

CRCM Model and Corresponding Extension to SENKIN

Sept. 7, 2007; A. Miyoshi

The rapid compression machine (RCM) is widely used to investigate the autoignition characteristics of fuel-air mixtures. Compared to the shock tube, its advantage is that it can cover the temperature and pressure range of compressed gases in practical engines. However, the clear disadvantages are that the gas is compressed in finite time history and that the heat loss and the fluid dynamic effects cannot be ignored. For CRCM (Chemical Rapid Compression Machine), which is aimed to reduce the transport effect of standard RCM, the mathematical and/or numerical models are clearly required for its development and in the analysis. In this document, CRCM models as well as the corresponding extension to Chemkin-II^[1] SENKIN^[2] code will be described.

1. Compression and Expansion of Gases

1.1. Ideal gas assumption

Figure 1.1 shows the compression factor,

$$Z = \frac{pV_m}{RT} \quad (1.1)$$

of dry air calculated from the virial equation.^[3] The non-ideality of the air is small in the experimental temperature range (300–1200 K) and pressure range (0.1–5 MPa), and the ideal gas assumption will be used throughout this document.

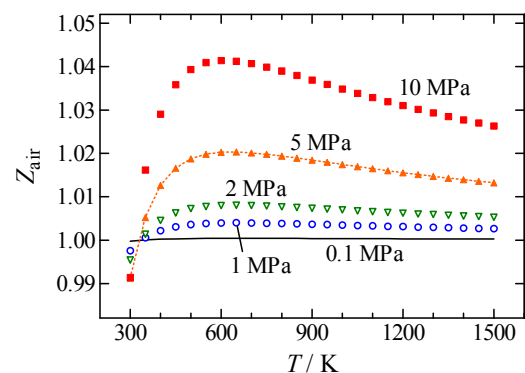


Fig. 1.1. Compression factor of dry air.

1.2. Adiabatic and isothermal processes

Temperature change of gas during the adiabatic and reversible processes (compression or expansion) can be derived from the energy equation.

$$C_V dT = -p dV \quad (1.2)$$

By assuming constant isovolumetric heat capacity, C_V , and ideal gas, the well-known solution (Poisson adiabatic equation) to the differential equation is derived as,

$$pV^\gamma = \text{const.}, \quad TV^{\gamma-1} = \text{const} \quad (1.3)$$

where γ is the heat capacity ratio,

$$\gamma = \frac{C_p}{C_V} \quad (1.4)$$

The isothermal equation,

$$pV = \text{const.}, \quad T = \text{const.} \quad (1.5)$$

can be regarded as a special case of eq. (1.3) with $\gamma = 1$. In many cases, practical processes are not either

^[1] R. J. Kee, F. M. Rupley, and J. A. Miller, *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*, SAND89-8009B-UC-706, Sandia National Laboratories, 1995.

^[2] A. E. Lutz, R. J. Kee, and J. A. Miller, *SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics With Sensitivity Analysis*, SAND87-8248-UC-401, Sandia National Laboratories, 1995.

^[3] K. Kadoya, N. Matsunaga, and A. Nagashima, *J. Phys. Chem. Ref. Data*, **14**, 947–970 (1985).

adiabatic (eq. 1.3) nor isothermal (eq. 1.5), but obey the relation in between the two limiting cases, and are expressed empirically by,

$$pV^n = \text{const.}, \quad TV^{n-1} = \text{const} \quad (1.6)$$

with n in between 1 and the heat capacity ratio γ .

The empirical exponent n is often referred as *polytropic index*. The work associated with the process following eq. (1.6) is,

$$w = \frac{p_0 V_0}{n-1} \left[\left(\frac{V_0}{V_1} \right)^{n-1} - 1 \right] \quad (1.7)$$

where suffixes 0 and 1 denote the initial and final conditions.

Figure 1.2 show the molar isobaric heat capacity, $C_{p,m}$ of typical gases which were calculated from the Chemkin thermodynamic data base^[4] (He, Ar, H₂, N₂, O₂, H₂O, CO₂, CH₄, C₃H₈, and *n*-C₆H₁₄) or calculated by NASA PAC99^[5] distributed with CEA program^[6] (Ne, Kr, Xe, CF₄, and SF₆) with molecular properties listed in JANAF-3.^[7] (See *Appendix A2* for detail.) It is clear that the constant heat capacity is not a good assumption except for the monoatomic rare gases. For sample gas mixture compressed in CRCM, eq. (1.3) should not be used but the pressure and temperature must be calculated by the precise numerical integration of eq. (1.2) with heat loss terms, if necessary. This is properly done by the VTIM codes of SENKIN.

