



## Chapter 9

# Reacting Flow Equations

In the continuum-flow regime, the motion of gases with chemical reaction and energy exchange processes can be modeled with the standard methods of fluid mechanics using the conservation of a mass, momentum and energy supplemented with the transport equations for individual species. These equations have to be augmented with chemical reaction mechanisms and associated reaction rates. A consistent set of thermodynamic data must be provided for each of the chemical species and energy states considered in the model. The goal of the present chapter is to present the governing equations and various simplification which are useful for analyzing specific situations.

Our analytical treatment of reacting flow behind shock and detonation waves follows the approach taking by Kirkwood and his collaborators (Some key papers are collected in [Kirkwood, 1967](#)) and the subsequent work at Los Alamos that is summarized in [Fickett and Davis \(1979\)](#). The analysis is based on the useful fictions of local thermodynamic equilibrium and either steady quasi-one dimensional flow or unsteady zero-dimensional (control volume) systems, considering only convective transport and neglecting molecular diffusion. Although limited in application, this approach has been a useful foundation for beginning research in high-temperature gas dynamics before going on to apply the numerical methods necessary for realistic treatments of the unsteady, multi-dimensional flows encountered in technology and nature.

The approach in this chapter is to develop fundamental equations in the most general form for a fluid described by a complete thermodynamic equation of rate, general reaction mechanism and the conservation laws of fluid mechanics. Our formulation of the basic equations follows that of [Kirkwood and Wood \(1954\)](#) and the analysis of the structure of the reaction zone behind shock waves and detonations by [Wood and Salsburg \(1960\)](#). Our treatment emphasizes the key role of the *thermicity* in coupling chemical reaction and fluid motion. After developing the general analytical framework, the expressions are specialized to the case of an ideal gas and examples are given of idealized detonation reaction zone structures and control volume models of explosions. The thermodynamic property evaluations are expressed in term of the language of ideal solution theory and partial molar properties used in the standard chemical engineering approach to evaluating mixture thermodynamic properties.

### 9.1 Reacting Compressible Flow

The field equations that describe mass, momentum, energy and species transport for a reacting compressible flow can be written in many different but equivalent forms ([Kee et al. Ch. 3 2003](#), [Poinsot and Veynante Ch. 1 2001](#)). The starting point for all of these versions is the conservation form that can be obtained directly from control volume balance statements.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (9.1)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P + \nabla \cdot \boldsymbol{\tau} \quad (9.2)$$

$$\frac{\partial}{\partial t}(e + |\mathbf{u}|^2/2) + \nabla \cdot [\rho \mathbf{u}(h + |\mathbf{u}|^2/2)] = -\nabla \cdot \mathbf{q} + \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{u}) \quad (9.3)$$

$$\frac{\partial \rho Y_k}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_k) = -\nabla \cdot \mathbf{j}_k + \dot{\Omega}_k \quad k = 1, 2, \dots, K \quad (9.4)$$

where  $\rho$  is the mass density,  $P$  is the pressure,  $\otimes$  is the tensor product,  $\mathbf{u}$  is the velocity vector,  $h = e + P/\rho$  is the enthalpy,  $e$  the internal energy,  $Y_k$  the mass fraction of species  $k$ . The net species production rate  $\dot{\Omega}_k$ , which has units of mass per unit volume and time. The practice in chemical kinetics is to compute the net rates of production as in terms of moles or molecules per unit volume and time. The term  $\dot{\Omega}_k = \mathcal{W}_k \dot{\omega}_k$ , where  $\mathcal{W}_k$  the molar mass of species  $k$  and the net molar production rate per unit volume  $\dot{\omega}_k$ .

The viscous stress tensor  $\boldsymbol{\tau}$  is defined in terms of the velocity gradients and the standard assumption is that the bulk viscosity vanishes and only the mixture viscosity  $\mu$  is relevant:

$$\boldsymbol{\tau} = -\frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^\top) \quad (9.5)$$

where  $\mathbf{I}$  is the identity tensor. In cartesian tensor notation

$$\tau_{ij} = -\frac{2}{3}\mu \frac{\partial u_k}{\partial x_k} \delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (9.6)$$

The mixture viscosity is a function of composition and temperature and is usually approximated using a mixture averaging formula. The species mass diffusion flux can be defined in terms of a *peculiar* velocity  $\mathbf{V}_k$ , i.e., the effective velocity of a species  $k$  relative to the mass average velocity  $\mathbf{u}$ .

$$\mathbf{j}_k = \rho Y_k \mathbf{V}_k \quad (9.7)$$

The thermal energy flux is defined as the sum of the usual diffusive flux due to a temperature gradient, thermal conductivity  $\lambda$  and the transport of enthalpy due to the diffusive flux of each species

$$\mathbf{q} = -\lambda \nabla T + \sum_{k=1}^K \mathbf{j}_k h_k. \quad (9.8)$$

In order to complete the equation set, we must add the appropriate equation of state, for example  $h = h(P, \rho, \mathbf{Y})$ . This can be as simple as the perfect gas equation of state or may be a dense fluid equation of state derived from an analytical expressions or tabular data based on detailed thermochemical information and molecular simulation. We also need models and data to compute diffusion fluxes and the transport coefficients  $\mu$  and  $\lambda$ , there are various levels of approximation and well developed methodologies for ideal gases (Kee et al., 2003) and empirical extensions for dense fluids.

The net molar reaction rates  $\dot{\omega}(T, P, \mathbf{Y})$  must also be specified. This requires an appropriate set of chemical species, a reaction mechanism and reaction rates describing the significant reactions between these species. This can be as simple as an irreversible one-step mechanism  $A \rightarrow B$ , the ideal dissociating gas model or the multi-species, multi-reaction mechanisms used to describe the reactions in high-temperature reentry or laboratory flows or the oxidation of hydrocarbon fuels.

Note that the chemistry appears explicitly only in the last term of Eqn. 9.4 and also note that the first three equations, Eqns. 9.1, 9.2, 9.3 apparently do not involve chemical reaction explicitly. These first three equations are sufficient for modeling two special cases. If we assume that reaction does not occur, then we have fixed composition  $\mathbf{Y} = \text{constant}$ , this is the situation of *frozen* or nonreactive flow. If we assume that the species at each point in space reacts infinitely fast and the composition shifts to match

local thermodynamics state,  $\mathbf{Y} = \mathbf{Y}_{eq}(P, T)$ , this is the case of *equilibrium* flow. In the general situation, chemical reaction will occur at a finite rate and will influence the flow through the dependence of the enthalpy and pressure functions on the composition. This flow-chemistry coupling can be demonstrated explicitly by reformulating the governing equations and using the the equation of state.

These equations are an incomplete model for high-temperature flows with energy exchange between translation and internal (rotation, vibration, electronic and ionization states) molecular or atomic energy states. Additional rate equations and detailed considerations of molecular and atomic collisions are needed to formulate adequate models of these processes (Zel'dovich and Raizer 1966, Vincenti and Kruger 1965, Clarke and McChesney 1964). The approximate theory for some simple situations is given in Ch. 11 of this report. Thermal radiation transport is an important issue for re-entry into planetary atmospheres and strongly radiating and absorbing gases in explosion products and near strong shock waves. Modeling these situations requires not only including thermal radiation interactions as a source term in the energy equation (9.3) but also solving an additional set of model equations for radiation transport (Zel'dovich and Raizer 1966, Pai 1966). If the gas density is sufficiently low, as in the high-altitude stages of atmospheric re-entry, an approach based on the solution to the Boltzmann equation and kinetic theory is required (Bird 1994, Boyd and Schwartzenruber 2017). For very dense fluids or liquids, it is necessary to simulate molecular dynamics using Newtonian mechanics with forces derived from approximate molecular interaction potentials and statistical averaging over ensembles of molecules.

