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## **Combustion modeling**

1. Introduction to governing equations thermodynamics, kinetics and transport properties

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# References

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## 1. Governing equations for reactive flows

- a) Continuity and momentum
- b) Species (including models for diffusion velocities)
- c) Energy (enthalpy and temperature formulations)

## 2. Thermodynamic data, kinetics, and transport properties

- a) Thermodynamics and NASA polynomials
- b) Kinetics: stoichiometry, reaction rates, formation rates
- c) Transport properties: viscosity, thermal conductivity, diffusion coefficients, mixture-averaged properties, fitting

## 3. The CHEMKIN<sup>®</sup> standard

- a) Introduction
- b) Thermodynamic data
- c) Kinetics
- d) Transport properties

## 1. Governing equations for reactive flows

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# Continuity equation

We begin from the continuity equation, corresponding to the conservation of mass [Bird2007, Kee2017]:

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

$\nabla \cdot (\rho \mathbf{u})$       Divergence of momentum flux

$$\nabla \cdot (\rho \mathbf{u}) = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \quad \text{Cartesian coordinates}$$

$$\nabla \cdot (\rho \mathbf{u}) = \frac{\partial u_i}{\partial x_i} \quad \text{Einstein's notation (summation implied)}$$

# Material (or Lagrangian) derivative

The continuity equation can be recast by introducing the Material or Lagrangian derivative [Bird2007, Kee2017]:

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

$$\frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho + \rho \nabla \cdot \mathbf{u} = 0$$

$$\frac{D\rho}{Dt} \stackrel{\text{def}}{=} \frac{\partial \rho}{\partial t} + \mathbf{u} \cdot \nabla \rho$$

Material or Lagrangian derivative

$$\boxed{\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{u} = 0}$$

Continuity equation



# Momentum equations (I)

The momentum equation for a variable density, variable properties, Newtonian fluid reads as follows [Bird2007, Kee2017]:

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla \cdot \mu \left( \nabla \mathbf{u} + \nabla \mathbf{u}^T - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right) + \rho \mathbf{g}$$

By introducing the material derivative:

$$\rho \frac{D\mathbf{u}}{Dt} + \rho \mathbf{u} \otimes \nabla \mathbf{u} = -\nabla p + \nabla \cdot \mu \left( \nabla \mathbf{u} + \nabla \mathbf{u}^T - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right) + \rho \mathbf{g}$$

The equation is a vector equation for three components

# Momentum equations (II)

The operators are specific to the coordinate reference system. For example, for Cartesian coordinates:

$$\mathbf{u} \otimes \mathbf{u} = (u_x, u_y, u_z)^T (u_x, u_y, u_z) = \begin{pmatrix} u_x u_x & u_x u_y & u_x u_z \\ u_y u_x & u_y u_y & u_y u_z \\ u_z u_x & u_z u_y & u_z u_z \end{pmatrix}$$

$$\nabla \mathbf{u} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)^T (u_x, u_y, u_z) = \begin{pmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_y}{\partial x} & \frac{\partial u_z}{\partial x} \\ \frac{\partial u_x}{\partial y} & \frac{\partial u_y}{\partial y} & \frac{\partial u_z}{\partial y} \\ \frac{\partial u_x}{\partial z} & \frac{\partial u_y}{\partial z} & \frac{\partial u_z}{\partial z} \end{pmatrix}$$



# Species mass conservation

The conservation equations for species are typically written in terms of mass fractions [Bird2007, Kee2017]:

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{u}_i Y_i) = \dot{\Omega}_i$$

where  $\rho \mathbf{u}_i Y_i$  is the total mass flux of species  $i$

The velocity  $\mathbf{u}_i$  is the sum of two components: the mass-averaged bulk velocity  $\mathbf{u}$  and the diffusion velocity  $\mathbf{u}_i^d$ :

$$\mathbf{u}_i = \mathbf{u} + \mathbf{u}_i^d \quad \text{where } \mathbf{u} \stackrel{\text{def}}{=} \sum \mathbf{u}_i Y_i$$

Since the sum of mass fractions is by definition equal to 1, we have:

$$\sum \mathbf{u}_i^d Y_i = 0$$

# Mass conservation

The conservation equations for species can be summed over all the species to recover the continuity equation:

$$\sum \left\{ \frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{u}_i Y_i) - \dot{\Omega}_i \right\} = 0$$

$$\left\{ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right\} + \sum \{ \nabla \cdot (\rho \mathbf{u}_i^d Y_i) - \dot{\Omega}_i \} = 0$$

$$\left\{ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right\} + \cancel{\nabla \cdot \left( \rho \sum \mathbf{u}_i^d Y_i \right)} - \cancel{\sum \dot{\Omega}_i} = 0$$

This result has important computational implications because the conservation equations for mass fractions of individual species maintain consistency with the continuity equation by virtue of the definition of the diffusion velocities [Bisetti2015]

# Closures for diffusion velocities

Let us now expand the conservation equations for individual species:

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{u}_i Y_i) - \dot{\Omega}_i = \frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_i) + \nabla \cdot (\rho \mathbf{u}_i^d Y_i) - \dot{\Omega}_i = 0$$

After considering the continuity equation:

$$\rho \frac{\partial Y_i}{\partial t} + \rho \mathbf{u} \cdot \nabla Y_i = -\nabla \cdot (\rho \mathbf{u}_i^d Y_i) + \dot{\Omega}_i$$

We need a closure equation for the diffusion velocity. In combustion there exist several options, with different levels of detail/accuracy:

- Stefan-Maxwell equations
- Fick's law
- Constant Lewis' number
- Hirschfelder-Curtiss approximation

# The Stefan-Maxwell equations (I)

The Stefan-Maxwell equations provide the most accurate description of mass diffusion. If the contributions of pressure, body forces, and Soret effects are neglected, we have:

$$\nabla X_i = \sum \frac{X_i X_j}{\mathcal{D}_{ij}} (\mathbf{u}_i^d - \mathbf{u}_j^d)$$

$X_i$  is the mole fraction of species  $i$

$\mathcal{D}_{ij}$  are the binary diffusivities calculated using the Chapman-Enskog kinetic theory of gases

# The Stefan-Maxwell equations (II)

The Stefan-Maxwell equations are usually not applied in numerical codes because of their large computational cost. Indeed they are implicit equations, requiring the solution of a linear system of  $3N$  equations (in each point of the computational domain), where  $N$  is the number of species [Kee2017].

As an example, in case of  $N = 3$  species, the linear system to be solved at each grid point, every time is:

$$\begin{pmatrix} \frac{X_1 X_2}{\mathcal{D}_{12}} + \frac{X_1 X_3}{\mathcal{D}_{13}} & -\frac{X_1 X_2}{\mathcal{D}_{12}} & -\frac{X_1 X_3}{\mathcal{D}_{13}} \\ -\frac{X_1 X_2}{\mathcal{D}_{12}} & \frac{X_1 X_2}{\mathcal{D}_{12}} + \frac{X_2 X_3}{\mathcal{D}_{23}} & -\frac{X_2 X_3}{\mathcal{D}_{23}} \\ -\frac{X_1 X_3}{\mathcal{D}_{13}} & -\frac{X_2 X_3}{\mathcal{D}_{23}} & \frac{X_1 X_3}{\mathcal{D}_{13}} + \frac{X_2 X_3}{\mathcal{D}_{23}} \end{pmatrix} \begin{pmatrix} \mathbf{u}_1^d \\ \mathbf{u}_2^d \\ \mathbf{u}_3^d \end{pmatrix} = \begin{pmatrix} \nabla X_1 \\ \nabla X_2 \\ \nabla X_3 \end{pmatrix}$$

# The Fick's law

If we set equal values for all binary diffusivities, i.e.  $\mathcal{D}_{ij} = \mathcal{D}$ , it can be shown that the Stefan-Maxwell equations reduce to the Fick's law for every species [Kee2017]:

$$\mathbf{u}_i^d = -\mathcal{D} \frac{\nabla Y_i}{Y_i}$$

In particular, after substituting the Fick's law into the conservation equations for species, we have:

$$\rho \frac{\partial Y_i}{\partial t} + \rho \mathbf{u} \cdot \nabla Y_i = \nabla \cdot (\rho \mathcal{D} \nabla Y_i) + \dot{\Omega}_i$$

Obviously, the closure reported above is consistent with the continuity equation:

$$\sum \mathbf{u}_i^d Y_i = -\sum \mathcal{D} \nabla Y_i = -\mathcal{D} \nabla \sum Y_i = 0$$

# Hirschfelder-Curtiss approximation (I)

The rigorous solution of the linear equations corresponding to the Stefan-Maxwell approach can be replaced by the Hirschfelder-Curtiss approximation:

$$\mathbf{u}_i^d X_i = -\mathcal{D}_i \nabla X_i$$

where:

$$\mathcal{D}_i = \frac{1 - Y_i}{\sum_{j \neq i} \frac{X_j}{\mathcal{D}_{ij}}}$$

The diffusion fluxes become:

$$\rho \mathbf{u}_i^d Y_i = -\rho \mathcal{D}_i \frac{Y_i}{X_i} \nabla X_i = -\rho \mathcal{D}_i Y_i \frac{\nabla(WX_i)}{W} = -\rho \mathcal{D}_i \nabla Y_i - \rho \mathcal{D}_i Y_i \frac{\nabla W}{W}$$



# Hirschfelder-Curtiss approximation (II)

In particular, after substituting the Fick's law into the conservation equations for species, we have:

$$\rho \frac{\partial Y_i}{\partial t} + \rho \mathbf{u} \cdot \nabla Y_i = \nabla \cdot (\rho \mathcal{D}_i \nabla Y_i) + \nabla \cdot \left( \rho \mathcal{D}_i Y_i \frac{\nabla W}{W} \right) + \dot{\Omega}_i$$

In addition to the Fickian term  $\rho \mathcal{D}_i \nabla Y_i$  there is an additional term  $\rho \mathcal{D}_i Y_i \frac{\nabla W}{W}$  which is often neglected

The Hirschfelder-Curtiss approximation does not necessarily imply the closure of diffusion fluxes. It may be tempting to simply correct the mass fractions to sum to unity periodically during the integration of the reactive Navier-Stokes equations. This is often a “bad idea” that may lead to unexpected solution behavior, and convergence issues [Bisetti2015].

# Constant Lewis' number

The Hirschfelder-Curtiss model can be simplified by letting  $\mathcal{D}_i = \frac{\mathcal{D}}{Le_i}$ , where  $Le_i$  is the species Lewis' number  $Le_i = \frac{\alpha}{\mathcal{D}} = \frac{\lambda}{\rho C_P \mathcal{D}_i}$ . The diffusion fluxes become:

$$\rho \mathbf{u}_i^d Y_i = -\rho \mathcal{D}_i \frac{Y_i}{X_i} \nabla X_i = -\rho \frac{\mathcal{D}}{Le_i} \nabla Y_i - \rho \frac{\mathcal{D}}{Le_i} Y_i \frac{\nabla W}{W}$$

In many computational codes, the Lewis' number is kept constant throughout the computational domain

Species	H2O	CH4	N2	CO	O2	CO2	H	O	OH
Le	1.055	1.260	1.436	1.414	1.424	1.737	0.228	0.906	0.924

# Implications for mass conservation (I)

Regardless of the definition of  $\mathcal{D}_i$ , the Hirschfelder-Curtiss model does not ensure, in general, the closure of diffusion fluxes, i.e.  $\sum \mathbf{u}_i^d Y_i \neq 0$

This leads to the artificial production or consumption of total mass, which needs to be avoided. A widely adopted remedy is to enforce mass conservation by correcting the velocity  $\mathbf{u}$  with  $\mathbf{u}^c$ :

$$\rho \frac{\partial Y_i}{\partial t} + \rho(\mathbf{u} + \mathbf{u}^c) \cdot \nabla Y_i = -\nabla \cdot (\rho \mathbf{u}_i^d Y_i) + \dot{\Omega}_i$$

The correction velocity can be easily calculated:

$$\begin{aligned} \mathbf{u}^c &= -\sum \mathbf{u}_i^d Y_i = \sum \mathcal{D}_i \frac{Y_i}{X_i} \nabla X_i = \sum \mathcal{D}_i \frac{W_i}{W} \nabla X_i = \sum \mathcal{D}_i \frac{\nabla(Y_i W)}{W} \\ &= \sum \mathcal{D}_i Y_i \frac{\nabla W}{W} + \sum \mathcal{D}_i \nabla Y_i \end{aligned}$$

# Implications for mass conservation (II)

- Adding the correction velocity  $\mathbf{u}^c$  to a reactive flow solver that uses explicit time integration is very simple and effective. However, in case of an implicit time solver, the adoption of the correction velocity is more complicated, because where  $\mathbf{u}^c$  introduces a direct coupling among convective and diffusive fluxes [Bisetti2015]
- The expression for the correction velocity is a function of the model used for the diffusive velocity, so one needs to be careful in actual implementations.
- Mass conservation bears important implications on enthalpy (i.e., energy) conservation, since mass transport implies transport of heat of formation.