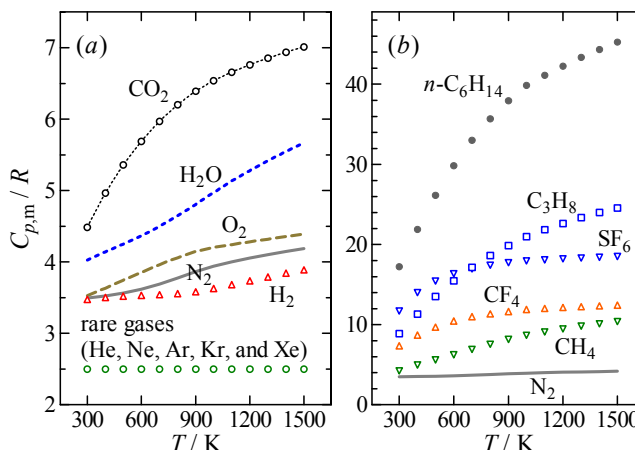


Fig. 1.2. Temperature dependence of the heat capacity.

2. Mechanical model for CRCM

Figure 2.1 shows the CRCM apparatus schematically. Initially, the driver tank is filled with dry air of pressure p_T . After opening the pneumatic valve at $t = 0$, the volume and pressure of the driver gas follow the equations (2.1) and (2.2) in terms of the driver-piston position x .

$$V_d = V_T + A_d x \quad (2.1)$$

$$p_d = p_T \left(\frac{V_T}{V_d} \right)^{\gamma_d} \quad (2.2)$$

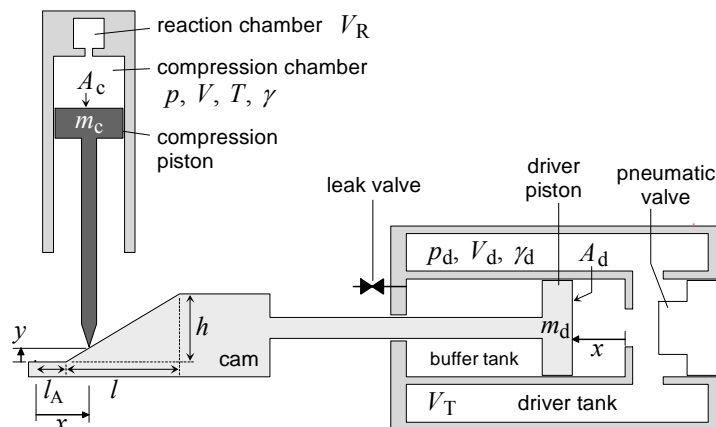


Fig. 2.1. A schematic of the CRCM apparatus.

The position y of the compression piston varies according to the cam-shape function s .

^[4] R. J. Kee, F. M. Rupley, and J. A. Miller, *The Chemkin Thermodynamic Data Base*, SAND87-8215B-UC-4, Sandia National Laboratories, 1994.

^[5] B. J. McBride and S. Gordon, *Computer Program for Calculating and Fitting Thermodynamic Functions*, NASA Reference Publication 1271, 1992.

^[6] S. Gordon and B. J. McBride, *Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications*, NASA Reference Publication 1311 (1996).

^[7] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurlop, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables, Third Edition," *J. Phys. Chem. Ref. Data*, **14**, Supplement 1 (1985).

$$y = s(x) \quad (2.3)$$

An example of the shape function is shown in Fig. 2.2 and its explicit form is shown in *Appendix A1*. The volume and pressure of sample gas are expressed by,

$$V = V_0 - A_c y \quad (2.4)$$

$$p = p_0 \left(\frac{V_0}{V} \right)^\gamma \quad (2.5)$$

where $V_0 = V_R + A_c h$.

As described at the end of previous section, constant- γ is a crude first-order approximation but will be used in the preliminary analyses. Since eqs. (2.1)–(2.5) give solution as a function of x , desired final solution can be obtained by expressing x as a function of time, t .

2.1. Solution via energy conservation

Here, for a while, the heat transfer from the compressed gas will be ignored. For the case that the buffer tank is full-open, that is, the pressure in the buffer tank is equal to the ambient pressure, p_a , the kinetic energy, thus the velocity, of two moving parts can be derived from the energy conservation equation. The work provided by the driver piston is,

$$w_d(x) = \frac{p_T V_T}{\gamma_d - 1} \left[1 - \left(\frac{V_T}{V_d} \right)^{\gamma_d - 1} \right] - p_a (V_d - V_T) - f_{f,d} x \quad (2.6)$$

and the work done to the compressor piston, including the work against the gravity, is,

$$w_c(y) = \frac{p_0 V_0}{\gamma - 1} \left[\left(\frac{V_0}{V} \right)^{\gamma - 1} - 1 \right] - p_a (V_0 - V) + m_c g_n y + f_{f,c} y \quad (2.7)$$

The total kinetic energy of two moving parts is,

$$w_k = \frac{1}{2} m_d \dot{x}^2 + \frac{1}{2} m_c \dot{y}^2 = \frac{1}{2} (m_d + s_1^2 m_c) \dot{x}^2 \quad (2.8)$$

where s_1 is the slope of the cam.

