!-------------------------------------------------------------

! (14) Grain surface reactions

!-------------------------------------------------------------

do J=type\_id\_start(14),type\_id\_stop(14)

IMOD1=0

IMOD2=0

BARR=1.0d0

! --------- Thermal hopping diffusion method

DIFFUSION\_RATE\_1(J)=THERMAL\_HOPING\_RATE(reactant\_1\_idx(J))

DIFFUSION\_RATE\_2(J)=THERMAL\_HOPING\_RATE(reactant\_2\_idx(J))

! --------- Check for JH,JH2, and JO

if (REACTION\_COMPOUNDS\_NAMES(1,J).EQ.YJH) IMOD1=1

if (REACTION\_COMPOUNDS\_NAMES(1,J).EQ.YJH2) IMOD1=2

if (REACTION\_COMPOUNDS\_NAMES(1,J).EQ.YJO) IMOD1=3

if (REACTION\_COMPOUNDS\_NAMES(2,J).EQ.YJH) IMOD2=1

if (REACTION\_COMPOUNDS\_NAMES(2,J).EQ.YJH2) IMOD2=2

if (REACTION\_COMPOUNDS\_NAMES(2,J).EQ.YJO) IMOD2=3

! --------- QM for JH,JH2 only - others are too heavy

if (IMOD1+IMOD2.NE.0) then

! ------------ QM1 - Tunnelling (if it's faster than thermal)

if (GRAIN\_TUNNELING\_DIFFUSION.EQ.1) then

tunneling\_rate = TUNNELING\_RATE\_TYPE\_1(reactant\_1\_idx(J))/nb\_sites\_per\_grain

if ((IMOD1.NE.0).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_1(J))) then

DIFFUSION\_RATE\_1(J)=tunneling\_rate

endif

tunneling\_rate = TUNNELING\_RATE\_TYPE\_1(reactant\_2\_idx(J))/nb\_sites\_per\_grain

if ((IMOD2.NE.0).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_2(J))) then

DIFFUSION\_RATE\_2(J)=tunneling\_rate

endif

endif

! ------------ QM2 - Tunnelling: use estimated width of lowest energy band (if it's faster than thermal)

if (GRAIN\_TUNNELING\_DIFFUSION.EQ.2) then

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_1\_idx(J))/nb\_sites\_per\_grain

if ((IMOD1.NE.0).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_1(J))) then

DIFFUSION\_RATE\_1(J)=tunneling\_rate

endif

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_2\_idx(J))/nb\_sites\_per\_grain

if ((IMOD2.NE.0).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_2(J))) then

DIFFUSION\_RATE\_2(J)=tunneling\_rate

endif

endif

! ------------ QM3 - Fastest out of thermal, QM1, QM2 rates

if (GRAIN\_TUNNELING\_DIFFUSION.EQ.3) then

if (IMOD1.NE.0) then

tunneling\_rate = TUNNELING\_RATE\_TYPE\_1(reactant\_1\_idx(J))/nb\_sites\_per\_grain

if (tunneling\_rate.GT.DIFFUSION\_RATE\_1(J)) then

DIFFUSION\_RATE\_1(J) = tunneling\_rate

endif

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_1\_idx(J))/nb\_sites\_per\_grain

if (tunneling\_rate.GT.DIFFUSION\_RATE\_1(J)) then

DIFFUSION\_RATE\_1(J) = tunneling\_rate

endif

endif

if (IMOD2.NE.0) then

tunneling\_rate = TUNNELING\_RATE\_TYPE\_1(reactant\_2\_idx(J))/nb\_sites\_per\_grain

if (tunneling\_rate.GT.DIFFUSION\_RATE\_2(J)) then

DIFFUSION\_RATE\_2(J) = tunneling\_rate

endif

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_2\_idx(J))/nb\_sites\_per\_grain

if (tunneling\_rate.GT.DIFFUSION\_RATE\_2(J)) then

DIFFUSION\_RATE\_2(J) = tunneling\_rate

endif

endif

endif

! ------------ QM2 - Tunnelling - case of atomic oxygen O : use estimated width of lowest energy band (if it's faster than thermal)

if (GRAIN\_TUNNELING\_DIFFUSION.EQ.4) then

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_1\_idx(J))/nb\_sites\_per\_grain

if ((IMOD1.eq.3).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_1(J))) then

DIFFUSION\_RATE\_1(J)=tunneling\_rate

endif

tunneling\_rate = TUNNELING\_RATE\_TYPE\_2(reactant\_2\_idx(J))/nb\_sites\_per\_grain

if ((IMOD1.eq.3).AND.(tunneling\_rate.GT.DIFFUSION\_RATE\_2(J))) then

DIFFUSION\_RATE\_2(J)=tunneling\_rate

endif

endif

endif

BARR=1.0d0

! --------- Calculate activation energy barrier multiplier

if (ACTIVATION\_ENERGY(J).GE.1.0D-40) then

ACTIV = ACTIVATION\_ENERGY(J) / actual\_dust\_temp

! ------------ Choose fastest of classical or tunnelling

if (ACTIV.GT.SURF\_REACT\_PROBA(J)) then

ACTIV = SURF\_REACT\_PROBA(J)

endif

BARR=EXP(-ACTIV)

if(is\_reac\_diff==1) then

prob\_reac = max(VIBRATION\_FREQUENCY(reactant\_1\_idx(J)),VIBRATION\_FREQUENCY(reactant\_2\_idx(J))) \* &

