

Cubic Equations for Z

A popular starting point for analytical $Z(V, T, \mathbf{N})$ expressions is the van der Waals equation (Abbott, 1989), which has been the basis of further development of a range of *cubic* equations (Abbott, 1973), so named because Z is determined as the root of a cubic polynomial. Members of the cubic equation family that are widely used in chemical engineering (Reid et al., 1987, Smith et al., 1996) include van der Waals, Redlich-Kwong, Peng-Robinson, and Soave. These equations can all be written in the form

$$P = \frac{NRT}{V - Nb} - \frac{N^2a}{V^2 + VNd + N^2d} \quad (9.114)$$

The conventional interpretation is that the first term on the right-hand side represents the effect of the finite size of the molecules, the second represents the effect of attraction associated with the intermolecular forces. The parameters a, b, c, d are functions of the molecular properties, composition and temperature; constraints on these functions and relationships to the critical properties, vapor pressure, acentric factors and virial coefficients are discussed by Abbott (1973). The application of cubic equations to the computation of detonation properties for high-pressure gases is described by Schmitt and Butler (1995a,b) and the calculation of the thermodynamics properties based on selected cubic equations is explained in detail by Schmitt (1994), Schmitt et al. (1994). Cubic equations are successful (Schmitt and Butler, 1995a) in describing detonation parameters such as CJ wave speeds for hydrocarbon-oxygen-diluent mixtures as a function of initial pressure up to 500 atm. Measurable deviations from ideal gas predictions are observed for initial pressures greater than 10-20 atm and the CJ speeds increase with increasing pressure, reaching values that are 50% larger than the ideal gas values at 300 atm (Schmitt and Butler, 1995a). For even higher pressures and condensed explosives, specialized $P(V, T, \mathbf{N})$ equations such as JCZ and BKW are utilized (Hobbs et al., 1999); these are also applicable to high-pressure gaseous detonations.

Redlich-Kwong EOS

A commonly considered cubic EOS for estimating real gas effects is the Redlich-Kwong model, this is implemented in Cantera 2.5 and the thermodynamic functions can be accessed through the Python interface. In molar volume coordinates, the EOS is defined by two parameters a and b

$$P = \frac{\mathcal{R}T}{\bar{V} - b} - \frac{a}{T^{1/2}\bar{V}(\bar{V} + b)} \quad (9.115)$$

The coefficients a and b can be related to the properties of the thermodynamic critical point. These properties are implicitly defined by the vanishing of the first and second derivatives of pressure with respect to volume:

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_{T_c, P_c} = 0 \quad (9.116)$$

$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_{T_c, P_c} = 0 \quad (9.117)$$

$$a = \Omega_a \frac{\mathcal{R}^2 T_c^2}{P_c} \quad \Omega_a = \frac{1}{9(2^{1/3} - 1)} = 0.42748 \dots \quad (9.118)$$

$$b = \Omega_b \frac{\mathcal{R} T_c}{P_c} \quad \Omega_b = \frac{2^{1/3} - 1}{3} = 0.08664 \dots \quad (9.119)$$

The coefficients a and b have been determined empirically for a number of pure substances (Reid et al., 1987) at modest temperatures by fitting experimental (P, V, T) data. For combustion simulations we are interested in gas mixtures containing many species such as radicals and intermediates and thermodynamics conditions for which it is not possible to directly measure the (P, V, T) EOS and obtain values of a and b . The state determined by (9.116) for a mixture is more properly referred to as a “pseudo-critical” point as the near-critical behavior observed in mixtures is often much more complex than the pure substance case.

We also require an analytical model of how the coefficients a and b depend on composition in order to implement reacting flow models, which as discussed below, require partial molar properties. In order to

compute value of a and b for mixtures, mixture averaging of individual species properties using mole or mass fractions is used. A common approach is to use rules (attributed to van der Waals) similar to those proposed for combining molecular interaction potential parameters.

$$a = \sum_i \sum_k X_i X_k \sqrt{a_i a_k} \quad (9.120)$$

$$b = \sum_k X_k b_k \quad (9.121)$$

The coefficients a_i and b_i for each species are, when available, based on tabulated values for pure substances. For the many combustion species for which EOS data is not available, the values of a_i and b_i must be computed using critical properties (9.116) estimated either from molecular potential parameters (9.111) or group contribution methods based on molecular structure (Joback and Reid, 1987, Reid et al., 1987). The a and b values for a mixture can be used in (9.118) and (9.119) as an alternative to (9.110) or (9.111) to define pseudo-critical point values (Table 9.3).

Table 9.3: Pseudo-critical parameters for stoichiometric CH₄-air mixtures computed using a and b values for Redlich-Kwong equation of state.

	$T_{c,m}$ (K)	$P_{c,m}$ (MPa)	$\rho_{c,m}$ (kg·m ⁻³)	$Z_{c,m}$
reactants	135	3.74	279	0.33
products	190	5.28	281	0.33

Departure Functions, Fugacity and Activity

Departure functions (Reid et al., 1987, Schmitt et al., 1994) are defined as additive corrections to the ideal gas properties to obtain real gas properties at a given temperature and pressure. For any thermodynamic property M , we define the departure as

$$M^d(T, P, \mathbf{N}) = M(T, P, \mathbf{N}) - M^{ig}(T, P, \mathbf{N}) . \quad (9.122)$$

Residual functions (Reynolds, 1979, Van Ness and Abbott, 1982) are an alternative terminology for these corrections and usually defined with the opposite sign, $M^r = M^{ig} - M$.

Departure for G

For fixed composition the Gibbs energy dependence on temperature and pressure can be found (Van Ness and Abbott, 1982) by integrating the fundamental relationship in the form

$$dG = -SdT + VdP . \quad (9.123)$$

Because $G(T, P)$ is a state function we are free to choose a convenient path of integration from the reference state (T°, P°) to the state (T, P) and the answer will independent of the path chosen. The choosen path is to first integrate in temperature at a fixed pressure P° and then integrate in pressure at the fixed final temperature T . The ideal gas limit is $P^\circ \rightarrow 0$, in practical terms, a gas is ideal, i.e., $Z \approx 1$, at $P^\circ = 1$ standard atmosphere if the temperature is sufficiently high compared to the effective critical temperature.

$$G(T, P) = \underbrace{G(T^\circ, P^\circ) + \int_{T^\circ}^T -S^{ig}(T', P^\circ) dT' + \dots \int_{P^\circ}^P V^{ig}(T, P') dP' + \dots}_{G^{ig}} \lim_{P^\circ \rightarrow 0} \underbrace{\int_{P^\circ}^P (V(T, P') - V^{ig}(T, P')) dP'}_{G^d} , \quad (9.124)$$

$$= G^{ig} + G^d , \quad (9.125)$$

The ideal gas has $Z = 1$, so that

$$V^{ig} = \frac{N\mathcal{R}T}{P} . \quad (9.126)$$

The compressibility factor can be expressed as

$$Z = Z(T, V/N, \mathbf{X}) \quad \text{or} \quad Z = Z(P, T, \mathbf{X}) , \quad X = (X_1, X_2, \dots, X_K) , \quad X_k = N_k/N , \quad (9.127)$$

where X_k is the mole fraction of species k . This is necessary and possible because Z is an intensive variable that does not depend on the amount of substance N so volume can only enter as a specific volume V/N and composition as mass or mole fractions. This is consistent with the cubic equation of state with the parameters a, b, c, d functions only of temperature and the mole (or mass) fractions. Rewriting the second integrand in (9.124) in terms of compressibility, we have

$$\frac{G^d}{\mathcal{R}T} = \int_0^P (NZ(T, P', \mathbf{N}) - N) \frac{dP'}{P'} . \quad (9.128)$$