## Material Derivative Formulation

Rather than work directly with Eqs. 9.1 - 9.4, it is more convenient to expand the derivatives with the usual rules of calculus to obtain the following variant of the governing equations. In doing this, a more convenient notation is the material or substantial derivative, defined as

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \mathbf{u} \cdot \nabla f . \quad (9.9)$$

where  $f$  is any differentiable field property. Substitution of this definition and simplifying, we obtain

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{u} \quad (9.10)$$

$$\frac{D\mathbf{u}}{Dt} = -\frac{1}{\rho} \nabla P + \nabla \cdot \tau \quad (9.11)$$

$$\frac{Dh}{Dt} = \frac{1}{\rho} \frac{DP}{Dt} - \frac{1}{\rho} \nabla \cdot \mathbf{q} + \frac{1}{\rho} \Upsilon \quad (9.12)$$

$$\frac{DY_k}{Dt} = -\frac{1}{\rho} \nabla \cdot \mathbf{j}_k + \frac{1}{\rho} \dot{\Omega}_k \quad (k = 1, \dots, K) \quad (9.13)$$

The term  $\Upsilon$  represents viscous energy dissipation per unit volume and is the tensor product of the velocity gradient and viscous stress tensor

$$\Upsilon = \tau : \nabla \mathbf{u} . \quad (9.14)$$

In cartesian tensor notation, this is

$$\Upsilon = \sum_j \sum_k \tau_{ik} \frac{\partial u_i}{\partial u_k} \quad (9.15)$$

## Entropy

The coupling between chemistry and fluid dynamics can be more explicitly displayed by substituting an evolution equation for entropy  $s$  instead or enthalpy  $h$ . Introduce the *fundamental property relation of thermodynamics* for a fixed mass of material:

$$dh = Tds + \frac{dP}{\rho} + \sum_{k=1}^K g_k dY_k \quad (9.16)$$

where  $g_k = \mu_i/\mathcal{W}_i$  is the Gibbs energy per mass of species  $i$ . The changes  $dh$ ,  $ds$ , etc. refer to variations within a certain mass of material or *fluid element*. For the next step we will take the changes in properties to be represent the time rate of change following a fixed identity of material using the material derivative,. With this correspondence  $dh \rightarrow Dh/Dt$ , etc., we can then combine Eqns. 9.16, 9.12 and 9.13 to obtain an equation for entropy which can be used in place of the energy equation.

$$\frac{Ds}{Dt} = -\frac{1}{\rho T} \left[ \nabla \cdot \mathbf{q} - \Upsilon - \sum_{k=1}^K g_k \nabla \cdot \mathbf{j}_k + \sum_{k=1}^K g_k \dot{\Omega}_k \right] \quad (9.17)$$

The entropy change has four components, entropy change due to heat transfer from adjacent fluid elements or boundaries, entropy generation due to viscous dissipation caused by velocity gradients and viscosity, entropy change due to species diffusion, and entropy changes associated with chemical reaction. Entropy changes or generation associated with gradients in the flow result in *irreversibility* that always increases the entropy of a fluid element. Small changes in the thermodynamic state often can be considered reversible and can either increase or decrease the entropy. The entropy changes in (9.17) result in both reversible and irreversible increases in entropy.

*Diabatic*<sup>1</sup> flows with external heat addition or removal (*Rayleigh flow*) and viscous flows inside ducts (*Fanno flow*) can be treated in a quasi-one-dimensional framework (see Ch. 11) as flows with additional entropy sources in (9.22) to mimic the integrated effects of entropy generation in (9.17). Although volumetric heat addition is often considered in elementary discussions of combustion as a surrogate for the conversion of chemical to thermal energy, that is an incomplete and misleading approach to modeling reacting flows.

### Euler's Equations

The role of diffusion in high-speed reacting flow can be important in the multi-dimensional, unsteady flows that are observed in the laboratory Shepherd (2009) and detailed simulations Ziegler (2011) of detonations and the many situations in high-temperature gas dynamics associated with reentry or shock wave interactions that result in shear layers and strong property gradients transverse to the main flow. However, in purely one-dimensional flows behind shock waves, diffusive transport of mass, momentum and energy are negligible for even a very modest flow Mach number (relative to the shock) in the reaction zone. Singh et al. (2003-10-02/2003-10-21) demonstrate this through numerical simulation of reaction zone structure based on Eqs. 9.1 - 9.4 with realistic properties for the case of methane-air as well as scaling analyses and magnitude estimation of the dominate balance between reaction, diffusion and convection.

Eliminating the diffusive transport terms, we obtain the governing equations for inviscid, compressible fluid motion, frequently referred to as *Euler's Equations*.

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{u} \quad (9.18)$$

$$\frac{D\mathbf{u}}{Dt} = -\frac{1}{\rho} \nabla P \quad (9.19)$$

$$\frac{Dh}{Dt} = \frac{1}{\rho} \frac{DP}{Dt} \quad (9.20)$$

$$\frac{DY_k}{Dt} = \frac{1}{\rho} \mathcal{W}_k \dot{\omega}_k \quad (k = 1, \dots, K) \quad (9.21)$$

If the flow is adiabatic and the entropy changes due to molecular diffusion (energy and species), and viscous dissipation are negligible, then the general entropy expression (9.17) reduces to

$$\frac{Ds}{Dt} = -\frac{1}{T} \sum_{k=1}^K \mu_k \dot{\omega}_k \quad (9.22)$$

where we are now using the more conventional symbol for Gibbs energy per mole or *chemical potential*  $\mu_k = \mathcal{W}_k g_k$ . This expression is consistent with the Euler equations and indicates that the entropy in a smooth,

<sup>1</sup>A diabatic flow is one that exchanges energy in the form of heat with the surroundings. This is in contrast to adiabatic flows which are thermally insulated from the surroundings.

inviscid flow changes only due to chemical reaction. Of course, in a discontinuous flow i.e., one with shocks, there can be jumps in entropy without any chemical reaction.

## 9.2 Adiabatic Change Relation

Changes in pressure, density, entropy and species are not independent but are related through the equation of state. Consider using an equation of state in the form

$$P = P(s, \rho, \mathbf{Y})$$

and relate small changes in pressure to changes in  $\rho$ ,  $s$  and  $\mathbf{Y}$ .

$$dP = \left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}} d\rho + \left( \frac{\partial P}{\partial s} \right)_{\rho, \mathbf{Y}} ds + \sum_{k=1}^K \left( \frac{\partial P}{\partial Y_k} \right)_{s, \rho, Y_{i \neq k}} dY_k \quad (9.23)$$

The coefficient of the first term on the right-hand side is just the definition of the *frozen* sound speed squared

$$\left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}} = a_f^2. \quad (9.24)$$

The coefficient of the second term on the right-hand side can be expressed in terms of standard thermodynamic quantities using the definitions and identities in App. E

$$\left( \frac{\partial P}{\partial s} \right)_{\rho, \mathbf{Y}} = \rho a_f^2 \frac{T \beta}{c_p}, \quad (9.25)$$

the coefficient of thermal expansion is

$$\beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_{P, \mathbf{Y}}, \quad (9.26)$$

and the specific heat at constant pressure is

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_{P, \mathbf{Y}}. \quad (9.27)$$

An alternative but equivalent formulation is to express this derivative in terms of the Grüneisen coefficient  $\mathcal{G}$

$$\left( \frac{\partial P}{\partial s} \right)_{\rho, \mathbf{Y}} = \rho T \mathcal{G}. \quad (9.28)$$

