

1 Addition 5 January 2007:

The energy dependent branching Ratios $R_j^\lambda(E)$

For C_xH_y, SiH_y molecules and their ions, fits for the total cross sections $\sigma^{tot}(E)$ for many of the electron impact collision processes in the databases [1, 2, 3] have been given in the following generic form:

$$\sigma_\lambda^{tot}(MH_y) = A_0 F_M^\lambda(y) \left(1 - \frac{E_{th}}{E}\right)^{\alpha_\lambda} \frac{1}{E} \ln(e + cE) \quad (\times 10^{-16} cm^2) \quad (1)$$

with A_0, α_λ and c constants, $F_M^\lambda(y)$ a function of y , the number of hydrogen atoms in the hydride molecule. M stands for C, C_2, C_3, Si and λ labels the type of process, such as dissociative excitation, dissociative ionization, etc. (DE, I-DI, DE^+ and DI^+), loc.cit.

All studied electron impact collision processes in these databases have many reaction channels, all of which [except the direct ionization and the pure electron capture] are related to the molecular dissociation. The total cross section of a given type of process for a given MH_y molecule is the sum of partial cross sections of individual reaction channels of that process for the considered molecule. The contribution of a particular reaction channel j to the total cross section σ_λ^{tot} of the process λ at a given collision energy E , is given by the branching ratio

$$R_j^\lambda(E) = \frac{\sigma_j^\lambda(E)}{\sigma_\lambda^{tot}(E)}, \quad (2)$$

where $\sigma_j^\lambda(E)$ is the partial cross section of channel j . Obviously, this relation can be used to determine $\sigma_j^\lambda(E)$ when $\sigma_\lambda^{tot}(E)$ and $R_j^\lambda(E)$ are known.

As was correctly pointed out to us by Tamara Moiseev, Politecnico di Milano, Jan. 2007, the formulas for $R_j^\lambda(E)$ mentioned in the three reports quoted above can lead to un-physical behavior such as negative cross sections above the threshold energies, or even singularities (cross sections going to plus or minus infinity) near the physically correct cross section maximum. See next subsection for one such example. **In this memo we provide new formulas for the branching ratios which do not suffer from these defects, and which have been implemented in HYDKIN (www.hydkin.de) in January 2007. Prior to this correction only constant branching ratios have been used in HYDKIN, so that this unphysical behaviour was absent, however the precision of the partial cross sections near their threshold energies was unnecessarily reduced.**

1.1 The branching ratio formulas in the published databases

As pointed out in the references it was shown experimentally that the cross section branching ratios R_j^λ for these molecules remain the same in the

entire energy region above $\sim 20 - 30$ eV (within the uncertainties of the data, 8-10 %). The observed energy invariance of channel branching ratios for these processes indicates that the basic dynamical mechanism for all reaction channels is the same, and the differences in the values of R_j^λ are related to structural factors.

Hence the assumption of energy independence of all R_j^λ is a highly plausible first approximation. The resulting unitarity relation for the branching ratios,

$$\sum_j R_j^\lambda = 1, \quad (3)$$

has then been used together with an ordering of partial processes according to the reaction thresholds

$$E_{th,1} < E_{th,2} < E_{th,3} < \dots E_{th,k} < \dots \quad (4)$$

in the following arguments:

- It is obvious that in the energy region $E_{th,1} < E \leq E_{th,2}$, when only the channel with lowest threshold is open, R_1^λ should be one, while Eq. (3) gives a smaller value.
- The partial cross section $\sigma_1^\lambda(E)$ calculated as $R_1^\lambda \cdot \sigma_\lambda^{tot}(E)$ will be reduced. More generally, in any part of the energy region when not all reaction channels are open, the true unitarity condition

$$\sum_{\text{all } k} \sigma_k^\lambda(E) = \sigma_\lambda^{tot}(E) \quad (5)$$

for the cross sections themselves (not just for the R_j^λ) is not satisfied.

- In order to satisfy the unitarity condition at any collision energy, the factors R_k^λ have to be modified. This requirement translates into a requirement that R_k^λ depend on energy.

One way to modify R_k^λ in order to account for unitarity (3) in the threshold regions is the replacement of R_k^λ by

$$\tilde{R}_1^\lambda(E) = \frac{R_1^\lambda}{1 - \chi_1 (E_{th,1}/E)^\beta}, \quad \chi_1 = 1 - R_1 \quad (6a)$$

$$\tilde{R}_k^\lambda(E) = \frac{R_k^\lambda}{1 - \chi_k (E_{th,k}/E)^\beta}, \quad \chi_k = 1 - \frac{R_k^\lambda}{1 - \sum_{j=1}^{k-1} \tilde{R}_j^\lambda(E)} \quad (6b)$$

where β is a (positive) parameter. The $\tilde{R}_k^\lambda(E)$ defined by Eqs. (6) have the