Defining the volume departure as

$$V^d = V - V^{ig} = \frac{N\mathcal{R}T}{P} (Z - 1) , \quad (9.129)$$

from this definition and (9.128), we obtain

$$\frac{V^d}{\mathcal{R}T} = \left[\frac{\partial(G^d/\mathcal{R}T)}{\partial P} \right]_T . \quad (9.130)$$

Using these relationships in (9.123), we obtain

$$\frac{H^d}{\mathcal{R}T} = -T \left[\frac{\partial(G^d/\mathcal{R}T)}{\partial T} \right]_P = -NT \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP'}{P'} . \quad (9.131)$$

Departure functions for other properties can be determined from (9.128) and (9.131) and thermodynamic identities. In nondimensional form, these are:

$$\frac{S^d}{\mathcal{R}} = \frac{H^d}{\mathcal{R}T} - \frac{G^d}{\mathcal{R}T} , \quad (9.132)$$

$$\frac{E^d}{\mathcal{R}T} = \frac{H^d}{\mathcal{R}T} - N(Z - 1) , \quad (9.133)$$

$$\frac{A^d}{\mathcal{R}T} = \frac{G^d}{\mathcal{R}T} - N(Z - 1) . \quad (9.134)$$

Departure Functions for $P(V, T, \mathbf{N})$ EOS

The departure functions computed using Gibbs energy are appropriate for an equation $Z(P, T, \mathbf{N})$. However, for equations of the form $Z(V, T, \mathbf{N})$ such as the cubic family, it is better to start from the Helmholtz energy $A(T, V, \mathbf{N})$ and carry out integrations in volume rather than pressure. An alternative is to use the expression for A^d in terms of G^d and transform to V coordinates for the integration of the departure term. From the previous section, the departure function for A is

$$\frac{A^d}{\mathcal{R}T} = \int_0^P (NZ(T, P') - N) \frac{dP'}{P'} - N(Z - 1) . \quad (9.135)$$

The integral term in (9.135) can be rewritten in terms of volume instead of pressure to facilitate computation using a $P(V, T, \mathbf{N})$ equation of state. Starting from the definition of compressibility Z , at fixed T and \mathbf{N} , we have

$$\frac{dP}{P} + \frac{dV}{V} = \frac{dZ}{Z} \quad (9.136)$$

Substitution into the integral and transforming to volume integration, we find that

$$\frac{A^d}{\mathcal{R}T} = -N \int_v^\infty (Z - 1) \frac{dV'}{V'} - N \ln Z \quad (9.137)$$

The departure for entropy can be computed from the fundamental relationship of thermodynamics for A

$$S^d = - \left(\frac{\partial A^d}{\partial T} \right)_V . \quad (9.138)$$

$$= N\mathcal{R} \int_\infty^V \left[T \left(\frac{\partial Z}{\partial T} \right)_V + Z - 1 \right] \frac{dV'}{V'} . \quad (9.139)$$

The departure functions for other thermodynamic potentials can be computed from the relationships (9.134) derived previously and the expressions for A^d and S^d . The internal energy departure function is

$$\frac{E^d}{\mathcal{R}T} = -T \left(\frac{\partial(A^d/\mathcal{R}T)}{\partial T} \right)_V , \quad (9.140)$$

and to complete the set of relations, we can show that

$$N(Z - 1) = V \left(\frac{\partial(A^d/\mathcal{R}T)}{\partial V} \right)_T . \quad (9.141)$$

Explicit expressions for the departure functions are given in Reid et al. (1987) for several equations of state, including Redlich-Kwong and variations.

Fugacity

An important application of departure functions is the computation of chemical potential and the application to chemical equilibrium through the minimization of Gibbs energy

$$G = \sum_{k=1}^K N_k \bar{G}_k , \quad (9.142)$$

at constant (T, P) subject to the conservation of atoms.

$$\sum_{k=1}^K \mu_k dN_k = 0 . \quad (9.143)$$

where the chemical potential is defined from the partial molar Gibbs energy

$$\mu_i \equiv \bar{G}_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{k \neq i}} . \quad (9.144)$$

Expand G in terms of the departure function to obtain

$$\mu_i = \left(\frac{\partial G^{ig}}{\partial N_i} \right)_{T, P, N_{k \neq i}} + \left(\frac{\partial G^d}{\partial N_i} \right)_{T, P, N_{k \neq i}} . \quad (9.145)$$

Identifying the derivative of the departure function as a partial molar property we obtain

$$\mu_i = \mu_i^{ig} + \bar{G}_i^d . \quad (9.146)$$

From (9.124) the partial molar departure function is

$$\bar{G}_i^d = \int_0^P (\bar{Z}_i - 1) \frac{dP'}{P'} , \quad (9.147)$$

where we define the partial molar compressibility factor as

$$\bar{Z}_i = \left(\frac{\partial(NZ)}{\partial N_i} \right)_{T,P,N_{k \neq i}} . \quad (9.148)$$

In analogy with the ideal gas expression for chemical potential

$$\mu_i^{ig} = \mu_i^\circ(T) + \mathcal{R}T \ln(X_i P / P^\circ) , \quad (9.149)$$

the *fugacity* f_i is defined by

$$\mu_i = \mu_i^\circ(T) + \mathcal{R}T \ln(f_i / P^\circ) . \quad (9.150)$$

The *fugacity coefficient* ϕ_i is defined by

$$\phi_i = \frac{f_i}{X_i P} , \quad (9.151)$$

which leads to the definition

$$\mu_i - \mu_i^{ig} = \mathcal{R}T \ln \phi_i . \quad (9.152)$$

Expressing ϕ_i in terms of the Gibbs energy departure function

$$\ln \phi_i = \frac{1}{\mathcal{R}T} \int_0^P (\bar{Z}_i - 1) \frac{dP'}{P'} . \quad (9.153)$$

Using the Helmholtz departure function to define ϕ_i , we obtain an expression that is useful for computing with an equation of state in the form $P(T, V, \mathbf{N})$

$$\ln \phi_i = -\frac{1}{\mathcal{R}T} \int_\infty^V \left[\left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{k \neq i}} - \frac{\mathcal{R}T}{V} \right] \frac{dV'}{V'} - \ln Z \quad (9.154)$$

