Attachment of Water and Alcohol Molecules Onto Water and Alcohol Clusters

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Unimolecular Evaporation Model

We derive in the following the expression of the evaporation rate used in our Monte Carlo simulations to describe unimolecular evaporation of water clusters. Namely we consider a parent cluster of size n with internal energy E which evaporates a single fragment with relative kinetic energy ε. The daughter cluster has a size n-1 and its internal energy is E-ε-D, where D is the dissociation energy of the cluster of size n.

The evaporation rate is obtained from the detailed balance principle:

$$\frac{\Gamma_e}{\omega_f \omega_{n-1}} = \frac{\Gamma_c}{\omega_n} \qquad \text{Eq. 1}$$

where Γ_e is the evaporation rate, Γ_c the collision rate, and ω_f, ω_n and ω_{n-1} are the density of states for the fragment, the parent cluster and the daughter cluster, respectively.

Let's consider a cluster as an ensemble of s degenerate harmonic oscillators of frequency ν, *s* being the number of degrees of freedom.

The density of states ω_n of the parent cluster with internal energy E is:

$$\omega_n(E) = \frac{\partial N(E)}{\partial E} = \frac{E^{s-1}}{(h\nu)^s (s-1)!} \qquad \text{Eq. 2}$$

whereas the one of the daughter cluster is:

$$\omega_{n-1}(E-\varepsilon-D) = \frac{(E-\varepsilon-D)^{s'-1}}{(h\nu)^{s'}(s'-1)!} \qquad \text{Eq. 3}$$

where ε is the relative kinetic energy between the fragment and the daughter cluster and D is the dissociation energy.

In the above expressions, the zero point energy is taken into account as the internal energy E is the sum of the zero point energy E_0 plus the thermal energy E_{th}[1].

The translational density of states for the fragment is:

$$\omega_f = \frac{4\pi\mu^2 v}{\rho h^3} \qquad \text{Eq. 4}$$

where v is the relative velocity to the daughter cluster, μ the reduced mass and ρ the density.

Finally we need the collision rate given by:

$$\Gamma_c = \rho\sigma v \qquad \text{Eq. 5}$$

where σ is the collision cross-section.

The evaporation rate of a fragment with velocity v is then:

$$\Gamma_e = \frac{8\pi\mu\sigma}{h^3}\varepsilon\frac{\omega_{n-1}}{\omega_n} \qquad \text{Eq. 6}$$

Using relation Eq. 2, equation Eq. 5 is rewritten as:

$$\Gamma_e = \frac{8\pi\mu\sigma}{h^3}\varepsilon(h\nu)^{s-s'}\frac{(E-\varepsilon-D)^{s'-1}}{E^s}\frac{(s-1)!}{(s'-1)!} \qquad \text{Eq. 7}$$

So far, the number of degrees of freedom has not been stated explicitly. If one considers clusters as made of atoms, the number of degrees of freedom is s=3n-6 and s'=3(n-1)-6. However, the case of molecular clusters is of course more complicated. Even if ones neglect the internal vibrationnal modes of the molecules, one should also consider libration modes, rotation modes, etc. Furthermore for complex systems such as water, the number of active degrees of freedom evolves with temperature. For instance the number of degrees of freedom deduced from the heat capacity of bulk ice evolves from 0.5 and 4.5 when the temperature goes from 25 K to 270 K. It should also be noted that all modes might not couple efficiently to dissociative modes. Finally, in such a crude model, which neglects for instance anharmonicity, one should consider the number of degrees of freedom as an effective number. We will continue our derivation of the evaporation rate by taking the number of degrees of freedom as s=αn-6 and s'=α(n-1)-6. By stating explicitly the number of degrees of freedom, Eq. 7 becomes:

$$\Gamma_e = \frac{8\pi\mu\sigma}{h^3}\varepsilon(h\nu)^{\alpha}\frac{(E-\varepsilon-D)^{\alpha(n-1)-7}}{E^{\alpha n-7}}\prod_{i=\alpha(n-1)-6}^{\alpha n-7} i \qquad \text{Eq. 8}$$

Equation Eq. 8 gives the evaporation rate of a cluster of size n which evaporates a monomer at a relative kinetic energy ε. The total evaporation rate is obtained by integrating Eq. 8 over all possible relative kinetic energies, namely between 0 and E-D-E_0, which gives:

$$\Gamma_{TOT} = \frac{8\pi\mu\sigma}{h^3}(h\nu)^{\alpha} \prod_{i=\alpha(n-1)-6}^{\alpha n-7} i \times \left[\frac{(E-D)^{\alpha(n-1)-5}}{(\alpha(n-1)-6)(\alpha(n-1)-5)E^{\alpha n-7}} - \frac{{E_0}^{\alpha(n-1)-5}}{(\alpha(n-1)-6)(\alpha(n-1)-5)E^{\alpha n-7}} - \frac{(E-E_0-D)E_0^{\alpha(n-1)-6}}{(\alpha(n-1)-6)E^{\alpha n-7}} \right], \text{ if } E_{\text{th}} > \text{D}$$

Eq. 9

$$=0, \text{ if } E_{\text{th}} < \text{D}$$

The simulations presented in the paper have been done with the above formula by taking α=3, as if all molecular internal degrees of freedom molecules were frozen; this choice is supported by recent theoretical studies, which demonstrate that it is actually the case in the temperature range investigated in the present paper[2].

More importantly, the initial internal energies of individual clusters are chosen such that the cluster ensemble is at temperature T, so that the average energy E_T of the ensemble follows the Einstein's model of heat capacity:

$$E_T = (\alpha n - 6)h\nu\left(\frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1}\right)$$

Eq. 10

After the initial internal temperature of the clusters is set, each individual cluster has its own microcanonical evolution during its propagation in the different electrical fields of the simulated experiment. The electric field potential is calculated using a relaxation method to solve the Laplace equation in cylindrical coordinates with potential electrodes as boundary conditions. The equations of motion are calculated using a Runge-kutta 4th order algorithm. At each time step, the probability for a collision and an evaporation event is evaluated, and both the size and the internal energy of the cluster are modified accordingly. The Boltzmann velocity distribution of the gaseous molecules at room temperature in the collision cell is taken into account. Care has also been taken to ensure that the evaporated fragment kinetic energy follows the probability given by:

$$P(\varepsilon) = \Gamma_e / \Gamma_{TOT}$$

Eq. 11

References

(1) Forst W., *Unimolecular Reactions: a Concise Introduction*, Cambridge University Press, 2003

(2) Chen, H.; Hansen, K. Low Temperature Heat Capacity of Water Clusters. *Chem. Phys. Lett.* **2014**, *610–611*, 369–374.