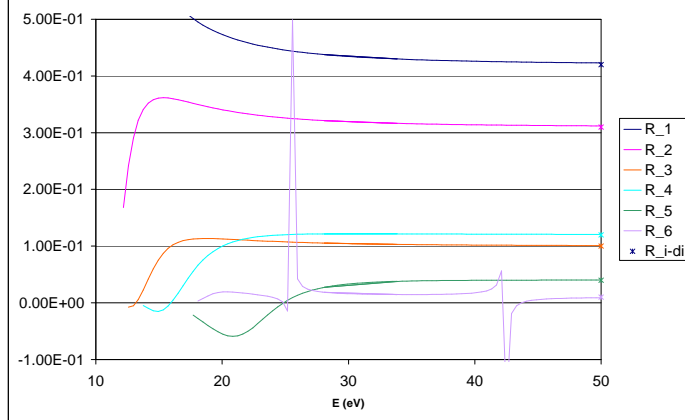


Figure 1: Branching ratios $\tilde{R}_j(E)$ for partial cross sections of the SiH_4 dissociative ionization channel, according to original formulas in [3], ordered according to relation (4). Also indicated by symbols at the right abscissa: the constant branching ratios R_j given in Table 2 of [3]. Note the singular behavior of R_6 , and the negative values of R_3 , R_4 and R_5 near and above their thresholds.

following properties:

$$(i) \quad \tilde{R}_k^\lambda(E) \rightarrow R_k^\lambda, \quad \text{for } E \rightarrow \infty \quad (7a)$$

$$(ii) \quad \sum_{j=1}^k \tilde{R}_j^\lambda(E_k) = 1, \quad (7b)$$

$$(iii) \quad \tilde{R}_1^\lambda(E) \rightarrow 1, \quad \text{for } E \rightarrow E_{th,1} \quad (7c)$$

Hence, the unitarity of \tilde{R}_k^λ is satisfied at every threshold (and for $E \gg E_{th,max}$), but, as evident from the expression for $\tilde{R}_1^\lambda(E)$, Eq. (6a), it is violated at energies between the thresholds.

It has then erroneously been argued in [1, 2, 3] that “except for $\tilde{R}_1^\lambda(E)$, however, this violation of unitarity for $E \neq E_{th,j}$ is relatively small, and for each specific reaction channel can be minimized by a suitable choice of parameter β . An optimum choice for β is $\beta \simeq 1.5(\pm 0.2)$ ”.

This assertion was formally correct but physically insufficient. The resulting energy dependent branching ratios can be negative or show singular behavior even in the physically most relevant energy region between threshold and cross section maximum. In Figure 1 the six branching ratios $\tilde{R}_j(E)$, $j = 1, \dots, 6$ for dissociative ionization of SiH_4 (see Table 2 in [3]) are plotted. The channels are ordered according to relation (4).

1.2 The new energy dependent branching ratios used in HY-DKIN

We start by noting that E_{th} in Eq. (1) for the total cross section is always the minimum of all $E_{th,j}$, i.e., $E_{th} = E_{th,1}$ of the partial reaction channels according to relation (4). Furthermore we note that when evaluating the partial cross section of channel j , the E_{th} in Eq. (1) should be replaced by the proper $E_{th,j}$ for that channel in order to provide proper threshold behavior for each partial cross section as well.

Hence, instead of the definition Eq. (2) we will define the new energy dependent branching ratios as

$$\sigma_j(E) = \tilde{R}_j(E) \cdot \sigma(E, E_{th,j})$$

with $\sigma(E, E_{th,j})$ defined as the total cross section Eq. (1) but with E_{th} replaced by the individual channel threshold $E_{th,j}$.

Consequently the fit expressions for the partials have different energy dependencies already before multiplication with a branching ratio. Hence unitarity relation (3) for the branching ratios is not applicable and only the unitarity relation for the cross section themselves, Eq. (5), needs to be fulfilled. We now define the energy dependent branching ratios [still assuming the ordering (4)] in the following way: In a first step we produce energy dependent branching ratios $\hat{R}_k(E)$ according to

$$\begin{aligned} \hat{R}_1(E) &= 0 & \text{for } E < E_1 \\ \hat{R}_1(E) &= 1 & \text{for } E \geq E_1 \\ & \cdot \\ & \cdot \\ & \cdot \\ \hat{R}_k(E) &= 0 & \text{for } E < E_k \\ \hat{R}_k(E) &= R_k/R_1 & \text{for } E \geq E_k \end{aligned} \tag{8}$$

with R_j being the (energy independent) branching ratios given in the database reports [1, 2, 3]. In a second step we apply a common normalizing function $\alpha(E)$ which is the same for all channels j , and which will be determined from the cross section unitarity relation (5). Hence the normalizing function $\alpha(E)$ is defined as:

$$\alpha(E) = \frac{\sigma^{tot}(E)}{\sum_j \hat{\sigma}_j(E)} \tag{9}$$

where $\hat{\sigma}_j$ is evaluated according to [compare with Eq. (1)]:

$$\hat{\sigma}_j(E) = \hat{R}_j(E) \cdot \sigma(E, E_{th,j}) \quad (10a)$$

$$= \hat{R}_j(E) \cdot A_0 F_M^\lambda(y) \left(1 - \frac{E_{th,j}}{E}\right)^{\alpha_\lambda} \frac{1}{E} \ln(e + cE) \quad (10b)$$

