

## Text Format of Reactions

### Reaction Types

**Ordinary reactions.** The description of an ordinary reaction has one line that contains a reaction equation and values  $A$ ,  $n$ ,  $E$ .

*Example.*

```
CH2O + H = CHO + H2    2.300E+10    1.05    13700.    !J.Warnatz, 1997
```

The forward reaction rate is  $q = k_{for}[\text{CH}_2\text{O}][\text{H}]$ . Here and further, the species name in brackets denotes the species concentration. For calculation of the forward rate constant  $k_{for}$  the Arrhenius formula is used.

$$k_{for} = AT^n \exp(-E/RT).$$

**Three-body reactions.** These reactions contain the term M in the reaction equation. The description of the reaction includes a line with third-body names and their enhanced efficiencies  $C_j$ .

*Example.*

```
CH2O + M = CHO + H + M    5.000E+16    0.0    320000.    !J.Warnatz, 1997
H2/1.0/ H2O/6.5/ O2/0.40/ N2/0.4/ CO/0.75/ CO2/1.50/ CH4/3.0/
```

The forward reaction rate is  $q = k_{for}[\text{M}][\text{CH}_2\text{O}]$ ,  $[\text{M}] = \sum [\text{X}_j] C_j$ . The summation is over all species. If a species is not declared in the third-body list, its efficiency is 1. The maximum number of declared third-bodies is 10.

**Pressure dependent reactions.** Chemked identifies only one type of the reactions with the pressure dependent rate constants, the unimolecular / recombination reactions. The pressure dependent reactions have the special term (+M) in the reaction equation. A species name can also be used in the parenthesis instead of the M symbol. In these reactions, the Lindeman and Troe relations for the rate constants are employed.

The Lindeman type of the rate constant

*Example.*

```
N2O (+M) <=> N2 + O (+M) 1.300E+11    .0    59620.00 !GRI-Mech 2.11
LOW / 6.200E+14    .000    56100.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
```

```

h + o2 (+h2) = ho2 (+h2) 4.52E+13    0.0    0.0    !N.M.Marinov 1995
low / 1.52E+19    -1.133    0.0 /

```

The forward reaction rate is  $q = k_{eff} [N_2O]$ . The pressure dependent forward rate constant is  $k_{eff} = k_L$ ,

$$k_L = \frac{k_{for}}{1 + 1/P_r}, \quad P_r = k_{for,low}[M]/k_{for},$$

where  $k_{for}$  and  $k_{for,low}$  are the high and low pressure limits of the forward rate constant. The Arrhenius parameters for the  $k_{for}$  constant are placed as before on the first line, and the parameters for the  $k_{for,low}$  constant are placed on the second line after the LOW keyword.

### The Troe type of rate constant

#### *Example.*

```

SI2H6 (+M) = SIH4 + SIH2 (+M) 1.81E10 1.7 50203. !NIST Mechanisms
LOW/5.09E53    -10.37    56034./
TROE/4.375E-5    438.5    2726.    438.2/
SIH4/4./ SI2H6/4./

```

The forward reaction rate is  $q = k_{eff} [SI_2H_6]$ . The forward rate constant is  $k_{eff} = k_L F_T$ .

$$\log_{10} F_T = \left[ 1 + \left( \frac{\log_{10} P_r + x}{n - y(\log_{10} P_r + x)} \right)^2 \right]^{-1} \log_{10} F_C$$

$$x = -0.4 - 0.67 \cdot \log_{10} F_C$$

$$n = 0.75 - 1.27 \cdot \log_{10} F_C$$

$$y = 0.14$$

$$F_C = (1 - a) \exp(-T/b) + a \exp(-T/c) + \exp(-d/T),$$

where  $F_C$  is a 4 parameter expression, the parameters  $a$ ,  $b$ ,  $c$ ,  $d$  are placed on an individual line and follow the TROE keyword.

Remark -----

It is the case that the last term in the  $F_C$  expression is omitted. Then the corresponding line of the reaction description should contain 3 parameters after the TROE keyword. This is the status flag for the Chemked solver to use the 3-parameter  $F_C$  expression.

-----

## Reactions with Reverse Rate Parameters

### Example.

```
OH + M = O + H + M          9.88E+17    -0.74    102100
    REV / 4.71E+18          -1          0 /
    H2/2.5/ H2O/12./ AR/0.75/
HO2 + H <=> H2 + O2         1.66E+13          0      823
    REV / 3.16E+12          0.35    55510 /
```

The three Arrhenius parameters for the reverse rate constant follow the keyword REV. This option overrides the reverse rate that would be normally computed through the equilibrium constant. **This reaction type can not be combined with pressure dependent reactions.**

**Reactions with photon radiation.** This reaction contains the special term HV. The HV (or hv) term isn't a species name and must not be declared in the thermodynamic database.

