}_{\kappa_{p(t)}}^{-1}$. Further, one can also establish the evolution equation for the natural configuration $\kappa_{p(t)}(B)$ in terms of the lower and the upper convected derivatives, i.e.,

$$\begin{aligned} & \overset{\nabla}{\mathbf{B}}_{\kappa_{p(t)}} \left(\eta_1 \mathbf{I} + \frac{\eta_2}{2} \det(\mathbf{B}_{\kappa_{p(t)}}) \mathbf{B}_{\kappa_{p(t)}}^{-2} \mathbf{T}^2 \right) - \frac{\eta_2}{2} \det(\mathbf{B}_{\kappa_{p(t)}}) \mathbf{B}_{\kappa_{p(t)}}^{-1} \mathbf{T}^2 \overset{\Delta}{\mathbf{B}}_{\kappa_{p(t)}}^{-1} \mathbf{B}_{\kappa_{p(t)}} \\ &= \left\{ \text{tr}(\mathbf{T}) \mathbf{B}_{\kappa_{p(t)}} - 2\mathbf{T} \left(\mathbf{I} + \det(\mathbf{F}_{\kappa_{p(t)}}) \sum_{i=1}^N (\chi_i)^2 \frac{E_i^{(1)} \theta_0}{\theta} \mathbf{B}_{\kappa_{p(t)}}^{-1} \mathbf{T} + \det(\mathbf{B}_{\kappa_{p(t)}}) \right) \right. \\ & \quad \left. \times \sum_{i=1}^N (\chi_i)^3 \frac{E_i^{(2)} \theta_0^2}{\theta^2} \mathbf{B}_{\kappa_{p(t)}}^{-2} \mathbf{T}^2 \right\}. \end{aligned} \quad (5.15)$$

Now, we shall determine the nature of the extremum (5.13). To that end, assuming sufficient smoothness for the rate of dissipation function, one can show that the Hessian of augmented function Γ with respect to the tensor $\mathbf{D}_{\kappa_{p(t)}}$ evaluated at the stationary point $\mathbf{D}_{\kappa_{p(t)}}^o$ with $\hat{\lambda} = -2$ is given through

$$\begin{aligned} \frac{\partial^2 \Gamma}{\partial \mathbf{D}_{\kappa_{p(t)}} \partial \mathbf{D}_{\kappa_{p(t)}}} \Big|_{\mathbf{D}_{\kappa_{p(t)}}^o, \hat{\lambda} = -2} &= (1 + \hat{\lambda}) \{ 2\eta_1 \mathbf{Z} + 2\eta_2 \mathbf{Z} (\mathbf{S}^2 \boxtimes \mathbf{I}) \mathbf{Z} \} \\ &= - \{ 2\eta_1 \mathbf{Z} + 2\eta_2 \mathbf{Z} (\mathbf{S}^2 \boxtimes \mathbf{I}) \mathbf{Z} \}, \end{aligned} \quad (5.16)$$

where \mathbf{Z} is a fourth-order symmetrizer tensor⁸ and the square tensor product⁹ is defined as $(\mathbf{A} \boxtimes \mathbf{B})\mathbf{C} := \mathbf{A}\mathbf{C}\mathbf{B}^T$, $\forall \mathbf{C} \in \text{Lin}(V, V)$, where \mathbf{A}, \mathbf{B} and \mathbf{C} are second-order tensors (see Jog [17]) and V is a vector space. Using the Cartesian basis, the components of the Eq. (5.16) is rewritten in a convenient form:

$$\begin{aligned} \frac{\partial^2 \Gamma}{\partial (\mathbf{D}_{\kappa_{p(t)}})_{pq} \partial (\mathbf{D}_{\kappa_{p(t)}})_{ij}} &= -2 \left\{ \eta_1 \frac{1}{2} (\delta_{ip} \delta_{jq} + \delta_{iq} \delta_{jp}) + \eta_2 \frac{1}{4} [(\mathbf{S}^2)_{ip} \delta_{jq} \right. \\ & \quad \left. + (\mathbf{S}^2)_{iq} \delta_{jp} + (\mathbf{S}^2)_{jq} \delta_{ip} + (\mathbf{S}^2)_{jp} \delta_{iq}] \right\}. \end{aligned} \quad (5.17)$$

Since the tensors \mathbf{S} and \mathbf{I} are symmetric, it is easy to see that the right-hand side of Eq. (5.17) represents the components of a fourth-order tensor with a major and two minor symmetries. The right-hand side of Eq. (5.16) is negative definite because on applying the definition for a negative definite tensor,¹⁰ one can show that $-2\{\eta_1 \text{tr}(\mathbf{A}^2) + \eta_2 \text{tr}(\mathbf{A}^2 \mathbf{S}^2)\} < 0$, \forall nonzero $\mathbf{A} \in \text{Lin}(V, V)$, i.e., the extremum $\mathbf{D}_{\kappa_{p(t)}}^o$ is a maximum. In other words, for each time t , there is a unique tensor $\mathbf{D}_{\kappa_{p(t)}}$ associated with the evolution Eq. (5.14) for the natural configuration $\kappa_{p(t)}(B)$ in such a way that it satisfies the constraint due to the second law of thermodynamics and it maximizes the rate of dissipation.

Alternatively, one can represent a three-dimensional fourth-order tensor with a major and minor symmetries as a symmetric, six-dimensional second-order tensor (see Moakher [23]). The six-dimensional, symmetric second-order tensor has the same eigen values as that of the fourth-order tensor with a major

⁸The symmetrizer tensor \mathbf{Z} is defined as $\mathbf{Z}\mathbf{A} := \frac{\mathbf{A} + \mathbf{A}^T}{2}$, $\forall \mathbf{A} \in \text{Lin}(V, V)$, where V is a vector space. The action of a fourth-order tensor $\mathbf{A} \otimes \mathbf{B}$ on second-order tensors is defined as $(\mathbf{A} \otimes \mathbf{B})\mathbf{C} := \text{tr}(\mathbf{B}\mathbf{C}^T)\mathbf{A}$, $\forall \mathbf{C} \in \text{Lin}(V, V)$, where \mathbf{A} and \mathbf{B} are second-order tensors.

⁹The action of a fourth-order tensor on any fourth-order tensor can be obtained by defining the action of the fourth-order tensor on a second-order tensor. One can show that the action of a fourth-order tensor $\mathbf{A} \otimes \mathbf{B}$ on another fourth-order tensor $\mathbf{C} \boxtimes \mathbf{D}$ is given through $(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \boxtimes \mathbf{D}) = \mathbf{A} \otimes (\mathbf{C}^T \mathbf{B} \mathbf{D})$, and $(\mathbf{C} \boxtimes \mathbf{D})(\mathbf{A} \otimes \mathbf{B}) = \mathbf{C} \mathbf{A} \mathbf{D}^T \otimes \mathbf{B}$, where $\mathbf{A}, \mathbf{B}, \mathbf{C}$ and \mathbf{D} are second-order tensors.

¹⁰A fourth-order tensor \mathbf{A} with major and minor symmetries is said to be positive definite if $\mathbf{A}\mathbf{B} \cdot \mathbf{B} > 0$, \forall nonzero $\mathbf{B} \in \text{Lin}^{\text{sym}}(V, V)$, where $\text{Lin}^{\text{sym}}(V, V)$ is the space of symmetric second-order tensors. A fourth-order tensor \mathbf{A} with a major and minor symmetries is said to be negative definite if $\mathbf{A}\mathbf{B} \cdot \mathbf{B} < 0$, \forall nonzero $\mathbf{B} \in \text{Lin}^{\text{sym}}(V, V)$.

and minor symmetries. If the six eigen values of the six-dimensional second-order tensor are positive, then the fourth-order tensor is positive definite, and vice versa.