# Enthalpy equation (I)

Under the assumption of negligible viscous heating effects, negligible external heat sources and assuming that the same external force (e.g. gravity) acts upon all the species, the transport equation for the mixture's enthalpy per unit mass is [Bisetti2015, Kee2017]:

$$\rho \frac{\partial h}{\partial t} + \rho \mathbf{u} \cdot \nabla h = -\nabla \cdot \mathbf{q} + \frac{Dp}{Dt}$$

The enthalpy per unit mass for a mixture of ideal gases appearing in the equation above is defined as:

$$h(T, \mathbf{Y}) = \sum h_i(T) Y_i$$

The heat flux  $\mathbf{q}$  for multicomponent mixture is the sum of two contributions, one associated to the thermal conduction and one associated to the mass diffusion fluxes:

$$\mathbf{q} = -\lambda \nabla T + \rho \sum h_i(T) Y_i \mathbf{u}_i^d$$

In order to enforce strict energy conservation, consistency between the conservation equations for species and the enthalpy equation, must be ensured, by selecting a proper and consistent definition of the term  $\nabla \cdot \mathbf{q}$  and diffusion velocities  $\mathbf{u}_i^d$

# Enthalpy equation with Fick's law

If Fick's law  $\mathbf{u}_i^d = -\mathcal{D} \frac{\nabla Y_i}{Y_i}$  is accounted for, the heat flux becomes:

$$\mathbf{q} = -\lambda \nabla T - \rho \mathcal{D} \sum h_i(T) \nabla Y_i$$

Upon substitution into the enthalpy equation, we obtain:

$$\rho \frac{\partial h}{\partial t} + \rho \mathbf{u} \cdot \nabla h = \frac{Dp}{Dt} + \nabla \cdot (\lambda \nabla T) + \nabla \cdot \left( \rho \mathcal{D} \sum h_i \nabla Y_i \right)$$



# Canonical enthalpy equation

An additional simplification consists in assuming that  $\lambda = \rho \mathcal{D} C_p$ :

$$\rho \frac{\partial h}{\partial t} + \rho \mathbf{u} \cdot \nabla h = \frac{Dp}{Dt} + \nabla \cdot (\rho \mathcal{D} C_p \nabla T) + \nabla \cdot \left( \rho \mathcal{D} \sum h_i \nabla Y_i \right) = \frac{Dp}{Dt} + \nabla \cdot (\rho \mathcal{D} \nabla h)$$

This results into the canonical conservation equation for the enthalpy:

$$\rho \frac{\partial h}{\partial t} + \rho \mathbf{u} \cdot \nabla h = \frac{Dp}{Dt} + \nabla \cdot (\rho \mathcal{D} \nabla h)$$

Special attention must be posed in using the equation above, since it is the result of a series of simplifications, including those on mass transport of species.

# The importance of enthalpy equation

There are combustion applications where the system's behavior is controlled by chemical kinetics, which is very sensitive to temperature, and lack of enthalpy conservation results in subtle changes in temperature and system behavior!

Furthermore, **enthalpy conservation** can (and should!) be checked when implementing or using a new numerical combustion code [Bisetti2015].

# The temperature transport equation (I)

The temperature is not a conserved variable. However, it is often convenient to replace the enthalpy equation with an equivalent equation for temperature, especially in the context of low Mach number approximation [Kee2017].

Let us start from the definition of enthalpy per unit of mass of an ideal mixture of gases:

$$h(T, Y) = \sum h_i(T) Y_i$$

By applying the chain rule to the material derivative, we have:

$$\rho \frac{Dh}{Dt} = \rho C_P \frac{DT}{Dt} + \rho \sum h_i \frac{DY_i}{Dt}$$


# The temperature transport equation (II)

Substituting the derivative of enthalpy in the enthalpy equation, we have:

$$\rho \frac{Dh}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T - \nabla \cdot \left( \rho \sum h_i(T) Y_i \mathbf{u}_i^d \right)$$

$$\rho C_p \frac{DT}{Dt} + \rho \sum h_i \frac{DY_i}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T - \nabla \cdot \left( \rho \sum h_i(T) Y_i \mathbf{u}_i^d \right)$$

$$\rho C_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T - \sum h_i \rho \frac{DY_i}{Dt} - \nabla \cdot \left( \sum h_i(T) \rho Y_i \mathbf{u}_i^d \right)$$


$$\rho \frac{DY_i}{Dt} = -\nabla \cdot (\rho \mathbf{u}_i^d Y_i) + \dot{\Omega}_i$$

Conservation of  
species

# The temperature transport equation (III)

After substituting the equation of conservation of species:

$$\rho C_P \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T + \sum h_i \nabla \cdot (\rho \mathbf{u}_i^d Y_i) - \sum h_i \dot{\Omega}_i - \nabla \cdot \left( \sum h_i(T) \rho Y_i \mathbf{u}_i^d \right)$$

The sum of the two blue terms can be also rewritten as:

$$\sum h_i \nabla \cdot (\rho \mathbf{u}_i^d Y_i) - \nabla \cdot \left( \sum h_i(T) \rho Y_i \mathbf{u}_i^d \right) = - \sum \rho \mathbf{u}_i^d Y_i \cdot \nabla h_i = - \sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T$$

Thus:

$$\rho C_P \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T - \sum h_i \dot{\Omega}_i - \sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T$$

Where  $-\sum h_i \dot{\Omega}_i$  is defined as the reaction heat  $\dot{Q}$

# The temperature transport equation (IV)

The temperature transport equation is then:

$$\rho C_P \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T + \dot{Q} - \sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T$$

- The  $\frac{Dp}{Dt}$  term reflects the effect of pressure changes on the enthalpy
- The  $\nabla \cdot \lambda \nabla T$  is a classic diffusive term
- The reaction heat  $\dot{Q} = -\sum h_i \dot{\Omega}_i$  represents the change of temperature due to the reactions
- The last term  $-\sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T$  represents the change of temperature due to mass (i.e. enthalpy) transport. Depending on the closure model for the diffusion velocities, various forms of the temperature equation arise

# Simplifications in the temperature transport equation

If Fick's law  $\mathbf{u}_i^d = -\mathcal{D} \frac{\nabla Y_i}{Y_i}$  is accounted for, the last term in the temperature transport equation becomes:

$$-\sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T = \rho \mathcal{D} \sum C_{Pi} \nabla Y_i \cdot \nabla T$$

If we also assume that the specific heat is the same for all the species, i.e.  $C_{Pi} = C_P$ , the term above becomes equal to 0. Thus, we obtain a very common form of the temperature equation:

$$\rho C_P \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot \lambda \nabla T + \dot{Q}$$

Special attention must be taken in adopting the equation above because of the strong simplifications: i) Fick's law (i.e. same diffusion coefficient for all the species); ii) same specific heat for all the species [Bisetti2015]



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# Governing equations

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

Viscosity

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p + \nabla \cdot \left( \mu \left( \nabla \mathbf{u} + \nabla \mathbf{u}^T - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} \right) \right) + \rho \mathbf{g}$$

Formation rates

$$\rho \frac{\partial Y_i}{\partial t} + \rho \mathbf{u} \cdot \nabla Y_i = \nabla \cdot (\rho \mathcal{D}_i \nabla Y_i) + \dot{\Omega}_i$$

Diffusion coefficients

Reaction heat (i.e. enthalpies)

$$\rho C_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \nabla \cdot (\lambda \nabla T) - \sum \rho \mathbf{u}_i^d Y_i C_{Pi} \cdot \nabla T + \dot{Q}$$

Thermal  
conductivity

Specific  
heats

# Thermodynamics, kinetics and transport properties

In order to solve the governing equations, thermodynamic data transport properties of species and chemical reactions must be known [RD2000, Kee2017].

## Thermodynamic data

- Constant pressure specific heat, enthalpy, entropy

## Kinetics

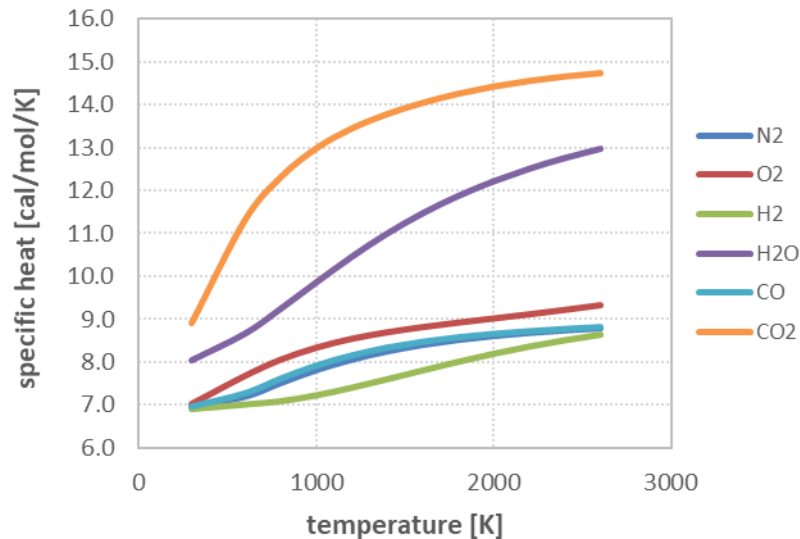
- Set of elementary and/or global reactions, together with kinetic parameters (frequency factors, activation energies, etc.)

## Transport properties

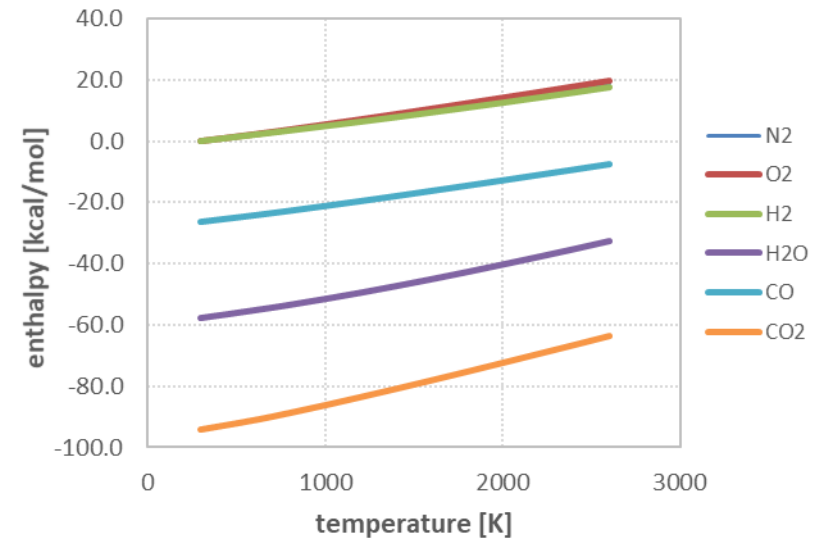
- Viscosity, thermal conductivity, mass diffusion coefficients, thermal diffusion coefficients

# Thermodynamic properties (I)

## Specific heats at constant pressure



## Enthalpies

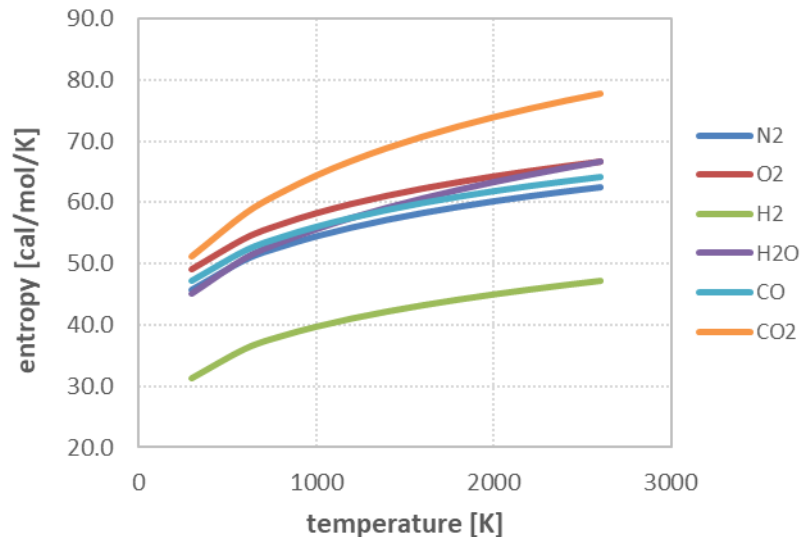


$$H_i = \Delta H_{f,i}^0 + \int_{T_0}^T C_{P,i}(T) dT$$

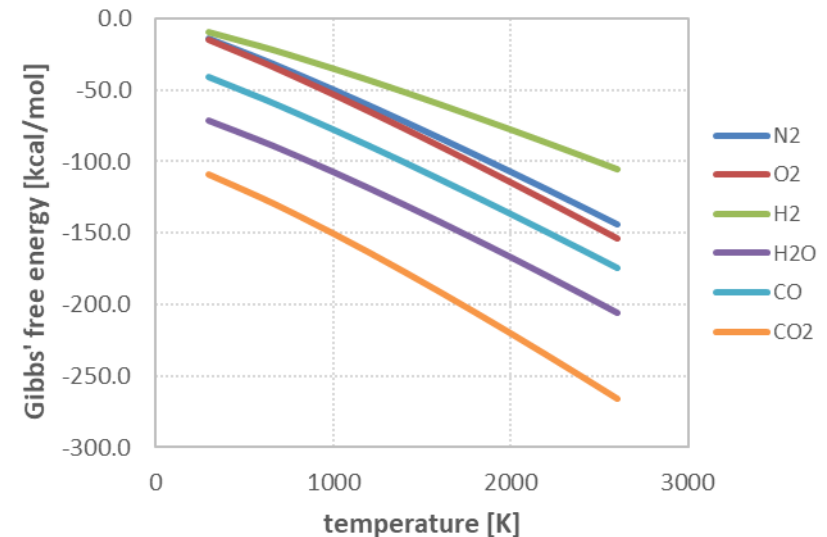
$T$  is the temperature and  $\Delta H_{f,k}^0$  is the enthalpy of formation of species  $i$  at the reference temperature  $T_0$ . The standard reference state used to tabulate formation enthalpies is usually set to  $T_0 = 298.15 \text{ K}$ .

# Thermodynamic properties (II)

## Entropies



## Gibbs' free energies



Any thermodynamic quantity (internal energy, Helmholtz's free energy, Gibbs' free energy, constant volume specific heat, etc.) can be estimated on the basis of **constant pressure specific heat, enthalpy, and entropy only**:

$$\text{Gibbs' free energy} \quad G_k(T) = H_k(T) - TS_k(T)$$

# The thermodynamic properties: NASA format

Thermodynamic data for each species in the chemical system are provided according to the so-called “**NASA format**” [RD2000].