The variation of the chemical potentials with pressure and temperature can be evaluated if the partial molar volume and entropy are known. Applying the reciprocity relationships of thermodynamics to the fundamental relation we obtain

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{P,\mathbf{N}} = -\bar{S}_k , \quad (9.155)$$

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T,\mathbf{N}} = \bar{V}_k . \quad (9.156)$$

Differentiating the expression for the Gibbs potential and using the fundamental relationship for dG we obtain

$$\sum_{k=1}^K N_k d\mu_k = -SdT + VdP . \quad (9.157)$$

This is known as the Gibbs-Duhem relationship. Using the partial molar sum representation of S and G and considering arbitrary variations in composition, the relationship for each component can be written

$$d\mu_k = -\bar{S}_k dT + \bar{V}_k dP . \quad (9.158)$$

Equilibrium

Equilibrium in real gases requires expressing the chemical potential in terms of the fugacity or fugacity coefficients instead of partial pressures which are used in the ideal gas formulation discussed in Section 4.8.

$$\mu_i = \mu_i^\circ(T) + \mathcal{R}T \ln(f_i/P^\circ) \quad (9.159)$$

$$= \mu_i^\circ(T) + \mathcal{R}T \ln(\phi_i X_i P/P^\circ) . \quad (9.160)$$

For a single equilibrium relation with stoichiometric coefficients ν_i , the equilibrium condition for a real gas will be

$$0 = \sum_i \nu_i [\mu_i^\circ(T) + \mathcal{R}T \ln(\phi_i X_i P/P^\circ)] \quad (9.161)$$

or (setting $P^\circ = 1$)

$$\Pi_i f_i^{\nu_i} = \exp \left(- \frac{\sum_i \nu_i \mu_i^\circ(T)}{\mathcal{R}T} \right) . \quad (9.162)$$

In terms of partial pressures

$$\Pi_i P_i^{\nu_i} = \underbrace{\frac{1}{\Pi_i \phi_i^{\nu_i}}}_{\text{real gas correction}} \underbrace{\exp \left(- \frac{\sum_i \nu_i \mu_i^\circ(T)}{\mathcal{R}T} \right)}_{\text{ideal gas}} . \quad (9.163)$$

or

$$\Pi_i P_i^{\nu_i} = K_p^{rg} \quad (9.164)$$

Define the ideal gas pressure-based equilibrium constant as

$$K_p^{ig} = \exp \left(- \frac{\sum_i \nu_i \mu_i^\circ(T)}{\mathcal{R}T} \right) \quad (9.165)$$

to obtain the real-gas pressure-based equilibrium constant as a modification to the ideal gas value

$$K_p^{rg} = \frac{K_p^{ig}}{\Pi_i \phi_i^{\nu_i}} . \quad (9.166)$$

Computations of reaction rates often require the equilibrium constant expressed in terms of molar concentrations in order to compute the reverse reaction rate from the forward rate. In doing so, there are two effects that can be significant for real gases: 1) the molar concentration for a real gas at the same partial pressure will differ from the ideal gas values when $Z \neq 1$; 2) the equilibrium constant for a real gas differs from the ideal gas value when $\phi_i \neq 1$. The molar concentrations are:

$$[i] = \frac{N_i}{V} \quad (9.167)$$

or in terms of the partial pressures

$$[i] = \frac{P_i}{Z\mathcal{R}T} . \quad (9.168)$$

The concentration-based equilibrium constant is

$$K_c^{rg} \equiv \Pi_i [i]^{\nu_i} , \quad (9.169)$$

which can be expressed as

$$K_c^{rg} = \frac{1}{\prod_i (\phi_i Z)^{\nu_i}} K_c^{ig} , \quad (9.170)$$

in terms of the ideal gas concentration-based equilibrium constant

$$K_c^{ig} = \frac{1}{(\mathcal{R}T)^{\Delta\nu}} K_p^{ig} . \quad (9.171)$$

Real-gas reacting flow model equations

The real gas analogues of the model equations for ideal gas reacting flow are derived starting from the fundamental relationships of thermodynamics.

$V(T, P, N)$ expansion

A useful general result is the expansion of $V(T, P, N)$ in a Taylor series.

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P, \mathbf{N}} dT + \left(\frac{\partial V}{\partial P} \right)_{T, \mathbf{N}} dP + \left(\frac{\partial V}{\partial N_k} \right)_{P, T, N_{i \neq k}} dN_k \quad (9.172)$$

The coefficients can be expressed in terms of standard thermodynamic properties and definitions

$$\left(\frac{\partial V}{\partial T} \right)_{P, \mathbf{N}} = V\beta . \quad (9.173)$$

$$\left(\frac{\partial V}{\partial P} \right)_{V, \mathbf{N}} = -V \frac{c_p}{c_v} K_s = -V \frac{\gamma}{\rho a_f^2} , \quad (9.174)$$

$$\left(\frac{\partial V}{\partial N_k} \right)_{V, N_{i \neq k}} = \bar{V}_k . \quad (9.175)$$

Solving for the temperature derivative and changing from mole to mass fraction for the composition variables we obtain

$$dT = \frac{1}{\beta} \left[\gamma \frac{dP}{\rho a_f^2} - \frac{d\rho}{\rho} - \sum_k \frac{\bar{V}_k}{\bar{V}} \frac{W}{W_k} dY_k \right] . \quad (9.176)$$

The ideal gas version of this expression is

$$dT = T \left[\frac{dP}{P} - \frac{d\rho}{\rho} - \sum_k \frac{W}{W_k} Y_k \right] \quad (\text{ideal gas}) \quad (9.177)$$

consistent with the results obtained directly using the ideal gas EOS in Section 9.7.

Constant pressure reaction

For an adiabatic, constant-pressure reaction process of a fixed mass, the enthalpy is constant and we can generalize the ideal gas results given previously by starting from

$$dH = 0 , \quad (9.178)$$

and considering $H = H(P, T, \mathbf{N})$ for a real gas equation of state. Expanding the derivative and using the definition of partial molar properties, we obtain

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P, \mathbf{N}} dT + \left(\frac{\partial H}{\partial P} \right)_{T, \mathbf{N}} dP + \sum_{k=1}^K \bar{H}_k dN_k . \quad (9.179)$$

Considering the time evolution of a closed, adiabatic reacting system with fixed enthalpy $dH = 0$ and pressure $dP = 0$, we obtain:

$$\frac{dT}{dt} = -\frac{1}{C_P} \sum_{k=1}^K \bar{H}_k \frac{dN_k}{dt}, \quad (9.180)$$

where the heat capacity is

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P, \mathbf{N}} \quad (9.181)$$

$$= \sum_{k=1}^K N_k \left(\frac{\partial \bar{H}_k}{\partial T} \right)_{P, N_{i \neq k}}. \quad (9.182)$$