$$s_1 = \frac{ds(x)}{dx} \quad (2.9)$$

From the energy conservation, the kinetic energy must be,

$$w_k = w_d - w_c \quad (2.10)$$

Figure 2.3 show w_d and w_c calculated with typical parameters shown in

Nomenclature except for $l_c = 1 \text{ mm}$, $f_{f,d} = f_{f,c} = 0$. The value of p_T was chosen to be the minimum ($= 1.924 \text{ bar}$). Since the condition, $w_d \geq w_c$, must be fulfilled until the end of compression around $x = x_2 = l_A + W$, the minimum p_T can be estimated by,

$$p_T(\text{min}) = \frac{\gamma_d - 1}{V_T} \times \frac{w_c(h) + p_a [V_d(x_2) - V_T]}{1 - [V_T / V_d(x_2)]^{\gamma_d - 1}} \quad (2.11)$$

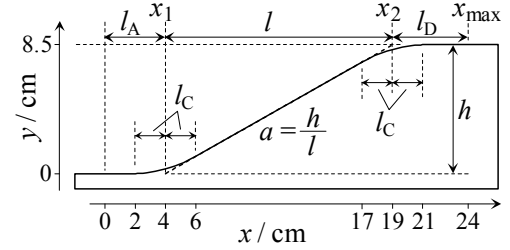


Fig. 2.2. An example of cam shape function.

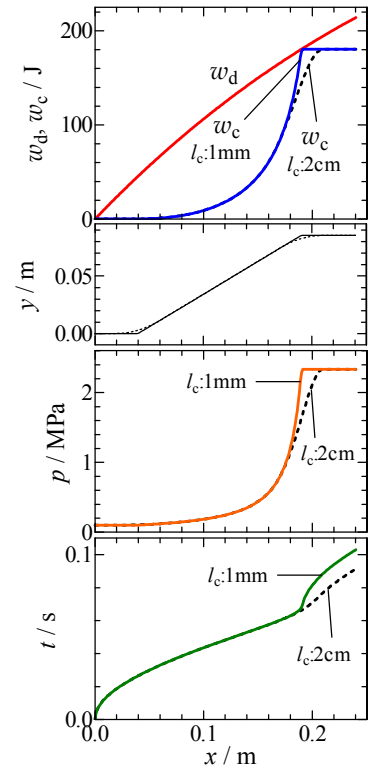


Fig. 2.3. An example solution from energy conservation.

It should be noted that eq. (2.11) is exact only for $l_c = 0$ and p_T may be even smaller for large l_c . An example of w_c calculated at $l_c = 2$ cm is shown in Figure 2.3. Since the velocity of driver-piston \dot{x} can be calculated as a function of x using eqs. (2.6)–(2.10), relation between t and x can be derived by numerical integration.

$$t(x) = \int_0^x \frac{dx}{\dot{x}} \quad (2.12)$$

An example of $t(x)$ is also shown in Fig. 2.3.

2.2. Solution of differential equation

Although the formulae above are essentially analytical except for the last numerical integration in eq. (2.12) and are comprehensive, they cannot be used when time-domain phenomena, e.g., heat losses, are included. For such purposes, the numerical solution of the differential equation is needed.

Since the two coordinates x and y are rigidly connected according to the cam shape, and the total kinetic energy is given by eq. (2.8), the motion of two moving part can be expressed by a single coordinate x and the effective mass,

$$m_{\text{eff}} = m_d + s_1^2 m_c \quad (2.13)$$

The force applied to the cam in x -direction from the driver piston is,

$$f_d = A_d(p_d - p_a) - f_{f,d} \quad (2.14)$$

and force applied in y direction from the compression piston and by the gravity is,

$$f_c = -A_c(p - p_a) - m_c g_n - f_{f,c} \quad (2.15)$$

The force associated with the change of effective mass, or the change of α , in x -direction is,

$$f_m = -s_1 s_2 m_c \dot{x}^2 \quad (2.16)$$

where s_2 is the second derivative of cam-shape function,

$$s_2 = \frac{d^2 s(x)}{dx^2} = \frac{ds_1}{dx} \quad (2.17)$$

Since the force in y -direction is transferred to x -direction with the conversion factor s_1 , as shown in Fig. 2.4, the total force applied is,

$$f = f_d + s_1 f_c + f_m \quad (2.18)$$

Then the differential equation for x becomes,

$$\begin{aligned} \frac{dx}{dt} &= \dot{x} \\ \frac{d\dot{x}}{dt} &= \frac{f}{m_{\text{eff}}} \end{aligned} \quad (2.19)$$

The solution can be obtained numerically.