This formulation will be useful in considering quasi-one-dimensional flows with friction and heat interactions. The coefficients of the sum in the third term on the right-hand side can be expressed in terms of derivatives which can be readily computed from the independent variables ( $T, P, \mathbf{Y}$ ).

$$\left( \frac{\partial P}{\partial Y_k} \right)_{s, \rho, Y_{i \neq k}} = \rho a_f^2 \left\{ -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{T, P, Y_{i \neq k}} - \frac{\beta}{c_p} \left[ \left( \frac{\partial h}{\partial Y_k} \right)_{T, P, Y_{i \neq k}} - g_k \right] \right\} \quad (9.29)$$

Rearranging and collecting terms, the final result is

$$dP = a_f^2 d\rho + \rho a_f^2 \frac{\beta}{c_p} \left( T ds + \sum_k g_k dY_k \right) + \rho a_f^2 \underbrace{\sum_k \left[ -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{T, P, Y_{i \neq k}} - \frac{\beta}{c_p} \left( \frac{\partial h}{\partial Y_k} \right)_{T, P, Y_{i \neq k}} \right]}_{\sigma_k} dY_k \quad (9.30)$$

Following Fickett and Davis (1979), we refer to this as the *adiabatic change equation*. The term

$$Tds + \sum_k g_k dY_k$$

represents any entropy changes other than those associated with chemically reaction. For example, from (9.17), we obtain

$$Tds + \sum_k g_k dY_k = -\frac{1}{\rho} \left( \nabla \cdot \mathbf{q} - \Upsilon - \sum_{k=1}^K g_k \nabla \cdot \mathbf{j}_k \right) dt$$

For an inviscid, adiabatic flow, the right hand side vanishes and we can substitute  $ds$  from Eqn. 9.22 into (9.30) to obtain

$$\frac{DP}{Dt} = a_f^2 \frac{D\rho}{Dt} + \rho a_f^2 \dot{\sigma}. \quad (9.31)$$

The *thermicity*  $\dot{\sigma}$  represents all the interactions of the chemical reaction with the flow and is defined by

$$\dot{\sigma} = \sum_{k=1}^K \sigma_k \frac{DY_k}{Dt};.$$

Thermicity which has dimensions of reciprocal time ( $s^{-1}$ ) and as we will see in the following sections, is the key quantity that determines the structure of the reaction zone in steady flows and the coupling between chemical reaction and the flow in unsteady cases.

### 9.3 Thermicity

The thermicity coefficients  $\sigma_k$  are thermodynamic properties and can be evaluated once the state  $(P, \rho, \mathbf{Y})$  is known. From the previous derivation we have

$$\sigma_k = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{P,T,Y_i \neq k} - \frac{\beta}{c_p} \left( \frac{\partial h}{\partial Y_k} \right)_{P,T,Y_i \neq k} \quad (9.32)$$

In terms of these coefficients the thermicity is

$$\dot{\sigma} = \sum_k \left[ -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{P,T,Y_i \neq k} - \frac{\beta}{c_p} \left( \frac{\partial h}{\partial Y_k} \right)_{P,T,Y_i \neq k} \right] \frac{DY_k}{Dt} \quad (9.33)$$

Note that this relation is completely general and is independent of any assumptions about the equation of state or the reaction mechanism. Alternative formulations for the thermicity coefficients can be obtained using thermodynamic identities and the standard methods of transformation of variables.

Considering expanding  $h(P, \rho, \mathbf{Y})$  to obtain

$$dh = \left( \frac{\partial h}{\partial P} \right)_{\rho, \mathbf{Y}} dP + \left( \frac{\partial h}{\partial \rho} \right)_{P, \mathbf{Y}} d\rho + \sum_{k=1}^K \left( \frac{\partial h}{\partial Y_k} \right)_{P, \rho, Y_i \neq k} dY_k \quad (9.34)$$

and eliminating the enthalpy using Eqn. 9.20 to obtain the following version of the adiabatic change relation

$$\left( \frac{1}{\rho} - \left( \frac{\partial h}{\partial P} \right)_{\rho, \mathbf{Y}} \right) dP = \left( \frac{\partial h}{\partial \rho} \right)_{P, \mathbf{Y}} d\rho + \sum_{k=1}^K \left( \frac{\partial h}{\partial Y_k} \right)_{P, \rho, Y_i \neq k} dY_k. \quad (9.35)$$

This can be further simplified with the following thermodynamic identities

$$a_f^2 = \frac{\left( \frac{\partial h}{\partial \rho} \right)_{P, \mathbf{Y}}}{\frac{1}{\rho} - \left( \frac{\partial h}{\partial P} \right)_{\rho, \mathbf{Y}}} \quad \left( \frac{\partial h}{\partial \rho} \right)_{P, \mathbf{Y}} = -\frac{c_p}{\rho \beta} \quad (9.36)$$

which results in the following alternative expression for the thermicity coefficient

$$\sigma_k = -\frac{\beta}{c_p} \left( \frac{\partial h}{\partial Y_k} \right)_{P,\rho,Y_i \neq k} \quad (9.37)$$

A similar derivation can be carried out (Kao, 2008) with internal energy  $e(P, v, \mathbf{Y})$  rather than enthalpy leading to

$$\sigma_k = -\frac{\mathcal{G}}{a_f^2} \left( \frac{\partial e}{\partial Y_k} \right)_{P,v,Y_i \neq k} \quad (9.38)$$

where the Grüneisen coefficient, see Section 7.10, is

$$\mathcal{G} = \frac{v}{\left( \frac{\partial e}{\partial P} \right)_{v,\mathbf{Y}}} \quad (9.39)$$

and the sound speed can be computed from  $e(P, v)$

$$a_f^2 = v^2 \frac{\left( \frac{\partial e}{\partial v} \right)_{P,\mathbf{Y}} + P}{\left( \frac{\partial e}{\partial P} \right)_{v,\mathbf{Y}}} \quad (9.40)$$

Using the identities in Appendix E, the final result can be simplified to

$$\sigma_k = -\frac{\beta}{c_p} \left( \frac{\partial e}{\partial Y_k} \right)_{P,v,Y_i \neq k} \quad (9.41)$$

which also follows directly from the previous result for enthalpy using the definition  $h = e + Pv$ . Yet another approach using partial molar properties is presented in Appendix D and Section 9.8.

### Ideal Gas

For an ideal gas, we can simplify the thermicity coefficients substantially.

$$\left( \frac{\partial h}{\partial Y_k} \right)_{P,T,Y_i \neq k} = h_k(T), \quad \beta = \frac{1}{T}, \quad c_p = \sum_{k=1}^K Y_k c_{p,k} \quad (9.42)$$

$$-\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{P,T,Y_i \neq k} = \frac{\mathcal{W}}{\mathcal{W}_k}, \quad \mathcal{W} = \left( \sum_{k=1}^K \frac{Y_k}{\mathcal{W}_k} \right)^{-1}. \quad (9.43)$$

The thermicity coefficients simplify to

$$\sigma_k = \frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_p T}, \quad (9.44)$$

which is straight forward to evaluate from available thermodynamic functions. The final expression for ideal gas thermicity is

$$\boxed{\dot{\sigma} = \sum_{k=1}^K \left( \frac{\mathcal{W}}{\mathcal{W}_k} - \frac{h_k}{c_p T} \right) \frac{DY_k}{Dt}.} \quad (9.45)$$

An alternative expression in term of the specific internal energy  $e_k$  and ratio of heat capacities  $\gamma = c_p/c_v$  is

$$\boxed{\dot{\sigma} = \frac{1}{\gamma} \sum_{k=1}^K \left( \frac{\mathcal{W}}{\mathcal{W}_k} - \frac{e_k}{c_v T} \right) \frac{DY_k}{Dt}.} \quad (9.46)$$

### Physical significance of thermicity

Thermicity represents the combined physical and chemical response of a reacting system to changes in chemical composition and more generally exchange of energy between the mean flow associated with the intermolecular energy associated with rotation, vibration, electronic and ionization states of molecules and atoms. It can be applied to any sort of reacting flow, endothermic or exothermic, steady or unsteady. It was originally introduced in the context of modeling the processes behind shock fronts, particularly detonations. Other applications including reacting flow in nozzles, flow in the stagnation or shock layer region in hypersonic blunt body flows, the reaction zone between oblique and curved shocks or detonations, and limiting cases of reaction constrained to occur along specified thermodynamic paths.