From the definition of departure function, the enthalpy can be expressed as

$$H = H^{ig} + H^d. \quad (9.183)$$

Defining the partial molar departure function as

$$\bar{H}_k^d = \left(\frac{\partial \bar{H}^d}{\partial N_k} \right)_{T, P, N_{i \neq k}}, \quad (9.184)$$

and using the standard expression for the ideal gas enthalpy

$$H^{ig} = \sum_{k=1}^K N_k H_k^{ig}(T), \quad (9.185)$$

we obtain an expression for the coefficients in the energy equation

$$\bar{H}_k = H_k^{ig} + \bar{H}_k^d, \quad (9.186)$$

In an similar fashion we can define the molar specific heat capacity as the sum of the ideal gas value and a departure function

$$C_{p,k} = C_{p,k}^{ig} + \bar{C}_{p,k}^d, \quad (9.187)$$

$$\bar{C}_{p,k}^d = \left(\frac{\partial \bar{H}_k^d}{\partial T} \right)_{P, \mathbf{N}}. \quad (9.188)$$

To compare this result with the ideal gas expression derived previously, define the molar specific heat capacity as

$$\bar{C}_p = \frac{C_P}{N}, \quad (9.189)$$

$$= \sum_{k=1}^K X_k \bar{C}_{p,k} \quad (9.190)$$

and compute the time rate of change of the species amounts from the net molar production rates $\dot{\omega}_k$ and system volume V

$$\frac{dN_k}{dt} = V \dot{\omega}_k. \quad (9.191)$$

which can be expressed in terms of the total number of moles, N , the mass density ρ and mean molar mass \mathcal{W}

$$= N\mathcal{W}\frac{\dot{\omega}_k}{\rho} . \quad (9.192)$$

Introducing the specific heat capacity per unit mass $c_p = \bar{C}_p/\mathcal{W}$, we obtain the analog of (11.28), the ideal gas expression for an adiabatic ($\dot{q} = 0$), constant-pressure ($P = \text{constant}$) reaction

$$\frac{dT}{dt} = -\frac{1}{\rho c_p} \sum_{k=1}^K \bar{H}_k \dot{\omega}_k . \quad (9.193)$$

$$(9.194)$$

In the case of constant-pressure combustion, the temperature evolution equations for ideal gas and real gases are identical in form but the interpretation of the symbols is different as shown in Table 9.4. Mass densities and concentrations used in computing $\dot{\omega}$ also need to be computed appropriately using the compressibility factor.

Table 9.4: Correspondence between terms in the constant-pressure, adiabatic temperature evolution equation for real gas and ideal gas models.

symbol	real gas	ideal gas
\bar{H}_k	$H_k^{ig} + \bar{H}_k^d$	H_k^{ig}
\bar{C}_p	$\sum_{k=1}^K X_k C_{p,k}^{ig} + \sum_{k=1}^K X_k \bar{C}_{p,k}^d$	$\sum_{k=1}^K X_k C_{p,k}^{ig}$
ρ	$\frac{P}{ZRT}$	$\frac{P}{RT}$
$[k]$	$X_k \frac{P}{ZRT}$	$X_k \frac{P}{RT}$

The simplicity of the correspondence between ideal gas and real gas in this case is due to the use of (T, P, \mathbf{N}) as the variables and the natural role that partial molar properties plays in the expansion in these coordinates. Contrast the simplicity of this derivation with the complexity of the derivation³ in Appendix B of Tang and Brezinsky (2006) as a consequence of choosing (T, V, \mathbf{N}) as the thermodynamic state variables.

By defining the partial molar enthalpy per unit mass as

$$\bar{h}_k = \frac{\bar{H}_k}{\mathcal{W}_k} , \quad (9.195)$$

we can write the energy equation as

$$\frac{dT}{dt} = -\frac{1}{\rho c_p} \sum_{k=1}^K \bar{h}_k \mathcal{W}_k \dot{\omega}_k . \quad (9.196)$$

or

$$= -\frac{1}{c_p} \sum_{k=1}^K \bar{h}_k \frac{dY_k}{dt} . \quad (9.197)$$

³The Tang and Brezinsky result, Eq. B8, is also inconsistent with the present derivation because of an error associated with transforming derivatives when changing independent variables from (T, V, \mathbf{N}) to (T, P, \mathbf{N}) between equations B2-B6 and B8.

For an ideal gas, this is simply

$$\frac{dT}{dt} = -\frac{1}{c_p} \sum_{k=1}^K h_k \frac{dY_k}{dt} . \quad (9.198)$$

This is the form of the expression used in the `cpsys.m` and `cpsys.py` routines.

Constant volume reaction

The real-gas, constant-volume, adiabatic reactor energy equation is derived Ch. 7 of [Schmitt et al. \(1994\)](#) using the (T, P, \mathbf{N}) as the independent variables. It is instructive to carry out the derivation in (T, V, \mathbf{N}) and carry out the appropriate thermodynamic transformations to show that it is possible to obtain the identical result.

Considering the internal energy $E = E(V, T, \mathbf{N})$ for a real gas equation of state, we carry out the Taylor series expansion

$$dE = \left(\frac{\partial E}{\partial T} \right)_{V, \mathbf{N}} dT + \left(\frac{\partial E}{\partial V} \right)_{T, \mathbf{N}} dV + \sum_{k=1}^K \left(\frac{\partial E}{\partial N_k} \right)_{T, V, N_{i \neq k}} dN_k . \quad (9.199)$$

And apply the constant-volume and adiabatic conditions

$$dV = 0 , \quad (9.200)$$

$$dE = 0 , \quad (9.201)$$

to obtain the temporal evolution equation for temperature

$$\frac{dT}{dt} = -\frac{1}{\left(\frac{\partial E}{\partial T} \right)_{V, \mathbf{N}}} \sum_{k=1}^K \left(\frac{\partial E}{\partial N_k} \right)_{T, V, N_{i \neq k}} \frac{dN_k}{dt} . \quad (9.202)$$

We can identify the denominator on the right-hand side as the heat capacity at constant volume

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V, \mathbf{N}} = \sum_{k=1}^K N_k \left(\frac{\partial \bar{E}_k}{\partial T} \right)_{V, \mathbf{N}} = N \sum_{k=1}^K X_k \left(\frac{\partial \bar{E}_k}{\partial T} \right)_{V, \mathbf{N}} = N \bar{C}_V , \quad (9.203)$$

where the molar specific heat capacity is

$$\bar{C}_V = \sum_{k=1}^K X_k \left(\frac{\partial \bar{E}_k}{\partial T} \right)_{V, \mathbf{N}} \quad (9.204)$$

The numerator can be written in terms of a partial molar properties by considering $E(P, T, \mathbf{N})$, $P(V, T, \mathbf{N})$ and using the chain rule of differentiation.

$$\left(\frac{\partial E}{\partial N_k} \right)_{T, V, N_{i \neq k}} = \left(\frac{\partial E}{\partial N_k} \right)_{T, P, N_{i \neq k}} + \left(\frac{\partial E}{\partial P} \right)_{T, \mathbf{N}} \left(\frac{\partial P}{\partial N_k} \right)_{V, T, N_{i \neq k}} \quad (9.205)$$