3. Dimensionless Expressions

For the practical computation of the model in the previous section as well as to clarify the independent parameters, dimensionless expressions of the model are derived here. The unit pressure is chosen to be p_a . That

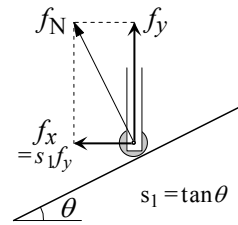


Fig. 2.4.

is, for example, the dimensionless pressures are defined as, $P = \frac{P}{p_a}$, $P_d = \frac{P_d}{p_a}$, $P_T = \frac{P_T}{p_a}$, and so on. In this

document, dimensionless numbers are denoted by the large / capital letters of corresponding quantities, except that the dimensionless volume is represented by 'U'. Along the x-coordinate, we choose l as unit length, A_d as unit area, $A_d l$ as unit volume, $p_a A_d l$ as unit energy, and $p_a A_d / l$ as unit mass. Similarly, along the y-coordinate, h , A_c , $A_c h$, $p_a A_c h$, and $p_a A_c / h$ are taken to be unit length, unit volume, unit energy, and unit mass, respectively. Since the units different from x-direction are chosen for y-direction, a conversion factor, $\varepsilon = \frac{A_c h}{A_d l}$, of energy

or volume is defined and used. Dimensionless expressions corresponding to (2.1)–(2.19) are as follows.

$$U_d = U_T + X, \quad P_d = P_T \left(\frac{U_T}{U_d} \right)^{\gamma_d} \quad (3.1), (3.2)$$

$$Y = S(X) \quad (3.3)$$

$$U = U_0 - Y, \quad P = P_0 \left(\frac{U_0}{U} \right)^{\gamma} \quad (3.4), (3.5)$$

where $U_0 = U_R + 1$

$$W_d(X) = \frac{P_T U_T}{\gamma_d - 1} \left[1 - \left(\frac{U_T}{U_d} \right)^{\gamma_d - 1} \right] - X - F_{f,d} X \quad (3.6)$$

$$W_c(Y) = \frac{P_0 U_0}{\gamma - 1} \left[\left(\frac{U_0}{U} \right)^{\gamma - 1} - 1 \right] - Y + M_c G_n Y + F_{f,c} Y \quad (3.7)$$

$$W_k = \frac{1}{2} M_d \dot{X}^2 + \frac{1}{2} \varepsilon M_c \dot{Y}^2 = \frac{1}{2} (M_d + \varepsilon S_1^2 M_c) \dot{X}^2 \quad (3.8)$$

$$S_1 = \frac{dS(X)}{dX} \quad (3.9)$$

$$W_k = W_d - \varepsilon W_c \quad (3.10)$$

$$P_T(\min) = \frac{\gamma_d - 1}{U_T} \times \frac{\varepsilon W_c(1) + X + F_{f,d} X}{1 - [U_T / U_d(X_2)]^{\gamma_d - 1}} \quad (3.11)$$

$$t(X) = \int_0^X \frac{dX}{\dot{X}} \quad (3.12)$$

$$M_{\text{eff}} = M_d + \varepsilon S_1^2 M_c \quad (3.13)$$

$$F_d = P_d - 1 - F_{f,d}, \quad F_c = -(P - 1) - M_c G_n - F_{f,c} \quad (3.14), (3.15)$$

where $G_n = g_n / h$

$$F_m = -\varepsilon S_1 S_2 M_c \dot{X}^2 \quad (3.16)$$

$$S_2 = \frac{d^2 S(X)}{dX^2} = \frac{dS_1}{dX} \quad (3.17)$$

$$F = F_d + \varepsilon S_1 F_c + F_m \quad (3.18)$$

$$\frac{dX}{dt} = \dot{X}, \quad \frac{d\dot{X}}{dt} = \frac{F}{M_{\text{eff}}} \quad (3.19)$$

In these expressions, eighteen parameters in eq. (2.1)–(2.19) ($g_n, p_a, V_T, A_d, P_T, \gamma_d, f_{f,d}, m_d, V_R, A_c, p_0, \gamma, f_{f,c}, m_c, h, l, l_A$, and l_C) are reduced to fourteen parameters ($G_n, U_T, P_T, \gamma_d, F_{f,d}, M_d, U_R, P_0, \gamma, F_{f,c}, M_c, \varepsilon, L_A$, and L_C).

4. Heat Transfer

Another important phenomenon which must be considered in the CRCM model is the heat transfer, especially from the compressed sample gas to the chamber wall.

