

APPENDIX A

The Morse Potential

The Morse potential is commonly written in two equivalent forms^{5,6}

$$\phi = \phi_0 \left\{ \exp \left[-\frac{2C}{\sigma} (r-r_e) \right] - 2 \exp \left[-\frac{C}{\sigma} (r-r_e) \right] \right\} \quad (\text{A1})$$

$$\phi = \phi_0 \left\{ \exp \left[-\frac{2\beta}{r_e} (r-r_e) \right] - 2 \exp \left[-\frac{\beta}{r_e} (r-r_e) \right] \right\} \quad (\text{A2})$$

where the zero-point of energy is taken at infinite separation of the molecular constituents. Thus the depth of the potential well is ϕ_0 , often denoted by D_e , and called the dissociation energy measured from the minimum. r_e is the separation distance r at which $\phi = -\phi_0$, or the equilibrium internuclear separation, σ is the distance where $\phi = 0$ and

$$C = \frac{\sigma \ln 2}{r_e - \sigma} \quad (\text{A3})$$

is a measure of the shape of the potential curve near the minimum. From comparison of Eqs. (A1) and (A2) and using (A3) we see that

$$\beta = C + \ln 2 \quad (\text{A4})$$

The Morse potential has a finite value at the origin, given by

$$\phi(0) = 4\phi_0 e^C (e^C - 1) \quad (\text{A5})$$

This is an unrealistic potential near the origin, unimportant for the computation of vibrational energy levels but important for use in intermolecular collisions if the relative energy of the colliding species is an appreciable fraction of $\phi(0)$. The true intermolecular potential behaves more like the Coulomb potential as $r \rightarrow 0$. One modification which renders this form more suitable for collision problems is to replace Eq. (A1) or (A2) by $\phi = \infty$ (hard sphere) when $r \leq r_\sigma$, a finite value of $r > 0$, but less than σ . Ref. 6 defines this

distance by

$$r_{\sigma} = 0.3\sigma = 0.3r_e \left(\frac{C}{C + 2m_2} \right) \quad (\text{A6})$$

In this way the authors of Ref. 6 are able to extend their tables of collision integrals to higher values of $T^* \equiv kT/\phi_0$ than would be physically realistic with the pure Morse potential.

It is worth noting here the relationship of the above contents for the Morse potential to certain spectroscopic quantities. We have

$$\omega_e = \beta \left(\frac{D_e \hbar}{\pi c \mu} \right)^{\frac{1}{2}} \quad (\text{A7})$$

and

$$\omega_e x_e = \frac{\hbar \beta^2}{4\pi c \mu} \quad (\text{A8})$$

where μ is the reduced mass, c the speed of light, and ω_e and $\omega_e x_e$ are vibrational constants in the formula for vibrational energy term $G(v)$

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \quad (\text{A9})$$

No higher powers of $v + \frac{1}{2}$ occur for the Morse potential. The rotational constant B_e is related to the equilibrium internuclear distance r_e by

$$B_e = \frac{\hbar}{4\pi c \mu r_e^2} \quad (\text{A10})$$

Finally, the true dissociation energy D_0 (measured from the 1st vibrational level) is related to the other constants by

$$D_0 = D_e - \frac{1}{2} \omega_e + \frac{1}{4} \omega_e x_e \quad (\text{A11})$$

All the above spectroscopic constants are given in cm^{-1} .

Tables of collision integrals have been prepared by Smith and Munn⁵ (SM) for the potential form in Eq. (A1) and by Samulov and Tsitelauri⁶ (ST) for that of Eq. (A2) with the modification of $\phi = \infty$ at $r \leq r_{\sigma}$. The range of variables