5.4. Chemical kinetics

For a given functional form for G , the inequality (5.1c) restricts \dot{n}_i 's, in that \dot{n}_i 's must be chosen such that $\sum_{i=1}^N \mu_i \dot{n}_i \leq 0$ in addition to the constraints imposed by Eq. (4.17). Further, after choosing suitable values for \dot{n}_i 's, one can calculate the total rate of entropy production due to the chemical reactions using Eq. (5.1c). Alternatively, one can prescribe a non-negative function for ζ_{chem} . Then, the equation (5.1c) becomes an equality constraint for \dot{n}_i 's. We shall require that ξ_{chem} must be zero for a fixed composition, and positive when compositional changes occur. To that end, we shall define ξ_{chem} as follows:

$$-\rho_{\kappa_t} \mu_i \dot{n}_i = \hat{\xi}_{\text{chem}}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}, \{\dot{n}_i\}) = \xi_{\text{chem}} = A_{ij} \dot{n}_j \dot{n}_i, \quad (5.18)$$

where the set $\{n_i\}$ denotes the members n_1, n_2, \dots, n_N and the set $\{\dot{n}_i\}$ denotes the members $\dot{n}_1, \dot{n}_2, \dots, \dot{n}_N$. The above equation is tantamount to assuming that ξ_{chem} is a quadratic polynomial in N variables, namely \dot{n}_1 through \dot{n}_N , and for convenience, may be expressed using the matrix representation. Further, Einstein's summation convention is followed and the matrix A is positive definite with scalar, real-valued entries, i.e.,

$$A = \begin{Bmatrix} f_{11}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & f_{12}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & \cdots & f_{1N}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) \\ f_{21}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & f_{22}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & \cdots & f_{2N}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) \\ \vdots & \vdots & \ddots & \vdots \\ f_{N1}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & f_{N2}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) & \cdots & f_{NN}(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}) \end{Bmatrix}. \quad (5.19)$$

Notice that the matrix A , for a given quadratic polynomial, has fixed entries, in that, for a given chemical system and the constitutive assumption invoked for ξ_{chem} , the entries associated with the matrix A do not change with the choice of basis vectors. Unless expressed otherwise, for each of the repeated indices, the summation is carried out from the index 1 to N . Note that ξ_{chem} is also a function of the density of the mixture because it can account for the fact that the higher the volumetric concentration the higher the rate of entropy production due to chemical reactions, should chemical reactions occur. By requiring A to be positive definite, the Eq. (5.18) is non-negative for all non-zero $\{\dot{n}_i\}$ and is equal to zero if and only if $\{\dot{n}_i\} = \{0\}$. Also, notice that $\hat{\xi}_{\text{chem}}$ is a quadratic function with respect to $\{\dot{n}_i\}$. Notice that for a given $\rho_{\kappa_t}, \theta, \{n_i\}$ and \mathbf{S} , the set $\{\dot{n}_i\}$ can assume any value as long as it satisfies the constraints, i.e., Eqs. (4.6c) or (5.18) and (4.17), which immediately implies that infinite choices for $\{\dot{n}_i\}$ are possible. In this section, we shall arrive at suitable equations for the evolution of the composition of the system.

We shall assume that for a given $\rho_{\kappa_t}, \theta, \{n_i\}$ and \mathbf{S} , $\{\dot{n}_i\}$ is chosen such that the function $\hat{\xi}_{\text{chem}}$ is maximized subject to the constraints, the Eqs. (4.17) and (5.18), i.e.,

$$\begin{aligned} \Phi(\rho_{\kappa_t}, \theta, \{n_i\}, \mathbf{S}, \{\dot{n}_i\}, \bar{\lambda}, \{\lambda_i\}) &= A_{ij} \dot{n}_j \dot{n}_i + \bar{\lambda}(A_{ij} \dot{n}_j \dot{n}_i + \rho_{\kappa_t} \mu_i \dot{n}_i) \\ &+ \sum_{j=1}^{N-M'} \lambda_j \left(\sum_{i=1}^{M'} \beta_{ji} \dot{n}_i - \dot{n}_{M'+j} \right) \end{aligned} \quad (5.20a)$$

$$= A_{ij} \dot{n}_j \dot{n}_i + \bar{\lambda}(A_{ij} \dot{n}_j \dot{n}_i + \rho_{\kappa_t} \mu_i \dot{n}_i) + \sum_{i=1}^{N-M'} Y_{ij} \dot{n}_j \lambda_i, \quad (5.20b)$$

where $\bar{\lambda}$ and λ_j , $j = 1, 2, \dots, N - M'$ are Lagrange multipliers introduced to enforce the constraints, i.e., Eqs. (4.17) and (5.18), respectively. The matrix Y is defined as

$$Y = \left\{ \begin{array}{cccccccc} \beta_{11} & \beta_{12} & \cdots & \beta_{1M'} & -1 & 0 & \cdots & 0 \\ \beta_{21} & \beta_{22} & \cdots & \beta_{2M'} & 0 & -1 & \cdots & 0 \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ \beta_{(N-M')1} & \beta_{(N-M')2} & \cdots & \beta_{(N-M')M'} & 0 & 0 & \cdots & -1 \end{array} \right\}. \quad (5.21)$$

For a given chemically reacting system, the entries of the matrix Y are constants and do not vary with the choice of basis vectors. Since the last $N - M'$ columns of the matrix Y are linearly independent, and the fact that the rank of the same matrix can be at most $N - M'$ implies that the rank of the matrix Y is $N - M'$.

A necessary condition for the existence of an extremum is given through $\frac{\partial \Phi}{\partial \dot{n}_i} = 0$, $i = 1, 2, \dots, N$, i.e.,

$$\left(\frac{1 + \bar{\lambda}}{\lambda} \right) (A_{ij} + A_{ji}) \dot{n}_j + \rho_{\kappa_t} \mu_i + \frac{1}{\lambda} \sum_{j=1}^{N-M'} Y_{ji} \lambda_j = 0, \quad i = 1, 2, \dots, N. \quad (5.22)$$

Now, we shall proceed to determine the Lagrange multipliers. By multiplying Eq. (5.22) with \dot{n}_i and summing over the index i from $i = 1$ to N , and comparing the result with the constraint (5.18), $\frac{1 + \bar{\lambda}}{\lambda}$ is determined to be $\frac{1}{2}$. Further, by premultiplying Eq. (5.22) by $\left\{ \frac{(A_{ij} + A_{ji})}{2} \right\}^{-1}$ (by definition, A is non-singular), one arrives at

$$\dot{n}_i = -\rho_{\kappa_t} (P^{-1})_{ij} \mu_j - \frac{1}{\lambda} \sum_{k=1}^{N-M'} (P^{-1})_{ij} Y_{kj} \lambda_k, \quad i = 1, 2, \dots, N, \quad (5.23)$$

where $P = \frac{(A_{ij} + A_{ji})}{2}$. The $N - M'$ values for $\frac{\lambda_i}{\lambda}$ are determined by premultiplying the Eq. (5.23) by the matrix Y and using the constraints, i.e., Eq. (4.17), one arrives at

$$Y_{ij} (P^{-1})_{jk} \left(\rho_{\kappa_t} \mu_k + \sum_{l=1}^{N-M'} Y_{lk} \tilde{\lambda}_l \right) = 0, \quad (5.24)$$

where $\tilde{\lambda}_i = \frac{\lambda_i}{\lambda}$.