4.1. Turbulent heat transfer

For forced convection conditions, the rate of heat-transfer from gas to the container wall is described by,⁸

$$\dot{q} = h_c \sigma (T - T_w) \quad (4.1)$$

The heat-transfer coefficient h_c is related to the thermal conductivity λ and the thickness of the thermal boundary layer δ_h by a simple boundary layer model,

$$h_c = \frac{\lambda}{\delta_h} \quad (4.2)$$

Therefore, the main problem is in the estimation of δ_h or the Nusselt dimensionless number Nu ,

$$Nu = \frac{D}{\delta_h} = \frac{h_c D}{\lambda} \quad (4.3)$$

In many empirical correlations for tubular, Nu is related to Reynolds and Prandtl numbers, Re and Pr , respectively, and the ratio of the viscosity at bulk to surface temperature, η_b / η_0 , as,

$$Nu = a Re^l Pr^m (\eta_b / \eta_0)^n \quad (4.4)$$

The Reynolds and Prandtl numbers are,

$$Re = \frac{\rho v D}{\eta} \quad (4.5)$$

$$Pr = \frac{c_p \eta}{\lambda} \quad (4.6)$$

For highly turbulent condition, Sieder and Tate proposed parameters for eq. (4.4) as: $a = 0.026$, $l = 0.8$, $m = 1/3$, and $n = 0.14$.

4.2. Correlation for CRCM conditions

For gases relevant to CRCM, η_b / η_0 in eq. (4.4) is around or less than 2, as shown in Fig. 4.1, and exponent l is rather small (~ 0.14), the factor $(\eta_b / \eta_0)^n$ does not significantly depend on the temperature or differ among gases. Also as shown in Fig. 4.2, the Prandtl number of gases is almost always around 0.7. For the calculation of transport coefficients, see *Appendix A3*. For these reasons, the last two factors in eq. (4.4) are often omitted for gases. For example, Woschni's correlation,^[9] which is widely used in the internal combustion engine modeling, assumes that $a = 0.035$, $l = 0.8$, and $m = n = 0$ in eq. (4.4). Thus the following correlation with $a \sim 0.3$ and $l \sim 0.8$ will be a reasonable choice for CRCM conditions.

$$Nu = a Re^l \quad (4.7)$$

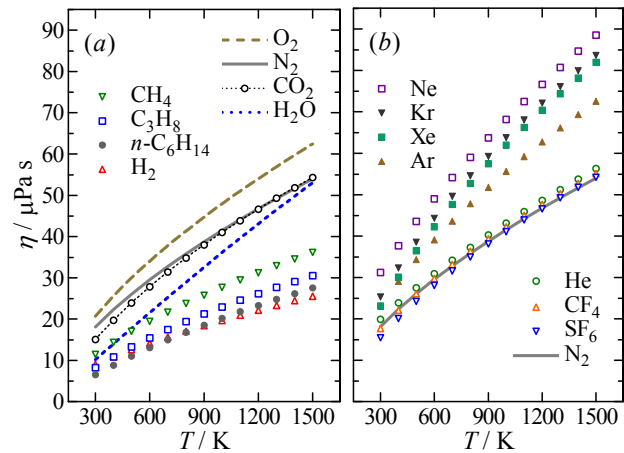


Fig. 4.1. Viscosity of gases.

[8] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, New York, 1960.

[9] J. B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988.

or

$$h_c = \frac{\lambda}{D} Nu = a \frac{\lambda}{D} Re^l \quad (4.8)$$

4.3. Effect of gas composition

Buffer gas for sample gas is often changed for the purpose of changing γ in RCM experiments. However, the effect of the buffer gas on the heat transfer properties is also important and may be used to control the heat loss in CRCM experiments.

For this purpose, properties of stoichiometric *n*-hexane/O₂/buffer mixtures were calculated. The ratio [O₂] : [buffer] was kept similar to dry air, 0.2095 : 0.7905. The density, ρ , of gas mixture was calculated for the compressed gas with compression ratio 10 from 300 K, 1 bar. The vD and A/V were assumed to be $0.16 \text{ m}^2 \text{ s}^{-1}$ and 150 m^{-1} , respectively, which correspond to the compression piston of diameter of 9.4 cm moving in a speed of full stroke (8.5 cm) in 50 ms, and $4 \times 4 \times 4 \text{ cm}$ cubic reaction chamber. Parameters $a = 0.035$ and $l = 0.8$ were used for eqs. 4.7 and 4.8. The heat transfer coefficient, h_c , is not the final quantity determining the decay of temperature of the compressed gas since the temperature decay also depends on the heat capacity of the gas. Thus the quantity $h_c AC_V^{-1}$ in the unit of s^{-1} was plotted in Fig. 4.3.

5. SENKIN extension

5.1. CRCM input

The CRCM extension to Senkin code is invoked by specifying keyword 'CRCM' instead of 'CONP', 'CONV', etc.

CRCM

Among the eighteen parameters in eq. (2.1)–(2.19), fourteen parameters can be specified as follows.