Going further, we can assign to components to this response, corresponding to the two terms in the summations over species in the thermicity.

$$\dot{\sigma} = \underbrace{\sum_k \left[ -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial Y_k} \right)_{P,T,Y_i \neq k} \frac{DY_k}{Dt} \right]}_{\text{I.}} + \underbrace{\left[ - \sum_k \frac{\beta}{c_p} \left( \frac{\partial h}{\partial Y_k} \right)_{P,T,Y_i \neq k} \frac{DY_k}{Dt} \right]}_{\text{II.}}$$

These components represent: I) changes in volume due to changes in composition; II) exchange of internal energy with the mean flow due to changes in composition. Both of these changes are manifested as a source term in the adiabatic change equation and can be conceptualized as contributing to the time rate of change of density and pressure due to chemical reaction processes in the flow. For inviscid flows, this is the sole manner in which the reaction processes are coupled to the flow.

Term I can be rewritten in terms of the change in specific volume  $v$  with time at constant pressure and temperature to explicitly show how this is a source term of volume created by the chemical reaction processes.

$$(I) = \frac{1}{v} \left( \frac{dv}{dt} \right)_{P,T}$$

The contribution to the thermicity change in a time increment  $\Delta t$  is the relative volume change

$$\Delta \dot{\sigma}_I = \frac{\Delta v}{v}$$

In a fixed mass of fluid treated as an ideal gas, this can be further manipulated to obtain

$$(I) = -\frac{1}{W} \left( \frac{dW}{dt} \right)_{P,T} = \frac{1}{n} \left( \frac{dn}{dt} \right)_{P,T} \quad \text{ideal gas}$$

illustrating the direct connection of term (I) to the change  $dn$  in the total number of species per unit mass due to the reaction process.

$$(I) = \frac{1}{v} \left( \frac{dv}{dt} \right)_{P,T} = \begin{cases} > 0 & \text{if } dn/dt > 0 \\ < 0 & \text{if } dn/dt < 0 \end{cases}$$

We see that reaction processes that result in an increase in the number of species make a positive contribution to thermicity analogous to exothermic chemical reactions and those processes that result in a decrease in the number of species make a negative contribution to the thermicity analogous to endothermic reactions.

Term II can be rewritten in terms of the change in specific enthalpy  $h$  with time at constant pressure and temperature.

$$(II) = -\frac{\beta}{c_p} \left( \frac{dh}{dt} \right)_{P,T}$$

The change  $dh$  in enthalpy is due to reaction processes making and breaking chemical bonds. Sign of the  $dh$  is determined by the heat of reaction:  $dh < 0$  for exothermic reactions,  $dh > 0$  for endothermic reactions.

The energy released or absorbed from the mean flow is transformed in a temperature change  $dT = dh/c_p$  through the mixture specific heat capacity  $c_p$ , the temperature increment creates generates differential volume expansion  $dv/v = \beta dT$  through the coefficient of thermal expansion  $\beta$ . The contribution to the thermicity

due to a change in enthalpy  $\Delta h$  in time  $\Delta t$  is the relative volume change associated with the enthalpy increment

$$\Delta\dot{\sigma}_{II} = \frac{\Delta v}{v} = -\frac{\beta}{c_p} \Delta h$$

The sign of thermicity created by the enthalpy change is determined by the energetics the chemical reaction processes.

$$(II) = -\frac{\beta}{c_p} \left( \frac{dh}{dt} \right)_{P,T} = \begin{cases} > 0 & \text{exothermic reactions } dh/dt < 0 \\ < 0 & \text{endothermic reactions } dh/dt > 0 \end{cases}$$

For an ideal gas  $\beta = 1/T$  and this provides an alternate explanation of term (II) as the change in enthalpy compared to a reference thermal energy content  $c_p T$

$$(II) = -\frac{\beta}{T} \left( \frac{dh}{dt} \right)_{P,T} = -\frac{1}{c_p T} \left( \frac{dh}{dt} \right)_{P,T} \quad \text{ideal gas} \quad (9.47)$$

### Equivalent Thermal Energy Addition

An alternative interpretation of the thermicity is in terms of defining an a fictitious thermal energy or “heat” addition that simulates the combustion process. The basis of this is to consider the reversible entropy change due to a thermal energy source  $\dot{q}$  which represents thermal energy transferred into the fluid per unit volume and time. For a nonreactive flow, the time rate of change in entropy of a fluid element is

$$\frac{Ds}{Dt} = \frac{\dot{q}}{\rho T} . \quad (9.48)$$

The adiabatic change equation can then be expressed as

$$\frac{DP}{Dt} = a^2 \frac{D\rho}{Dt} + G\dot{q} . \quad (9.49)$$

Comparison with the thermicity formulation of the adiabatic change equation, we obtain the equivalence

$$\dot{\sigma} = G \frac{\dot{q}}{\rho a^2}$$

For an ideal gas, this expression is

$$\dot{\sigma} = \frac{\gamma - 1}{\gamma} \frac{\dot{q}}{P}$$

### Limiting Cases

Three limiting cases of thermodynamic constraints are often considering in modeling combustion systems. In the following, the processes are all assumed to be adiabatic.

#### 1. Constant Pressure

Constraining the pressure to be constant, the thermicity is converted to specific volume changes. The adiabatic change equation becomes an evolution equation for specific volume

$$\left( \frac{dv}{dt} \right)_P = +v\dot{\sigma}$$

or density

$$\left( \frac{d\rho}{dt} \right)_P = -\rho\dot{\sigma}$$

## 2. Constant Volume

Constraining the specific volume to be constant, the thermicity is converted to specific volume changes to pressure changes. The adiabatic change equation becomes an evolution equation for pressure.

$$\left( \frac{dP}{dt} \right)_\rho = +\rho a^2 \dot{\sigma}$$

## 3. Steady flow

In steady, adiabatic flow, the conservation of momentum and mass imply that pressure and specific volume changes are coupled with the constraint taking the form of the Rayleigh line  $\mathcal{R}$ . Differentiating (6.17), we obtain:

$$\left( \frac{dP}{dt} \right)_{\mathcal{R}} = -(\rho w)^2 \frac{dv}{dt} = w^2 \frac{d\rho}{dt}$$

Using this constraint in the adiabatic change equation, we obtain

$$\left( \frac{d\rho}{dt} \right)_{\mathcal{R}} = -\rho \frac{a^2}{a^2 - w^2} \dot{\sigma}$$

and

$$\left( \frac{dP}{dt} \right)_{\mathcal{R}} = -\rho w^2 \frac{a^2}{a^2 - w^2} \dot{\sigma}$$

When the initial conditions are values immediately behind a shock wave, these equations form the ZND model of steady shock and detonation structure. There are numerous variations on these equations associated with variable area flow, flows with friction and thermal energy exchange, flows behind oblique and curved shocks and constraints of imposed pressure or volume changes. These cases are discussed in Chapter 11.

## 4. Unsteady flow

The thermicity appears as a source term in the when density is eliminated from the Euler equations, see Section 9.5 for a discussion of the implications for computing one-dimensional flow with the method of characteristics.