The last term can be expressed in terms of conventional thermodynamic properties using classical thermodynamics

$$\left(\frac{\partial E}{\partial P} \right)_{T, \mathbf{N}} \left(\frac{\partial P}{\partial N_k} \right)_{V, T, N_{i \neq k}} = - \left(\frac{T\beta}{\kappa_T} - P \right) \bar{V}_k , \quad (9.206)$$

The term in parentheses represents one of the corrections due to a real gas equation of state and vanishes in the case of an ideal gas. The terms in this expression are the coefficient of thermal expansion

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P, \mathbf{N}}, \quad (9.207)$$

the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, \mathbf{N}}, \quad (9.208)$$

and the partial molar volume

$$\bar{V}_k = \left(\frac{\partial V}{\partial N_k} \right)_{T, P, N_{i \neq k}}. \quad (9.209)$$

An alternative expression for the combination of terms in parentheses can be derived from classical thermodynamics

$$\frac{T\beta}{\kappa_T} = T \left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{N}}. \quad (9.210)$$

This combination of terms can be expressed in terms of the derivative of the compressibility factor

$$T \left(\frac{\partial P}{\partial T} \right)_{V, \mathbf{N}} = P \left[1 + \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_{V, \mathbf{N}} \right]. \quad (9.211)$$

The final expression for the temperature temporal derivative is

$$\frac{dT}{dt} = -\frac{1}{N\bar{C}_V} \sum_{k=1}^K \left[\bar{E}_k - \left(\frac{T\beta}{\kappa_T} - P \right) \bar{V}_k \right] \frac{dN_k}{dt}. \quad (9.212)$$

Or in terms of the compressibility factor

$$\frac{dT}{dt} = -\frac{1}{N\bar{C}_V} \sum_{k=1}^K \left[\bar{E}_k - P \frac{T}{Z} \left(\frac{\partial Z}{\partial T} \right)_{V, \mathbf{N}} \bar{V}_k \right] \frac{dN_k}{dt}. \quad (9.213)$$

Using the same consideration as in the previous section, we can write this in terms of the net molar production rate, mass density and mass specific heat capacity at constant volume

$$\frac{dT}{dt} = -\frac{1}{\rho c_v} \sum_{k=1}^K \left[\bar{E}_k - \left(\frac{T\beta}{\kappa_T} - P \right) \bar{V}_k \right] \dot{\omega}_k. \quad (9.214)$$

This is identical to Eq. (7.17) of [Schmitt et al. \(1994\)](#). Contrast this with the ideal gas version

$$\frac{dT}{dt} = -\frac{1}{\rho c_v} \sum_{k=1}^K E_k \dot{\omega}_k, \quad (9.215)$$

$$\frac{dT}{dt} = -\frac{1}{c_v} \sum_{k=1}^K e_k \frac{dY_k}{dt} \quad (9.216)$$

The final version is the form of the expression used in the [cvsys.m](#) and [cv.py](#)

ZND model

The derivation of the ZND model equations terms of mass fraction derivatives was given previously in Section 9.2 and presented in terms of partial molar properties in [Schmitt and Butler \(1995b\)](#), the complete derivation can be found in [Schmitt \(1994\)](#). The only difference between the ideal and real gas formulations is in the computation of thermicity using in (9.81)-(9.84). A derivation of thermicity for the real gas case is given Appendix D. The result in terms of the partial molar fractions is

$$\dot{\sigma} = \sum_k \left(\frac{\mathcal{W}}{\mathcal{W}_k} \frac{\bar{V}_k}{\bar{V}} - \frac{\beta}{c_p} \frac{\bar{H}_k}{\mathcal{W}_k} \right) \frac{dY_k}{dt}. \quad (9.217)$$

Comparing this with the previous derivation (9.32) and equating corresponding terms, we find that

$$\frac{\mathcal{W}}{\mathcal{W}_k} \frac{\bar{V}_k}{\bar{V}} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial Y_k} \right)_{P,T,Y_{i \neq k}}, \quad (9.218)$$

$$\frac{\beta}{c_p} \frac{\bar{H}_k}{\mathcal{W}_k} = \frac{\beta}{c_p} \left(\frac{\partial h}{\partial Y_k} \right)_{P,T,Y_{i \neq k}}. \quad (9.219)$$

Direct computation of the quantities on the right-hand side is facilitated by using the transformation $dN_K = M dY_k / \mathcal{W}_k$ to obtain the relationship between PMP of an extensive property B and the corresponding mass specific property $b = B/M$

$$\bar{B}_k = \left(\frac{\partial B}{\partial N_k} \right)_{P,T,N_{i \neq k}} = \mathcal{W}_k \left(\frac{\partial b}{\partial Y_k} \right)_{T,P,Y_{i \neq k}}; \quad (9.220)$$

$$(9.221)$$

Using this transformation verifies that the mass and mole based expressions for the terms in thermicity are equivalent.

From the definition of the compressibility factor, we can express the first term in the thermicity using the partial molar derivative of Z

$$\frac{\bar{V}_k}{\bar{V}} = 1 + \frac{1}{Z} \bar{Z}_k. \quad (9.222)$$

The second term in the sum has three components, c_p , β , \bar{H}_k , all of which will have departure from ideal gas values due to real gas effects. The effects on specific heat capacity and enthalpy require detailed computation using the departure functions, while the effect on thermal expansion coefficient can be computed from the compressibility

$$\beta = \frac{1}{T} + \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_{P,Y} \quad (9.223)$$

$$(9.224)$$

The real gas thermicity expression reduces to the ideal gas version (9.33) in the limit of $Z \rightarrow 1$ with the following correspondence between ideal and real gas quantities.

The evolution of temperature for the ZND model of a real gas can be computed using the ZND model equations for P (9.82), ρ (9.81) and (9.176). The result is

$$\frac{dT}{dt} = \frac{1}{\beta} \left[\frac{1 - \gamma M^2}{\eta} \dot{\sigma} - \sum_k \frac{\bar{V}_k}{\bar{V}} \frac{\mathcal{W}}{\mathcal{W}_k} \frac{dY_k}{dt} \right] \quad (9.225)$$

Table 9.5: Correspondence between terms in the thermicity expression for real gas and ideal gas models.

symbol	real gas	ideal gas
\bar{H}_k	$H_k^{ig} + \bar{H}_k^d$	H_k^{ig}
\bar{C}_P	$\sum_{k=1}^K X_k C_{P,k}^{ig} + \sum_{k=1}^K X_k \bar{C}_{P,k}^d$	$\sum_{k=1}^K X_k C_{P,k}^{ig}$
β	$\frac{1}{T} + \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_{P, \mathbf{Y}}$	$\frac{1}{T}$
$\frac{\bar{V}_k}{\bar{V}}$	$1 + \frac{1}{Z} \bar{Z}_k$	1

Chapter 10

Reactions and Reaction Rates

Chemical reaction rates in gases are determined from a network of reactions and associated reaction rates which are assembled into a *reaction mechanism*. The types of individual reactions and empirical rate descriptions are described as is the computation of net reaction rates for each species within the reaction network. The concept of detailed balance is introduced to relate forward and reverse reactions to equilibrium constants.

