Custom Rate Constants - Beyond TS1 and TS2

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November 25, 2024

1 Using this Document

Contained are notes on the coversion of all custom rate constant equations from CAM to standard MICM reaction types, building on the custom rate constant equation notes for TS1 and TS2. The original rate constant functions are taken from the CAM source code, at `cam/src/chemistry/mozart/mo_usrrxt.F90`. These notes represent a snapshot in time, and the CAM code will likely have changed since this document was written. The code snippets are included to provide context.

2 usr_MCO3_XNO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (796,796)
      tp(:)             = 300._r8 * tinv(:)


/cam/src/chemistry/mozart/mo_usrrxt.F90 (958,966)
!-----------------------------------------------------------------
!     ... mco3 + no2 -> mpan
!-----------------------------------------------------------------
      if( usr_MCO3_NO2_ndx > 0 ) then
         rxt(:,k,usr_MCO3_NO2_ndx) = 1.1e-11_r8 * tp(:) / m(:,k)
      end if
      if( usr_MCO3_XNO2_ndx > 0 ) then
         rxt(:,k,usr_MCO3_XNO2_ndx) = 1.1e-11_r8 * tp(:) / m(:,k)
      end if
```

As discussed in the TS1 document sections 11 and 19, this appears to have been replaced by a Troe reaction. The proposed reworking of this function (TS1 section 19) included removing M from the reactants and products and using a standard Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{1}$$

with $A = 1.1 \times 10^{-11}$, $B = -1$, $C = 0$, $D = 300$, and $E = 0$.

However, it appears that the CAM preprocessor may ignore M as a reactant, meaning that this reaction would require a new reaction type in Music Box.

Should a new reaction type be added to Music Box for this reaction? Or is this no longer used?

3 usr_XOOH_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1046,1052)
!-----------------------------------------------------------------
!       ... xooh + oh -> h2o + oh
!-----------------------------------------------------------------
      if( usr_XOOH_OH_ndx > 0 ) then
         call comp_exp( exp_fac, 253._r8*tinv, ncol )
         rxt(:,k,usr_XOOH_OH_ndx) = temp(:ncol,k)**2._r8 * 7.69e-17_r8 * exp_fac(:)
      end if
```

This can be rearranged as an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{2}$$

with $A = 7.69 \times 10^{-17}$, $B = 2$, $C = 253$, $D = 1$, and $E = 0$.

4 usr_OA_O2

/cam/src/chemistry/mozart/mo_usrrxt.F90 (800,808)

```
!-----------------------------------------------------------------
! ... o + o2 + m --> o3 + m (JPL15-10)
!-----------------------------------------------------------------
       if( usr_O_O2_ndx > 0 ) then
          rxt(:,k,usr_O_O2_ndx) = 6.e-34_r8 * tp(:)**2.4_r8
       end if
       if( usr_OA_O2_ndx > 0 ) then
          rxt(:,k,usr_OA_O2_ndx) = 6.e-34_r8 * tp(:)**2.4_r8
       end if
```

Same as `usr_O_O2` (TS1 section 5).

5 usr_XNO2NO3_M and usr_NO2XNO3_M

/cam/src/chemistry/mozart/mo_usrrxt.F90 (849,875)

```
!-----------------------------------------------------------------
! ... n2o5 + m --> no2 + no3 + m (JPL15-10)
!-----------------------------------------------------------------
       if( usr_N2O5_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_N2O5_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) * 1.724138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_N2O5_M_ndx) = 0._r8
          end if
       end if
       if( usr_XNO2NO3_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_XNO2NO3_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) *1.724138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_XNO2NO3_M_ndx) = 0._r8
          end if
       end if
       if( usr_NO2XNO3_M_ndx > 0 ) then
          if( tag_NO2_NO3_ndx > 0 ) then
             call comp_exp( exp_fac, -10840.0_r8*tinv, ncol )
             rxt(:,k,usr_NO2XNO3_M_ndx) = rxt(:,k,tag_NO2_NO3_ndx) * 1.734138e26_r8 * exp_fac(:)
          else
             rxt(:,k,usr_NO2XNO3_M_ndx) = 0._r8
          end if
       end if
```

Same as `usr_N2O5_M` (TS1 section 7)