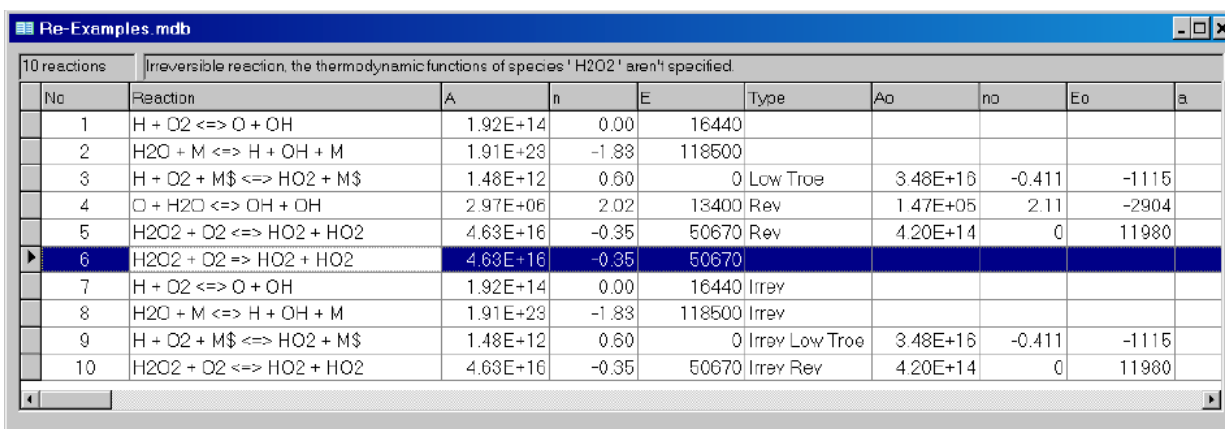
### Example.

```
NO(A) = NO(X) + hv 5E+08 0. 0. !I.S.McDermid 1982
```

These reactions are processed in assumption of free escaping of radiation. In this case the reaction is irreversible.

## Reaction Table

In Chemked, reactions are displayed in tables of databases where the rate constant parameters are placed in the corresponding fields. An example of this table is presented in the following figure.



No	Reaction	A	n	E	Type	Ao	no	Eo	a
1	H + O2 <=> O + OH	1.92E+14	0.00	16440					
2	H2O + M <=> H + OH + M	1.91E+23	-1.83	118500					
3	H + O2 + M\$ <=> HO2 + M\$	1.48E+12	0.60	0	Low Troe	3.48E+16	-0.411	-1115	
4	O + H2O <=> OH + OH	2.97E+06	2.02	13400	Rev	1.47E+05	2.11	-2904	
5	H2O2 + O2 <=> HO2 + HO2	4.63E+16	-0.35	50670	Rev	4.20E+14	0	11980	
6	H2O2 + O2 => HO2 + HO2	4.63E+16	-0.35	50670					
7	H + O2 <=> O + OH	1.92E+14	0.00	16440	Irrev				
8	H2O + M <=> H + OH + M	1.91E+23	-1.83	118500	Irrev				
9	H + O2 + M\$ <=> HO2 + M\$	1.48E+12	0.60	0	Irrev Low Troe	3.48E+16	-0.411	-1115	
10	H2O2 + O2 <=> HO2 + HO2	4.63E+16	-0.35	50670	Irrev Rev	4.20E+14	0	11980	

An example of reaction table

The pressure dependent reactions and the reactions with reverse rate parameters have the following designations.

Reaction Type		Keyword
Lindeman form		Low
Lindeman form with Troe function		Low Troe
With reverse rate parameters		Rev

These keywords are placed in the **Type** fields of the table.

## Reversible and Irreversible Properties of Reaction

In Chemked you can process reversible and irreversible reactions; the way to display these reactions in the reaction table is shown in the figure above.