CDRV V_T D_d l f_{fd} m_d
 CCMP V_R D_c h f_{fc} m_c
 CCAM l_A l_C
 CDGA p_T γ_d

Two constants are always assumed to be, $g_n = 980.665 \text{ cm s}^{-2}$ and $p_a = 1 \text{ atm} (= 101325 \text{ Pa})$. No input for p_0 is required since it is read and calculated from 'PRES' input. Another parameter, the heat capacity ratio, γ , is calculated from the sample gas composition and temperature as a function of time. It should be noted that the

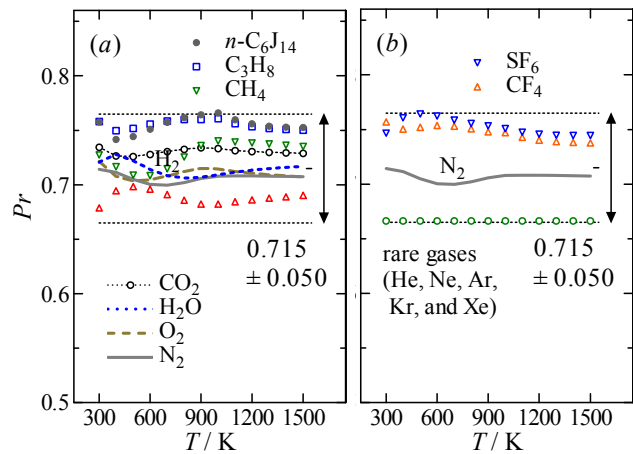


Fig. 4.2. Prandtl number of gases.

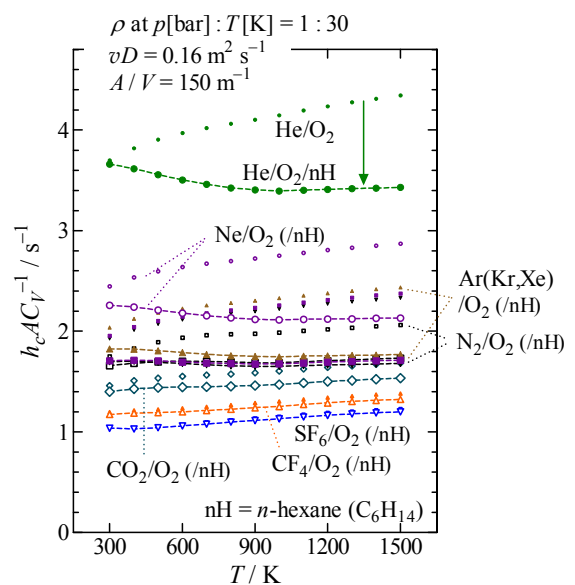


Fig. 4.3. Heat decay rate for several mixtures.

diameters, D_d and D_c , of pistons must be specified in input instead of areas, A_d and A_c , which are calculated accordingly.

$$A_d = \frac{\pi D_d^2}{4} \quad \text{and} \quad A_c = \frac{\pi D_c^2}{4} \quad (5.1)$$

If any of the keyword line except for 'CRCM' was not found, the default values in Table 5.1 is assumed. The unit for parameters is cgs, as aligned to the other input of SENKIN, except for the pressure, for which the unit is atm. They are also listed in Table 5.1.

5.2. Heat transfer

By default, CRCM extension ignores the heat loss except that the following heat loss keyword input is found in SENKIN input.

CHTL *a l* σ_0 σ_R T_w

where a and l are correlation parameters in eq. (4.7). Initial and final surface areas of sample compression chamber are specified by σ_0 and σ_R , respectively. The surface area for heat transfer is interpolated as a function of Y as,

$$\sigma = \sigma_0 - (\sigma_0 - \sigma_R)Y \quad (5.2)$$

The last parameter, T_w , is the temperature of the wall of the reaction chamber. The Reynolds number for the evaluation of eq. (4.7) is calculated using characteristic gas velocity, v_c , and compression piston diameter, D_c .

$$Re = \frac{\rho v_c D_c}{\eta} \quad (5.3)$$

The characteristic velocity was chosen to be the current piston speed during the acceleration period, but kept at the peak piston speed during deceleration period or after the piston is stopped.

5.3. Transport properties

When 'CHTL' card is found in input, the CRCM extension assumes the transport coefficients, η and λ , are same as those of initial sample gas mixture. The program has coefficients of eqs. (A3.1) and (A3.2) for gases listed in Table 5.2 internally, and tries to find species names specified in 'REAC' cards case-insensitively in the internal library. For example, 'Ar' matches with 'AR' and 'cC6H12' matches with 'CC6H12'. However, mechanism files may use different names for fuels listed in Table 5.2. For such cases, alias definition cards may be used to select proper species in the internal library.