The time rate of the change of each species mass density $\rho_i = Y_i \rho$ is determined by the mass source term $\mathcal{W}_i \dot{\omega}_i$ on the right-hand side of the species equations (9.21). The fluid motion is coupled to the chemical reaction through the thermicity (9.33) which can be written as a sum of terms, each of which is proportional to the time rate of change of the species mass fraction. The source term for (9.21) has units of mass (of species i) per unit time per unit volume of the gas. The term is written as the product of the molar mass \mathcal{W}_i and the molar source term ω_i , which traditionally is specified in units of $\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$. The terminology of chemical reactions and reaction rates is a legacy of chemistry and chemical engineering which measure the quantity of substance in terms of moles and the concentration in terms of moles per unit volume (the concentration of species A is written $[A]$) in usually given in legacy units of $\text{mol}\cdot\text{cm}^{-3}$. The key to computing a chemically reacting flow is to have a prescription for computing the source term.

In order to compute the source term, we need to select a set of species, a reaction mechanism and associated reaction rates. Only *elementary* reactions, that is, physically plausible reactions mediated by molecular collisions, are of interest for detailed reaction modeling. These come in three varieties: uni-molecular, bi-molecular and ter-molecular; see Laidler (1987) for an introduction to chemical kinetics and the theory of reaction rates.

10.1 Unimolecular reactions

Unimolecular is a term that is used to describe a reaction that appears to obey *first order* rate laws, that is, the rate of disappearance of the reactant is proportional to the amount of reactant. For example, an initial step of the decomposition of the explosive molecule nitromethane under high pressure conditions is the thermal decomposition which can be expressed as



and if rate of reaction is k_∞ , the rate of disappearance of nitromethane can be expressed as

$$\frac{d[\text{CH}_3\text{NO}_2]}{dt} = -k_\infty[\text{CH}_3\text{NO}_2] \quad (10.1)$$

This reaction, like many other reactions that appear to be unimolecular, actually depend on bimolecular collisions to provide the energy to overcome the bonding that stabilizes the molecule (the activation energy for this reaction is 58.5 kcal/mol), and create an excited state that decomposes into the observed products. When the collisions are sufficiently rapid compared to the rate of decomposition, decomposition is the limiting or rate-controlling step and the pressure does not appear explicitly in the rate law. As the pressure

is decreased and collisions become rarer, the collisions are the rate limiting step and the collisions with the other molecules (denoted M) in the gas need to be explicitly taken account of in the reaction



and the rate of disappearance of nitromethane depends on pressure ($P = [\text{M}]\mathcal{R}T$).

$$\frac{d[\text{CH}_3\text{NO}_2]}{dt} = -k_o[\text{CH}_3\text{NO}_2][\text{M}] \quad (10.2)$$

The transition from unimolecular to bimolecular with decreasing pressure is a general situation that occurs with reactions that appear uni-molecular at high pressure and are truly elementary.¹ The representation of these reaction rates for use in comprehensive combustion models requires measuring or estimating the high-pressure (k_∞) and low-pressure (k_o) rate constants and an interpolating function of pressure and temperature that fits the intermediate data. The meaning of high and low pressure as well as the interpolating function are discussed subsequently in Section 10.3.

True unimolecular reactions can occur due to the spontaneous emission or absorption of photons. These are relevant to predicting optical emission and absorption or photochemical initiation of combustion. Some examples that are important in high-temperature gas dynamics and combustion of the decay of an excited atomic or molecular electronic state and the emission of a photon are:



with emission in a band between 305-315 nm.



with emission in a band between 425-435 nm.



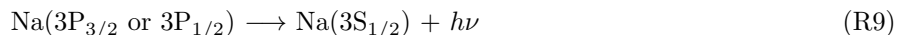
with emission in a band between 405-415 nm.



with emission in a band between 465-475 nm, part of the *Swan bands*.



with emission in the *gamma* band between 180-270 nm.



with emission in two adjacent lines (termed the D-doublet or D-lines) at 588.995 and 589.5924 nm. Although sodium is sometimes deliberately introduced into flows, it is a ubiquitous contaminant and the D-lines are prominent in high-temperature gas spectra.

The rate of disappearance of an excited state, generically written as A^* , is proportional to the amount of that state.

$$\frac{d[\text{A}^*]}{dt} = -k_{rad}[\text{A}^*]. \quad (10.3)$$

In the context of transitions between two quantum states, from a single upper level to lower level, the constant k_{rad} is known as the Einstein A-coefficient. In the absence of competing processes, k_{rad} is the inverse of the excited state radiative lifetime

$$k_{rad} = \frac{1}{\tau_{rad}}. \quad (10.4)$$

¹There are many empirical models of reactions, particularly of explosives, which are modeled as uni-molecular but these are approximations of composite molecular processes not true elementary reactions.

The order of magnitude of the radiative life time is 10^{-6} s for OH^* and NO^* , and 10^{-8} s for Na^* . The quantity $k_{\text{rad}}[\text{A}^*]$ is the number of photons emitted per second and for a single frequency emission, each photon will have energy $h\nu$. The spontaneous emission of photons occurs uniformly in all directions so that the energy emission rate J per unit volume and unit solid angle is given by

$$J = \frac{1}{4\pi} h\nu k_{\text{rad}}[\text{A}^*] \quad \text{W} \cdot \text{sr}^{-1} \quad (10.5)$$

Comprehensive models [Hanson et al. \(2016\)](#), [Zel'dovich and Raizer \(1966\)](#) of radiative emission in high-temperature gases requires considering the competing processes of creation and destruction of the excited species as well as the absorption and re-emission that occurs during the transport of radiation through the surrounding gas. Additional reaction processes include the production of excited species by recombination of atoms or bimolecular reactions, and nonradiative transitions or quenching due to collisions. The most sophisticated models consider the manifold of electronic and molecular states and all the possible transitions between these states in order to predict the wavelength dependence of emission.

10.2 Bi-molecular or two-body reactions

Bi-molecular reactions involve the collision of two reactant molecules to produce two distinct reactant molecules. In the following example (considered the most important reaction in combustion) the reactants are H and O_2 and the products are OH and O.



These form the majority of the reactions considered in detailed reaction mechanisms. These reactions rearrange or shuffle the atoms but do not decrease or increase the number of molecules in the system. Energy will be released or absorbed depending on the heat of reaction. The molar rates of creation of the products are equal because each reaction between an H and an O_2 will always create an OH and one O. The rates of reactions associated with the reaction (R10) are:

$$\frac{d[\text{OH}]}{dt} = \frac{d[\text{O}]}{dt} \quad (10.6)$$

$$= -\frac{d[\text{H}]}{dt} \quad (10.7)$$

$$= -\frac{d[\text{O}_2]}{dt} \quad (10.8)$$

For bi-molecular reactions, the rate of reaction is equal to the collision rate between the molecules times the probability of a reactive collision. This can be expressed a reaction rate constant times the product of the molar concentration of the reactants. For the reaction (R10), the rate constant is k_f with the subscript indicating the *forward* reaction proceeding from left to right.

$$\frac{d[\text{OH}]}{dt} = k_f [\text{H}][\text{O}_2] \quad (10.9)$$

The rate constant for a mixture in local thermodynamic equilibrium is only a function of the temperature and is conventionally parameterized and fit to the modified Arrhenius form.

$$k = AT^n \exp(-E/\mathcal{R}T), \quad (10.10)$$

where the pre-exponential A , temperature exponent n , and the activation energy E are theoretically or experimentally determined constants.