Theorem 5.1. *The matrix $Y P^{-1} Y^T$ is invertible.*

Proof. Let $\text{row}_i(Y)$, $i = 1, 2, \dots, N - M'$ and $\text{col}_i(P^{-1})$, $i = 1, 2, \dots, N$ be the rows of the matrix Y and columns of P^{-1} , respectively. Then, the matrix multiplication operation $Y P^{-1}$ is represented by the $(N - M') \times N$ matrix with the entries corresponding to the i th row being given through $\{\text{row}_i(Y) \cdot \text{col}_1(P^{-1}) \quad \text{row}_i(Y) \cdot \text{col}_2(P^{-1}) \quad \dots \quad \text{row}_i(Y) \cdot \text{col}_N(P^{-1})\}$, where $\text{row}_i(Y) \cdot \text{col}_j(P^{-1}) = \sum_{p=1}^N Y_{ip} (P^{-1})_{pj}$, i.e., ij th component of the matrix $Y P^{-1}$. Now, we shall determine the rank of the matrix $Y P^{-1}$ by multiplying each row by a scalar, summing the resultant expression and equating it to the zero vector, i.e.,

$$\left\{ \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) \cdot \text{col}_1(P^{-1}) \quad \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) \cdot \text{col}_2(P^{-1}) \quad \dots \quad \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) \cdot \text{col}_N(P^{-1}) \right\} = \vec{0}_N, \\ \alpha_i \in \mathfrak{R}, \quad i = 1, 2, \dots, N - M', \tag{5.25}$$

where $\vec{0}_N$ represents the N -dimensional zero vector. The above equation implies that for the k th entry, $k = 1, 2, \dots, N$, $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) = \vec{0}_N$ or $\text{col}_k(P^{-1}) = \vec{0}_N$ or $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y)$ is ‘perpendicular’ to $\text{col}_k(P^{-1})$. Since $\text{row}_i(Y)$, $i = 1, 2, \dots, N - M'$ are linearly independent, there are no non-zero α_i ’s for which $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) = \vec{0}_N$. None of the columns of the matrix P^{-1} , i.e., $\text{col}_k(P^{-1})$, $k = 1, 2, \dots, N$ can be zero because the matrix P (and its inverse) is positive definite. Therefore, the columns of P^{-1} cannot be zero. Recall that the vector $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y)$ spans $N - M'$ sub-space of the N dimensional space spanned by the columns of P^{-1} . Further, since the rank of P^{-1} is N , there are no non-zero vectors belonging to the N dimensional space that are ‘perpendicular’ to all the columns of the matrix P^{-1} , only the zero vector is ‘perpendicular’ to all the columns. Consequently, the vector $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y)$ cannot be simultaneously perpendicular to all the columns of P^{-1} . Therefore, the only possibility to satisfy Eq. (5.25) is by letting $\alpha_1 = \alpha_2 = \dots = \alpha_{N-M} = 0$, i.e., the rank of the matrix YP^{-1} is $N - M'$.

Now, we shall determine the rank of square matrix $YP^{-1}Y^T$ of size $N - M'$, which is obtained by post-multiplying YP^{-1} with Y^T . Let $\text{row}_i(YP^{-1})$, $i = 1, 2, \dots, N - M'$, represent the rows of the matrix YP^{-1} . Using the definition of linear independence of vectors, similar to that detailed in the preceding paragraph, i.e.,

$$\left\{ \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(YP^{-1}) \cdot \text{row}_1(Y) \quad \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(YP^{-1}) \cdot \text{row}_2(Y) \quad \dots \quad \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(YP^{-1}) \cdot \text{row}_{N-M'}(Y) \right\} = \vec{0}_{N-M'}, \quad \alpha_i \in \mathfrak{R}, \quad i = 1, 2, \dots, N - M'. \tag{5.26}$$

Since $\text{row}_i(YP^{-1})$, $i = 1, 2, \dots, N - M'$ are linearly independent, $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(YP^{-1}) = \vec{0}_N$ if and only if $\alpha_1 = \alpha_2 = \dots = \alpha_{N-M'} = 0$, and $\text{row}_i(Y)$, $i = 1, 2, \dots, N - M'$ are basis vectors and cannot be the vector $\vec{0}_N$. The other way to satisfy Eq. (5.26) is if the vector $\sum_{i=1}^{N-M'} \alpha_i \text{row}_i(YP^{-1}) \in \text{Null}(Y)$, which, upon using the Rank-Nullity theorem, one determines that $\text{Null}(Y)$ must be of dimension M' . Further, the N dimensional space can be decomposed into a $N - M'$ dimensional space (\mathcal{V}) spanned by basis $\text{row}_i(Y)$, $i = 1, 2, \dots, N - M'$ and the M' -dimensional, orthogonal sub-space \mathcal{V}^\perp spanned by the basis $\text{row}_i(Y^\perp)$, $i = 1, 2, \dots, M'$, where each of the vectors belonging to \mathcal{V}^\perp is perpendicular to all the vectors spanned by the basis $\text{row}_i(Y)$ ’s, it can be deduced that $\text{Null}(Y) \equiv \mathcal{V}^\perp$. Recall that $\text{row}_i(YP^{-1})$ ’s are a basis for a $N - M'$ dimensional space, and since $\text{row}_i(YP^{-1})$, $i = 1, 2, \dots, N - M'$ is assumed to span $\text{Null}(Y)$ (or \mathcal{V}^\perp), it immediately implies that $N - 1 \geq M' \geq N/2$ if N is even and $N - 1 \geq M' \geq (N + 1)/2$ if N is odd. However, as the matrix P^{-1} is positive definite and symmetric, $(P^{-1})_{ij}(\text{row}_k(Y))_j(\text{row}_k(Y))_i = \text{row}_k(YP^{-1}) \cdot \text{row}_k(Y) > 0$, $k = 1, 2, \dots, N - M'$, which implies that $\text{row}_i(YP^{-1}) \notin \text{Null}(Y)$, $i = 1, 2, \dots, N - M'$, and consequently, in general, it does not imply that the vectors $\text{row}_i(YP^{-1})$ ’s span the same sub-space as that spanned by $\text{row}_i(Y)$ ’s. Further, since, $\text{row}_i(YP^{-1}) \notin \text{Null}(Y)$, $i = 1, 2, \dots, N - M'$, it implies that an inner product of any non-zero vector belonging to the sub-space spanned by $\text{row}_i(YP^{-1})$ ’s with all the $\text{row}_i(Y)$ ’s cannot be equal to zero simultaneously, which implies that the only way to satisfy Eq. (5.26) is by letting $\alpha_1 = \alpha_2 = \dots = \alpha_{N-M'} = 0$. Therefore, the matrix $YP^{-1}Y^T$ is invertible. \square

From this point forward, the summation up to $N - M'$ is also understood. The Eq. (5.24) implies that $Y_{ij} = 0$ or $P_{ij}^{-1} = 0$ or $\rho_{\kappa_i} \mu_i + Y_{ji} \tilde{\lambda}_j = 0$ or every row of matrix Y is simultaneously orthogonal to all the columns of P^{-1} or every row of matrix P^{-1} is orthogonal to the vector with components $\rho_{\kappa_i} \mu_i + Y_{ji} \tilde{\lambda}_j$ or $\rho_{\kappa_i} Y_{ip} (P^{-1})_{pq} \mu_q + Y_{ip} (P^{-1})_{pq} Y_{rq} \tilde{\lambda}_r = 0$. Since the matrices Y and P^{-1} are of full rank, $Y_{ij} \neq 0$ and $(P^{-1})_{ij} \neq 0$. The vector with components $\rho_{\kappa_i} \mu_i + Y_{ji} \tilde{\lambda}_j \neq 0$ because, if it were equal to the vector zero, it implies that $\dot{n}_i = 0$, and there can be no change in the composition of chemical mixture. Due to reasons discussed in the Theorem (5.4), $Y_{ip} (P^{-1})_{pj} \neq 0$, $(P^{-1})_{ij} (\rho_{\kappa_i} \mu_j + Y_{pj} \tilde{\lambda}_p) \neq 0$, and, for a given specific Gibbs potential G , ξ_{chem} and stoichiometry, the Lagrange multiplier $\tilde{\lambda}_i$ is uniquely determined to be:

$$\tilde{\lambda}_i = -\rho_{\kappa_i} \left((Y P^{-1} Y^T)^{-1} \right)_{ip} (Y P^{-1})_{pq} \mu_q, \quad i = 1, 2, \dots, N - M'. \quad (5.27)$$