CTAL *name*_{chem} *name*_{transp}

where, *name*_{chem} is a name in mechanism input (processed by 'chem') and *name*_{transp} is the corresponding name in internal library. For example, when the mechanism file uses the name 'c-c6h12' for cyclohexane, an alias card,

CTAL c-c6h12 cC6H12

Table 5.1. Constants, defaults, and units for CRCM extension.

parameter	default	unit
constant:		
g_n	980.665	cm s ⁻²
p_a	1	atm
parameter:		
V_T	13120	cm ³
D_d	13	cm
l	15	cm
$f_{i,d}$	0	dyn
m_d	10500	g
V_R	64	cm ³
D_c	9.4	cm
h	8.5	cm
$f_{f,c}$	0	dyn
m_c	3000	g
l_A	4	cm
l_C	2	cm
p_T	1.9	atm
γ_d	1.2	
heat transfer:		
a	0.035	
l	0.8	
σ_0	416	cm ²
σ_R	96	cm ²
T_w	300	K
buffering:		
l_B	24	cm
D_{rod}	1.8	cm
c_{leak}	1	cm ⁵ dyn ⁻¹ s ⁻¹

is used to assign the fuel transport data. It should be noted that the alias definition overrides the name matching with internal library. For example, when the mechanism file uses name 'c4h10' for isobutane, an alias card,

```
CTAL c4h10 iC4H10
```

may be used to avoid the improper matching with 'C4H10' (*n*-butane) in the library.

For the case when a gas in the sample gas is not any molecules in the library, the coefficients in eqs. (A3.1) and (A3.2) can be directly specified in the input using 'CTCF' card.

```
CTCF name a1η a2η a3η a4η
      M b1λ b2λ b3λ b4λ
```

where *name* is the name of the species, *a*_{1η} to *a*_{4η} are coefficients for (A3.1), *b*_{1λ} to *b*_{4λ} are coefficients for (A3.2), and *M* is the molecular weight. When this input is found, transport coefficients are calculated with these values irrespective of the name matching with library or matching with the alias.

Table 5.2. Gases in CRCM internal transport library

name	descr.	name	descr.
O2	O ₂	iC4H10	isobutane
N2	N ₂	neoC5H12	neopentane
CO2	CO ₂	C2H2	acetylene
H2O	H ₂ O	C2H4	ethylene
He	He	C3H4p	methyl acetylene
Ne	Ne	C3H6	propylene
Ar	Ar	CH3OH	methanol
Kr	Kr	C2H5OH	ethanol
Xe	Xe	nC3H7OH	n-propanol
CF4	CF ₄	CH3OCH3	dimethyl ether
SF6	SF ₆	C2H5OC2H5	diethyl ether
H2	H ₂	CH3COCH3	acetone
CH4	methane	CH3COOCH3	methyl acetate
C2H6	ethane	CH3COOC2H5	ethyl acetate
C3H8	propane	cC6H12	cyclohexane
C4H10	<i>n</i> -butane	cC6H11CH3	methyl cyclohexane
C5H12	<i>n</i> -pentane	C3H4c	cyclopropene
C6H14	<i>n</i> -hexane	C6H6	benzene
		C6H5CH3	toluene

5.4. Role of the buffer tank

The role of the buffer tank can be described by replacing eq. (2.14) with,

$$f_d = A_d p_d - A_b p_b - (A_d - A_b) p_a - f_{f,d} \quad (5.4)$$

The volume of the buffer tank is,

$$V_b = A_b (l_B - x) \quad (5.5)$$

The variation of *p*_b can be described by the differential equation,

$$\frac{dp_b}{dt} = \frac{p_b A_b \dot{x}}{V_b} - \frac{c_{leak} p_b (p_b - p_a)}{V_b} \quad (5.6)$$

The effect of the buffer tank can be calculated by using a 'CBUF' card,

```
CBUF lB Drod cleak
```

The cross section of the buffer tank is calculated as,

$$A_b = \pi \frac{D_d^2 - D_{rod}^2}{4} \quad (5.7)$$

Nomenclature

<i>g</i> _n	standard acceleration of gravity	typical values 9.80665 m s ⁻²
<i>p</i> _a	ambient pressure	101325 Pa
<i>t</i>	time	
driver section		
<i>V</i> _T	volume of air reservoir tank	0.01312 m ³
<i>D</i> _d	diameter of driver piston	0.13 m

