Term-by-term calculation of partition functions for each species in the ammonia synthesis reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ compared to RASPA manual (section 8.3, table 8.2 pp. 158-161). Calculations correspond to $T = 573$ K.

$$\frac{q}{V} = \frac{q_{trans}}{V} q_{rot} q_{vib} q_{elec} e^{\frac{D_0}{RT}} \tag{1}$$

$$\frac{q_{trans}}{V} = \left(\frac{2\pi m k_b T}{h^2}\right)^{\frac{3}{2}} \tag{2}$$

$$q_{rot}(diatomic) = \frac{T}{\sigma \Theta_{rot}} \tag{3}$$

$$q_{rot}(polyatomic) = \frac{\pi^{\frac{1}{2}}}{\sigma} \left(\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right)^{\frac{1}{2}} \tag{4}$$

$$q_{vib}|_{V=0} = \prod_{j=1}^{\alpha} \frac{1}{1 - e^{-\frac{\Theta_{vib,j}}{T}}} \tag{5}$$

$$q_{elec} \approx g_{e1} \tag{6}$$

V = volume [m^3]

D_0 = atomization/dissociation energy [kcal mol^{-1}]

R = gas constant [$1.987 \bullet 10^{-3}$ kcal mol^{-1} K^{-1}]

T = temperature [573 K]

m = mass [kg]

k_b = Boltzmann constant [$1.381 \bullet 10^{-23}$ J K^{-1}]

h = Planck's constant [$6.626 \bullet 10^{-34}$ J s]

σ = symmetry number

Θ_{rot} = rotational temperature [K]

α = number of vibrational modes

Θ_{vib} = vibrational temperature [K]

g_{e1} = ground state degeneracy

Table 1. Molecular constants from *Statistical Mechanics*, McQuarrie. Tables also reproduced in *Molecular Thermodynamics*, McQuarrie and Simon, Table 4.2 (p. 151), Table 4.4 (p. 162). Parentheses in Θ values indicate degeneracy (omitted if 1).

Species	m (u)	Θ_{rot} (K)	Θ_{vib} (K)	σ	$D_{0, absolute}$ (kcal mol^{-1})	Reference
N_2	28.0134	2.88	3374	2	225.1	McQuarrie, Table 6-1, p. 95
H_2	2.016	85.3	6332	2	103.2	McQuarrie, Table 6-1, p. 95
NH_3	17.031	13.6(2), 8.92	4800, 1360, 4880(2), 2330(2)	3	276.8	McQuarrie, Table 8-1, p. 132

N_2:

$$m = 28.0134\,u * \frac{1\,kg}{6.022 * 10^{26}\,u}$$
$$= 4.65 * 10^{-26}\,kg$$

$$\frac{q_{trans}}{V} = \left(\frac{2\pi(4.65 * 10^{-26}\,kg)(1.381 * 10^{-23}\,J * K^{-1})(573\,K)}{(6.626 * 10^{-34}\,J * s)^2}\right)^{\frac{3}{2}}$$
$$= 3.82 * 10^{32}\,m^{-3} * \frac{1\,m^3}{10^{30}\,Å^3}$$
$$= 382\ Å^{-3}$$

$$q_{rot} = \frac{573\,K}{2(2.88\,K)}$$
$$= 99.5$$

$$q_{vib}|_{V=0} = \frac{1}{1 - e^{-\frac{3374\,K}{573\,K}}}$$
$$= 1.00$$

$$q_{elec} \approx 1$$

D_0 = 0 (N_2 is element at standard state, and RASPA uses D_0 relative to elements)

$$e^{\frac{0}{RT}} = 1$$

$$\frac{q}{V} = (382\ Å^{-3})(99.5)(1.00)(1)(1)$$
$$= 3.81271 * 10^4\ Å^{-3}\ (matches\ RASPA\ manual, Table\ 8.2, p.160)$$