Now, we shall determine the nature of the extremum, i.e., Eq. (5.23). To that end, by substituting Eq. (5.27) in Eq. (5.23), one arrives at the evolution equation for each of the chemical species:

$$\begin{aligned} \dot{n}_i &= -\rho_{\kappa_i} (P^{-1})_{ij} \left\{ \delta_{jr} - Y_{pj} \left((Y P^{-1} Y^T)^{-1} \right)_{pq} (Y P^{-1})_{qr} \right\} \mu_r \\ &= -\rho_{\kappa_i} (P^{-1})_{ip} \{ \delta_{pq} - \mathcal{P}_{pq} \} \mu_q, \quad i = 1, 2, \dots, N, \end{aligned} \quad (5.28)$$

where δ_{ij} is an identity matrix of size N and the square matrix $\mathcal{P} := Y^T$

$(Y P^{-1} Y^T)^{-1} Y P^{-1}$. One can also rewrite Eq. (5.28) in terms of concentration expressed in moles per unit volume, i.e., using Eqs. (3.10), (3.11) and (5.28), one can show the following matrix equation:

$$\dot{\tilde{n}}_i + \tilde{n}_i \text{div}(\mathbf{v}) + \rho_{\kappa_i}^2 (P^{-1})_{ip} \{ \delta_{pq} - \mathcal{P}_{pq} \} \mu_q = 0, \quad i = 1, 2, \dots, N. \quad (5.29)$$

Referring to Eq. (5.28), for a given ρ_{κ_i} , θ , $\{n_i\}$ and \mathbf{S} , there is a unique $\{\dot{n}_i\}$ satisfying the constraints (5.18) and (4.17), which maximizes the function $\hat{\xi}_{\text{chem}}$. Before commenting on this further, let us examine the geometrical implications of Eq. (5.28).

Eventhough Zeleznik and Gordon [40] considered a more general system with l elements making up m compounds (existing in p phases) reacting through r chemical reactions, the effect of deformation on chemical reactions, and vice versa, was not considered in their study. Further, extremization of the rate of entropy production due to chemical reaction to obtain the evolution equation for the composition of mixture is new and was not considered by them.

5.4.1. Geometrical properties of evolution equation. Notice that $\mathcal{P}\mathcal{P} = \mathcal{P}$, which implies that the matrix \mathcal{P} is idempotent. On using a property of idempotent matrices, i.e., the rank of such a matrix is equal to its *trace*, one can determine, using the properties of the *trace* operator that $\text{Rank}(\mathcal{P}) = \text{trace} \left\{ (Y P^{-1} Y^T) (Y P^{-1} Y^T)^{-1} \right\} = \text{trace}(I_{N-M'}) = N - M'$, where $I_{N-M'}$ is an identity matrix of size $N - M'$. Now, we shall show that \mathcal{P} is a projection. Let $\vec{v} = \sum_{i=1}^{N-M'} \alpha_i \text{row}_i(Y) = Y^T \vec{\alpha}$, $\vec{\alpha} \in \mathfrak{R}^{N-M'}$, where $\mathfrak{R}^{N-M'}$ is an arbitrary real-valued $N - M'$ -tuple. Further, $\mathcal{P}\vec{v} = \mathcal{P}Y^T \vec{\alpha} = Y^T \vec{\alpha} = \vec{v}$ and upon using the rank-nullity theorem, $\dim(\text{null}(\mathcal{P})) = M'$. Thus, \mathcal{P} acts as an identity matrix for all the vectors belonging to the $N - M'$ dimensional sub-space spanned by the $\text{row}_i(Y)$'s. Any $\vec{u} \in \mathcal{V} \oplus \mathcal{V}^\perp$ can be represented as $\vec{u} = Y^T \vec{\alpha} + (Y^\perp)^T \vec{\beta} = \vec{v} + \vec{v}^\perp$, $\vec{\alpha} \in \mathfrak{R}^{N-M'}$, $\vec{\beta} \in \mathfrak{R}^{M'}$, where Y^\perp is a $M' \times N$ matrix with basis vectors $\text{row}_i(Y^\perp)$, $i = 1, 2, \dots, M'$ making up the rows of matrix Y^\perp . The action of \mathcal{P} on \vec{u} , i.e., $\mathcal{P}\vec{u} = Y^T \vec{\alpha} = \vec{v}$ implies that the matrix \mathcal{P} projects an arbitrary vector \vec{u} onto the sub-space \mathcal{V} . Further, it is clear from the properties of \mathcal{P} that $\mathcal{P} \neq I_N$, and hence, one obtains, in general, non-trivial solutions for the evolution Eq. (5.28). Similarly, one can show that the matrix $I_N - \mathcal{P}$ is also idempotent and projects any $\vec{u} \in \mathcal{V} \oplus \mathcal{V}^\perp$ onto \mathcal{V}^\perp .

It is clear that if $\vec{\mu}$ always lies in the sub-space spanned by $\text{row}_i(Y)$'s, then $\dot{\vec{n}} = \vec{0}_N$, i.e., the chemical reactions do not occur. On the other hand, if $\vec{\mu} \in \mathcal{V} \oplus \mathcal{V}^\perp$, then the projection $I_N - \mathcal{P}$ projects $\vec{\mu}$ onto

\mathcal{V}^\perp , and if $\vec{\mu} \in \mathcal{V}^\perp$, then $(I_N - \mathcal{P})\vec{\mu} = \vec{\mu}$. By understanding the geometrical properties of Eq. (5.28), to obtain non-trivial solutions, it is clear that the specific Gibbs potential must be defined such that its gradient (the vector containing chemical potential of all species) should not always lie in the sub-space spanned by the $\text{row}_i(Y)$'s.

Now, we shall determine the nature of the differential equation, i.e., Eq. (5.28). To show that the point \vec{n} satisfying the constraints, i.e., Eqs. (4.17) and (5.18), is a regular point (see [4]), one computes the gradient of $A\vec{n} \cdot \vec{n} + \rho_{\kappa_t} \vec{\mu} \cdot \vec{n}$ with respect to \vec{n} and evaluates the gradient at $\vec{n} = -\rho_{\kappa_t} P^{-1} \{I_N - \mathcal{P}\} \vec{\mu}$, which is given through $-2\rho_{\kappa_t} (I_N - \mathcal{P})\vec{\mu} + \rho_{\kappa_t} \vec{\mu} = -2\rho_{\kappa_t} \vec{\mu}^\perp + \rho_{\kappa_t} \vec{\mu}$. It is clear that unless $\vec{\mu} \in \mathcal{V}$, one cannot express $-2\rho_{\kappa_t} \vec{\mu}^\perp + \rho_{\kappa_t} \vec{\mu}$ as a linear combination of the gradient of $Y\vec{n}$, i.e., $\text{row}_i(Y)$, $i = 1, 2, \dots, N - M'$, and hence, $\vec{n} = -\rho_{\kappa_t} P^{-1} \{I_N - \mathcal{P}\} \vec{\mu}$ is a regular point. Further, assuming smoothness of $\Phi(\theta, \{n_i\}, \{\dot{n}_i\}, \bar{\lambda}, \{\lambda_i\})$, a necessary and sufficient condition for the existence of a maximum satisfying the constraints (4.17) and (5.18) is that Hessian of the function Φ with respect to \vec{n} , evaluated at a regular point $\vec{n} = -\rho_{\kappa_t} P^{-1} \{I_N - \mathcal{P}\} \vec{\mu}$, $\bar{\lambda} = -2$ and $\vec{\lambda} = 2\rho_{\kappa_t} (Y P^{-1} Y^T)^{-1} (Y P^{-1}) \vec{\mu}$, is negative definite, i.e.

$$\frac{\partial^2 \Phi}{\partial \vec{n} \partial \vec{n}} = 2(1 + \bar{\lambda})P = -2P, \tag{5.30}$$

which implies that Eq. (5.30) is negative definite. In summary, we have shown that there exists a unique \dot{n}_i given by Eq. (5.28), which maximizes the rate of entropy production due to chemical reactions.