### Reversible Reactions

a. Thermodynamic properties of all reactants and all products are specified in the thermodynamic database. In this case the equilibrium constant of the reaction is known, and the reverse rate constant  $k_{rev}$  is calculated throughout the forward rate constant  $k_{for}$  and the equilibrium constant  $K_c$ .

$$k_{rev} = k_{for} / K_c$$

This reaction is reversible; examples are presented in the reaction table (No 1-3); these reactions have no special designation. The CHEMKIN representation is shown here

```

H + O2 <=> O + OH          1.92E+14          0          16440
H2O + M <=> H + OH + M      1.91E+23         -1.83         118500
    H2/0.73/ H2O/12./ AR/0.38/
H + O2 (+M) <=> HO2 (+M)    1.48E+12          0.6          0
    LOW / 3.48E+16      -0.411      -1115 /
    TROE / 0.5      1.E-30      1.E+30      1.E+100 /
    H2/1.3/ H2O/14./ AR/0.67/

```

b. A reaction is reversible if the Arrhenius parameters of the reverse rate constant are explicitly specified. This property is true even if the thermodynamic data for reactants or products are not available. Examples are presented in the reaction table (No 4,5); the reactions have keywords **Rev**. The CHEMKIN representation is shown here

O + H2O	<=>	OH + OH	2.97E+06	2.02	13400
REV /	1.47E+05	2.11	-2904 /		
H2O2 + O2	<=>	HO2 + HO2	4.63E+16	-0.35	50670
REV /	4.20E+14	0	11980 /		

*Note.* In reversible reactions the delimiter between reactants and products contains left and right angle brackets, <=>.

## Irreversible Reactions

Thermodynamic properties of at least one reactant or one product are not specified; this reaction is irreversible. An example is presented in the reaction table (No 6); the CHEMKIN representation is shown here

H2O2 + O2	=>	HO2 + HO2	4.63E+16	-0.35	5067
-----------	----	-----------	----------	-------	------

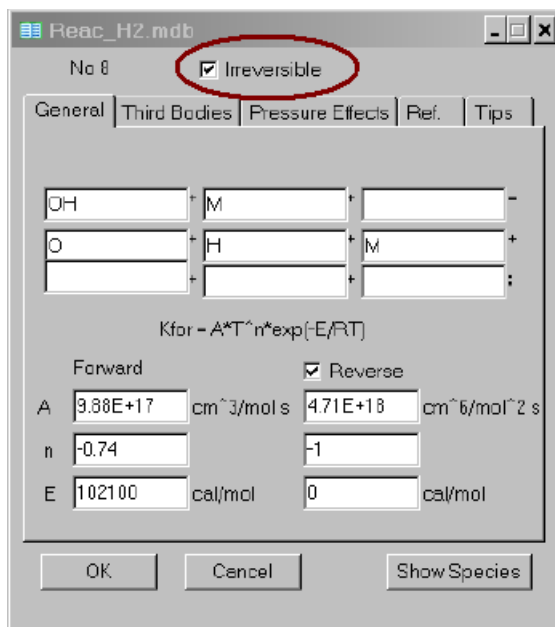
In the example, we have not specified the polynomial coefficients for calculating thermodynamic properties of H2O2.

*Note.* In this reaction type the delimiter between reactants and products contains only right angle bracket, =>.

## User Specified Irreversibility.

You may change the reaction property from reversible to irreversible.

1. Double click the name of the reaction you want to make irreversible. The input window appears.
2. Check the Irreversible check box; click OK.



In the Type field of the reaction table, the **Irrev** keyword will be added to existing keywords (reaction table, No. 7-10).

This operation does not change the reaction description in the table. For example, if the delimiter between reactants and products was  $\rightleftharpoons$ , it does not change although the reaction becomes irreversible. However in the CHEMKIN representation, the delimiter changes to the form  $\Rightarrow$ .

```
H2O + M => H + OH + M          1.91E+23      -1.83      118500
H2/0.73/ H2O/12./ AR/0.38/
H + O2 (+M) => HO2 (+M)        1.48E+12         0.6         0
LOW / 3.48E+16      -0.411      -1115 /
TROE / 0.5      1.E-30      1.E+30      1.E+100 /
H2/1.3/ H2O/14./ AR/0.67/
H2O2 + O2 => HO2 + HO2          4.63E+16      -0.35      50670
REV / 4.20E+14          0      11980 /
```

To return the reversible property, you should open the input window, delete the check mark in the Irreversible check box; click OK.

**Important.** The reversible and irreversible properties of reactions are taken into account when forming reaction mechanism for solver file.

## Valid and Invalid Properties of Reactions

A reaction has **Invalid** property in the following cases.

- At least one reactant, product or third-body isn't declared in the thermodynamic database or has the **Invalid** property.
- Chemical elements don't balance.

Otherwise the reaction has the **Valid** property. In the reaction table, the invalid reactions are highlighted.