6 usr_XHNO3_OH

/cam/src/chemistry/mozart/mo_usrrxt.F90 (877,897)

```
!-----------------------------------------------------------------
! set rates for:
!   ... hno3 + oh --> no3 + h2o
!           ho2no2 + m --> ho2 + no2 + m
!-----------------------------------------------------------------
       if( usr_HNO3_OH_ndx > 0 ) then
```

```
         call comp_exp( exp_fac, 1335._r8*tinv, ncol )
         ko(:) = m(:,k) * 6.5e-34_r8 * exp_fac(:)
         call comp_exp( exp_fac, 2199._r8*tinv, ncol )
         ko(:) = ko(:) / (1._r8 + ko(:)/(2.7e-17_r8*exp_fac(:)))
         call comp_exp( exp_fac, 460._r8*tinv, ncol )
         rxt(:,k,usr_HNO3_OH_ndx) = ko(:) + 2.4e-14_r8*exp_fac(:)
      end if
      if( usr_XHNO3_OH_ndx > 0 ) then
         call comp_exp( exp_fac, 1335._r8*tinv, ncol )
         ko(:) = m(:,k) * 6.5e-34_r8 * exp_fac(:)
         call comp_exp( exp_fac, 2199._r8*tinv, ncol )
         ko(:) = ko(:) / (1._r8 + ko(:)/(2.7e-17_r8*exp_fac(:)))
         call comp_exp( exp_fac, 460._r8*tinv, ncol )
         rxt(:,k,usr_XHNO3_OH_ndx) = ko(:) + 2.4e-14_r8*exp_fac(:)
      end if
```

Same as `usr_HNO3_OH` (TS1 section 18).

7 usr_XHO2NO2_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (898,913)
      if( usr_HO2NO2_M_ndx > 0 ) then
         if( tag_NO2_HO2_ndx > 0 ) then
            call comp_exp( exp_fac, -10900._r8*tinv, ncol )
            rxt(:,k,usr_HO2NO2_M_ndx) = rxt(:,k,tag_NO2_HO2_ndx) * exp_fac(:) / 2.1e-27_r8
         else
            rxt(:,k,usr_HO2NO2_M_ndx) = 0._r8
         end if
      end if
      if( usr_XHO2NO2_M_ndx > 0 ) then
         if( tag_NO2_HO2_ndx > 0 ) then
            call comp_exp( exp_fac, -10900._r8*tinv, ncol )
            rxt(:,k,usr_XHO2NO2_M_ndx) = rxt(:,k,tag_NO2_HO2_ndx) * exp_fac(:) / 2.1e-27_r8
         else
            rxt(:,k,usr_XHO2NO2_M_ndx) = 0._r8
         end if
      end if
```

Same as `usr_HO2NO2_M` (TS1 section 8).

8 usr_XPAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (968,985)
!-----------------------------------------------------------------
! ... pan + m --> ch3co3 + no2 + m (JPL15-10)
!-----------------------------------------------------------------
      call comp_exp( exp_fac, -14000._r8*tinv, ncol )
      if( usr_PAN_M_ndx > 0 ) then
         if( tag_CH3CO3_NO2_ndx > 0 ) then
            rxt(:,k,usr_PAN_M_ndx) = rxt(:,k,tag_CH3CO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
         else
            rxt(:,k,usr_PAN_M_ndx) = 0._r8
         end if
      end if
      if( usr_XPAN_M_ndx > 0 ) then
         if( tag_CH3CO3_NO2_ndx > 0 ) then
            rxt(:,k,usr_XPAN_M_ndx) = rxt(:,k,tag_CH3CO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
```

```
      else
         rxt(:,k,usr_XPAN_M_ndx) = 0._r8
      end if
   end if
```

Same as `usr_PAN_M` (TS1 section 17).