In addition to the equations given above for pressure and density (or specific volume), equations for the evolution of temperature can be formulated, the perfect gas versions of these equations are given in Section 9.7 and the real gas versions are given in Section 9.8.

## 9.4 Equilibrium and Frozen Flow

In frozen flow, the composition  $\mathbf{Y} = \text{constant}$ , and  $D\mathbf{Y}/Dt = 0$ . From the adiabatic change relation, the pressure and density changes in frozen flow are related by

$$\frac{DP}{Dt} = a_f^2 \frac{D\rho}{Dt} \quad \text{and} \quad a_f^2 = \left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}}, \quad (9.50)$$

along particle paths. If the entropy is uniform throughout the flow then this applies broadly to any states in the flow

$$dP = a_f^2 d\rho. \quad (9.51)$$

In particular, this relationship can be used in the momentum equation to replace spatial gradients in pressure with gradients in density

$$\nabla P = a_f^2 \nabla \rho \quad (9.52)$$

and with an expression  $a_f(\rho)$ , the mass and momentum equations form a complete description of adiabatic, irrotational compressible flow ([Liepmann and Roshko, 1957](#), Ch. 7).

An equilibrium flow without diffusive transport has a fixed elemental composition and species composition that shifts with changing thermodynamic state  $\mathbf{Y} = \mathbf{Y}^{eq}(P, \rho)$ . The equilibrium isentrope  $P$ - $\rho$  relationship is defined implicitly by

$$P = P(\rho, \mathbf{Y}^{eq}(P, \rho); s = \text{constant}) . \quad (9.53)$$

The slope of the isentrope can be computed from the adiabatic change relationship

$$dP = a_f^2 d\rho + \rho a_f^2 \sum_{i=1}^K \sigma_i dY_i^{eq} , \quad (9.54)$$

and the dependence of the composition on thermodynamic state

$$dY_i = \left( \frac{\partial Y_i^{eq}}{\partial P} \right)_\rho dP + \left( \frac{\partial Y_i^{eq}}{\partial \rho} \right)_P d\rho . \quad (9.55)$$

Solving for the slope of the equilibrium isentrope, we obtain

$$\left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}^{eq}} = a_f^2 \frac{1 + \rho \sum_{i=1}^K \sigma_i \left( \frac{\partial Y_i^{eq}}{\partial \rho} \right)_P}{1 - \rho a_f^2 \sum_{i=1}^K \sigma_i \left( \frac{\partial Y_i^{eq}}{\partial P} \right)_\rho} \quad (9.56)$$

This expression is often referred to as the *equilibrium sound speed*

$$a_e^2 = \left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}^{eq}} . \quad (9.57)$$

The interpretation is that this is the speed of propagation of low frequency sound waves in a reactive flow and is valid as long as the period of the wave is much larger than the characteristic chemical reaction times so that the composition shifts to remain in equilibrium as pressure and density change within the wave.

In the equilibrium limit, the chemical reaction processes that maintain equilibrium must proceed faster than all other flow processes. From a molecular point of view, a condition of equilibrium is that the forward and reverse reaction rates balance or equivalently, the net reaction rates for all species vanish  $\dot{\omega}_i(\mathbf{Y}^{eq}, P, \rho) = 0$ . From the previous discussion on thermodynamics, this means that the entropy is constant along particle paths in the equilibrium flow limit and it is sensible to speak of an isentropic but reacting flow. This is of course, an idealization and the consequence of a limiting process. The reaction rates must be non-zero in order for the species to shift to maintain chemical equilibrium as temperature and pressure vary with time in a transient flow. As long as the reaction rates are all significantly faster than the rate of change of temperature and pressure, the species distributions will be sufficiently close to the chemical equilibrium values to justify using exact thermodynamic equilibrium species distributions. A detailed discussion of this issue is given in Ch. 6 of [Cooper \(2004\)](#) in the context of chemical reactions within the Taylor-Zeldovich expansion.

The frozen sound speed is the speed of propagation of high frequency sound waves which have a period that is sufficiently small compared to the characteristic chemical reaction times that the composition remains fixed as the pressure and density change within the wave. The dependence of sound speed on frequency leads to dispersion of wave packets propagating in reactive flows as discussed at length by [Vincenti and Kruger \(1965\)](#) in the context of both chemical reactions and vibrational-translational energy exchange processes.

## 9.5 Nonsteady Flow

The real value of the entropy formulation is the connection that can be established between chemical reaction and thermodynamic state changes. This can be most clearly illustrated by considering a one-dimensional flow and formulating the equations in characteristic form.

Starting with the adiabatic change equation and the definition of thermicity (9.33), the governing equation set for reacting, inviscid flow can be written

$$\frac{DP}{Dt} + \rho a_f^2 \nabla \cdot \mathbf{u} = \rho a^2 \dot{\sigma} \quad (9.58)$$

$$\rho \frac{D\mathbf{u}}{Dt} + \nabla P = 0 \quad (9.59)$$

$$\frac{DY_k}{Dt} = \frac{\mathcal{W}_k \dot{\omega}_k}{\rho} \quad k = 1, 2, \dots, K \quad (9.60)$$

$$\frac{Ds}{Dt} = -\frac{1}{\rho T} \sum_k \mu_k \dot{\omega}_k \quad (9.61)$$

This equation set has to be supplemented by a relationship for frozen sound speed

$$a_f^2 \equiv \left( \frac{\partial P}{\partial \rho} \right)_{s, \mathbf{Y}} \quad (9.62)$$

a reaction mechanism, and thermochemical data for computing the equation of state in the form  $P(\rho, s, \mathbf{Y})$ .

These equations can be further manipulated to obtain the *characteristic* form for planar (one-dimensional) geometries:

$$\begin{aligned} \frac{dP}{dt} \pm \rho a_f \frac{du}{dt} &= \rho a_f^2 \dot{\sigma} \quad \text{on} \quad \frac{dx}{dt} = u \pm a_f \\ \frac{ds}{dt} &= -\frac{1}{\rho T} \sum_k \mu_k \dot{\omega}_k \quad \text{on} \quad \frac{dx}{dt} = u \\ \frac{dY_k}{dt} &= \frac{\mathcal{W}_k \dot{\omega}_k}{\rho} \quad \text{on} \quad \frac{dx}{dt} = u \quad (k = 1, \dots, K) \end{aligned} \quad (9.63)$$

The effect of chemical reaction is felt through the source terms on the right-hand side of the equation. Amplification or decay of signals will occur in addition to the propagation effects described for nonreacting flow. The thermicity appears as the key function coupling chemical reaction and acoustic wave propagation.