H_2:

$$m = 2.016\,u * \frac{1\,kg}{6.022 * 10^{26}\,u}$$
$$= 3.35 * 10^{-27}\,kg$$

$$\frac{q_{trans}}{V} = \left(\frac{2\pi(3.35 * 10^{-27}\,kg)(1.381 * 10^{-23}\,J * K^{-1})(573\,K)}{(6.626 * 10^{-34}\,J * s)^2}\right)^{\frac{3}{2}}$$
$$= 7.38 * 10^{30}\,m^{-3} * \frac{1\,m^3}{10^{30}\,Å^3}$$
$$= 7.38\ Å^{-3}$$

$$q_{rot} = \frac{573\,K}{2(85.3\,K)}$$
$$= 3.36$$

$$q_{vib}|_{V=0} = \frac{1}{1 - e^{-\frac{6332\,K}{573\,K}}}$$
$$= 1.00$$

$$q_{elec} \approx 1$$

D_0 = 0 (N_2 is element at standard state, and RASPA uses D_0 relative to elements)

$$e^{\frac{0}{RT}} = 1$$

$$\frac{q}{V} = (7.38\ \text{Å}^{-3})(3.36)(1.00)(1)(1)$$
$$= 2.47837 * 10^1\ \text{Å}^{-3}\ (matches\ RASPA\ manual, Table\ 8.2, p. 160)$$

NH_3:

$$m = 17.031\,u * \frac{1\,kg}{6.022 * 10^{26}\,u}$$
$$= 2.83 * 10^{-26}\,kg$$

$$\frac{q_{trans}}{V} = \left(\frac{2\pi(2.83 * 10^{-26}\,kg)(1.381 * 10^{-23}\,J * K^{-1})(573\,K)}{(6.626 * 10^{-34}\,J * s)^2}\right)^{\frac{3}{2}}$$
$$= 1.81 * 10^{32}\,m^{-3} * \frac{1\,m^3}{10^{30}\,\text{Å}^3}$$
$$= 181\ \text{Å}^{-3}$$

$$q_{rot} = \frac{\pi^{\frac{1}{2}}}{3}\left(\frac{(573\,K)^3}{(13.6\,K)^2(8.92\,K)}\right)^{\frac{1}{2}}$$
$$= 200$$

$$q_{vib}|_{V=0} = \frac{1}{1 - e^{-\frac{1360\,K}{573\,K}}}\left(\frac{1}{1 - e^{-\frac{2330\,K}{573\,K}}}\right)^2 \frac{1}{1 - e^{-\frac{4800\,K}{573\,K}}}\left(\frac{1}{1 - e^{-\frac{4880\,K}{573\,K}}}\right)^2$$
$$= 1.14$$

$$q_{elec} \approx 1$$

$$NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$$

$$D_0 = D_{0,NH_3,absolute} - \sum D_{0,constituent\ elements,absolute}$$
$$= 276.8\frac{kcal}{mol} - \left(\frac{1}{2}\left(225.1\frac{kcal}{mol}\right) + \frac{3}{2}\left(103.2\frac{kcal}{mol}\right)\right)$$
$$= 9.45\frac{kcal}{mol}$$

$$e^{\frac{9.45\frac{kcal}{mol}}{\left(1.987*\frac{10^{-3}kcal}{mol\,K}\right)(573K)}} = 4021$$

$$\frac{q}{V} = (181\ \text{Å}^{-3})(200)(1.14)(1)(4021)$$
$$= 1.66002 * 10^{8}\ \text{Å}^{-3}\ (RASPA\ manual\ shows\ 1.498133 * 10^{8}\ \text{Å}^{-3}, Table\ 8.2, p.160)$$

Table 2. Summary of term-by-term hand calculations versus RASPA manual values (Table 8.2, p. 161).

	Atkinson					RASPA
Species	**q_{trans}/V (Å^{-3})**	**q_{rot}**	**q_{vib}**	**$e^{D_o/RT}$**	**q/V (Å^{-3})**	**q/V (Å^{-3})**
N_2	3.8220E+02	9.9479E+01	1.0028E+00	1	3.81271E+04	3.81253E+04
H_2	7.3788E+00	3.3587E+00	1.0000E+00	1	2.47837E+01	2.48054E+01
NH_3	1.8118E+02	1.9951E+02	1.1422E+00	4020.5	1.66002E+08	1.498133E+08