9 usr_XMPAN_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (987,1003)
!-----------------------------------------------------------------
! ... mpan + m --> mco3 + no2 + m (JPL15-10)
!-----------------------------------------------------------------
   if( usr_MPAN_M_ndx > 0 ) then
      if( tag_MCO3_NO2_ndx > 0 ) then
         rxt(:,k,usr_MPAN_M_ndx) = rxt(:,k,tag_MCO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
      else
         rxt(:,k,usr_MPAN_M_ndx) = 0._r8
      end if
   end if
   if( usr_XMPAN_M_ndx > 0 ) then
      if( tag_MCO3_NO2_ndx > 0 ) then
         rxt(:,k,usr_XMPAN_M_ndx) = rxt(:,k,tag_MCO3_NO2_ndx) * 1.111e28_r8 * exp_fac(:)
      else
         rxt(:,k,usr_XMPAN_M_ndx) = 0._r8
      end if
   end if
```

Same as `usr_MPAN_M` (TS1 section 11).

10 usr_C2O3_NO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1444,1449)
   if ( usr_C2O3_NO2_ndx > 0 ) then
      ko(:)   = 2.6e-28_r8 * m(:,k)
      kinf(:) = 1.2e-11_r8
      rxt(:,k,usr_C2O3_NO2_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log10(ko/kinf))**2))
   end if
```

This is a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{3}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 2.6 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 1.2 \times 10^{-11}$, $B_{inf} = 0$, and $C_{inf} = 0$.

11 usr_C2H4_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1454,1458)
   if ( usr_C2H4_OH_ndx > 0 ) then
```

```
      ko(:)   = 1.0e-28_r8 * m(:,k)
      kinf(:) = 8.8e-12_r8
      rxt(:,k,usr_C2H4_OH_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log(ko/kinf))**2))
   end if
```

This is a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{4}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 1.0 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 8.8 \times 10^{-12}$, $B_{inf} = 0$, and $C_{inf} = 0$.

12 usr_XO2N_HO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1459,1461)
      if ( usr_XO2N_HO2_ndx > 0 ) then
         rxt(:,k,usr_XO2N_HO2_ndx) = rxt(:,k,tag_XO2N_NO_ndx)* (continued)
           rxt(:,k,tag_XO2_HO2_ndx)/(rxt(:,k,tag_XO2_NO_ndx)+1.e-36_r8)
      end if
```

Looking through the Chemistry Café, the `tag_XO2_HO2_ndx` appears to be an Arrhenius reaction with $A = 8 \times 10^{-13}$ and $C = 700$, and the `tag_XO2_NO_ndx` appears to also be an Arrhenius reaction with $A = 2.7 \times 10^{-12}$ and $C = 360$, but I can't find anything corresponding to `tag_XO2N_NO_ndx` in the database or the mechanisms that are stored with the CAM source code.

How should this rate constant be calculated?

13 usr_C2O3_XNO2

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1449,1453)
      if ( usr_C2O3_XNO2_ndx > 0 ) then
         ko(:)   = 2.6e-28_r8 * m(:,k)
         kinf(:) = 1.2e-11_r8
         rxt(:,k,usr_C2O3_XNO2_ndx) = (ko/(1._r8+ko/kinf)) * 0.6_r8**(1._r8/(1._r8+(log10(ko/kinf))**2))
      end if
```

This is a Troe reaction:

$$
\begin{aligned}
k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{5}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 2.6 \times 10^{-28}$, $B_0 = 0$, $C_0 = 0$, $A_{inf} = 1.2 \times 10^{-11}$, $B_{inf} = 0$, and $C_{inf} = 0$.

14 usr_CLm_H2O_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1909,1910)
        call comp_exp( exp_fac, -6600._r8 * tinv, ncol )
        rxt(:,k,usr_clm_h2o_m_ndx) = 2.e-8_r8 * exp_fac(:)
```

This is an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{6}$$

with $A = 2 \times 10^{-8}$, $B = 0$, $C = -6600$, and $E = 0$.

15 usr_CLm_HCL_M

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1912,1913)
        call comp_exp( exp_fac, -11926._r8 * tinv, ncol )
        rxt(:,k,usr_clm_hcl_m_ndx) =  tinv(:) * exp_fac(:)
```

This is an Arrhenius reaction:

$$k = Ae^{(\frac{C}{T})}(\frac{T}{D})^B(1.0 + E \times P), \tag{7}$$

with $A = 1$, $B = -1$, $C = -11926$, $D = 1$, and $E = 0$.

16 usr_oh_co

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (796,796)
       tp(:)              = 300._r8 * tinv(:)
```