EXP(-ACTIV)

prob\_deso = EVAPORATION\_RATES\_TEMPO(reactant\_1\_idx(J)) + &

EVAPORATION\_RATES\_TEMPO(reactant\_2\_idx(J))

IF(ANY(REACTION\_COMPOUNDS\_NAMES(:,j)(1:1).eq.'K')) prob\_deso = 0.0D+00

prob\_diff = (DIFFUSION\_RATE\_1(J) + DIFFUSION\_RATE\_2(J)) \* nb\_sites\_per\_grain

barr = prob\_reac+prob\_deso+prob\_diff

barr = prob\_reac / barr

endif

endif

! Modified rate have sense only for surface species

IF(any(REACTION\_COMPOUNDS\_NAMES(:,j)(1:1).eq."J")) THEN

! --------- Modify according to MODIFY\_RATE\_FLAG switch:

if (MODIFY\_RATE\_FLAG.NE.0) then

! ------------ if H+H->H2 is only modified rxn:

if ((MODIFY\_RATE\_FLAG.EQ.-1).AND.(IMOD1.NE.1.OR.IMOD2.NE.1)) then

IMOD1=0

IMOD2=0

endif

! ------------ if only H is modified:

if ((MODIFY\_RATE\_FLAG.EQ.1).AND.(IMOD1.NE.1)) IMOD1=0

if ((MODIFY\_RATE\_FLAG.EQ.1).AND.(IMOD2.NE.1)) IMOD2=0

! ------------ Set to modify all rates, if selected (just atoms)

if (MODIFY\_RATE\_FLAG.EQ.3) then

if ((REACTION\_COMPOUNDS\_NAMES(1,J).EQ.YJH).OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JHe ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JC ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JN ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JO ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JS ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JSi ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JFe ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JNa ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JMg ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JP ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JF ').OR.&

(REACTION\_COMPOUNDS\_NAMES(1,J).EQ.'JCl ')) IMOD1=3

if ((REACTION\_COMPOUNDS\_NAMES(2,J).EQ.YJH).OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JHe ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JC ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JN ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JO ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JS ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JSi ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JFe ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JNa ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JMg ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JP ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JF ').OR.&

(REACTION\_COMPOUNDS\_NAMES(2,J).EQ.'JCl ')) IMOD2=3

endif

! ------------ Modify rates (DIFFUSION\_RATE\_1 & DIFFUSION\_RATE\_2) according to their own evap/acc rates

YMOD1=Y(reactant\_1\_idx(J))

YMOD2=Y(reactant\_2\_idx(J))

call modify\_specific\_rates(J,IMOD1,IMOD2,BARR,YMOD1,YMOD2)

endif

endif

DIFF = DIFFUSION\_RATE\_1(J) + DIFFUSION\_RATE\_2(J)

reaction\_rates(J) = RATE\_A(J) \* branching\_ratio(J) \* BARR \* DIFF \* GTODN / actual\_gas\_density

!PRINT \*, "RATE\_A(J)",RATE\_A(J)

!PRINT \*, "branching\_ratio(J)",branching\_ratio(J)

!PRINT \*, "BARR",BARR

!PRINT \*, "DIFF",DIFF

!PRINT \*, "GTODN / actual\_gas\_density",GTODN/actual\_gas\_density

!PRINT \*, REACTION\_COMPOUNDS\_NAMES(1,J), REACTION\_COMPOUNDS\_NAMES(2,J)

!PRINT \*, "reaction\_rates(J) (ITYPE 14) for reaction:",J,'is=',reaction\_rates(J)

! If the number of mantle layer is > 1, we consider that t(diff) (the time required by a species to

! scan the entire grain sites) is given by the Number of sites on a layer time the number of layer time t(hop)

IF(any(REACTION\_COMPOUNDS\_NAMES(:,j)(1:1).eq."K").and.sumlaymant.gt.1.0d0) THEN

reaction\_rates(J) = reaction\_rates(J) / sumlaymant

ENDIF

! H2 formation by LH mechanism is turned off when the ad hoc formation of H2 is activated

IF ((reaction\_compounds\_names(1,J).EQ.YJH).AND.(reaction\_compounds\_names(2,J).EQ.YJH)) then

IF(IS\_H2\_ADHOC\_FORM.eq.1) reaction\_rates(J) = 0.0D+00

ENDIF

! "Encounter desorption" process for JH2 (Hincelin et al. 2014,A&A)

! The reaction JH2+JH2->JH2+H2 must be in the grain\_reactions.in file to be accounted

! in practice the dominant processes are really the thermal hoping and thermal desorption of H2.

if ((reaction\_compounds\_names(1,J).EQ.YJH2).AND.(reaction\_compounds\_names(2,J).EQ.YJH2)) then

PROBH2H2=EVAPORATION\_RATES\_TEMPO\_H2/(VIBRATION\_FREQUENCY(reactant\_1\_idx(J))\*EXP(-diff\_binding\_ratio\_surf\*ED\_H2/&

actual\_dust\_temp)/nb\_sites\_per\_grain+ EVAPORATION\_RATES\_TEMPO\_H2)

reaction\_rates(J)=reaction\_rates(J)\*PROBH2H2

endif

! reaction\_rates(J)=0.D0

enddo