Elementary reactions can always proceed in either the forward direction(10) or in the reverse direction



and the associated reaction rate is k_r . The rates of reaction associated with (R11) are:

$$\frac{d[H]}{dt} = \frac{d[O_2]}{dt} \quad (10.11)$$

$$= -\frac{d[OH]}{dt} \quad (10.12)$$

$$= -\frac{d[O]}{dt} \quad (10.13)$$

$$= k_r[OH][O] \quad (10.14)$$

The forward and reverse reactions together are usually written as a single reaction equation with double arrows



The *net* reaction rate is the difference between the contributions of the forward and reverse rates, for (R12), these are:

$$\frac{d[OH]}{dt} = k_f[H][O_2] - k_r[OH][O], \quad (10.15)$$

$$\frac{d[O]}{dt} = k_f[H][O_2] - k_r[OH][O], \quad (10.16)$$

$$\frac{d[H]}{dt} = -k_f[H][O_2] + k_r[OH][O], \quad (10.17)$$

$$\frac{d[O_2]}{dt} = -k_f[H][O_2] + k_r[OH][O]. \quad (10.18)$$

The forward and reverse reactions generally proceed at very different rates due to the distinct dependence of the forward and reverse rate constants on temperature as well as the concentration of the species in the gas mixture. Setting aside the obvious effect of concentrations on reaction rates, the differences in rate constants reflects the relative size of the energy barriers (measured by the magnitude of the activation energy) and the probability of a geometrically favorable collision. Many elementary reactions actually go through a series of intermediate steps which have been averaged over to arrive at a reaction rate. For example, (R10) proceeding through the creation of an intermediate complex HO_2^* of the H and O_2 molecules,



which is actually in a potential well (lower energy) compared to both products and reactants (180 kJ/mol lower) (Melius and Blint, 1979, Miller, 1981, Quémener et al., 2010, Guo, 2012). The overall reaction is endothermic, with an enthalpy change of about +70 kJ/mol, which is consistent with the activation energy inferred from the measured reaction rate temperature dependence.

Forward and reverse rates are determined in separate measurements and for combustion reactions, there has been a multi-decade collective effort (Gardiner, 1984, Baulch et al., 1992, 1994, 2005) to evaluate these measurements and make consensus recommendations for rates. The measured rates for (R10) are shown in Fig. 10.1. Baulch et al. (2005) recommend a reaction rate of $3.43 \times 10^{-10} T^{-0.097} \exp(-7560/T)$ in units of $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ for (R10) over the range 800-3500 K. Note the use of alternate units in the rate, the units can be converted to the convention most often used in Cantera (length = cm, time = s, quantity = mol, activation energy = cal/mol) using the Avogadro number $6.02214 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}$ and energy equivalence $1.9872 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. For reaction (11), Baulch et al. (2005) recommend a reaction rate of $2.0 \times 10^{-10} T^{-0.352} \exp(113/T)$ over the range 250-3000 K.

Although the forward and reverse reaction rates can be independently measured and specified for an elementary reaction, these rates may not be consistent with thermodynamic equilibrium. In equilibrium, the net rate of reaction vanishes for all species. For our example reaction,

$$\frac{d[OH]}{dt} = \frac{d[O]}{dt} = \frac{d[H]}{dt} = \frac{d[O_2]}{dt} = 0, \quad (10.19)$$

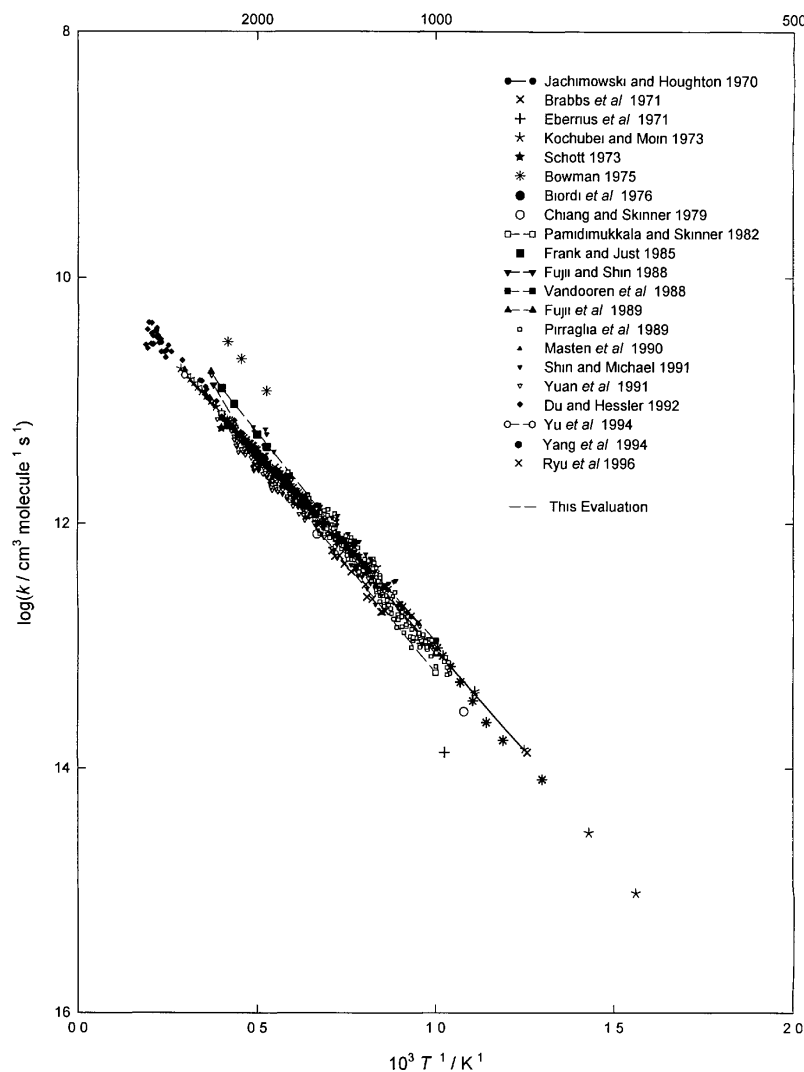


Figure 10.1: Measured reaction rates for $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ from [Baulch et al. \(2005\)](#).

