Fragmentation rate constant for an atom-like product

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We adopt the notation presented in Zapadinsky *et al.*, *J. Phys. Chem. A* **2019**, *123*, 611–624. The cluster formation rate is then given by the following expression (cf. Eq. 32 in the same article):

$$k_p(\varepsilon-\epsilon_r)=\frac{2\sqrt{2}\pi}{V\sqrt{\mu_p}\,\rho_p(\varepsilon-\epsilon_r)}\iiint\limits_{\substack{0\le\epsilon_r+\epsilon_t\le\varepsilon-\epsilon_r\\0\le b\le b_{\max}}} d\varepsilon_t\,d\varepsilon_r\,db\,b\,\sqrt{\varepsilon_t}\,\rho_{pt}(\varepsilon_t)\,\rho_{pr}(\varepsilon_r)\cdot\rho_{pv}(\varepsilon-\epsilon_r-\varepsilon_r-\varepsilon_t)\,. \quad (1)$$

In the case where one of the products is an atom, only its translational degrees of freedom are relevant. To conserve angular momentum, the rotational energy of the cluster must be fixed to a single value that depends on the translational energy in the center-of-mass frame:

$$\varepsilon_r=\mu_p b^2\frac{\varepsilon_t}{I_1}\,. \quad (2)$$

This constraint is imposed by expressing the rotational density of states of the cluster as a Dirac delta function:

$$\rho_{pr}(\varepsilon_r)=\delta\left(\varepsilon_r-\mu_p b^2\frac{\varepsilon_t}{I_1}\right)\,. \quad (3)$$

Substituting Eq. (3) into Eq. (1), the integral simplifies to:

$$k_p(\varepsilon-\epsilon_r)=\frac{2\sqrt{2}\pi}{V\sqrt{\mu_p}\,\rho_p(\varepsilon-\epsilon_r)}\iint\limits_{\substack{0\le\varepsilon_t\left(1+\frac{\mu_p b^2}{I_1}\right)\le\varepsilon-\epsilon_r\\0\le b\le b_{\max}}} d\varepsilon_t\,db\,b\,\sqrt{\varepsilon_t}\,\rho_{pt}(\varepsilon_t)\cdot\rho_{pv}\left(\varepsilon-\epsilon_r-\varepsilon_t\left(1+\frac{\mu_p b^2}{I_1}\right)\right)\,. \quad (4)$$

The translational density of states is given by:

$$\rho_{pt}(\varepsilon_t)=\frac{4\sqrt{2}\pi V\mu_p^{3/2}\sqrt{\varepsilon_t}}{(2\pi\hbar)^3}\,, \quad (5)$$

which leads to:

$$k_p(\varepsilon-\epsilon_r)=\frac{2\mu_p}{\pi\hbar^3\rho_p(\varepsilon-\epsilon_r)}\iint\limits_{\substack{0\le\varepsilon_t\left(1+\frac{\mu_p b^2}{I_1}\right)\le\varepsilon-\epsilon_r\\0\le b\le b_{\max}}} d\varepsilon_t\,db\,b\,\varepsilon_t \cdot\rho_{pv}\left(\varepsilon-\epsilon_r-\varepsilon_t\left(1+\frac{\mu_p b^2}{I_1}\right)\right)\ . \tag{6}$$

We now perform the substitution:

$$\tilde{\varepsilon}_t=\varepsilon_t\left(1+\frac{\mu_p b^2}{I_1}\right)\ , \tag{7}$$

which transforms the expression into:

$$k_p(\varepsilon-\epsilon_r)=\frac{2\mu_p}{\pi\hbar^3\rho_p(\varepsilon-\epsilon_r)}\iint\limits_{\substack{0\le\tilde{\varepsilon}_t\le\varepsilon-\epsilon_r\\0\le b\le b_{\max}}} d\tilde{\varepsilon}_t\,db\,b\,\tilde{\varepsilon}_t\left(\frac{I_1}{I_1+\mu_p b^2}\right)^2\rho_{pv}\left(\varepsilon-\epsilon_r-\tilde{\varepsilon}_t\right)\ . \tag{8}$$

Taking the limit $b_{\max}\to+\infty$ and performing the integration over b gives:

$$k_p(\varepsilon-\epsilon_r)=\frac{I_1}{\pi\hbar^3\rho_p(\varepsilon-\epsilon_r)}\int_0^{\varepsilon-\epsilon_r}d\tilde{\varepsilon}_t\,\tilde{\varepsilon}_t\,\rho_{pv}\left(\varepsilon-\epsilon_r-\tilde{\varepsilon}_t\right)\ . \tag{9}$$

The fragmentation rate at zero angular momentum is related to the formation rate by:

$$\gamma_0(\varepsilon-\epsilon_r)\rho_v(E_f+\varepsilon-\epsilon_r)=k_p(\varepsilon-\epsilon_r)\rho_p(\varepsilon-\epsilon_r)\ , \tag{10}$$

which yields:

$$\gamma_0(\varepsilon-\epsilon_r)=\frac{I_1}{\pi\hbar^3\rho_v(E_f+\varepsilon-\epsilon_r)}\int_0^{\varepsilon-\epsilon_r}d\tilde{\varepsilon}_t\,\tilde{\varepsilon}_t\,\rho_{pv}\left(\varepsilon-\epsilon_r-\tilde{\varepsilon}_t\right)\ . \tag{11}$$

Finally, the total fragmentation rate is obtained by averaging over the rotational energy distribution:

$$\gamma(\varepsilon)=\int_0^{\varepsilon}f_r(\epsilon_r)\gamma_0(\varepsilon-\epsilon_r)d\epsilon_r\ , \tag{12}$$

where the weighting function is given by:

$$f_r(\epsilon_r)=\frac{\rho_v(E-\epsilon_r)\sqrt{\epsilon_r}}{\int_0^E\rho_v(E-\epsilon_r)\sqrt{\epsilon_r}\,d\epsilon_r}\ . \tag{13}$$