TOPIC : Electronic partition functions

Pages (9-10)

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AT STP, i.e., T = 298 K

: $K_BT \simeq 9.43 \times 10^{-4}$ a.u.

$\simeq 9.43 \times 10^{-4}$ hartree

⇒ Electronic levels appear discritized for thermal energy & exchange of energy at thermal levels

Thus; electronic partition function, q_{elec} can be represented as :

$$\boxed{q_{elec} = \sum_i \omega_{ei}\, e^{-\beta \varepsilon_i}}$$

∀ ω_{ei} = degeneracy of energy level "ε_i"

Since all thermodynamic properties constitute equation with q_{elec} both in numerator and denominator and because of negative bound states of atomic & molecular system, ε_0 can be reset to zero. Thus $\boxed{q_{elec} = \omega_{e1} + \omega_{e2}\, e^{-\beta \Delta \varepsilon_{12}} + \cdots}$

Usually, Not more than one or two excited states contribute to "q_{elec}".

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TOPIC : Nuclear Partition Function

For transition among nuclear energy levels, required temperature, $T \simeq 10^{10} K$, Thus at STP, majorly Ground state involved.

$$\Rightarrow \boxed{q_{nucl} = \sum \omega_{nj} e^{-\beta \varepsilon_{nj}}}$$

Can be written as

$$\boxed{q_{nuclear} = \omega_{n1} + \cdots}$$

Higher terms can be ignored.

As Born-Oppenheimer approximation seperates electronic & nuclear coordinates, so does their respective partition functions

Hence total partition function of monoatomic gases can be written as

$$\boxed{Z_{monoatomic} = \frac{(q_{trans}\, q_{elec}\, q_{nucl})^N}{N!}}$$

where

$$q_{tran} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V = \frac{V}{\Lambda^3}$$

$$q_{ele} = \omega_{e1} + \omega_{e2} e^{-\beta \Delta \varepsilon_{12}}$$

$$q_{nucl} = \omega_{n1} + \cdots$$