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1757,1770)
       !-----------------------------------------------------------------------
       !     ... CO + OH --> CO2 + HO2
       !-----------------------------------------------------------------------
       if ( usr_oh_co_ndx > 0 ) then
          ko(:)     = 5.9e-33_r8 * tp(:)**1.4_r8
          kinf(:)   = 1.1e-12_r8 * (temp(:ncol,k) / 300._r8)**1.3_r8
          ko_m(:)   = ko(:) * m(:,k)
          k0(:)     = 1.5e-13_r8 * (temp(:ncol,k) / 300._r8)**0.6_r8
          kinf_m(:) = (2.1e+09_r8 * (temp(:ncol,k) / 300._r8)**6.1_r8) / m(:,k)
          rxt(:,k,usr_oh_co_ndx) = (ko_m(:)/(1._r8+(ko_m(:)/kinf(:)))) * &
               0.6_r8**(1._r8/(1._r8+(log10(ko_m(:)/kinf(:)))**2._r8)) + &
               (k0(:)/(1._r8+(k0(:)/kinf_m(:)))) * &
               0.6_r8**(1._r8/(1._r8+(log10(k0(:)/kinf_m(:)))**2._r8))
       endif
```

This rate constant is the sum of a Troe rate constant:

$$\begin{aligned} k &= \frac{k_0[\mathrm{M}]}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\ k_0 &= A_0 e^{(\frac{C_0}{T})} \left(\frac{T}{300}\right)^{B_0} \\ k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}} \end{aligned} \tag{8}$$

where $F_C = 0.6$, $N = 1$, $A_0 = 5.9 \times 10^{-33}$, $B_0 = -1.4$, $C_0 = 0$, $A_{inf} = 1.1 \times 10^{-12}$, $B_{inf} = 1.3$, and $C_{inf} = 0$, and a ternary chemical activation rate constant:

$$
\begin{aligned}
k &= \frac{k_0}{1 + k_0[\mathrm{M}]/k_{\mathrm{inf}}} F_C^{(1+1/N[log_{10}(k_0[\mathrm{M}]/k_{\mathrm{inf}})]^2)^{-1}} \\
k_0 &= A_0 e^{\left(\frac{C_0}{T}\right)} \left(\frac{T}{300}\right)^{B_0} \\
k_{inf} &= A_{inf} e^{\left(\frac{C_{inf}}{T}\right)} \left(\frac{T}{300}\right)^{B_{inf}}
\end{aligned}
\tag{9}
$$

where $F_C = 0.6$, $N = 1$, $A_0 = 1.5 \times 10^{-13}$, $B_0 = 0.6$, $C_0 = 0$, $A_{inf} = 2.1 \times 10^{9}$, $B_{inf} = 6.1$, and $C_{inf} = 0$.

17 usr_oh_dms

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1777,1784)
      !-----------------------------------------------------------------------
      !     ... DMS + OH --> 0.75 SO2 + 0.25 MSA
      !-----------------------------------------------------------------------
      if ( usr_oh_dms_ndx > 0 ) then
         o2(:ncol) = invariants(:ncol,k,inv_o2_ndx)
         rxt(:,k,usr_oh_dms_ndx) = 2.000e-10_r8 * exp(5820.0_r8 * tinv(:)) / &
              ((2.000e29_r8 / o2(:)) + exp(6280.0_r8 * tinv(:)))
      endif
```

This does not appear to fit any existing reaction types.

Should this be added as a reaction type to Music Box? If so, is there a reference to use for the documentation?

18 usr_COhc_OH, usr_COme_OH and usr_CO01_OH–usr_CO42_OH

```
/cam/src/chemistry/mozart/mo_usrrxt.F90 (1777,1784)
!-----------------------------------------------------------------
!      ... CO tags
!-----------------------------------------------------------------
      if( usr_CO_OH_b_ndx > 0 ) then
         if( usr_COhc_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_COhc_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_COme_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_COme_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_CO01_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO01_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
         if( usr_CO02_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO02_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if

         ...

         if( usr_CO41_OH_ndx > 0 ) then
            rxt(:ncol,:,usr_CO41_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
         end if
```

```
if( usr_CO42_OH_ndx > 0 ) then
   rxt(:ncol,:,usr_CO42_OH_ndx) = rxt(:ncol,:,usr_CO_OH_b_ndx)
end if
```

Same as `usr_CO_OH_b` (TS1 section 23).