Physically, this indicates that there are two types of propagating disturbances in the flow. Acoustic disturbances produce pressure changes  $\delta P$  that are proportional to velocity changes  $\delta u$  and modified by the chemical reaction through the thermicity

$$\delta P = \pm \rho a_f \delta u + \rho a_f^2 \dot{\sigma} \delta t \quad \text{on} \quad \delta x = (u \pm a_f) \delta t. \quad (9.64)$$

The disturbances created by a pulse of thermicity propagate with the sound speed  $\pm a$  relative to the flow, which is moving with velocity  $u$ . In a space-time diagram of the process, the acoustic disturbances propagate along characteristic directions  $C_{\pm}$

$$C_{\pm} : \frac{dx}{dt} = u \pm a. \quad (9.65)$$

Entropy disturbances  $\delta s$  and composition changes  $\delta Y_k$  due to chemical reaction or spatial nonuniformity propagate with the fluid velocity  $u$ . This can be interpreted as motion along the particle path characteristic

$$C_0 : \frac{dx}{dt} = u \quad (9.66)$$

In nonreactive flow  $\dot{\omega}_k = 0$ , the solution of the characteristic equations is obtained by using *Riemann Invariants*  $\mathcal{P}$  and  $\mathcal{Q}$  defined by

$$\left( \int \frac{dP}{\rho a_f} + u \right) = \mathcal{P} \quad (9.67)$$

$$\left( \int \frac{dP}{\rho a_f} - u \right) = \mathcal{Q} \quad (9.68)$$

For non-reactive flow, these quantities are constant along characteristics and the function

$$F(P) = \int_{P^\circ}^P \frac{dP'}{\rho a_f} \quad (9.69)$$

is unique. For reactive flow, these quantities are not invariant and the function  $F(P)$  is path dependent

$$\frac{d\mathcal{P}}{dt} = a_f \dot{\sigma} \quad \text{on} \quad \frac{dx}{dt} = u + a \quad (9.70)$$

$$\frac{d\mathcal{Q}}{dt} = a_f \dot{\sigma} \quad \text{on} \quad \frac{dx}{dt} = u - a \quad (9.71)$$

Numerical solutions of the reactive form of the characteristic equations were used by Fickett and co-workers in studying the one-dimensional stability of detonation with a model one-step reaction, (See p. 278, [Fickett and Davis, 1979](#)).

Although the characteristics  $C_\pm$  are defined using the frozen sound speed, the chemical reaction along the particle paths results in dispersion ([Vincenti and Kruger, 1965](#), Ch. 8, ) with low-frequency sound waves traveling at the equilibrium sound speed and high frequency sound waves traveling at the frozen sound speed relative to the mean flow. Impulsive small amplitude disturbances will spread out to form smooth compressive waves with a precursor traveling at the frozen sound speed and the bulk of the disturbance moving at the equilibrium sound speed.

## 9.6 Steady flow

In terms of thermicity, the unsteady Euler equations are

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{u} \quad (9.72)$$

$$\frac{D\mathbf{u}}{Dt} = -\frac{1}{\rho} \nabla P \quad (9.73)$$

$$\frac{DP}{Dt} = a_f^2 \frac{D\rho}{Dt} + \rho a_f^2 \dot{\sigma} \quad (9.74)$$

$$\frac{DY_k}{Dt} = \frac{1}{\rho} \mathcal{W}_k \dot{\omega}_k \quad (k = 1, \dots, K) \quad (9.75)$$

These can be simplified for steady one-dimensional reactive flow, with the following definitions:

$$\frac{\partial}{\partial t} = 0, \quad (9.76)$$

$$\mathbf{u} = w \hat{\mathbf{x}}, \quad (9.77)$$

$$\frac{D}{Dt} = w \frac{d}{dx}. \quad (9.78)$$

In a frame of reference moving with a fluid element, the relationship between space and time is given by the trajectory  $X(t)$  of the element as defined by the kinematic relationship

$$\frac{dX}{dt} = w(X(t)). \quad (9.79)$$

Instead of distance  $x$ , we can consider the motion in terms of the time  $t$  elapsed from a reference location. This is equivalent to the Lagrangian interpretation of the convective derivative

$$\frac{D}{Dt} = \frac{d}{dt} \quad \text{on} \quad \frac{dx}{dt} = w. \quad (9.80)$$

When considering shock-initiated reactions as in a detonation, it is usual to consider the time  $t$  as being relative to time the fluid element passed through the shock front. The equations of motion simplify to

$$\frac{d\rho}{dt} = -\rho \frac{\dot{\sigma}}{\eta}, \quad (9.81)$$

$$\frac{dP}{dt} = -\rho w^2 \frac{\dot{\sigma}}{\eta}, \quad (9.82)$$

$$\frac{dw}{dt} = w \frac{\dot{\sigma}}{\eta}, \quad (9.83)$$

$$\frac{dY_k}{dt} = \frac{1}{\rho} \mathcal{W}_k \dot{\omega}_k = \Omega_k \quad (k = 1, \dots, K). \quad (9.84)$$

The *sonic* parameter is defined in terms of the frozen sound speed

$$\eta = 1 - \frac{w^2}{a_f^2} \quad (9.85)$$

The sonic parameter is always less than one in the reaction zone behind a shock wave and if the sonic parameter approaches one, then the thermicity has to vanish or the solution will be singular:  $\dot{\sigma} \rightarrow 0$  as  $\eta \rightarrow 0$ .

These equations (9.81- 9.84) are the basis of the standard Zel'dovich-von Neumann-Döring (ZND) model of detonation structure and extensions to treat variable area, friction and heat transfer are the foundation of widely-used elementary models of steady reactive flow (See Ch. 2 of [Zhang, 2012](#)). This model and extensions described in Ch. 11 can be used for both endothermic and exothermic reaction, and is applicable both to the flows behind shock waves and as well as variable area flows encountered in high-speed flight and testing facilities.

## 9.7 Temperature

In this section we derive temperature evolution equations for steady reactive flow and the limiting cases of constant volume and constant pressure explosions. The derivations in this section are all based on the ideal gas model. A more general expression for relating changes in  $T$ ,  $P$ ,  $\rho$  and  $\mathbf{Y}$  valid for an arbitrary equation of state is given in Section 9.8.

The derivation begins with the ideal gas relations.

$$P = \rho RT \quad (9.86)$$

This leads to the following logarithmic derivation relationship.

$$\frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dR}{R} + \frac{dT}{T} \quad (9.87)$$

Here  $R$  is the specific gas constant,

$$R = \frac{\mathcal{R}}{\mathcal{W}} = \mathcal{R} \sum_{i=1}^{N_Y} \frac{Y_i}{\mathcal{W}_i}. \quad (9.88)$$

The derivative of  $R$  is related to the evolution of the species in the following way

$$\frac{dR}{R} = \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} dY_i \quad (9.89)$$

Now the temperature derivative in a steady flow is

$$\frac{dT}{dx} = T \left[ \frac{1}{P} \frac{dP}{dx} - \frac{1}{\rho} \frac{d\rho}{dx} - \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} \frac{dY_i}{dx} \right], \quad (9.90)$$

and if we insert the thermicity equations (Eqs. 9.81-9.84),

$$\frac{dT}{dx} = T \left[ -\frac{\rho w \dot{\sigma}}{P \eta} + \frac{1}{w \eta} \dot{\sigma} - \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} \frac{\dot{\Omega}_i}{w} \right]. \quad (9.91)$$

By grouping terms and recalling the definition of the frozen sound speed  $a_f^2 = \gamma P / \rho$ , the temperature equation becomes

$$\frac{dT}{dx} = \frac{T}{w} \left[ \left( 1 - \frac{\gamma w^2}{a_f^2} \right) \frac{\dot{\sigma}}{\eta} - \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} \dot{\Omega}_i \right]. \quad (9.92)$$

Finally, the ZND temperature equation is

$$\frac{dT}{dx} = \frac{T}{w} \left[ (1 - \gamma M^2) \frac{\dot{\sigma}}{\eta} - \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} \dot{\Omega}_i \right] \quad (9.93)$$

or

$$\frac{dT}{dt} \Big|_{X_p} = w \frac{dT}{dx} = T \left[ (1 - \gamma M^2) \frac{\dot{\sigma}}{\eta} - \sum_{i=1}^{N_Y} \frac{\mathcal{W}_i}{\mathcal{W}} \dot{\Omega}_i \right]. \quad (9.94)$$

## Limiting Behavior

The constant volume explosion is the limit of the steady reacting flow equations as velocity goes to infinity  $w \rightarrow \infty$ . The velocity only appears in the first term and its limit is

$$T \left( 1 - \gamma \frac{w^2}{a_f^2} \right) \frac{\dot{\sigma}}{\left( 1 - \frac{w^2}{a_f^2} \right)} \rightarrow T \gamma \dot{\sigma}. \quad (9.95)$$