These data are in the form of polynomial fits to temperature, for species enthalpy, entropy, and specific heat capacity.

$$\frac{C_P}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

**7 coefficients** are required to completely characterize the thermodynamic properties of **each species**

Additional thermodynamic quantities (free Gibbs energy, Helmotz energy, internal energy, etc.) can be evaluated from enthalpy, entropy, and specific heat capacity reported on the left

In the expressions above,  $T$  is the temperature in  $K$  and  $R$  is the universal constant of ideal gases

# Thermodynamic databases

Thermodynamic databases are a key component of efforts in numerical combustion. Three typical sources:

- Thermodynamics data are obtained as part of a “combustion model” comprising thermodynamics, transport, and kinetic models (e.g., the GRIMech 3.0 methane mechanism)
- NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species (NASA/TP2002-211556) Available at: <http://www.grc.nasa.gov/WWW/CEAWeb/>
- Prof. Burcat’s Data base: Ideal Gas Thermodynamic Data in Polynomial Form for Combustion and Air Pollution Use. Available at: <http://garfield.chem.elte.hu/Burcat/burcat.html> or <http://burcat.technion.ac.il/dir/>

Note that the report TP2002-211556 has a great introduction to the formats of thermodynamics data used in combustion codes, i.e., the so-called “NASA polynomials”, as well as an in-depth discussion of standard and reference states [Bisetti2015]



# Chemical kinetics (I)

Let us consider a chemical system with  $N$  species involved in  $N_R$  reactions:

$$\sum_{i=1}^N v_{ij}^f \psi_i \rightleftharpoons \sum_{i=1}^N v_{ij}^b \psi_i \quad j = 1, \dots, N_R$$

$\psi_i$       Species  $i$ -th

$v_{ij}^f$       Forward (molar) stoichiometric coefficient

$v_{ij}^b$       Backward (molar) stoichiometric coefficient

## Example: 2 reactions

$$\begin{cases} A + B \rightleftharpoons C \\ C \rightleftharpoons D \end{cases} \quad \boldsymbol{\psi} = \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} \quad \boldsymbol{v}^f = \begin{pmatrix} 1 & 0 \\ 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \boldsymbol{v}^b = \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 1 & 0 \\ 0 & 1 \end{pmatrix}$$

# Chemical kinetics (II)

Each chemical reaction must enforce mass conservation, i.e. the mass of reactants must be equal to the mass of products:

$$\sum_{i=1}^N v_{ij}^f W_i = \sum_{i=1}^N v_{ij}^b W_i \quad j = 1, \dots, N_R$$

$$\sum_{i=1}^N (v_{ij}^b - v_{ij}^f) W_i = 0 \quad j = 1, \dots, N_R$$

In order to have a more compact notation, it is often useful to introduce the net stoichiometric coefficients:

$$\sum_{i=1}^N v_{ij} W_i = 0 \quad j = 1, \dots, N_R$$
$$v_{ij} \stackrel{\text{def}}{=} v_{ij}^b - v_{ij}^f$$

# Reaction rates (I)

For each reaction we can introduce the so-called reaction rate (or rate of progress), i.e. a measure of the rate at which the reactants are transformed into the products:

$$r_j = k_j^f \prod_{i=1}^N C_i^{\eta_{ij}^f} - k_j^b \prod_{i=1}^N C_i^{\eta_{ij}^b} \quad j = 1, \dots, N_R$$

$k_j^f$  Forward kinetic constant of reaction j

$k_j^b$  Backward kinetic constant of reaction j

$C_j$  Concentration (molar) of species i

$\eta_{ij}^f$  Forward order or reaction of species i in reaction j

$\eta_{ij}^b$  Backward order or reaction of species i in reaction j

## Reaction rates (II)

For elementary reactions the reaction orders of reactants and products are equal to the stoichiometric coefficients:

$$r_j = k_j^f \prod_{i=1}^N C_i^{v_{ij}^f} - k_j^b \prod_{i=1}^N C_i^{v_{ij}^b} \quad j = 1, \dots, N_R$$

For elementary reactions the forward and backward kinetic constants are not independent, but they are connected by the equilibrium constant  $K_j^{eq}$ :

$$k_j^b = \left( \frac{RT}{p_0} \right)^{\sum v_{ij}} \frac{k_j^f}{K_j^{eq}}$$

Kinetic constants are not really constants! They are function of temperature (and in some cases pressure).

# Reaction rates (III)

The kinetic constant can be usually expressed using the modified Arrhenius' law:

$$k_j^f = A_j T^{\beta_j} \exp\left(-\frac{E_j}{RT}\right) = A_j T^{\beta_j} \exp\left(-\frac{T_j^a}{T}\right)$$

- $A_j$       Frequency factor of pre-exponential factor
- $\beta_j$       Temperature exponent
- $E_j$       Activation energy ( $T_j^a$  is the activation temperature)

- The modified Arrhenius law is an empirical fit to observed rate constants and there may be reactions that do not confirm to the Arrhenius format
- The actual units of  $k_j^f$  depend on the reaction orders of reactant species and vary reaction by reaction

# The equilibrium constant (I)

As mentioned before, for elementary reactions the forward and backward kinetic constants are not independent, but they are connected by the equilibrium constant  $K_j^{eq}$ :

$$K_j^{eq}(T) = \exp \left[ -\frac{1}{RT} \sum_{i=1}^N v_{ij} G_i(T, P_0) \right]$$

Gibbs free energy per unit mole:  $G_i(T, P_0) = H_i(T) - TS_i(T, P_0)$

The equilibrium constant is a function of temperature only and it is calculated at a reference pressure  $P_0$ , usually set to 1 atm.

The fact that the reverse rate constant of a reaction is computed from the equilibrium constant implies that chemical kinetics rates are affected by thermodynamic properties of the species [Bisetti2015].

# The equilibrium constant (II)

Since the equilibrium constant  $K_j^{eq}$  is defined as:

$$K_j^{eq}(T) = \prod_{i=1}^N \left( \frac{p_k}{p_0} \right)^{v_{ij}}$$

we can derive that:

$$K_j^{eq}(T) = \prod_{i=1}^N \left( \frac{p_k}{p_0} \right)^{v_{ij}} = \prod_{i=1}^N \left( \frac{C_i RT}{p_0} \right)^{v_{ij}} = \left( \frac{RT}{p_0} \right)^{\sum v_{ij}} \prod_{i=1}^N C_i^{v_{ij}} = \left( \frac{RT}{p_0} \right)^{\sum v_{ij}} \frac{k_j^f}{k_j^b}$$

Thus, the backward kinetic constant can be calculated from the forward kinetic constant and the equilibrium constants as:

$$k_j^b = \left( \frac{RT}{p_0} \right)^{\sum v_{ij}} \frac{k_j^f}{K_j^{eq}}$$

# The formation rates

The so-called **formation rate**  $\dot{\Omega}_i$  of each species can be easily calculated by considering all the reactions in which the species itself is involved:

$$\dot{\Omega}_i = W_i \sum_{j=1}^{NR} v_{ij} r_j$$

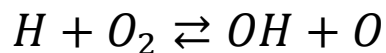
The sum of all the reaction rates  $\dot{\Omega}_i$  is equal to 0 since each chemical reaction enforces the conservation of mass:

$$\sum_{i=1}^N \dot{\Omega}_i = \sum_{i=1}^N W_i \sum_{j=1}^{NR} v_{ij} r_j = \sum_{j=1}^{NR} r_j \left( \sum_{i=1}^N v_{ij} W_i \right) = 0$$



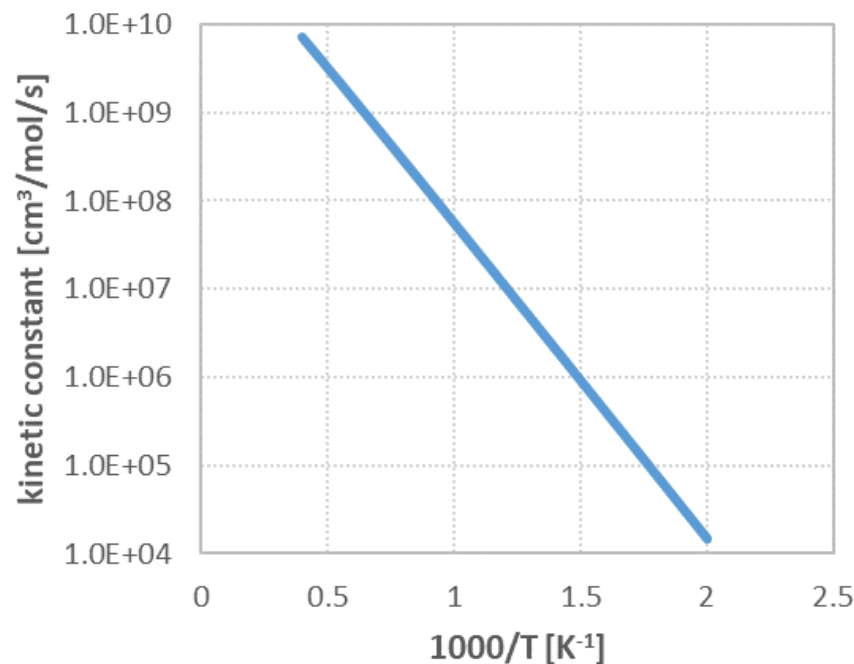
## Example: $H + O_2 \rightleftharpoons OH + O$

Let us to consider the forward kinetic constant for the following elementary reaction:



$$k_f = AT^n \exp\left(-\frac{E}{RT}\right)$$

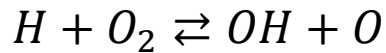
$$\left\{ \begin{array}{l} A = 9.60 \cdot 10^{14} \text{ [mol, cm, s]} \\ n = -0.20 \\ E = 16625 \text{ cal/mol} \end{array} \right.$$



When plotted as  $\log_{10}(k_f)$  versus  $\frac{1}{T}$ , it is clear that the rate constant appears as a straight line. The temperature exponent results in a slight curvature.

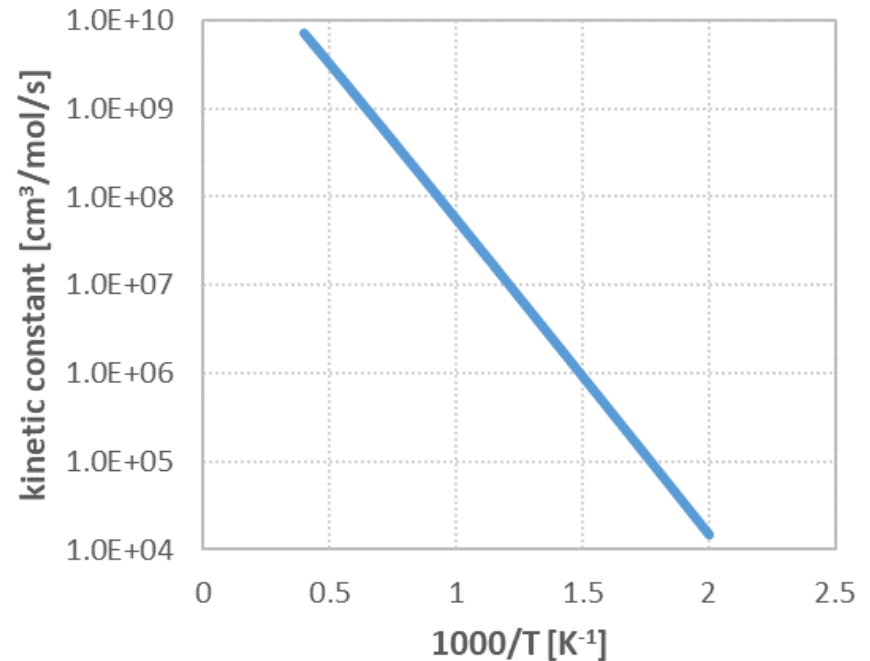
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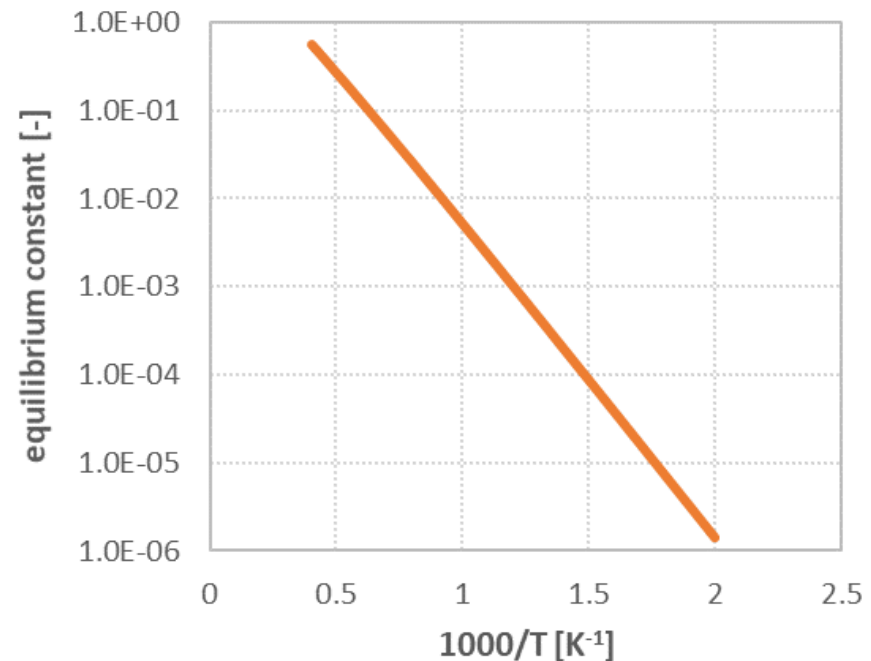


When plotted as  $\log_{10}(k_f)$  versus  $\frac{1}{T}$ , it is clear that the rate constant appears as a straight line. The temperature exponent results in a slight curvature.