($\times 10^{-16} \text{ cm}^2$)

with the same constants A_0, α_λ, c as for the corresponding total cross section, and with $\hat{R}_j(E)$ according to Eqs. (8). Finally the partial cross section for channel j is given as:

$$\sigma_j(\text{MH}_y) = \alpha(E) \cdot \hat{\sigma}_j(E) = \tilde{R}_j(E) \cdot \sigma(E, E_{th,j}) \quad (11)$$

Hence we have automatically fulfilled the unitarity relation (5), the correct near threshold behavior for each partial and total cross section, and, furthermore,

$$\frac{\tilde{R}_i(E)}{\tilde{R}_j(E)} = \frac{\hat{R}_i(E) \cdot \alpha(E)}{\hat{R}_j(E) \cdot \alpha(E)} = \frac{\hat{R}_i(E)}{\hat{R}_j(E)} = \frac{R_i}{R_j} \quad (12)$$

at **all** energies E at which the partial channels i, j are both open.

The procedure to evaluate a particular partial cross section $\sigma_j(E_0)$ at an energy E_0 proceeds as follows:

- First find all partial channels $1, \dots, k_0$ which are open at the energy E_0 .
- Set $\hat{R}_1(E_0) = 1$ and $\hat{R}_j(E_0)$ according to Eq. (12) for all $j = 2, \dots, k_0$.
- Form the sum $\sum_{j=1}^{k_0} \hat{R}_j(E_0) \sigma(E_0, E_{th,j})$, where the $\sigma(E_0, E_{th,j})$ are evaluated according to Equations (10) at energy E_0 .
- Use this sum to find the normalizing factor $\alpha(E_0)$ from Eq. (9) and set

$$\sigma_j(E_0) = \alpha(E_0) \hat{R}_j(E_0) \cdot \sigma(E_0, E_{th,j}) = \tilde{R}_j(E_0) \cdot \sigma(E_0, E_{th,j}).$$

In Figs. 2, 3 the new energy dependent branching ratios $\tilde{R}_j(E)$ according to that procedure are shown, again for the SiH_4 dissociative ionization channels, once for the near threshold energies and once for a wide energy range. Clearly, by construction, the new energy dependent branching ratios converge to the constant branching ratios given in the databases for large energies, because the differences in the near threshold energy dependencies in the various channel cross sections [due to different $E_{th,j}$ in the formula (1)] diminishes.

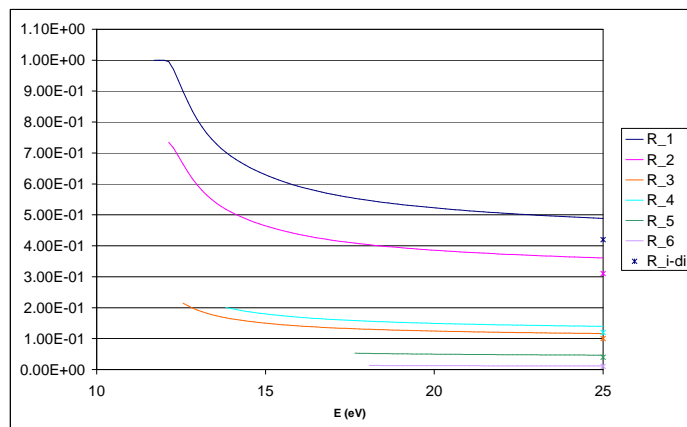


Figure 2: Branching ratios $\tilde{R}_j(E)$ for partial cross sections of the SiH_4 dissociative ionization channel, according to new formulas given here, ordered according to relation (4). Also indicated by symbols: the constant branching ratios R_j given in Table 2 of [3]

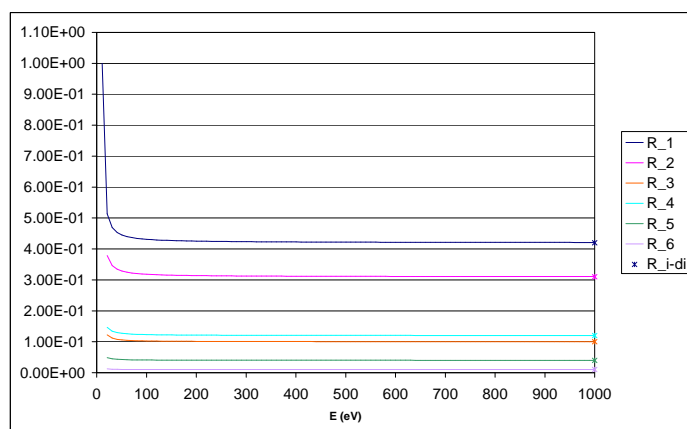


Figure 3: Same as Fig. 2, but for wider energy range, showing the convergence to the constant branching ratios at high energies.

References

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