When you form the reaction mechanism for a chemical kinetic problem, the invalid reactions will be ignored.

## Units of Concentration and Rate Constants

Description of each chemical reaction contains a set of parameters for calculating reaction rate constant. The basis for the calculation is the Arrhenius type formula.

$$k = AT^n \exp(-E/RT)$$

where  $k$  is reaction rate constant,  $R$  is the universal gas constant and  $T$  is temperature in K. The pre-exponential factor  $A$ , exponent  $n$  and activation energy  $E$  are stored in reaction database. The values  $A$  and  $E$  are not dimensionless and we have to specify their units. The unit of the pre-exponential factor (A-units) directly relate to the units of species concentrations. Among a great number of concentration units we have chosen mol/cm<sup>3</sup>. These units are most frequently used in published reaction mechanisms and they are the default units in the CHEMKIN subroutines.

The A-units depend on reaction order. If  $z$  is the order of a reaction then the A-units are (mol/cm<sup>3</sup>)<sup>1-z</sup> sec<sup>-1</sup>. We will denote these units as **mol-cm-sec**. The equilibrium constant units are (mol/cm<sup>3</sup>)<sup>a</sup> where  $a = z_{rev} - z_{for}$ ;  $z_{for}$  and  $z_{rev}$  are orders of forward and reverse reactions.

The Chemked units of the activation energy (E-units) are **cal/mol**.

**The pre-exponential factor units mol-cm-sec and the activation energy units cal/mol are the internal Chemked units and only they are used in the Chemked reaction databases.**

If the data you want to enter does not have the internal Chemked units, they should be converted to these units. Some help can be get using the **Paste Special** method; more information on this item can be found in the **Entering Data help topic**.

*Example* -----

```
OH + M = O + H + M          9.88E+17      -0.74      102100
    REV / 4.71E+18          -1          0 /
    H2/2.5/ H2O/12./ AR/0.75/
```

Concentrations [OH], [O], [H], [M] mol/cm<sup>3</sup>

$R = 1.19872$  cal/mol K

$k_{for} = 9.88E+17 * T^{0.74} \exp(-102100/RT)$  cm<sup>3</sup>/mol sec

$k_{rev} = 4.71E+18 * T^{-1}$  cm<sup>6</sup>/mol<sup>2</sup> sec

Equilibrium constant  $K_c = k_{for} / k_{rev}$  mol/cm<sup>3</sup>

Reaction rate  $k_{for} [OH][M] - k_{rev} [O][H][M]$  mol/cm<sup>3</sup> sec

-----

## Additional Precepts for Reactions in Chemked

1. In each reaction, the maximum number of reactants is 3 and the maximum number of products is 6.

2. The stoichiometric coefficients are not used.

*Example.*

When entering the reaction  $2O + M = O_2 + M$ , the symbols  $2O$  will be interpreted as an unknown name. The reaction should be written as  $O + O + M = O_2 + M$ .

3. In accordance with the CHEMKIN-II format, the pressure dependent reactions have a special term (+M) in reaction equations. In Chemked, the terms (+M) are replaced with + M\$, in order to process the M\$ symbols as other species names. When entering data from the clipboard, the replacement is made automatically. In the text output documents, the characters (+M) are printed.

*Example.*

CHEMKIN representation  $CH_3 + H (+M) = CH_4 (+M)$   
 $h + o_2 (+h_2) = ho_2 (+h_2)$

Chemked representation  $CH_3 + H + M\$ = CH_4 + M\$$   
 $h + o_2 + h_2\$ = ho_2 + h_2\$$

4. The sign '+' is commonly used for the positive ion designation. On the other hand, this symbols is a delimiter between species names in the reaction equation. To distinguish between these two cases, the following rule is taken. A species name may end with any number of '+'s without parentheses. The use of embedded '+'s in the species names is forbidden.

*Example.*

The equation  $C^{++e}=C^{+++e+e}$  will be interpreted as  $C^{+} + e = C^{++} + e + e$ .

5. The CHEMKIN description of reaction duplicates includes an additional line with the DUPLICATE (or DUP) keyword.

*Example.*

```
ho2 + ho2 = h2o2 + o2 4.20E+14 0.0 11982.0 !N.M.Marinov 1995
dup
ho2 + ho2 = h2o2 + o2 1.30E+11 0.0 -1629.0 !N.M.Marinov 1995
dup
```

When entering such a reaction, the DUPLICATE word will be written in the Comment field of the reaction table ahead of other comments. If the Comment field contains the DUPLICATE (or DUP) word at the first position then a line with this word will be created in the text output documents.