which implies that

$$0 = k_f[\text{H}]_{eq}[\text{O}_2]_{eq} - k_r[\text{OH}]_{eq}[\text{O}]_{eq}, \quad (10.20)$$

or

$$\frac{[\text{OH}]_{eq}[\text{O}]_{eq}}{[\text{H}]_{eq}[\text{O}_2]_{eq}} = \frac{k_f}{k_r}. \quad (10.21)$$

The left-hand side is known as the concentration *equilibrium constant*

$$K_c \equiv \left(\frac{[\text{OH}][\text{O}]}{[\text{H}][\text{O}_2]} \right)_{eq}, \quad (10.22)$$

and can be computed from thermodynamic data for each of the species (Denbigh, 1981, Sec. 4.4).

$$K_c = \frac{\exp\left(-\frac{\Delta G^\circ(T)}{\mathcal{R}T}\right)}{(\mathcal{R}T)^{\Delta\nu}}. \quad (10.23)$$

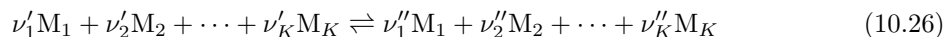
The argument of exponential is the net change in the pressure-independent portion of the molar Gibbs energy $G^\circ = H - TS^\circ$. For set of K species, this change is defined as

$$\Delta G^\circ = \sum_{k=1}^K \nu_k (H_k - TS_k^\circ) \quad (10.24)$$

where

$$\nu_k = \nu_k'' - \nu_k' \quad \text{and} \quad \Delta\nu = \sum_{k=1}^K \nu_k. \quad (10.25)$$

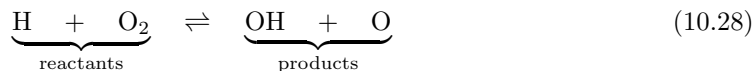
The *stoichiometric coefficients* ν_k' for reactants and ν_k'' for products are the species numeric multipliers in the equilibrium relationship or corresponding reaction equation of interest when written symbolically in terms of the species M_k as



or more concisely

$$\sum_{k=1}^K \nu_k' M_k \rightleftharpoons \sum_{k=1}^K \nu_k'' M_k. \quad (10.27)$$

The ν_k' and ν_k'' are either zero or positive integers for elementary reactions. In the case of the reaction (R12), the equilibrium relation is



and the stoichiometric coefficients are

$$\nu_{\text{H}}' = +1 \quad \nu_{\text{H}}'' = 0 \quad (10.29)$$

$$\nu_{\text{O}_2}' = +1 \quad \nu_{\text{O}_2}'' = 0 \quad (10.30)$$

$$\nu_{\text{OH}}' = 0 \quad \nu_{\text{OH}}'' = +1 \quad (10.31)$$

$$\nu_{\text{O}}' = 0 \quad \nu_{\text{O}}'' = +1 \quad (10.32)$$

The net change $\Delta\nu$ is zero for bimolecular reactions and non-zero for unimolecular or ter-molecular reactions. The stoichiometric coefficients can be used to more compactly express the relationships between changes in species amounts due to a reaction or shift in equilibrium by defining the net change in species i as $\nu_i = \nu_i'' - \nu_i'$. The net reaction rates normalized by ν_i are known as the *rate of progress* q and are identical for all species in the reaction

$$\frac{1}{\nu_1} \frac{d[M_1]}{dt} = \frac{1}{\nu_2} \frac{d[M_2]}{dt} = \cdots = \frac{1}{\nu_K} \frac{d[M_K]}{dt} = q = k_f \prod_{k=1}^K [M_k]^{\nu_k'} - k_r \prod_{k=1}^K [M_k]^{\nu_k''}. \quad (10.33)$$

For bimolecular reactions, the concentration equilibrium constant K_c is identical to the partial pressure equilibrium constant

$$K_p(T) = \exp\left(-\frac{\Delta G^\circ(T)}{\mathcal{R}T}\right) \quad (10.34)$$

$$= \prod_{k=1}^K (P_k)_{eq}^{\nu_k} . \quad (10.35)$$

where $P_{k,eq} = X_{k,eq}P$ is the equilibrium partial pressure of species k .

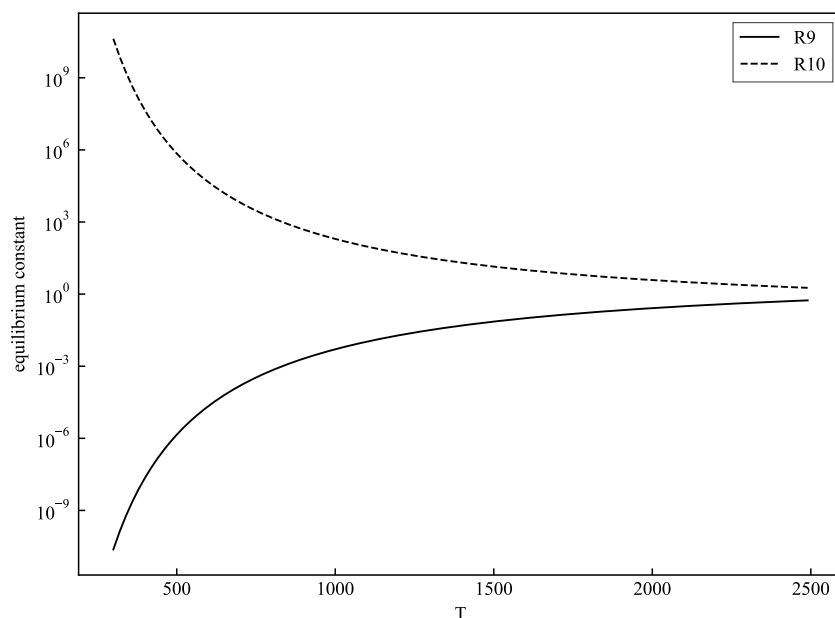


Figure 10.2: Equilibrium constants K_p for the forward and reverse reactions of $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$.

To avoid thermodynamic inconsistency, combustion modelers typically only specify either the forward or reverse rate and compute the other rate from the equilibrium relation, for example if the forward rate is specified, the reverse rate is computed as

$$k_r = \frac{k_f}{K_c} . \quad (10.36)$$

This is the case for almost all of the reaction mechanisms supplied with the SDToolbox. The choice of which direction to use as the reference reaction for specifying the rate often depends on which has been measured or estimated more reliably. For example, as shown in Fig. 10.1 there are extensive measurements over a wide temperature range for (R10) but measurements for (R11) are only available for temperatures less than 500 K. The reverse rate has been fit to an expression which is consistent at high temperatures with (10.36) as shown in Figure 10.3. At room temperature, the estimated rate k_f/K_c is almost 5 times larger than the recommended rate of Baulch et al. but within 20% for temperatures between 800 and 3000 K, which is the range of interest in most combustion situations.

10.3 Ter-molecular or three-body reactions

As discussed in the introduction, there are many reaction processes which require collisions with other gas molecules in order to create a reaction pathway to the products. These collisions either serve to add sufficient energy to overcome an energy barrier or stabilize a product molecular by removing energy. At sufficiently