## Example: $H + O_2 \rightleftharpoons OH + O$

The equilibrium constant for the same reaction can be calculated as previously explained:

$$K^{eq}(T) = \exp \left[ -\frac{1}{RT} \sum_{i=1}^N v_{ij} G_i(T, P_0) \right]$$



- Since the equilibrium constants is  $< 1$  in the temperature range here considered, this indicates that  $k^r > k^f$ , i.e. the recombination of the 2 radicals OH and O is thermodynamically favored
- The fact that  $\log_{10}(K^{eq})$  versus  $\frac{1}{T}$  is a straight line, indicates that  $\sum_{i=1}^N v_{ij} G_i(T, P_0)$  is a weak function of temperature.

# Transport properties

In general, all transport properties should be treated as functions of the thermo-chemical state of the mixture:  $T$ ,  $P$ , and  $Y$

- $\mu$  dynamic viscosity of the mixture
- $\lambda$  thermal conductivity of the mixture
- $\mathcal{D}_{ij}$  binary diffusion coefficients for species components

Widely adopted models for transport properties are based on the **Chapman-Enskog theory** for a multicomponent gas mixtures under thermal and chemical equilibrium (Chapman and Cowling, 1991).

The theory is centered around the concept of **binary interactions** between colliding molecules. Collisions are described well by **potential functions** (e.g., Lennard-Jones and Stockmayer potentials) in the regime of interest for most combustion applications [Bisetti2015, Kee2017].

# Dynamic viscosity of pure species

The viscosity of a pure species  $i$  can be estimated as [Bird2007, Kee2017]:

$$\mu_i = \frac{5}{16} \frac{\sqrt{\pi m_i k_B T}}{\pi \sigma_i^2 \Omega^{(2,2)}}$$

$\Omega^{(2,2)}$  is the **collision integral**, which is a function of the reduced temperature  $T_i^* = \frac{k_B T}{\varepsilon_i}$  and the reduced dipole moment  $\delta_i^* = \frac{\delta_i}{2 \varepsilon_i \sigma_i^3}$

- $\sigma$  is the Lennard-Jones collision diameter
- $\varepsilon$  is the Lennard-Jones potential well depth
- $\delta$  is the dipole moment

It is important to notice that  $\mu_i$  is a function of temperature only!

# Thermal conductivity

The viscosity of a pure species  $i$  can be estimated as [Bird2007, Kee2017]:

$$\lambda_i = \frac{25}{32} \sqrt{\frac{k_B T}{\pi m_i}} \frac{C_V}{N_{AV} \sigma_i^2 \Omega^{(2,2)}}$$

$\Omega^{(2,2)}$  is the **collision integral**, which is a function of the reduced temperature  $T_i^* = \frac{k_B T}{\varepsilon_i}$  and the reduced dipole moment  $\delta_i^* = \frac{\delta_i}{2 \varepsilon_i \sigma_i^3}$

- $\sigma$  is the Lennard-Jones collision diameter
- $\varepsilon$  is the Lennard-Jones potential well depth
- $\delta$  is the dipole moment

It is important to notice that  $\lambda_i$  is a function of temperature only!

# Binary diffusion coefficients

The viscosity of a pure species  $i$  can be estimated as [Bird2007, Kee2017]:

$$\mathcal{D}_{ij} = \frac{3}{8} \sqrt{\frac{\pi k_B^2 T^2}{m_{ij}}} \frac{1}{\pi P \sigma_{ij}^2 \Omega^{(1,1)}}$$

$\Omega^{(1,1)}$  is the **collision integral**, which is a function of the reduced temperature  $T_{ij}^* = \frac{k_B T}{\varepsilon_{ij}}$  and the reduced dipole moment  $\delta_{ij}^* = \frac{\delta_{ij}}{2\varepsilon_{ij}\sigma_{ij}^3}$

- $\sigma_{ij}$  is the Lennard-Jones collision diameter  $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$
- $\varepsilon_{ij}$  is the Lennard-Jones potential well depth  $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$
- $\delta_{ij}$  is the dipole moment (depends on the polarity of species)
- $m_{ij}$  is the reduced mass  $m_{ij} = \frac{m_i m_j}{m_i + m_j}$

It is important to notice that  $\mathcal{D}_{ij}$  is a (complex) function of temperature and (simple) function of pressure!

# Reduced collision integrals (I)

$$\begin{cases} \Omega^{(1,1)}(T^*) \approx a_1 T^{*-a_2} + (T^* + a_3)^{-a_4} \\ \Omega^{(2,2)}(T^*) \approx b_1 T^{*-b_2} + (T^* + b_3)^{-b_4} \end{cases}$$

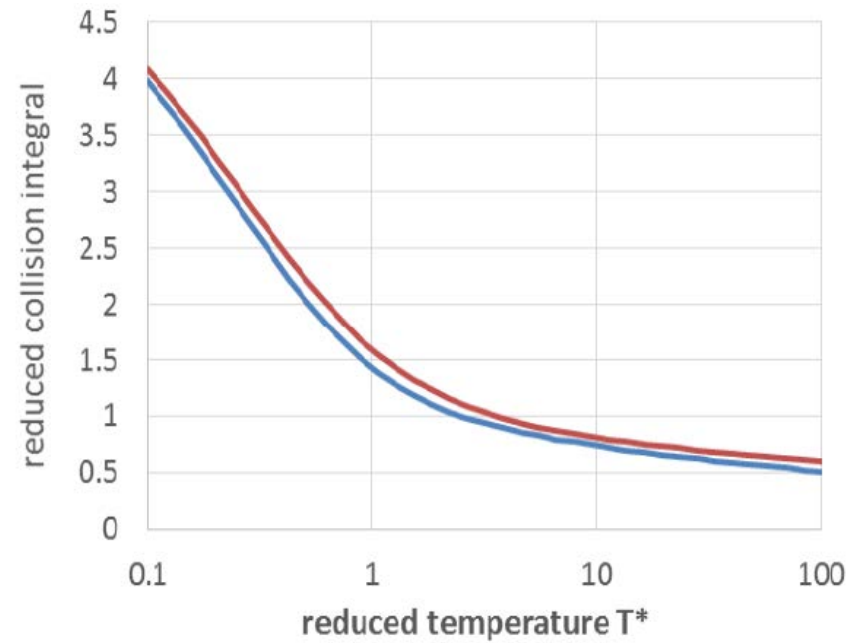
Reduced  
temperature

$$T^* = \frac{k_B T}{\varepsilon}$$

	j=1	j=2	j=3	j=4
$a_j$	1.0548	0.15550	0.55909	2.1705
$b_j$	1.0413	0.11930	0.43628	1.6041

**Monchick, Mason**, *Transport properties of polar gases*,  
Journal of Chemical Physics, 35, p. 1676 (1961)

Lennard-Jones 12-6 potential





# Reduced collision integrals (II)

$$\begin{cases} \Omega^{(1,1)}(T^*) \approx \left[ a_1 T^{*-a_2} + (T^* + a_3)^{-a_4} \right] f^{(1,1)} \\ \Omega^{(2,2)}(T^*) \approx \left[ b_1 T^{*-b_2} + (T^* + b_3)^{-b_4} \right] f^{(2,2)} \end{cases}$$

Stockmayer potential

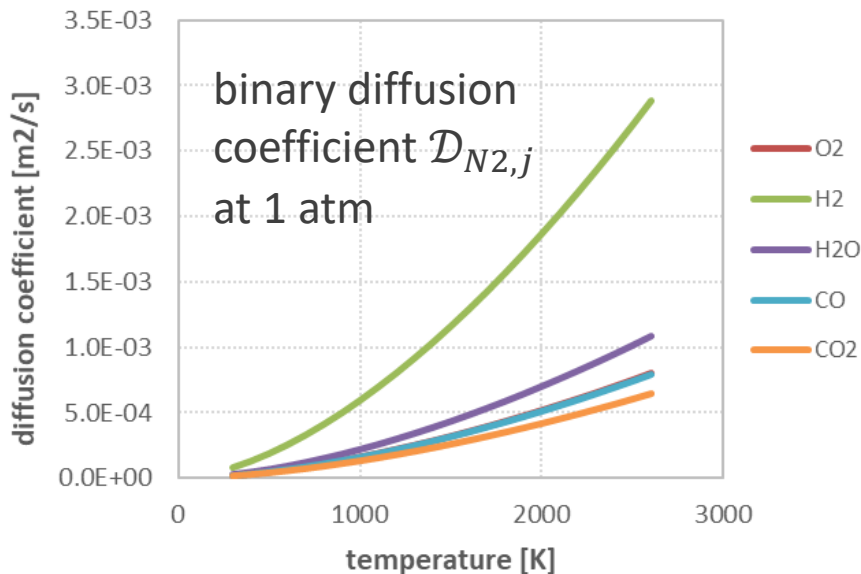
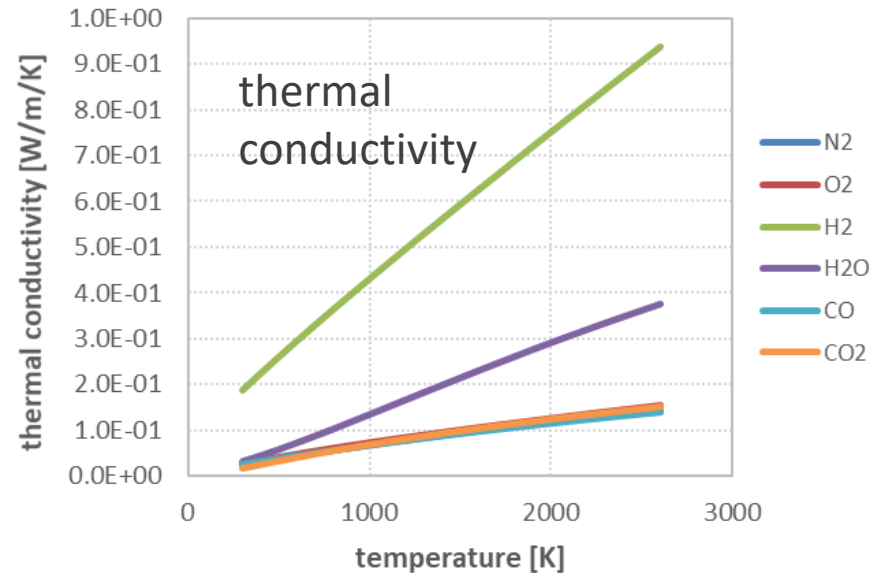
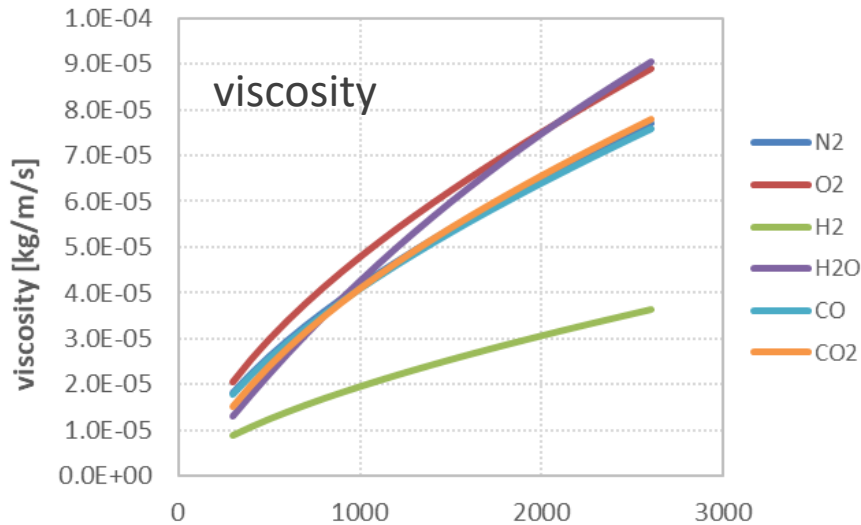
$$\begin{cases} f^{(1,1)}(T^*, \delta^*) = 1 + \frac{(e^{a_5/T^*} - e^{-a_6/T^*})(2\delta^*)^2}{2 + 5\delta^*} \\ f^{(2,2)}(T^*, \delta^*) = 1 + \frac{(e^{b_5/T^*} - e^{-b_6/T^*})(2\delta^*)^2}{2 + 5\delta^*} \end{cases}$$

Correction factors

**Monchick, Mason**, *Transport properties of polar gases*,  
Journal of Chemical Physics, 35, p. 1676 (1961)

	j=5	j=6
$a_j$	0.093193	1.5
$b_j$	0.095661	2.0

# Transport properties of pure species



The transport properties of individual species are monotonic, increasing functions of temperature, according to the Chapman-Enskog theory

# Thermal diffusion coefficients (I)

The Hirschfelder-Curtiss model can be refined by including an additional contribution associated to the Soret effect, i.e. the additional diffusion of species due to the temperature gradient:

$$\rho Y_i \mathbf{u}_i^d = -\rho \mathcal{D}_i \nabla Y_i - \rho \mathcal{D}_i Y_i \frac{\nabla W}{W} - \rho Y_i \mathbf{u}_i^T$$

where  $\mathbf{u}_i^T$  is the so-called **thermal diffusion velocity**.

According to the Chapman-Enskog theory, the thermal diffusion velocity is given by the following expression [Bird2007, Kee2017]:

$$\mathbf{u}_i^T = -\frac{\mathcal{D}_i \theta_i}{X_i} \frac{\nabla T}{T}$$

Where  $\theta_i$  is the **thermal diffusion ratio** of species  $i$ .

# Thermal diffusion coefficients (II)

The thermal diffusion ratio is the sum of binary thermal diffusion ratios:

$$\theta_i = \sum_{j \neq i}^N \theta_{ij}$$

Similarly to other transport properties, the binary thermal diffusion ratios are a function of collisional integrals:

$$\theta_{ij} = \frac{15}{2} \frac{(2A_{ij}^* + 5)(6C_{ij}^* - 5)}{A_{ij}^*(16A_{ij}^* - 12B_{ij}^* + 55)} \frac{W_i - W_j}{W_i + W_j} X_i X_j$$

The thermal diffusion coefficients are significant only for very light species.