5.4.2. Gibbs-Duhem equation. Suppose one assumes that the specific Gibbs potential function G to be homogeneous of degree one with respect to \vec{n} , i.e., $G(\theta, \alpha \vec{n}, \mathbf{S}) = \alpha G(\theta, \vec{n}, \mathbf{S})$ with θ and \mathbf{S} as parameters, and on using Euler's theorem for homogeneous functions, G can be represented as follows:

$$G = \frac{\partial G}{\partial \vec{n}} \cdot \vec{n} = \vec{\mu} \cdot \vec{n}. \tag{5.31}$$

As usual, by taking the derivative of Eq. (5.31) with respect to time and comparing with equation $\dot{G}(\theta, \vec{n}, \mathbf{S}) = \frac{\partial G}{\partial \theta} \dot{\theta} + \frac{\partial G}{\partial \vec{n}} \cdot \dot{\vec{n}} + \frac{\partial G}{\partial \mathbf{S}} \cdot \dot{\mathbf{S}}$, one arrives at the generalized Gibbs-Duhem equation:

$$\frac{\partial G}{\partial \theta} \dot{\theta} + \frac{\partial G}{\partial \mathbf{S}} \cdot \dot{\mathbf{S}} = -\eta \dot{\theta} - \frac{1}{2\rho_{\kappa_p(t)}} \mathbf{C}_{\kappa_p(t)} \cdot \dot{\mathbf{S}} = \dot{\vec{\mu}} \cdot \vec{n}. \tag{5.32}$$

It is worth noting that in deriving Eq. (5.28), we did not make any assumptions concerning the nature of function G . The only requirement is that for obtaining non-trivial solutions, the gradient of G with respect to \vec{n} should not always lie in the $N - M'$ dimensional sub-space spanned by $\text{row}_i(Y)$'s, i.e., sub-space \mathcal{V} .

5.4.3. De Donder affinity and conditions for equilibrium. At equilibrium, $\dot{\vec{n}} = \vec{0}_N$, and Eq. (5.28) reduces to $(I_N - \mathcal{P})\vec{\mu} = \vec{0}_N$, which implies that $\vec{\mu} \in \mathcal{V}$. From Eq. (4.16), it is clear that $Y_{ip} \nu_{jp} = \nu_{ip} Y_{jp} = 0$. It is also true that $\nu_{ij} Y_{pj} \alpha_p = \nu_{ij} \mu_j = 0$, $\forall \{\alpha_i\} \in \mathfrak{R}^{M'}$ because the chemical potential, under the condition of equilibrium, belongs to the sub-space \mathcal{V} , and can be represented as $\vec{\mu} = Y_{ij} \alpha_j$, $\{\alpha_i\} \in \mathfrak{R}^{M'}$. Further, if $\vec{\mu} \in \mathcal{V}$, then $\dot{\vec{n}} = \vec{0}_N$. Consequently, the equation $\nu \vec{\mu} = \vec{0}_{M'}$ can be rewritten as $\text{row}_i(\nu) \cdot \vec{\mu} = 0$, $i = 1, 2, \dots, M$ and are both necessary and sufficient conditions for equilibrium. The negative of the quantity $\text{row}_i(\nu) \cdot \vec{\mu}$ is known as the de Donder affinity of the i th reaction. Notice that not all i 's are independent, only M' of them are independent.

The conditions obtained for equilibrium are the same as that obtained by minimizing the Gibbs free energy, which is assumed to be homogeneous of degree one (see [7] for a single reaction and [40] for many reactions), at constant temperature and pressure. However, for obtaining the result $\nu \vec{\mu} = \vec{0}_{M'}$, we made no assumption about Gibbs free energy or the temperature field.

5.4.4. An application: rubber chemistry.

5.4.4.1. Introduction. Rubber, in its natural form, is a sticky liquid-like material with poor mechanical properties. To improve its mechanical behavior, natural rubber is crosslinked using sulfur to form a networked polymer. Such a process is called vulcanization. In 1841, Charles Goodyear vulcanized natural rubber with sulfur, which took several hours to complete. Later, certain chemicals such as thiocarbanilides were found to accelerate the rate of crosslinking reactions where sulfur was used as a crosslinking agent. Vulcanization using such chemicals is known as accelerated rubber vulcanization. Some examples of the class of accelerators are thiocarbanilides, thiurams, dithiocarbamates, amines, benzothiazoles and benzothiazolesulfenamides.

Numerous chemical reactions occur during vulcanization. The basic framework for chemical reactions that occur during accelerated sulfur vulcanization is described below (see Ghosh et al. [15]): The chemical reactions are grouped under three categories, namely accelerator chemistry, crosslinking and post-crosslinking chemistry. The accelerator combines with the sulfur to form an active sulfurating agent, which can react with an unsaturated site in a rubber chain to form a crosslink precursor, termed as accelerator-terminated pendent group. The formation of active sulfurating agent marks the end of the first category of reactions, namely accelerator chemistry. The crosslink precursors have many sulfur atoms (polysulfidic), usually, a distribution of sulfur atoms. The crosslink precursors get activated and combine with an unsaturated site in a neighboring rubber chain to form a crosslink. The crosslinks are also polysulfidic in nature. During post-crosslinking reactions, the newly formed crosslinks may degrade to form cyclic sulfides or other main-chain modification or desulfurate to form a more stable crosslinks with fewer sulfur atoms. For a detailed description of the chemical reaction mechanisms for accelerated rubber vulcanization by the action of different classes of accelerators, and vulcanization by the action of metal oxides and peroxides, we refer the reader to Coran [6].

Coran [5] proposed a lumped model for accelerated vulcanization of rubber, in that, only the most important chemical species are retained and several similar chemical species are lumped into a single species. Coran considered four chemical species, viz., accelerator and/or its reaction products, A , crosslink precursor, B , an activated crosslink precursor, B^* , and the vulcanizate, Vu . Each of the four species has a distribution of sulfur atoms, which are lumped into its respective species. The reaction scheme is as follows:



and



where k_1 through k_4 are the rate constants and α and β are introduced to adjust for the stoichiometry. It has been experimentally observed that the crosslinking reactions do not occur in a significant manner during the initial phase termed as an induction (scorch delay) region, which is significant for benzothiazole class of accelerators. During this phase, primarily the reactions pertaining to the accelerator chemistry occur, and almost all the accelerator is consumed prior to the formation of crosslinks. Coran [5] assumed that the accelerator and its reaction products with sulfur retard the formation of crosslinks. Reaction (5.33b) emulates the retarding action. It is clear from the reaction (5.33a) that the reactions associated with the accelerator and sulfur is not represented explicitly. By selecting a suitable value for the rate constant k_1 , one can ensure that the accelerator is consumed prior to the formation of crosslinks and by selecting a suitable value the rate constant k_4 (and the other rate constants), one can ensure that the induction region is emulated. It was observed that for natural rubber-based formulations, the peak concentration of the vulcanizate reduces with the increase in temperature. Recognizing this effect, Ding et al. [9] introduced a competitive reaction (5.33c), i.e.,



Later, Ding and Leonov [8] added a reaction to account for the phenomenon of reversion, which was observed during the vulcanization of natural rubber, i.e.,