Now we can rearrange the terms as follows to find the correct expression for the constant volume model.

$$\frac{dT}{dt} \Big|_{X_p} = T \left[ \gamma \sum_{i=1}^{N_Y} \left( \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i}{c_P T} \right) \dot{\Omega}_i - \sum_{i=1}^{N_Y} \frac{\mathcal{W}}{\mathcal{W}_i} \dot{\Omega}_i \right] \quad (9.96)$$

$$= T \sum_{i=1}^{N_Y} \left[ (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{\gamma}{c_P} \frac{h_i}{T} \right] \dot{\Omega}_i \quad (9.97)$$

$$= T \sum_{i=1}^{N_Y} \left[ (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{e_i + R_i T}{c_v T} \right] \dot{\Omega}_i \quad (9.98)$$

$$= T \sum_{i=1}^{N_Y} \left[ (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{e_i + R_i T}{c_v T} \right] \dot{\Omega}_i \quad (9.99)$$

$$= -\frac{1}{c_v} \sum_{i=1}^{N_Y} e_i \dot{\Omega}_i + T \sum_{i=1}^{N_Y} \left[ (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{\mathcal{R}}{W} \frac{\mathcal{W}}{\mathcal{W}_i} \frac{\gamma - 1}{R} \right] \dot{\Omega}_i \quad (9.100)$$

$$= -\frac{1}{c_v} \sum_{i=1}^{N_Y} e_i \dot{\Omega}_i + T \sum_{i=1}^{N_Y} \left[ (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} - (\gamma - 1) \frac{\mathcal{W}}{\mathcal{W}_i} \right] \dot{\Omega}_i \quad (9.101)$$

$$\frac{dT}{dt} \Big|_{X_p} = -\frac{1}{c_v} \sum_{i=1}^{N_Y} e_i \dot{\Omega}_i \quad (9.102)$$

On the other hand, the constant pressure model is the limit as the velocity goes to zero  $w \rightarrow 0$ . Again, the velocity only appears in the first term and its limit is

$$T \left( 1 - \gamma \frac{\frac{w^2}{a_f^2}}{1 - \frac{w^2}{a_f^2}} \right) \frac{\dot{\sigma}}{\left( 1 - \frac{w^2}{a_f^2} \right)} \rightarrow T \dot{\sigma}. \quad (9.103)$$

Now we can rearrange the terms as follows to find the correct expression for the constant pressure model.

$$\frac{dT}{dt} \Big|_{X_p} = T \left[ \sum_{i=1}^{N_Y} \left( \frac{\mathcal{W}}{\mathcal{W}_i} - \frac{h_i}{c_P T} \right) \dot{\Omega}_i - \sum_{i=1}^{N_Y} \frac{\mathcal{W}}{\mathcal{W}_i} \dot{\Omega}_i \right] \quad (9.104)$$

$$= T \sum_{i=1}^{N_Y} -\frac{h_i}{c_P T} \dot{\Omega}_i \quad (9.105)$$

$$\frac{dT}{dt} \Big|_{X_p} = -\frac{1}{c_P} \sum_{i=1}^{N_Y} h_i \dot{\Omega}_i \quad (9.106)$$

## 9.8 Real Gas Modeling

Real gases<sup>2</sup> are distinguished from ideal gases through the additional pressure (or equivalently volume) dependence of the thermodynamic potentials that arises from continuous intermolecular interactions. These interactions are important at sufficiently high densities so that the molecules and atom are constantly interacting through the electrostatic force fields as well as quantum mechanical effects. At intermediate densities and low temperatures, these interactions are attractive and result in a lower pressures than would be predicted by the ideal gas relations. At higher densities and temperatures, these interactions are repulsive and result in higher pressures than would be predicted by the ideal gas relations.

There are four key real gas effects on reactive flows:

- Departures from the ideal gas  $P(V, T)$  equation of state.

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<sup>2</sup>We use the term real gas to indicate any fluid substance (gas, dense gas or liquid) that can be described in terms of the thermodynamic parameters  $P$ ,  $V$  and  $T$ . The considerations in this section apply to any substance in this category.

2. Departures from the ideal gas properties for thermodynamic potentials  $E, H, A, G$  and entropy  $S$ .
3. Departures from ideal gas chemical potentials and equilibrium constants.
4. Shifts in chemical reaction mechanisms and rates due to the creation of new intermediates and pathways associated with stabilizing influence neighboring molecules.

The thermodynamic effects of items 1-3 can be described by defining a *compressibility factor*  $Z$ ,

$$Z = \frac{PV}{N\mathcal{R}T}, \quad (9.107)$$

In the attractive regime,  $Z < 1$  and in the repulsive regime,  $Z > 1$ . For ideal gases, the molecular interactions are highly intermittent, occurring through infrequent collisions so that  $Z = 1$  to high degree of accuracy. The functional dependence  $Z(T, P, N)$  for a pure substance at modest temperatures can be determined by measurements, which can be fit to model equations (Reid et al., 1987, Reynolds, 1979) of the form  $P(V/N, T)$ . As discussed the next section, these relationships can be extended to gas mixtures using empirical averaging methods to include the effects of composition  $P(V/N, T, \mathbf{X})$  or equivalently,  $P(V/N, T, \mathbf{Y})$ .

Using classical thermodynamics and a functional relationship  $Z = Z(T, V, \mathbf{N})$  for a reactive mixture, the departures associated with item 1 can be computed directly or implicitly, and for items 2 and 3, the relevant departure functions can be computed from partial derivatives of  $Z$ . Item 4 is much more challenging to address and requires using molecular dynamics and quantum mechanical modeling of molecular interactions to determine the corrections and limitations of using traditional reaction mechanisms with thermal reaction rates.

From the thermodynamicist and engineer's point of view, the effect of molecular interactions can be represented as compressibility effects and quantified through empirical relationships and extended to other properties using the methods of classical thermodynamics. From the physicist or chemist's point of view, the effect of molecular interactions can be represented by using molecular potentials to describe the interactions and use the methods of statistical thermodynamics to compute a partition function from which all thermodynamic properties can be derived. In practice, a mixture of these methods is used: rigorous statistical mechanics for ideal gas properties (described in Section 3) complemented by empirical equations of state and rigorous thermodynamics to correct for the effects of compressibility. This is the approach we will describe.

## Critical States and Properties

The effect of molecular interactions on a pure substance can be gauged by evaluating the nondimensional thermodynamic state, using the thermodynamic critical properties  $T_c$ ,  $P_c$  and  $V_c$  as reference conditions. In these terms the compressibility factor can be expressed as function of nondimensional reduced pressure  $P_r = P/P_c$ , volume  $V/V_c$ , temperature  $T_r = T/T_c$ , and mole fractions  $\mathbf{X}$ .

$$Z = Z(P_r, T_r, \mathbf{X}) \quad \text{or} \quad Z = Z(P_r, V_r, \mathbf{X}) \quad (9.108)$$

Thermodynamic critical states for selected molecules are given in Table 9.1. Additional values and estimation methods (important for radicals and reactive intermediates) are given in texts and monographs on thermodynamics (e.g., Kee et al., 2003, Reid et al., 1987, Reynolds, 1979).