Therefore only a limited number of the binary coefficients reported above needs to be calculated

$$\left\{ \begin{array}{l} A_{ij}^* = \frac{1}{2} \frac{\Omega_{ij}^{(2,2)}}{\Omega_{ij}^{(1,1)}} \\ B_{ij}^* = \frac{1}{3} \frac{5\Omega_{ij}^{(1,2)} - 4\Omega_{ij}^{(1,3)}}{\Omega_{ij}^{(1,1)}} \\ C_{ij}^* = \frac{1}{3} \frac{\Omega_{ij}^{(1,2)}}{\Omega_{ij}^{(1,1)}} \end{array} \right.$$

# Mixture-averaged properties (I)

The mixture averaged properties are usually estimated (i.e. approximated) from the pure species values using semi-empirical rules. This approach offers an attractive compromise between accuracy and computational effort [RD2000].

As an example, the Wilke's formula can be applied for estimating the dynamic viscosity of the mixture:

$$\mu = \sum_{i=1}^N \frac{X_i \mu_i}{\sum_{j=1}^N X_j \phi_{ij}}$$

where:

$$\phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{W_i}{W_j} \right)^{-1/2} \left[ 1 + \sqrt{\frac{\mu_i}{\mu_j}} \left( \frac{W_j}{W_i} \right)^{1/4} \right]^2$$

Note that the evaluation of viscosity requires a double-loop over all species. For mechanisms featuring a large number of species, the computational cost becomes prohibitive rather rapidly.

# Mixture-averaged properties (II)

The mixture averaged properties are usually estimated (i.e. approximated) from the pure species values using semi-empirical rules. This approach offers an attractive compromise between accuracy and computational effort.

For the thermal conductivity the combination averaging formula proposed by Mathur is usually adopted:

$$\lambda = \frac{1}{2} \left( \sum_{i=1}^N X_i \lambda_i + \frac{1}{\sum_{i=1}^N X_i / \lambda_i} \right)$$

**Wilke**, *A viscosity equation for gas mixtures*, Journal of Chemical Physics, 18, p. 517 (1950)

**Mathur, Saxena**, *Methods of calculating thermal conductivities of binary mixtures involving polyatomic gases*, Applied Science Resources, 17, p. 155 (1967)

# Mixture-averaged properties (III)

In case we consider the Hirschfelder-Curtiss approximation for evaluating the mass diffusion fluxes, as already reported, the mixture-averaged diffusion coefficients can be calculated as:

$$\mathcal{D}_i = \frac{1 - Y_i}{\sum_{j \neq i} \frac{X_j}{\mathcal{D}_{ij}}}$$

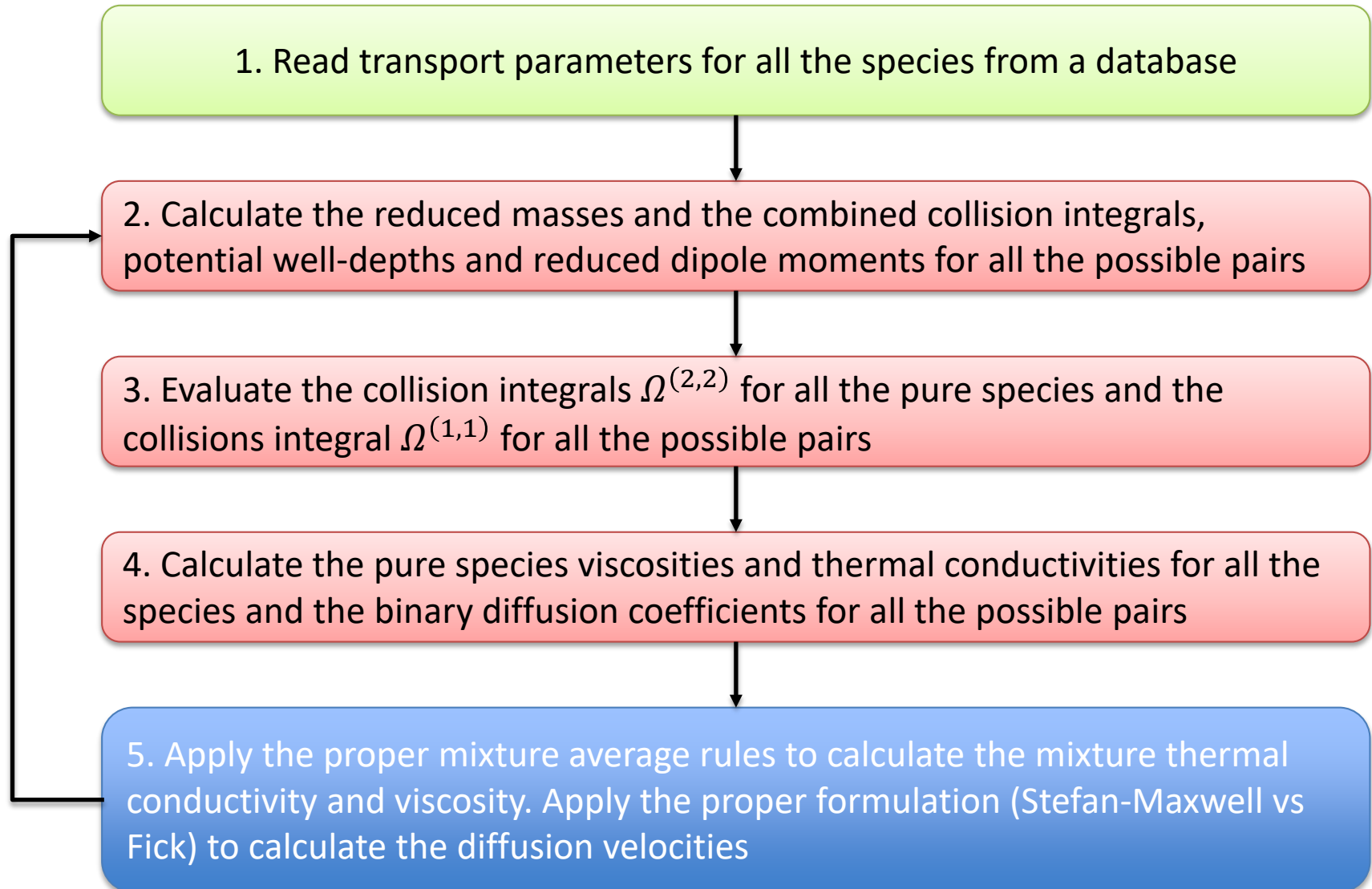
The thermal diffusion ratio is the sum of binary thermal diffusion ratios:

$$\theta_i = \sum_{j \neq i}^N \theta_{ij}$$

**Hirschfelder, Curtis, Bird**, *Molecular theory of gases and liquids*, New York, John Wiley and Sons (1954)

**Dixon-Lewis**, *A FORTRAN Computer Code Package for the evaluation of gas phase multicomponent transport properties*, Proceedings of the Royal Society, A304, p. 111-135 (1968)

# Calculation of transport properties





# The pure species fitting procedure (I)

In order to save computational time, a fitting procedure can be performed when a kinetic scheme is pre-processed (therefore only once) in order to write the pure species properties as polynomial functions [RD2000]

$$\ln(\mu_i) = \sum_{n=1}^4 a_{n,i} (\ln T)^{n-1}$$

$$\ln(\lambda_i) = \sum_{n=1}^4 b_{n,i} (\ln T)^{n-1}$$

$$\begin{cases} \ln(\tilde{\mathcal{D}}_{ij}) = \sum_{n=1}^4 c_{n,ij} (\ln T)^{n-1} \\ \mathcal{D}_{ij} = P \tilde{\mathcal{D}}_{ij} \end{cases}$$

We usually adopt third-order polynomials (i.e.  $N=4$ ), since the fitting error are less than 1% in most cases (as reported by Kee et al.)

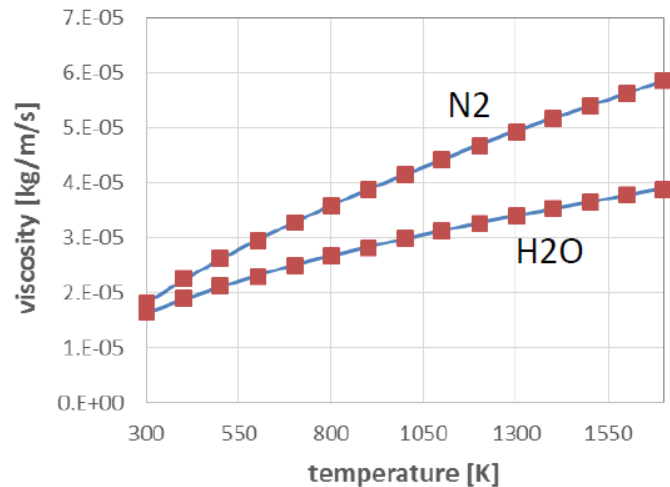
This fitting must be performed for all the species contained in the kinetic scheme. Therefore it cannot be done once and for all, but must be done every time we change the list of species in the kinetic scheme

# The pure species fitting procedure (II)

## VISCOSITY FITTING COEFFICIENTS

$\mu = \exp( A + B \cdot \log T + C \cdot (\log T)^2 + D \cdot (\log T)^3 ) \quad [\text{kg/m/s}]$

	A	B	C	D
1. HE	-1.336819e+01	1.705437e-01	6.411484e-02	-2.794003e-03
2. AR	-2.083165e+01	3.231053e+00	-3.384623e-01	1.476053e-02
3. N2	-1.853769e+01	2.232971e+00	-2.102014e-01	9.264622e-03
4. O2	-1.906650e+01	2.494518e+00	-2.440586e-01	1.072526e-02
...				

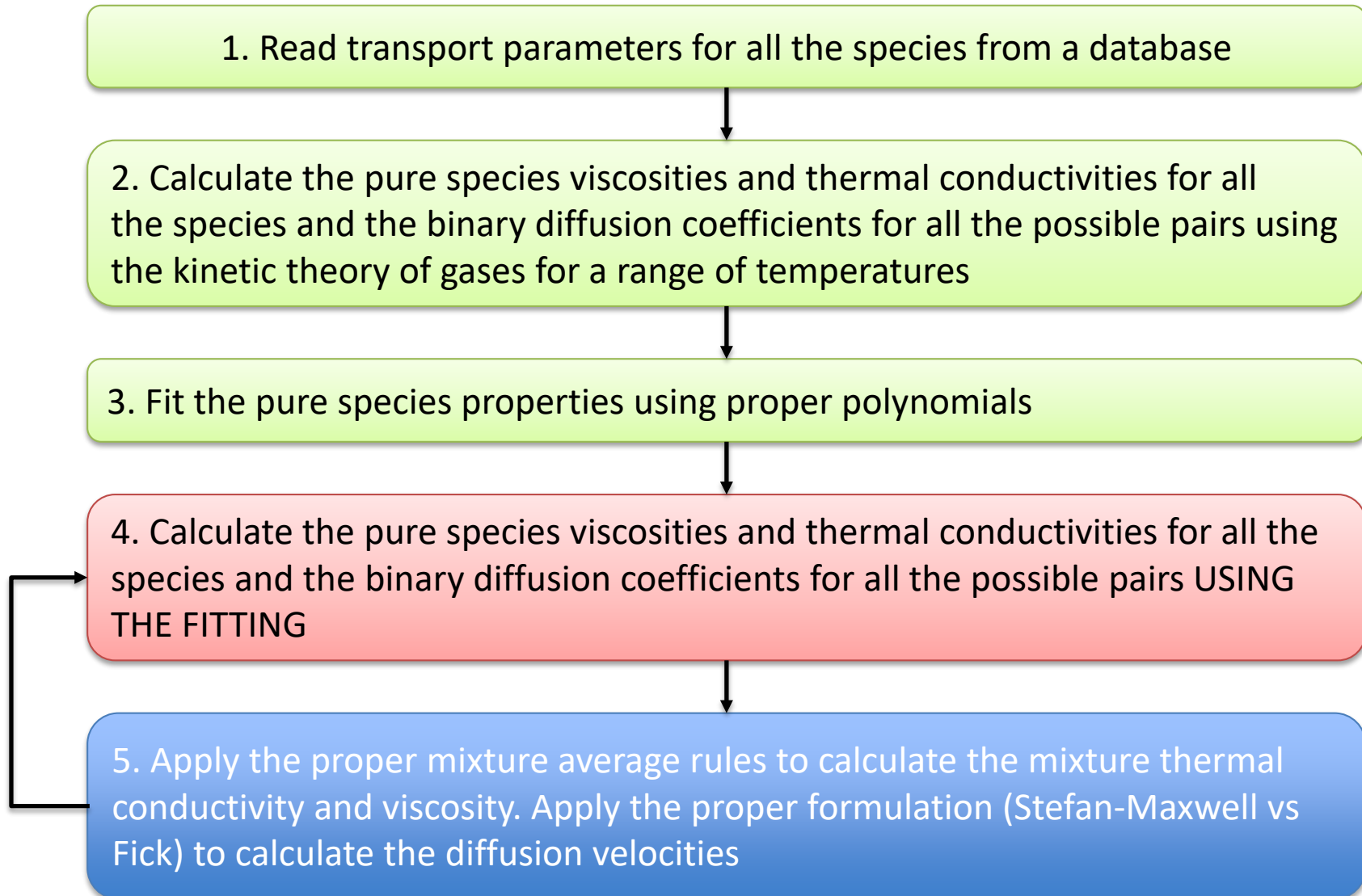


In case of full-multicomponent calculations, it is not necessary to calculate and fit the pure thermal conductivities, because they are used only in the mixture averaged formulation