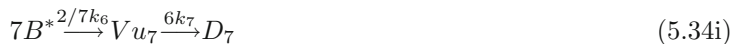
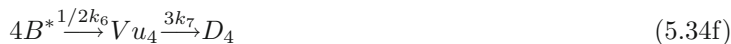
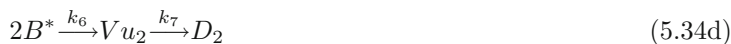


The reactions (5.33a)–(5.33d) do have some limitations, in that the distribution of the type of crosslinks cannot be predicted and the reaction (5.33d) indicates that all of the crosslinks degrade given sufficient time. It has been observed that (see Loo [19] and [20]) the monosulfidic crosslinks are very stable even at 200°C, which is attributed to the strong C–S bond compared to the much weaker S–S bond found in disulfidic and polysulfidic crosslinks. The vulcanization of rubber is usually carried out at about 140°C. Therefore, in normal processing range, not all the formed crosslinks degrade. Fan et al. [11] introduced a simple reaction scheme with three rate constants involving four species, namely polysulfidic pendent group, polysulfidic crosslink, mono and disulfidic crosslink, and main chain modifications (or dead ends). This model was able to capture the distribution of crosslinks reasonably well. However, this model is incapable of predicting the induction time (or scorch time), and therefore, cannot predict the time at which peak crosslink density is achieved. This model could be used if induction time is negligible. Ghosh et al. [15] developed a comprehensive reaction scheme by taking into account the detailed chemical reactions that occur during the induction, crosslinking and post-crosslinking region. There are 111 reactants and products. This reaction scheme can predict the distribution of crosslinks, apart from the others. However, one needs to solve a large system of nonlinear, ordinary differential equations (111 equations).

We propose a lumped model by taking into account the various types of crosslinks and derive a set of differential equations representing chemical kinetics using the equations developed in Sect. 5.4. Further, only di and polysulfidic crosslinks are allowed to degrade and desulfurate. Since vulcanization of many rubber products such as automobile tires, etc. takes place at constant deformation, the effect of deformation is neglected. However, the temperature will have a profound effect on the extent of vulcanization, which we take into account.

5.4.4.2. Modified reaction scheme. Geysler and McGill [12] showed that the reaction of tetramethylthiuram disulfide (TMTD), an accelerator, and sulfur (1:0.25 molar ratio) at 130°C produced polysulfides of TMTD, i.e., $(\text{CH}_3)_2\text{NC} = \text{SS}_x\text{S} = \text{CN}(\text{CH}_3)_2$, $x = 3, 4, \dots, 8$ in such a way that at all times, the concentration of polysulfide with $x = 3$ was the highest, followed by $x = 4$, etc. A similar trend was observed by Geysler and McGill [13] for TMTD/Sulfur/ZnO system, when ZnO is used as an activator. Morgan and McGill [24], using high-performance liquid chromatography (HPLC) analysis of equimolar concentration of 2-bisbenzothiazole-2,2-disulfide (MBTS)/Sulfur/ZnO system at 152°C, observed a similar trend for polysulfides of MBTS, another accelerator. Morgan and McGill [25], using 2,3-dimethyl-2-butene (TME) as a model compound for polyisoprene (rubber), employing HPLC analysis of 33.9 : 1.1 : 1 : 1 molar ratio of TME/MBTS/Sulfur/ZnO at 150°C, showed a similar trend for the polysulfidic pendent group $\text{TME} - \text{S}_x - \text{Bt}$, $x = 3, 4, \dots, 6$ and polysulfidic crosslinks $\text{TME} - \text{S}_x - \text{TME}$, $x = 3, 4, \dots, 10$. Geysler and McGill [14], for TME/TMTD/Sulfur/ZnO system, observed a similar trend for polysulfidic pendent groups. Based on these studies, we propose a reaction scheme that results in a distribution of di and polysulfidic crosslinks, which emulates the observations made on model compounds such as TME. If required, one may decouple the formation and degradation of disulfidic crosslinks, i.e., reaction (5.34d) from the set of reactions (5.34a)–(5.34j), by introducing two additional rate constants. Accordingly, Coran and co-worker's reaction scheme (5.33a)–(5.33d) may be modified as follows:





and



where k_1 through k_8 are rate parameters, Vu_i , $i = 1, 2, \dots, 8$ and D_i , $i = 1, 2, \dots, 8$ represents crosslinks and dead ends, respectively, containing i sulfur atoms. The expected rate constants associated with various chemical reactions are represented based on the chemical structure of the various constituents. Such information is used in the Sect. 5.4.4.3 to arrive at the differential equations representing the evolution of concentration of all the chemical species. As a result of the manner in which the lumping is carried out, the molar masses of the chemical species A , B , B^* , Vu_1 and D_1 are the same, whereas, that of the chemical species Vu_x , $x = 2, 3, \dots, 8$ and D_x , $x = 2, 3, \dots, 8$ are x times \mathcal{M} , where \mathcal{M} is the molar mass of species A . Notice that the reactions (5.34a) through (5.34q) are stoichiometrically balanced, i.e., ν_{ij} corresponding to each of the reactions is determined such that Eq. (3.6) is satisfied.¹¹ For conventional rubber compounds, it is reasonable to assume that up to octa sulfidic crosslinks are produced. In the above reactions, the chemical species A represents a number of rubber molecules and a molecule of active sulfurating agent that can aid in the formation of a crosslink with a single sulfur atom (monosulfidic). The active sulfurating agent in the lumped species A reacts with a rubber molecule to produce a pendent group. Thus, the lumped species B represents a molecule of pendent group along with many rubber molecules, which is assumed to be in abundance. A similar interpretation can be given to the activated form of B , i.e., B^* . The set of reactions (5.34a)–(5.34q) does not explicitly include the mechanisms for the formation of polysulfides of accelerator and pendent group. Instead, simplistically, it is assumed that disulfidic crosslinks are produced from two B^* , trisulfidic crosslinks are produced from three B^* , and so forth. One may assume that the rate at which Vu_3 , Vu_4 , Vu_5 , and so forth, are produced at 2/3rd, 1/2, 2/5th, etc., respectively, of the rate at which Vu_2 is produced. Further, we assume that only Vu_i , $i = 2, 3, \dots, 8$ can degrade (see Loo [19] and [20]) to its respective dead ends. The crosslink Vu_x , $x = 2, 3, \dots, 8$ has $x - 1$ $S-S$ bonds. By assuming that the bond strength of $S-S$ bonds in Vu_x , $x = 2, 3, \dots, 8$ to be the same, the rate at which Vu_x , $x = 3, 4, \dots, 8$ degrades must be $x - 1$ times the rate at which Vu_2 degrades. For

¹¹ As a result of the way in which lumping of chemical compounds is carried out, conservation of atoms is automatically satisfied, whenever balance of mass is satisfied. For example, two units of species B^* and one unit of Vu_2 will have the same number of atoms of each type.

the reasons discussed in the pages 625–627 of Ghosh et al. [15], the rate at which desulfurization occurs must be independent of the number of $S-S$ bonds, and hence, the reactions (5.34k) through (5.34q) have the same rate constant. After desulfurization, the released sulfur atom is again available for crosslinking, which is emulated through the release of chemical species A .