A_d	sectional area of driver piston	0.01327 m ²
p_T	Initial pressure of air reservoir tank	
γ_d	polytropic index of driver gas	1.2
$f_{f,d}$	dynamic frictional force of driver piston	(10~300 N)
m_d	mass of moving part of driver	10.5 kg
x	position of driver piston	
V_d	volume of driver gas	
p_d	pressure of driver section	
buffer section		
l_B	length of buffer section	0.24 m
D_{rod}	diameter of driver piston rod	0.018 m
A_b	sectional area of buffer section	0.01302 m ²
c_{leak}	gas leak coefficient	$1 \times 10^{-5} \text{ m}^3 \text{ Pa}^{-1} \text{ s}^{-1}$
V_b	volume of the buffer tank	
p_b	pressure of buffer tank	
sample compression section		
V_R	volume of reaction chamber	$6.4 \times 10^{-5} \text{ m}^3$
D_c	diameter of compression piston	0.094 m
A_c	sectional area of compression piston	0.006940 m ²
p_0	Initial pressure of sample gas	101325 Pa
γ	heat capacity ratio of sample gas	1.35
$f_{f,c}$	dynamic frictional force of compression piston	(10~300 N)
m_c	mass of moving part of compressor	3 kg
y	position of compression piston	
V	volume of sample	
p	pressure of sample	
cam		
l	cam slope width	0.15 m
h	cam slope height (= compression piston stroke)	0.085 m
l_A	cam acceleration length	0.04 m
l_D	cam deceleration length	0.05 m
l_C	cam curvature length	0.02 m
f_d	horizontal force from driver	
f_c	vertical force from compressor	
heat transfer		
q	heat	
σ	surface area of reactor	
T	sample gas temperature	
T_w	reactor wall temperature	
h_c	heat transfer coefficient	
δ_h	thickness of thermal boundary layer	
D	tube diameter	
η	viscosity	
λ	thermal conductivity	
ρ	density	
c_p	specific heat capacity	
v	gas velocity	
Nu	Nusselt number (= $h_c D / \lambda$)	
Pr	Prandtl number (= $c_p \eta / \lambda$)	
Re	Reynolds number (= $\rho v D / \eta$)	

Appendix

A1. Cam shape function

Explicit form of the cam shape function shown in Fig. 2.2 can be written as follows.

Some additional thermodynamic data for hydrocarbons were calculated by THERM program.^[10] An input for the genTherm program is shown in List A2.2.

List A2.2. Sample input for genTherm program (hydrocarbons)

Thermodata for CRCM (Aug 20, 2007)																					
C2H5OH	M	C	2	H	6	O	1	\$	C/C/H3	1	C/C/H2/O	1	O/C/H	1	\$	2	3				
CH3OCH3	M	C	2	H	6	O	1	\$	C/H3/O	2	O/C2	1	\$	2	18						
CH3COCH3	M	C	3	H	6	O	1	\$	C/CO/H3	2	CO/C2	1	\$	2	18						
iC4H10	M	C	4	H	10	\$			C/C3/H	1	C/C/H3	3	\$	3	81						
CH3COOC2H5	M	C	4	H	8	O	2	\$	C/CO/H3	1	CO/C/O	1	O/C/CO	1	C/C/H2/O	1	C/C/H3	1	\$	4	9
cC6H12	M	C	6	H	12	\$			CY/C6	1	C/C2/H2	6	\$	0	3						
cC6H11CH3	M	C	7	H	14	\$			CY/C6	1	C/C/H3	1	C/C2/H2	5	C/C3/H	1	\$	1	3		

A3. Calculation of transport properties

Transport properties of gases necessary for the evaluation of heat transfer terms were calculated using TRANFIT program^[11] in Chemkin-II using the transport property input (sample is shown List A3.1) and thermodynamic database described in Appendix A2. The transport input data available in Chemkin-II library were used if available. Other data were taken from the value derived from the experimental viscosity.^[12] The TRANFIT program fit the viscosity and thermal conductivity in the following forms, and the derived coefficients were used to calculate the transport properties.

$$\ln \eta = \sum_{i=1}^4 a_{i\eta} (\ln T)^{i-1} \quad (\text{A3.1})$$

$$\ln \lambda = \sum_{i=1}^4 b_{i\lambda} (\ln T)^{i-1} \quad (\text{A3.2})$$

The mixture averaged transport properties were calculated using the following formulae.

$$\eta = \frac{\sum_{i=1}^N x_i \eta_i}{\sum_{j=1}^N x_j \Phi_{ij}} \quad (\text{A3.3})$$

$$\text{where, } \Phi_{ij} = \frac{1}{8^{1/2}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\eta_i}{\eta_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2$$

$$\lambda = \frac{1}{2} \left(\sum_{i=1}^N x_i \lambda_i + \frac{1}{\sum_{i=1}^N x_i / \lambda_i} \right) \quad (\text{A3.4})$$

List A3.1. Input for TRANFIT

O2	1	107.400	3.458	0.000	1.600	3.800
N2	1	97.530	3.621	0.000	1.760	4.000
CO2	1	244.000	3.763	0.000	2.650	2.100
H2O	2	572.400	2.605	1.844	0.000	4.000
He	0	10.200	2.576	0.000	0.000	0.000
Ne	0	32.8	2.820	0.	0.	0.
Ar	0	136.500	3.330	0.000	0.000	0.000
Kr	0	178.9	3.655	0.	0.	0.
Xe	0	231.0	4.047	0.	0.	0.
CF4	2	134.0	4.662	0.	0.	1.

^[10] E. R. Ritter and J. W. Bozzelli, *Int. J. Chem. Kinet.*, **23**, 767–778 (1991).

^[11] R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller, *A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties*, SAND86-8246-UC-401, Sandia National Laboratories, 1995.

^[12] B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids, 5th Ed.*, McGraw-Hill, Boston, 2001.