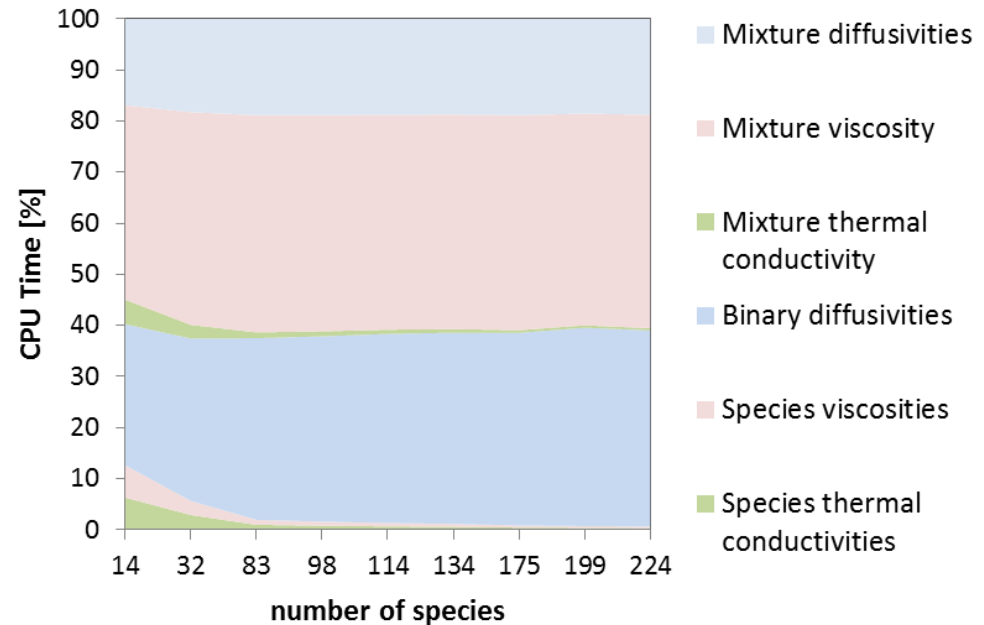
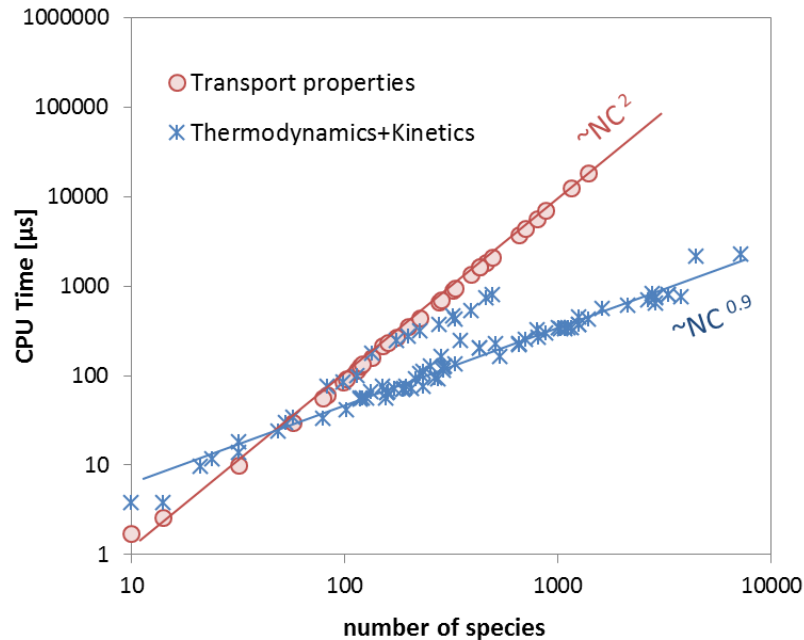
The binary thermal diffusion ratios are usually fitted through the following polynomial function:

$$\ln(\theta_{ij}) = \sum_{n=1}^4 d_{n,ij} T^{n-1}$$

# Calculation of transport properties



# Computational cost of transport properties



- The cost of evaluation of transport properties (in particular diffusion) increases **quadratically** with the number of species
- In fully-coupled methods proper techniques must be applied to **reduce the computational cost of transport properties** (they can be the **bottleneck** in evaluation of Jacobian matrix)



Lesson 4

## 1. Governing equations for reactive flows

- a) Continuity and momentum
- b) Species (including models for diffusion velocities)
- c) Energy (enthalpy and temperature formulations)

## 2. Thermodynamic data, kinetics, and transport properties

- a) Thermodynamics and NASA polynomials
- b) Kinetics: stoichiometry, reaction rates, formation rates
- c) Transport properties: viscosity, thermal conductivity, diffusion coefficients, mixture-averaged properties, fitting

## 3. The CHEMKIN<sup>®</sup> standard

- a) Introduction
- b) Thermodynamic data
- c) Kinetics
- d) Transport properties

CHEMKIN® is a proprietary software tool for solving complex chemical kinetics problems. It is used worldwide in the combustion, chemical processing, microelectronics and automotive industries, and also in atmospheric science.

- The original CHEMKIN, developed at Sandia National Laboratories, was published in 1980.
- A later version, known as CHEMKIN-II, expanded the basic capabilities, with inclusion of an accurate and efficient means of describing pressure-dependent reactions.
- The first commercial version, originally called CHEMKIN-III, greatly expanded the applicability of CHEMKIN through inclusion of global reaction kinetics.
- The current version of CHEMKIN® is developed by a US company, Reaction Design.

# The CHEMKIN® format

Since its original release during the '80s, CHEMKIN defined a format for writing detailed kinetic mechanisms, together with thermodynamic and transport data for species.

Today, the CHEMKIN format is widely accepted and used by the combustion kinetics as the standard format for writing detailed kinetic mechanisms.

**Reaction Design**, *Chemkin Theory Manual*, CK-THE-15151-1601-UG-1, January 2016

Web: [https://www.ems.psu.edu/~radovic/ChemKin\\_Theory\\_PaSR.pdf](https://www.ems.psu.edu/~radovic/ChemKin_Theory_PaSR.pdf)

# Why to use the CHEMKIN® format?

1. Efficient handling of large reaction mechanisms
2. Generalized framework, simple and standard inputs
3. Minimization of common mistakes
4. Common platform for distributing new kinetic schemes



# A “*kinetic mechanism*” in CHEMKIN® format

In order to have a kinetic mechanism in CHEMKIN® format, three different types of data are required: thermodynamic data, transport properties (not strictly necessary), and chemical reactions (i.e. kinetics)

Typically, these data are provided in three different files, which are written based on specific (and very strict) rules, which define the CHEMKIN® format

## Thermodynamic data

- Constant pressure specific heat, enthalpy, entropy

## Kinetics

- Set of elementary and/or global reactions, together with kinetic parameters

## Transport properties

- Only required for simulating systems in which transport occurs (flames, ICE, etc.)

# The thermodynamic properties (I)

Thermodynamic data for each species in the chemical system are provided according to the so-called “NASA format”.

These data are in the form of polynomial fits to temperature, for species enthalpy, entropy, and specific heat capacity.

$$\frac{C_P}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

**7 coefficients** are required to completely characterize the thermodynamic properties of **each species**

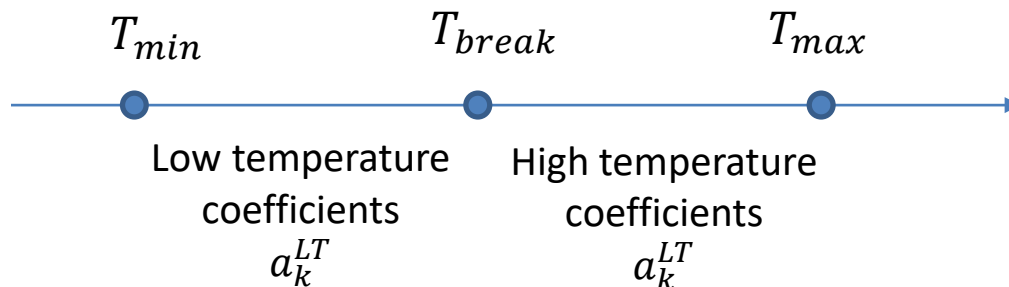
Additional thermodynamic quantities (free Gibbs energy, Helmotz energy, internal energy, etc.) can be evaluated from enthalpy, entropy, and specific heat capacity reported on the left

In the expressions above,  $T$  is the temperature in  $K$  and  $R$  is the universal constant of ideal gases

# The thermodynamic properties (II)

In order to ensure higher accuracy in the evaluation of thermodynamic properties, **two sets** of NASA coefficients are usually accounted for, by dividing the temperature field in 2 ranges

This means that each species is completely characterized by a total of **14 NASA coefficients**



Obviously, the two sets of coefficients have to be chosen in order to strictly ensure the continuity of thermodynamic properties at the intermediate temperature.

If possible, for numerical reasons, continuity of first order derivative is also a desired property

# Thermodynamic data in CHEMIN® format (I)

The first line specifies that the following data are a set of thermodynamic data, while the second line provides the three temperatures used in splitting the whole temperature space (low temperature, break temperature, and high temperature).

```
THERMO ALL
300.000 1000.000 5000.000

CH2CHO          SAND86O  1H   3C   2      G   300.000  5000.000  1000.000  1
0.05975670E+02 0.08130591E-01-0.02743624E-04 0.04070304E-08-0.02176017E-12  2
0.04903218E+04-0.05045251E+02 0.03409062E+02 0.10738574E-01 0.01891492E-04  3
-0.07158583E-07 0.02867385E-10 0.15214766E+04 0.09558290E+02  4
AL              62987AL  1      G   300.000  5000.000  1000.000  1
0.02559589E+02-0.10632239E-03 0.07202828E-06-0.02121105E-09 0.02289429E-13  2
0.03890214E+06 0.05234522E+02 0.02736825E+02-0.05912374E-02-0.04033937E-05  3
0.02322343E-07-0.01705599E-10 0.03886794E+06 0.04363879E+02  4
(CH2O)3         70590C  3H   6O   3      G   300.00  4000.00  1500.00  1
0.01913678E+03 0.08578044E-01-0.08882060E-05-0.03574819E-08 0.06605142E-12  2
-0.06560876E+06-0.08432507E+03-0.04662286E+02 0.06091547E+00-0.04710536E-03  3
0.01968843E-06-0.03563271E-10-0.05665403E+06 0.04525264E+03  4
END
```

# Thermodynamic data in CHEMIN® format (II)

name of species [1-16]	comments [19-24]	atomic comp. [25-44]					Phase [45]	Temperature intervals [46-73]			Line [80]
CH2CHO	SAND	O	1H	3C	2		G	300.000	5000.000	1000.000	1
0.05975670E+02 0.08130591E-01-0.02743624E-04 0.04070304E-08-0.02176017E-12											2
0.04903218E+04-0.05045251E+02 0.03409062E+02 0.10738574E-01 0.01891492E-04											3
-0.07158583E-07 0.02867385E-10 0.15214766E+04 0.09558290E+02											4

High Temperature (HT) NASA coefficients

Low Temperature (LT) NASA coefficients

Very strict syntax rules apply:

1. The data for each species requires **4 formatted lines** of length **80 characters**.
2. The data on the first line must be properly formatted, in fields with predefined length
3. The **7 HT NASA coefficients** must be followed by the **7 LT NASA coefficients**
4. The NASA coefficients have to be written in blocks of **15 chars**

# Transport properties (I)

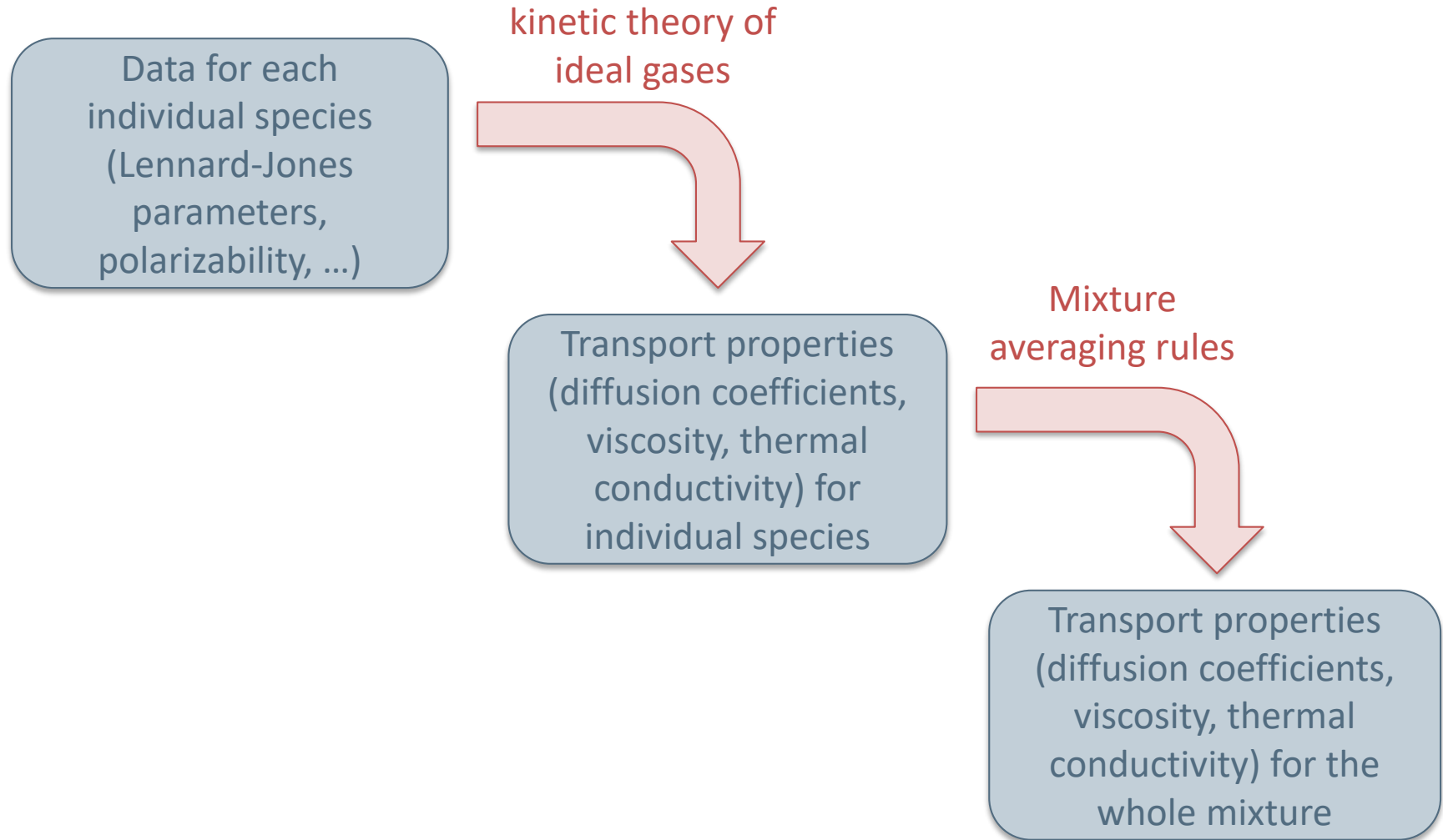
Characterizing the molecular transport of species, momentum, and energy in a multicomponent gaseous mixture requires the evaluation of **diffusion coefficients**, **viscosities**, **thermal conductivities**, and **thermal diffusion coefficients**.