Reactants and products for combustion systems are mixtures with a composition that varies during the reaction process. In order to compute the compressibility effects during the reaction process using a model relationship of the form (9.108), an averaging method is needed to combine pure substance properties to calculate effective or psuedo-critical states as a function of composition. Prescriptions for averaging are discussed by Reid et al. (1987). One simple method is *Kay's rule* for the effective critical temperature

$$T_{c,m} = \sum_{k=1}^K X_k T_{c,k} \quad (9.109)$$

where  $X_k$  is the mole fraction of species  $k$ . The *Prausnitz-Gunn rule* for effective (or pseudo-) critical pressure, compressibility, and volume is

$$P_{c,m} = Z_{c,m} \frac{RT_{c,m}}{v_{c,m}} \quad Z_{c,m} = \sum_{k=1}^K X_k Z_{c,k} \quad v_{c,m} = \sum_{k=1}^K X_k v_{c,k} \quad (9.110)$$

Table 9.1: Thermodynamic critical states for some common components of combustion reactants and products (Reid et al., 1987).

substance	$\mathcal{W}$ (kg/kmol)	$T_c$ (K)	$P_c$ (MPa)	$\rho_c$ (kg·m <sup>-3</sup> )	$Z_c$
CH <sub>4</sub>	16.043	190.6	4.61	162.0	0.2880
N <sub>2</sub>	28.014	126.2	3.40	313.2	0.2897
O <sub>2</sub>	31.999	154.6	5.043	435.2	0.2885
CO <sub>2</sub>	44.01	304.2	7.38	466.5	0.2753
CO	28.01	134.5	3.50	310.9	0.2819
H <sub>2</sub> O	18.02	647.0	22.09	322.5	0.2291
H <sub>2</sub>	2.0159	33.18	1.30	31.36	0.3060

Applying these relationships to a stoichiometric CH<sub>4</sub>-air mixture, the pseudo-critical values shown in Table 9.2 were obtained. The product composition was computed for constant-pressure combustion at 1 bar, values for constant volume or CJ detonation are comparable and the modest differences are due to the shift in composition with pressure.

Table 9.2: Effective thermodynamic critical parameters for stoichiometric CH<sub>4</sub>-air mixtures.

	$T_{c,m}$ (K)	$P_{c,m}$ (MPa)	$\rho_{c,m}$ (kg·m <sup>-3</sup> )	$Z_{c,m}$
reactants	138	3.79	316	0.289
products	238	6.57	329	0.277

For intermediate species, radicals and fuel molecules for which thermodynamic critical states are not available, the critical properties must be estimated. One method is to use the molecular potential parameters,  $\varepsilon$  (well depth),  $\sigma$  (well radius) given in the Cantera or Chemkin thermodynamic database files and used for computing molecular transport coefficients. These parameters are specified as `well_depth = ε/k_B` (K) and `diam = σ` (Å). For the purposes of rough approximation, the critical pressure and temperature can be estimated (all units in SI) using the following correlations Rowlinson and Swinton (1982).

$$T_c = 1.35 \frac{\varepsilon}{k_B} \quad (\text{K}) \quad (9.111)$$

$$P_c = 0.142 \frac{\varepsilon}{\sigma^3} \quad (\text{Pa}) \quad (9.112)$$

$$V_c = 2.857 N_A \sigma^3 \quad (\text{m}^3 \cdot \text{mol}^{-1}) \quad (9.113)$$

Other correlations are available, for example, Smit (1992) has analyzed molecular simulations of a fluid described by molecules interacting by intermolecular forces derived from a Lennard-Jones potential to obtain  $T_c = 1.316\varepsilon/k_B$  and  $V_c = 3.29N_A\sigma^3$ ,  $P_c$  and  $Z_c$  are determined by the equation of state. These simple estimation methods are very rough approximations to critical properties and should be used with caution, particularly with the many molecules and mixtures that require considering the effects of asymmetric molecular potentials that cannot be described by a central potential such as Lennard-Jones. For cubic equations, the values of  $Z_c$  depend only on the particular form of the equation Reid et al. (1987). For example van der Waals  $Z_c = 3/8$ , Redlich-Kwong  $Z_c = 1/3$  and Peng-Robinson  $Z_c = 0.3074$ .

The actual values of  $Z_c$  as well as the  $P(V, T)$  relationship in the near-critical region can be significantly different than predicted by simple cubic equation equations of state. There is a substantial chemical engineering literature on sophisticated equations of state for pure substances that can be used to make highly

reliable estimates of thermodynamic properties. However, there are significant issues in developing and applying more sophisticated approaches to multi-component mixtures characteristic of combustion systems. For this reason, cubic equations of state continue to be widely used in estimating compressibility effects for combustion at elevated pressures with the notable exception of condensed explosives.

Compressibility effects on products and reactants are often found to be quite different due to the much higher temperatures in combustion products as compared to reactants as well as effects of higher product pressure in the case of shock and detonation waves. For example, for CH<sub>4</sub>-air at an initial pressure of 100 bar, the initial reactant state can be considered a perfect gas at room temperature but there are substantial molecular interaction effects ( $Z \sim 2$ ) on the postshock (vN) state and the product CJ state ( $Z \sim 1.3$ ). The compressibility factor will increase with increasing density, reaching values as high as 15 to 20 for condensed explosives.

Computations and experiments reveal that:

1. At a given reactant density, the constant volume or detonation pressures are higher for a dense gas than for the ideal gas model.
2. Detonation velocity is higher for dense gases than for low density gases at the same initial composition and temperature.
3. Dense gas detonation velocities increase with increasing reactant density but computed ideal gas values reach a limiting value.
4. Compressibility factors of shocked reactants and products increase with increasing reactant density.
5. For modest density increases, the effect on compressibility factor is much more pronounced than the effect on enthalpy or internal energy.
6. For fuel-air mixtures, the initial pressure should be less than 10 to 20 bar if less than a 10% error in compressibility, i.e.,  $Z - 1 < 0.1$ , is to be allowed at the vN point. The initial pressure should be less than 2 bar if less than 1% error is allowable.

Physically, all of these effects are a consequence of the increasing importance of molecular repulsion with increasing density of the reactants and consequently, the products. This effect can be crudely approximated with a hard sphere model which prevents the molecules from being packed together any closer than the mean diameter. Detailed consideration of dense gas effects for detonations can be found in [Schmitt and Butler \(1995a,b\)](#)

## Equation of State

For chemical equilibrium and reactive flow computations a complete equation of state is required in the form of a thermodynamic potential (Sec. 2.1) that is a function of two independent thermodynamic variables and composition. For equilibrium computations, an expression for the Gibbs energy  $G(T, P, \mathbf{N})$  is sought. In the case of reacting flows, either the enthalpy  $H$ , internal energy  $U$  or Helmholtz energy  $A$  will be required in addition to  $G$ . In practice, only one of the potentials, for example  $A(T, V, \mathbf{N})$  will be computed and the other potentials computed by standard thermodynamic transformations (Ch. 2).

In order to construct a complete equation of state, we start from the low-pressure (large volume limit) of the ideal gas mixture (Section 2.2). In this limit, we can take advantage of the established databases of information for temperature and species dependence of ideal gas properties (Ch. 5) which are based on statistical mechanics and physical chemistry (Ch. 3). To estimate the continuous molecular interactions on the ideal gas properties, we will use an empirical expressions for  $Z(V, T, \mathbf{N})$  or  $Z(T, P, \mathbf{N})$  and thermodynamic identities to calculate *departure* or *residual* functions which are additive corrections to the ideal gas properties.

The computation of a complete real gas equations of state proceeds by considering a gas mixture with a fixed (frozen) composition, a set of ideal gas properties such as  $C_p^{ig}$ ,  $H^{ig}(T)$  and a analytical relationship for  $Z(V, T, \mathbf{N})$ . Because the composition is frozen, we suppress the dependence on composition when computing the departure functions although the total amount of substance will enter into the results. However, we will need to keep the composition dependence in mind and carry out differentiation with respect to the composition variables in order to develop the governing equations for reactive flow.