5.4.4.3. Differential equations. A typical rubber vulcanization process occurs at constant deformation. Therefore, we shall assume that the change in volume is zero, and consequently, there is no distinction between \dot{n}_j and $\dot{\tilde{n}}_j$. The reactions (5.34a)–(5.34q) contain 19 chemical species. The rank of ν_{ij} is 18. Therefore, according to the theorem (4.2), there is exactly one constraint involving the rate of change of concentration of 19 chemical species, or the rank of the matrix Y is $19 - 18 = 1$. Let A denote the first species, B the second, B^* the third, Vu_1 through Vu_8 denote the fourth through the eleventh, respectively, and D_1 through D_8 represents the twelfth through the nineteenth species. By substituting suitable values for molar masses corresponding to each of the chemical species, and on using Eq. (3.12), one arrives at

$$\frac{d[A]}{dt} + \frac{d[B]}{dt} + \frac{d[B^*]}{dt} + \sum_{i=1}^8 i \frac{d[Vu_i]}{dt} + \sum_{i=1}^8 i \frac{d[D_i]}{dt} = 0. \tag{5.35}$$

The above equation is the only required constraint and is ordered according to the numbering of the chemical species. Comparing Eqs. (4.17), (5.21) and (5.35), the matrix Y is given through

$$Y = \left\{ \begin{matrix} -1/8 & -1/8 & -1/8 & -1/8 & -1/4 & -3/8 & -1/2 & -5/8 & -3/4 \\ -7/8 & -1 & -1/8 & -1/4 & -3/8 & -1/2 & -5/8 & -3/4 & -7/8 & -1 \end{matrix} \right\}. \tag{5.36}$$

The rate of entropy production (times $\rho_{\kappa_t} \theta$) due to chemical reactions is assumed to be the same as that of Eq. (5.18), with $A_{ij} = I_{19}$, where I_{19} is the identity matrix in a nineteen dimensional space. Such an assumption is tantamount to assuming that the total rate of entropy production (times $\rho_{\kappa_t} \theta$) is the sum of the individual quadratic expression involving the rate of change of concentration of each of the chemical species per unit mass of mixture. Accordingly, the matrix P is given through $P = I_{19}$. Since the chemical reactions occur at constant deformation, $\mathbf{v} = \mathbf{0}$, and the Eq. (5.29) reduces to $\dot{\tilde{n}}_i = -\rho_{\kappa_t}^2 \mu_i^\perp$, $i = 1, 2, \dots, 19$, where μ_i^\perp are the entries associated with the projection of chemical potential vector μ onto \mathcal{V}^\perp . The components of the vector μ^\perp are assumed to be

$$\mu_1^\perp = -\frac{1}{\rho_{\kappa_t}^2} \left\{ -k_1(\theta)[A] - k_4(\theta)[A][B^*] + k_8(\theta) \left(\sum_{i=2}^8 [Vu_i] \right) \right\}, \tag{5.37a}$$

$$\mu_2^\perp = -\frac{1}{\rho_{\kappa_t}^2} \{ k_1(\theta)[A] - k_2(\theta)[B] + 2k_4(\theta)[A][B^*] \}, \tag{5.37b}$$

$$\mu_3^\perp = -\frac{1}{\rho_{\kappa_t}^2} \{ k_2(\theta)[B] - k_3(\theta)[B^*] - k_4(\theta)[A][B^*] - k_5(\theta)[B^*] - 14k_6(\theta)[B^*] \}, \tag{5.37c}$$

$$\mu_4^\perp = -\frac{1}{\rho_{\kappa_t}^2} \{ k_3(\theta)[B^*] + k_8(\theta)[Vu_2] \}, \tag{5.37d}$$

$$\mu_{i+3}^\perp = -\frac{1}{\rho_{\kappa_t}^2} \left\{ \frac{2k_6(\theta)}{i} [B^*] - (i-1)k_7(\theta)[Vu_i] + k_8(\theta) \{ [Vu_{i+1}] - [Vu_i] \} \right\}, \quad i = 2, 3, \dots, 7, \tag{5.37e}$$

$$\mu_{11}^\perp = -\frac{1}{\rho_{\kappa_t}^2} \left\{ \frac{k_6(\theta)}{4} [B^*] - 7k_7(\theta)[Vu_8] - k_8(\theta)[Vu_8] \right\}, \tag{5.37f}$$

$$\mu_{12}^\perp = -\frac{1}{\rho_{\kappa_t}^2} \{ k_5(\theta)[B^*] \} \tag{5.37g}$$

and

$$\mu_{i+11}^\perp = -\frac{1}{\rho_{\kappa_t}^2} \{(i-1)k_7(\theta)[Vu_i]\}, \quad i = 2, 3, \dots, 8. \quad (5.37h)$$

Not all of μ_i^\perp , $i = 1, 2, \dots, 19$ can be specified independently. This is because of the constraint $\rho_{\kappa_t} Y_{1j} \dot{n}_j = Y_{1j} \dot{n}_j + Y_{1j} \bar{n}_j \operatorname{div}(\mathbf{v}) = Y_{1j} \dot{n}_j = -\rho_{\kappa_t}^2 Y_{1j} \mu_j^\perp = 0$ obtained using Eqs. (3.2), (3.4), (5.28), (5.29) and $Y_{1j} \dot{n}_j = 0$, where the components of the matrix Y are given in Eq. (5.36). In other words, 18 components of μ^\perp can be specified independently, and the last component is specified such that the constraint is satisfied. The Eqs. (5.37a)–(5.37h) satisfy this constraint. One may determine the chemical potential of all the 19 species using the relation $\mu_i^\perp = (I_{19} - \mathcal{P})_{ij} \mu_j$. Recall that the matrix $I_{19} - \mathcal{P}$ is not invertible. Accordingly, the differential equations for the rate of change of concentration per unit volume is given through

$$\frac{d[A]}{dt} = -k_1(\theta)[A] - k_4(\theta)[A][B^*] + k_8(\theta) \left(\sum_{i=2}^8 [Vu_i] \right) \quad (5.38a)$$

$$\frac{d[B]}{dt} = k_1(\theta)[A] - k_2(\theta)[B] + 2k_4(\theta)[A][B^*] \quad (5.38b)$$

$$\frac{d[B^*]}{dt} = k_2(\theta)[B] - k_3(\theta)[B^*] - k_4(\theta)[A][B^*] - k_5(\theta)[B^*] - 14k_6(\theta)[B^*], \quad (5.38c)$$

$$\frac{d[Vu_1]}{dt} = k_3(\theta)[B^*] + k_8(\theta)[Vu_2] \quad (5.38d)$$

$$\frac{d[Vu_i]}{dt} = \frac{2k_6(\theta)}{i} [B^*] - (i-1)k_7(\theta)[Vu_i] + k_8(\theta)\{[Vu_{i+1}] - [Vu_i]\}, \quad i = 2 \text{ to } 7 \quad (5.38e)$$

$$\frac{d[Vu_8]}{dt} = \frac{k_6(\theta)}{4} [B^*] - 7k_7(\theta)[Vu_8] - k_8(\theta)[Vu_8] \quad (5.38f)$$

and

$$\frac{d[D_1]}{dt} = k_5(\theta)[B^*] \quad (5.38g)$$

$$\frac{d[D_i]}{dt} = (i-1)k_7(\theta)[Vu_i], \quad i = 2 \text{ to } 8. \quad (5.38h)$$

An Arrhenius expression is prescribed for each of the rate constants, i.e., $k_i(\theta) = A_o^i \exp\left(\frac{E_a^i}{R\theta}\right)$, $i = 1, 2, \dots, 8$, where R is the universal gas constant, A_o^i and E_a^i represent the pre-exponential and activation energy associated with the i^{th} rate parameter. The differential equations (5.38a)–(5.38h) represent a set of nonlinear, ordinary differential equations, which is of first order in each of the chemical species.

5.4.4.4. Results and discussion. To check the efficacy of the Eqs. (5.38a)–(5.38h), one needs to compare the predictions of the model with that of the experimental data. Loo [19] determined the distribution of mono, di and polysulfidic crosslinks for a conventional rubber compound containing 0.5:2.5 parts by weight of N-cyclohexyl-2-benzothiazole sulfenamide (CBS) and sulfur. Chemical probes were used to selectively cleave polysulfidic and disulfidic crosslinks in vulcanizates, vulcanized at 140, 160, 180 and 200°C. The concentration of each type of chemical crosslink as a function of time was determined using a combination of chemical probes and by measuring elastic properties. The data obtained, after converting mol/gRH to mol/m³, are shown in the Figs. (2, 3, 4, 5).