Although evaluation of pure species properties follows **standard kinetic theory** expressions, one can choose from a range of possibilities for evaluating mixture properties. Moreover, computing the **mixture properties** can be expensive, and depending on the use of the results, it is often advantageous to make simplifying assumptions to reduce the computational cost (Kee et al., 2003)

For most applications, gas mixture properties can be determined from pure species properties via certain approximate mixture averaging rules. More advanced and accurate approaches are possible, but usually the computational cost increases

**Reaction Design**, *TRANSPORT*, A software package for the evaluation of gas-phase, multicomponent transport properties, TRA-036-1, CHEMKIN Collection Release 3.6, September 2000, Web: <https://www3.nd.edu/~powers/ame.60636/transport.pdf>

# Transport properties (II)



# Transport data in CHEMKIN® format

AR	0	136.5	3.33	0.	0.	0.
C	0	71.4	3.298	0.	0.	0.
C2H2OH	2	224.7	4.162	0.	0.	1.
C2N	1	232.400	3.828	0.	0.	1.

The first 16 columns in each line of the database are reserved for the species name. Columns 17 through 80 are free-format, and they contain the molecular parameters for each species.

1. An index indicating whether the molecule has a monatomic, linear or nonlinear geometrical configuration. If the index is 0, the molecule is a single atom; 1 means the molecule is linear; 2 the molecule is nonlinear.
2. The Lennard-Jones potential well depth (in Kelvins)
3. The Lennard-Jones collision diameter (in Angstroms)
4. The dipole moment (in Debye)
5. The polarizability (in cubic Angstroms)
6. The rotational relaxation collision number at 298 K.
7. A “comment” line is one that has an exclamation mark (!) as the first non-blank character. In addition, on any line, any input that follows an exclamation mark is taken as a comment.



# Polynomial fitting of transport properties

To expedite the evaluation of transport properties, the temperature dependent parts of the pure species property expressions are fitted. This means that, rather than re-evaluating the complex expressions for the properties, only simple fits need to be evaluated. In particular, a **polynomial fit** of the logarithm of the property versus the logarithm of the temperature is adopted:

Viscosity	$\ln(\mu) = b_1^\mu + b_2^\mu(\ln T) + b_3^\mu(\ln T)^2 + b_4^\mu(\ln T)^3$	4 fitting coefficients
Thermal conductivity	$\ln(\lambda) = b_1^\lambda + b_2^\lambda(\ln T) + b_3^\lambda(\ln T)^2 + b_4^\lambda(\ln T)^3$	4 fitting coefficients
Binary diffusion coefficient with species j	$\ln(\mathcal{D}_j) = b_{j,1}^{\mathcal{D}} + b_{j,2}^{\mathcal{D}}(\ln T) + b_{j,3}^{\mathcal{D}}(\ln T)^2 + b_{j,4}^{\mathcal{D}}(\ln T)^3$	4N fitting coefficients

# Mixture averaging rules

In most cases the transport properties of the species can be evaluated by using the **standard kinetic theory** expressions (Hirschfelder, 1964). Then we can apply averaging rules to have the transport properties of the mixture

Thermal conductivity

$$\lambda = \frac{1}{2} \left[ \sum_{i=1}^N X_i \lambda_i + \left( \sum_{i=1}^N \frac{X_i}{\lambda_i} \right)^{-1} \right]$$

Mixture averaged diffusion coefficient

$$\mathcal{D}_{i,mix} = \frac{\sum_{j \neq i}^N X_j W_j}{W_{mix} \sum_{j \neq i}^N \frac{X_j}{\mathcal{D}_{ji}}}$$

Dynamic viscosity

$$\mu = \sum_{i=1}^N \frac{X_i \mu_i}{\sum_{j=1}^N X_j \phi_{i,j}} \quad \phi_{i,j} = \frac{1}{\sqrt{8}} \sqrt{\frac{W_j}{W_i + W_j}} \left[ 1 + \sqrt{\frac{\mu_i}{\mu_j}} \left( \frac{W_j}{W_i} \right)^{1/4} \right]^2$$

# The kinetics in CHEMKIN® format

## ELEMENTS

C      H      O  
N      AR      HE  
END

Section 1:  
List of elements

## SPECIES

HE                  AR                  N2                  O2                  H2  
H2O                H2O2                CO                  CO2                  O  
H                  OH                  HO2                  HCO  
END

Section 2:  
List of species

## REACTIONS

H+O2=OH+O                                  0.9600E+15                  -0.2                  16625.0  
O+H2=OH+H                                  0.4330E+14                  0.0                  10000.0  
CO+O(+M)=CO2(+M)                          0.9640E+11                  0.0                  3800.0  
LOW/    .2070E+27    -3.340                  7610.0/  
H2O/12.00/ H2/2.00/ CO/1.50/ CO2/2.00/ AR/0.50/  
END

Section 3:  
List of reactions

# Standard reactions in CHEMKIN® format

Basic rate  
expression:

$$r = r_f - r_b = k_f \prod_j C_j^{v_j^f} - k_b \prod_j C_j^{v_j^b}$$

Backward  
kinetic  
constant

$$k_b = \frac{k_f}{K_{eq}}$$

$$r = \left( k_f \right) \prod_j C_j^{v_j^f} - \left( \frac{k_f}{K_{eq}} \right) \prod_j C_j^{v_j^b}$$

$v_j^f$  forward stoichiometric coefficient of species j  
 $v_j^b$  backward stoichiometric coefficient of species j  
 $C_j$  concentration of species j  
 $K_{eq}$  equilibrium constant

**H + O2 = OH + O**  
 reactants      products

**0.9600E+15**  
 Frequency  
 factor A  
 [cm<sup>3</sup>/mol/s]

**-0.2**  
 Temperature  
 exponent n

**16625.0**  
 Activation  
 energy E  
 [cal/mol]

$$k_f = AT^n e^{-\frac{E}{RT}}$$

Arrhenius' law

# Basic reactions in CHEMKIN® format

## Reversible reaction

H + O2 = OH + O                      0.9600E+15           -0.2           16625.0

## Non-reversible reaction

H + O2 => OH + O                      0.9600E+15           -0.2           16625.0

## Third-body reaction

HCO +M = CO + H +M                      0.1200E+18           -1.0           17000.0  
H2O/5.00/   CO2/3.00/   H2/1.90/   CO/1.90/

## Pressure dependent reaction (fall-off)

OH+OH (+M) = H2O2 (+M)           0.7400E+14           -0.37           0  
LOW/   .1300E+19           -.900           -1700.0/  
TROE/ 0.7346 94.00           1756.           5182. /  
H2/2.00/   H2O/6.00/   CO/1.50/   CO2/2.00/   AR/.70/   HE/0.70/   N2/0.90/

# Third-body reactions in CHEMKIN® format

In some reactions a “**third body**” is required for the reaction to proceed. This is often the case in dissociation or recombination reactions, such as:



When a third body is needed, the concentration of the effective third body must appear in the expression for the reaction rate. Thus, the effective reaction rate  $r$  can be obtained from the plain reaction rate  $r'$  corrected by a factor  $[M]$  accounting for the third body:

$$r = [M]r'$$

$$r' = r_f - r_b = k_f \prod_j C_j^{v_j^f} - k_b \prod_j C_j^{v_j^b}$$

$$[M] = \sum_{j=1}^N \varepsilon_j C_j$$

For each species we have a so-called **third body efficiency**  $\varepsilon_j$

# Third-body reactions in CHEMKIN® format

```
HCO +M = CO + H +M          0.1200E+18      -1.0    17000.0
H2O/5.00/   CO2/3.00/   H2/1.90/   CO/1.90/
```

1. Third-body reactions are specified by putting **+M** on the left and right sides of the reaction
2. By default, the efficiency of each species is assumed equal to 1
3. Only efficiencies different than 1 are specified in a separate line (see the example above)

# Fall-off reactions in CHEMKIN® format

As an example of a unimolecular/recombination fall-off reaction, consider methyl recombination:



In the **high-pressure limit**, the appropriate description of the reaction is simply:



In the **low-pressure limit**, a third-body collision is required to provide the energy necessary for the reaction to proceed, i.e., the appropriate description is:



When such a reaction is at either limit, the simple Arrhenius' based rate expressions discussed are applicable. However, when the pressure and temperature are such that the reaction is between the limits, the rate expressions are more complicated. To denote a reaction that is in this **"fall-off" region**, we write the reaction with the positive **(+M)** enclosed in parentheses:





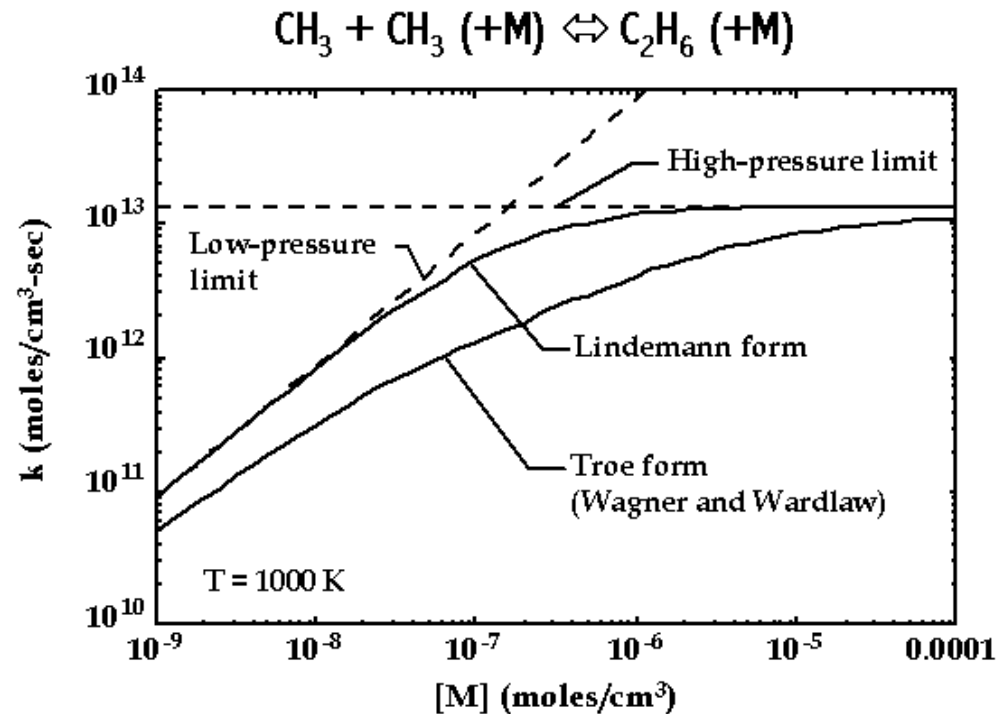
# Fall-off reactions in CHEMKIN® format

Arrhenius' rate parameters are required for both the high- and low-pressure limiting cases. The effective kinetic constant is obtained through a proper “blending” between the low-pressure  $k_{LP}$  and high-pressure  $k_{HP}$  kinetic constants:

$$k = k_{HP} \frac{P_r}{1 + P_r} F$$

$$P_r = \frac{k_{LP}[M]}{k_{HP}}$$

$$\begin{cases} k_{HP} = A_{HP} T^{\beta_{HP}} e^{-\frac{E_{HP}}{RT}} \\ k_{LP} = A_{LP} T^{\beta_{LP}} e^{-\frac{E_{LP}}{RT}} \end{cases}$$

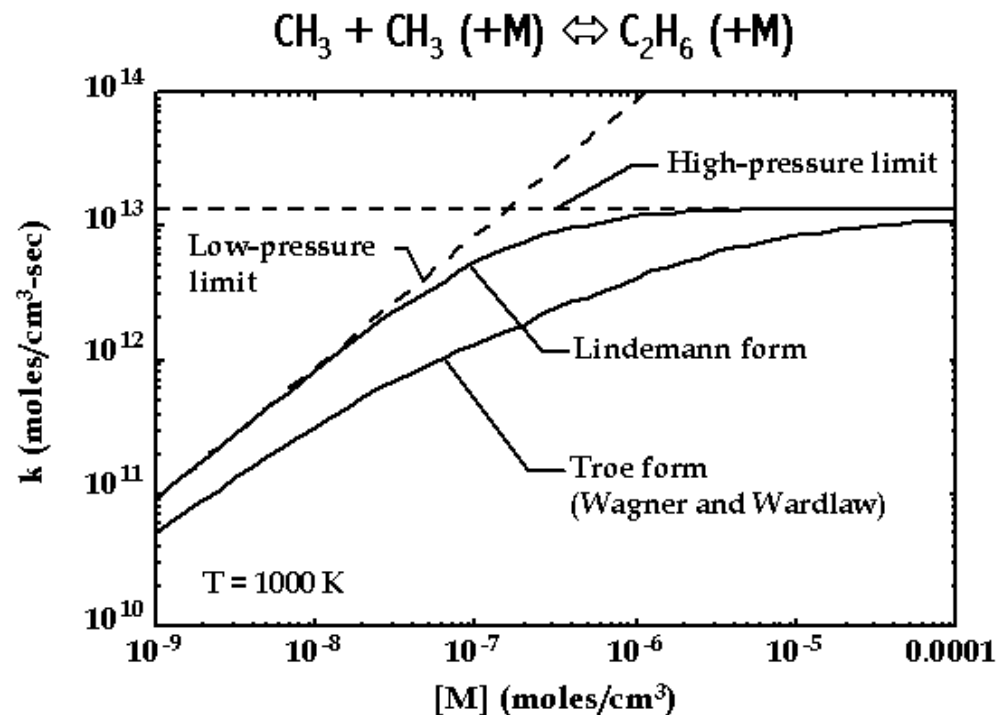


# Fall-off reactions in CHEMKIN® format

There are several methods of representing the rate expressions in this fall-off region:

1. The Lindemann form
2. The Troe form
3. The SRI form

According to the type of form adopted, the expression of  $F$  is different



# The Lindemann form

```
H+C2H4(+M)=C2H5(+M) 0.221E+14 0 2066
LOW / 6.369E27 -2.76 -54.0 /           ! Lindemann fall-off
H2/2/ CO/2/ CO2/3/ H2O/5/           ! third-body efficiencies
```

In the Lindemann's approach arrhenius rate parameters are required for both the high- and low-pressure (**LOW**) limiting cases. Third body efficiencies can be also specified for specific species (if different than 1)

In the Lindemann's approach, we simply have:

$$F = 1$$

# The Troe form

```
CH3+CH3(+M)=C2H6(+M) 9.03E16 -1.18 654.  
LOW / 3.18E41 -7.03 2762 /  
TROE / 0.6041 6927. 132. / ! TROE fall-off reaction  
H2/2/ CO/2/ CO2/3/ H2O/5/ ! third-body efficiencies
```

In the Troe's approach, we have:

$$\log F = \left\{ 1 + \left[ \frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right\}^{-1} \log F_{cent}$$

$$\begin{cases} c = -0.4 - 0.67 \log F_{cent} \\ n = 0.75 - 1.27 \log F_{cent} \\ d = 0.14 \\ F_{cent} = (1 - \alpha) e^{-\frac{T}{T^{***}}} + \alpha e^{-\frac{T}{T^*}} + e^{-\frac{T^{**}}{T}} \end{cases}$$

**TROE** must be followed by the slash-delimited 3 or 4 parameters  $\alpha$ ,  $T^{***}$ ,  $T^*$ ,  $T^{**}$

The fourth parameter is optional and if omitted, the last term in is not used.

# The SRI form

```
CH3+H(+M) = CH4(+M) 6.0E16 -1.0 0  
LOW/8.0E26 -3.0 0/  
SRI/0.45 797.0 979.0/  
H2/2/ CO/2/ CO2/3/ H2O/5/
```

In the SRI's approach, we have:

$$F = d \left[ a e^{-\frac{b}{T}} + e^{-\frac{T}{c}} \right]^X T^e$$

$$X = \frac{1}{1 + (\log P_r)^2}$$

**SRI** must be followed by either three, or five, slash-delimited parameters  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$ .

The fourth and fifth parameters are optional and if omitted, they are by default  $d = 1$  and  $e = 0$ .

# Global reactions in CHEMKIN® format (I)

- By default, in CHEMKIN® format every reaction is assumed to be an “elementary reaction”. This means that in the evaluation of the corresponding reaction rate, the concentration of each reactant or product species is raised to the power of its stoichiometric coefficient.
- Often, this elementary assumption does not apply to the global reactions of interest. For example, an experimental measurement may show that the rate of reaction is proportional to the concentration of a species raised to an arbitrary power (different from its stoichiometric coefficient).
- In such cases, CHEMKIN® format allows the user to declare that the reaction rate is proportional to the concentration of any species (regardless of whether that species even appears as a reactant or a product in the reaction) raised to any specified power.
- To modify the reaction order for the reaction in the forward or reverse direction, the user must declare the **FORD** or **RORD**

# Global reactions in CHEMKIN® format (II)

H2+0.5O2=>H2O	1.21E+18	-1.00	40000.
FORD / H2 0.25 /			
FORD / O2 1.5 /			

**FORD** is followed, in slash-delimited format, by the species name and the new reaction order. The reaction order for all other species maintain their default values.

In the example above, the reaction rate is calculated as:

$$r = kC_{H_2}^{0.25}C_{O_2}^{1.5}$$

CH4+0.5O2=>CO+2H2	7.82E+13	0.00	30000.
FORD / O2 1.25 /			

In the example above, the reaction rate is calculated as:

$$r = kC_{CH_4}^1C_{O_2}^{1.25}$$

# Global reactions in CHEMKIN® format (III)

```
A+B=AB          1.21E+18      -1.00      40000.  
RORD / AB 1.5/  
RORD / D  1/
```

**RORD** is followed, in slash-delimited format, by the species name and the new reaction order. The reaction order for all other species maintain their default values. Multiple occurrences of the RORD construct may appear on the auxiliary line.

In the example above, the reverse reaction rate is calculated as:

$$r = k_{rev} C_{AB}^{1.5} C_D^1$$

The user should exercise caution when specifying a change of reaction order, as such a change may produce unexpected and unphysical results in a kinetic simulation. For example, the user should consider the kinetics of the reverse reaction when changing reaction-orders for the forward reaction. Such a reaction may no longer satisfy microscopic reversibility.



# Additional reaction types

- **REV**: Explicit reverse reaction rates
- **PLOG**: Pressure Dependence Through Logarithmic Interpolation
- **CHEB**: Chebyshev Polynomial Rate Expressions
- **FIT1**: Power series within the exponential of a modified Arrhenius expression
- **JAN**: Janev-Langer reaction rates
- **LT**: Landau-Teller reaction rates
- **CABR**: Chemically Activated Bimolecular Reactions

# Explicit reverse reaction rates

```
C2F4 + M = CF2 + CF2 + M 1.126E-07 0. 27528.0
REV / 9.381E-14 0. 31404.1 /
```

- Supersedes the reverse rates that would normally be computed through the equilibrium constant
- `REV` must be followed by the three slash-delimited Arrhenius coefficients  $A_i, \beta_i, E_i$  to specify the reverse rate.

# Pressure dependence by Log interpolation (I)

A generalized method for describing the pressure dependence of a reaction rate based on direct interpolation of reaction rates specified at individual pressures.

The reaction rate is described in terms of the standard modified Arrhenius rate parameters. Different rate parameters are given for discrete pressures within the pressure range of interest.

When the actual reaction rate is computed, the rate parameters will be determined through logarithmic interpolation of the specified rate constants, at the current pressure from the simulation:

$$\ln k = \ln k_i + (\ln k_{i+1} - \ln k_i) \frac{\ln P - \ln P_i}{\ln P_{i+1} - \ln P_i}$$

This approach provides a very straight-forward way for users to include rate data from more than one pressure regime.

# Pressure dependence by Log interpolation (II)

```
H2CCCH+H=C3H2(S)+H2 2.9512E+09 1.28 13474.  
PLOG /0.03947 2.9512E+09 1.28 13474./  
PLOG /1. 1.0965E+10 1.13 13929./  
PLOG /10. 3.3113E+13 0.195 17579./  
PLOG /100. 3.3113E+13 0.195 17579./
```

- Using the **PLOG** keywords, you can enter any number of sets of Arrhenius reaction-rate coefficients at different reactor pressures.
- The **PLOG** data will override the Arrhenius coefficients provided on the reaction line.
- The **PLOG** keyword must be followed by the slash-delimited values for the pressure (in atm) at which the reaction rates are given and the three Arrhenius parameters,  $A_i$ ,  $\beta_i$ ,  $E_i$ , for that pressure.
- Multiple **PLOG** entries can be provided, but they must be included in ascending order of pressure.

## Pressure dependence by Log interpolation (III)

- If the rate of the reaction is desired for a pressure lower than any of those provided, the rate parameters provided for the lowest pressure are used.
- Likewise, if rate of the reaction is desired for a pressure higher than any of those provided, the rate parameters provided for the highest pressure are used.
- This logarithmic interpolation method can be used as an alternative approach to describing any type of pressure dependence. It has the advantage of being conceptually straightforward to implement.
- However, the resolution or accuracy of the pressure dependence will depend on the number of pressure points included for each reaction.

# Chebyshev reactions in CHEMKIN® format (I)

- The fall-off formalism previously described, i.e., the Lindemann, Troe, and SRI forms, although accurate for representing the falloff behavior of single well reactions, do not apply well to multiple-well reactions.
- A method based on the **Chebyshev expansions** are proposed by Venkatesh et al. (2000) for approximating the pressure and temperature-dependent behavior of multiple-well reactions.
- The Chebyshev expansions provide accurate approximations over any given temperature and pressure domain for single- and multiple-well reactions.
- However, these approximates should not be used for extrapolative studies outside their defined domain.
- Instead of using the modified Arrhenius form for the rate coefficient, the Chebyshev expansions approximate the logarithm of the rate coefficient directly as a **truncated bivariate Chebyshev series** in the reverse temperature and logarithm of the pressure.

## Chebyshev reactions in CHEMKIN® format (II)

Since the Chebyshev polynomials are only defined in the interval of  $[-1, +1]$ , the temperature and pressure boundaries for the approximation must be established first

$$\begin{cases} T_{min} \leq T \leq T_{max} \\ P_{min} \leq P \leq P_{max} \end{cases}$$

The domain is then mapped onto a square bounded by  $\pm 1$  using the transformations:

$$\begin{cases} \tilde{T} = \frac{2T^{-1} - T_{min}^{-1} - T_{max}^{-1}}{T_{max}^{-1} - T_{min}^{-1}} \\ \tilde{P} = \frac{2\log P - \log P_{min} - \log P_{max}}{\log P_{max} - \log P_{min}} \end{cases}$$

The logarithm of the rate coefficient is approximated by the Chebyshev expansions as

$$\log(k) = \sum_{n=1}^N \sum_{m=1}^M a_{nm} \varphi_n(\tilde{T}) \varphi_m(\tilde{P})$$

where the Chebyshev polynomials of the first kind of degree  $n - 1$  are given by:

$$\varphi_n(x) = \cos((n - 1)\arccos(x)) \quad n = 1, 2, \dots$$

## Chebyshev reactions in CHEMKIN® format (III)

- The integers  $N$  and  $M$  denote the number of basis functions along the temperature and the pressure axis, respectively.
- The accuracy of the approximates will increase monotonically with  $N$  and  $M$ .
- The coefficients  $a_{nm}$  of the Chebyshev expansions are determined from a least-squares fit to a set of rate coefficient data points,  $k(\tilde{T}, \tilde{P})$ , computed from a detailed theory such as the Rice-Ramsperger-Kassel-Marcus (RRKM) theory.



# Chebyshev reactions in CHEMKIN® format (IV)

```
C2H5 + O2 (+M) <=> C2H4E + HO2 (+M) 1.00E+00 .000 0.  
TCHEB / 300. 2500./  
PCHEB / 1.0 100.0/  
CHEB/ 7 3 1.0216E+01 -1.1083E+00 -1.9807E-01 7.8325E-01/  
CHEB/ 1.1609E+00 1.1762E-01 -9.5707E-02 1.0928E-01 1.1551E-01/  
CHEB/ -8.0290E-02 -1.0978E-01 3.7074E-04 -1.4830E-02 -6.0589E-02/  
CHEB/ -2.8056E-02 6.9203E-03 -9.7259E-03 -1.3556E-02 7.6648E-03/  
CHEB/ 6.6865E-03 -8.8244E-04/
```

**TCHEB** must be followed by the two slash-delimited values  $T_{min}$  and  $T_{max}$  (in K). If not specified, the default pressure limits are  $T_{min} = 300$  and  $T_{max} = 2500$ .

**PCHEB** must be followed by the two slash-delimited values  $P_{min}$  and  $P_{max}$  (in atm). If not specified, the default pressure limits are  $P_{min} = 0.001$  and  $P_{max} = 100$ .

**CHEB** must be followed by (slash delimited) parameters:

- for the first **CHEB**, the first value is  $N$ , the number of basis functions along the  $T$  axis;
- the second is  $M$ , the number of basis functions along the  $P$  axis;
- the remainder are the  $N \times M$  coefficients  $a_{nm}$  in the order  $a_{11}, a_{12}, \dots, a_{1M}, a_{21}, \dots, a_{nm}$

# Training Session 1 (optional)

- get **familiar with the standard CHEMKIN format** to write kinetic mechanisms (including thermodynamic and transport properties)
- recognize the **importance of pre-processing** thermodynamic, transport and kinetic data to check the existence of possible inconsistencies or unphysical behaviors
- learn how to calculate **adiabatic flame temperature** and equilibrium conditions for arbitrarily complex mixtures of gases
- recognize the importance of a proper selection of species to be included in the thermodynamic equilibrium calculation

# Additional references to CHEMKIN®

**Reaction Design**, *Chemkin Theory Manual*, CK-THE-15151-1601-UG-1, January 2016

Web: [https://www.ems.psu.edu/~radovic/ChemKin\\_Theory\\_PaSR.pdf](https://www.ems.psu.edu/~radovic/ChemKin_Theory_PaSR.pdf)

**Reaction Design**, *CHEMKIN, A software package for the analysis of gas-phase chemical and plasma kinetics*, CK-TUT-10112-1112-UG-1, CHE-036-1, CHEMKIN Collection Release 3.6, September 2000

Web: <https://www3.nd.edu/~powers/ame.60636/chemkin2000.pdf>

**Reaction Design**, *TRANSPORT, A software package for the evaluation of gas-phase, multicomponent transport properties*, TRA-036-1, CHEMKIN Collection Release 3.6, September 2000

Web: <https://www3.nd.edu/~powers/ame.60636/transport.pdf>

**Reaction Design**, *CHEMKIN Tutorials Manual*, CK-TUT-10112-1112-UG-1, December 2011

Web: [https://www.ems.psu.edu/~radovic/ChemKin\\_Tutorial\\_2-3-7.pdf](https://www.ems.psu.edu/~radovic/ChemKin_Tutorial_2-3-7.pdf)