Assuming that the density of the rubber mixture to be 1 g/cc, the concentration of sulfur is calculated to be $\frac{2.5 \times 10^6}{32 \times 111} = 704 \text{ mol/m}^3$. Since the species A is assumed to possess one sulfur atom, the initial concentration of A is 704 mol/m³. The initial concentration of the rest of the chemical species is set

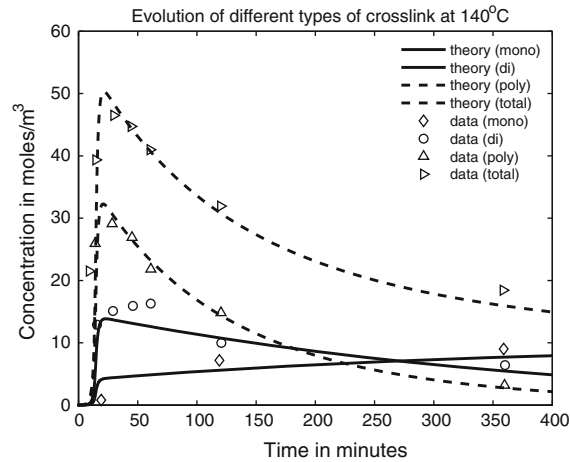


FIG. 2. Evolution of different type of crosslinks at 140°C

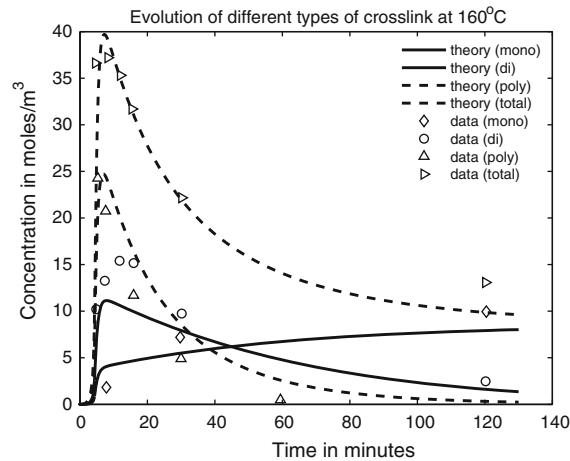


FIG. 3. Evolution of different type of crosslinks at 160°C

to zero. The set of ordinary differential equations, i.e., Eqs. (5.38a)–(5.38h) is solved numerically using MATLAB with suitable initial conditions. The two sets of rate parameters k_1 through k_8 are determined such that the data at 140 and 200°C is matched. The fits are shown in the Figs. (2) and (5). Assuming Arrhenius expression for the rate constants, the pre-exponential and activation energy can be determined (see Abhilash et al. [1]) and is shown in Table (1). The Figs. (3) and (4) show the predictions of the model. The predictions of the model agree reasonably well with that of experimental data. By decoupling the rate constants associated with the production and degradation of Vu_2 , one can obtain better results with respect to the prediction of concentration of di sulfidic crosslinks.

6. Conclusions

A fairly general thermodynamic framework has been put into place, which can be used to study the thermo-mechanical response of a viscoelastic materials undergoing large deformation and chemical reactions. For the first time, the rate of entropy production due to the chemical reactions is taken into

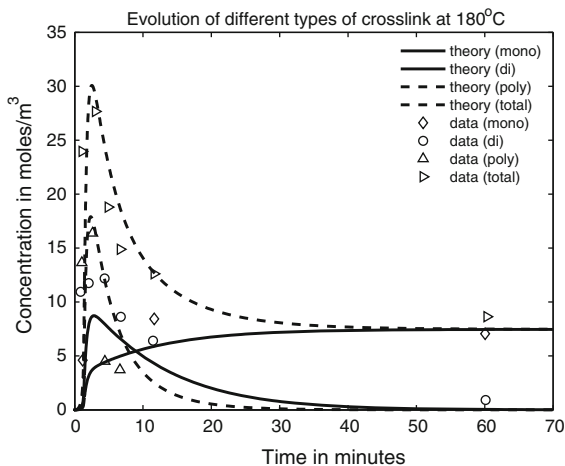


FIG. 4. Evolution of different type of crosslinks at 180°C

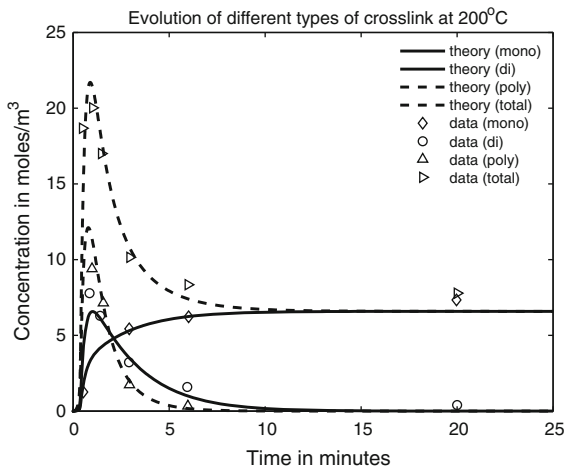


FIG. 5. Evolution of different type of crosslinks at 200°C

consideration, in addition to the rates of entropy production due to dissipation and conduction, and using the notion that the processes that are undergone by the body are those that maximize the rate of entropy production, the response of the viscoelastic body is studied. The framework also incorporates the stoichiometry associated with chemical reactions in a consistent manner. Such a framework can be used to study growth and degradation of biological tissues, degradation of polymeric materials, etc. The efficacy and usefulness of the procedure is evaluated by corroborating the predictions of the theory against a complex process in which chemical reactions play a key role, namely that of the vulcanization of rubber. Special constitutive equations of the implicit type were derived with regard to the thermo-mechanical behavior of a viscoelastic liquid, an outcome which is natural for Gibbs potential based formulations. For such constitutive equations, the relaxation time will be dependent upon the state of stress. There are plenty of problems of interest such as the effect of pressure on fluids, the effect of state of stress on the mechanical behavior of granular materials, the response of polymeric composites to extreme environmental conditions, for example high temperatures, that lead to oxidation, etc., which could be studied using

TABLE 1. *Pre-exponential and activation energy*

Rate parameter	Pre-exponential	Activation energy (J mol ⁻¹)
k_1 (min ⁻¹)	1.331×10^{23}	2.065×10^5
k_2 (min ⁻¹)	2.298×10^6	5.215×10^4
k_3 (min ⁻¹)	2.033×10^2	1.272×10^4
k_4 (min ⁻¹ mol ⁻¹ m ⁻³)	1.551×10^8	5.685×10^4
k_5 (min ⁻¹)	4.805×10^5	2.296×10^4
k_6 (min ⁻¹)	6.122×10^1	4.399×10^3
k_7 (min ⁻¹)	1.482×10^{14}	1.331×10^5
k_8 (min ⁻¹)	7.412×10^{13}	1.331×10^5

constitutive equations derived using this framework. It is worth noting that if one supplements the chemical reactions, for example, associated with degradation of the viscoelastic material, the interdependent effect of thermo-mechanical and chemical response, which the framework is capable of describing, could have been demonstrated as well. For the sake of simplicity, the effect of deformation on the chemical reactions was not included in this example; however, such an effect could be easily incorporated within the scope of the theory.

Acknowledgements

One of the authors, K. Kannan, would like to thank Indian Institute of Technology Madras (Grant no. MEE/0708/196/NFSC/KRIA) and MRF Limited for funding this research.

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(Received: September 1, 2010)