C8863
Free Energy Calculations

4. Statistical Thermodynamics – Ideal Gas

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Ideal Gas

Partition Function of Any System

thermodynamic
state

$\bar{M}$

What is the free energy of the state?

Canonical Partition Function (NVT)

$$Q = \sum_{i=1}^{K} e^{-\beta E_i} = \sum_{i=1}^{K} e^{-\frac{E_i}{k_B T}}$$

Helmholtz Energy F:

$$F = -k_B T \ln Q$$

K - sum over all microstates of prototype (due to very large number of atoms)

E_i is practically inaccessible due to size of system (due to very large number of atoms)

We need a simplification!

Ideal Gas

!!!!!!!!

Ideal gas is composed from **non-interacting molecules**, which are usually indistinguishable.

$$Q = q^N$$

distinguishable molecules

$$Q = \frac{q^N}{N!}$$

indistinguishable molecules

N – number of molecules
q – molecular partition function

Exercises:

- explain multiplication of molecular partition function
- explain factorial factor for indistinguishable molecules

Molecular Partition Function

Molecular Partition Function

$$q = \sum_{i=1}^{k} e^{-\beta \varepsilon_i} = \sum_{i=1}^{k} e^{-\frac{\varepsilon_i}{k_B T}}$$

k - sum over all microstates of molecule

ε_i is energy of molecular microstate

Energy of molecular microstates can be found by solving time-independent Schrodinger equation (SR).

$$\hat{H}\psi_i = \varepsilon_i \psi_i \quad \longrightarrow \quad \text{k-solutions, i.e., quantum states}$$

But SR cannot be solved for real chemical systems (> He, polyatomic systems).

=>

Further approximations are needed!

Born-Oppenheimer Approximation

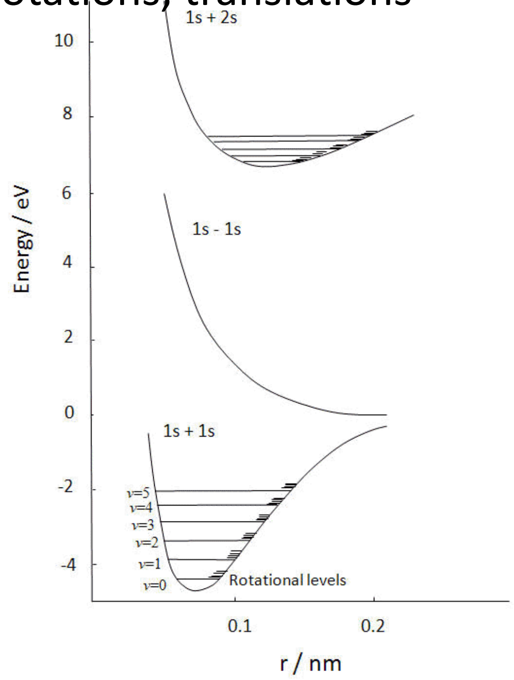
$$\hat{H}\psi_i = \varepsilon_i \psi_i$$

BO approximation

$$\hat{H}_e \Phi_m(\mathbf{r},\mathbf{R}) = E_m(\mathbf{R}) \Phi_m(\mathbf{r},\mathbf{R}) \qquad \hat{H}_R \chi_l(\mathbf{R}) = E_{VRT,l} \chi_l(\mathbf{R})$$

movement of electrons in static field of nuclei
electronic properties of molecule

movement of nuclei in effective field of electrons
vibrations, rotations, translations



electronic energy contribution

vibration, rotational, and translational energy contributions

$$\varepsilon_i = E_m(R_{opt,m}) + E_{VRT,l}$$

energy of quantum state (molecular microstate)

optimal geometry at which E_m is minimal

Molecular Partition Function - BO

Energies of molecular microstates:

$$\varepsilon_i = E_m(R_{opt,m}) + E_{VRT,l}$$

changing names

$$\varepsilon_i = \varepsilon_m^E + \varepsilon_l^{VRT}$$

Molecular partition function:

$$q = q^E q^{VRT}$$

$$q^E = \sum_{m=1}^{M} e^{-\beta \varepsilon_m^E} \qquad q^{VRT} = \sum_{l=1}^{L} e^{-\beta \varepsilon_l^{VRT}}$$

sum over all electronic quantum states

sum over all VRT quantum states

Electronic Partition Function

Electronic partition function:

$$q^E = \sum_{m=1}^{M} e^{-\beta \varepsilon_m^E}$$

sum over all electronic quantum states

Ground electronic state usually dominates over excited states:

$$\varepsilon_0^E \ll \varepsilon_1^E \ll \varepsilon_2^E \ldots$$

$$\boxed{q^E \approx e^{-\beta \varepsilon_0^E}}$$

This approximation is not valid for systems having

- low-lying excited states
- degenerate ground state

Zero Point Energy

It is convenient to reference energy of microstates to well defined state. This is usually the state with the lowest energy. The energy of this state is called **zero point energy**.

$$q = \sum_{i=1}^{K} e^{-\beta\varepsilon_i}$$

$$q = \sum_{i=1}^{K} e^{-\beta(\varepsilon'_i + \varepsilon_0)} = \underline{e^{-\beta\varepsilon_0}} \sum_{i=1}^{K} e^{-\beta\varepsilon'_i}$$

$$q' = \sum_{i=1}^{K} e^{-\beta\varepsilon'_i}$$

molecular partition function
referenced to ZPE

$$A_{ZPE} = E_{ZPE} = \varepsilon_0$$

zero point energy (free energy)

This can be applied to separately to each domain of molecular partition function.

Electronic Partition Function, again

Electronic partition function:

$$q^E = \sum_{m=1}^{M} e^{-\beta \varepsilon_m^E}$$

sum over all electronic quantum states

Ground electronic state usually dominates over excited states:

$$\varepsilon_0^E \ll \varepsilon_1^E \ll \varepsilon_2^E \ldots$$

$$\boxed{q^E \approx g_0}$$

$$\boxed{E_{ZPE} = e_0^E = E(R_0)}$$

E – potential energy

R_0 – optimal configuration (coordinates of atoms) at ground state

g_0 - degeneracy of ground state

This approximation is not valid for systems having

- low-lying excited states

Molecular Partition Function - VRT

$$\varepsilon_l^{VRT} = \varepsilon_v^{V} + \varepsilon_r^{R} + \varepsilon_t^{T}$$

this is an approximation, which follows the same idea as BO

$$\Big\downarrow$$

$$q^{VRT} = q^{V} q^{R} q^{T}$$

Each domain is represented by simplified quantum model:

- vibration by **harmonic oscillator**
- rotation by **rigid rotor**
- translation by **the particle in potential box**

Vibrations

Vibrational states of a normal mode :

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

n – quantum number (0,1,2,...,∞)
h – Planck constant
v – frequency

Vibrational partition function of a normal mode:

$$q^V = \frac{1}{1 - e^{-\beta h\nu}}$$

$$E_{ZPE} = \frac{1}{2} h\upsilon$$

Total vibrational partition function

$$q^V = \prod_{i=1}^{3N-c} \frac{1}{1 - e^{-\beta h\nu_i}}$$

c=5 – two atom molecule
c=6 – other molecules

Zero point energy:

$$E_{ZPE} = \frac{1}{2} \sum_{i=1}^{3N-c} h\upsilon_i$$

Rotations

Rotational energy (rigid rotor model)

$$E_J = J(J+1)hcB$$

J – main rotational quantum number (0,1,2,...)
c – speed of light
A,B,C – rotational constants

$$g_J = 2J+1$$

Each state is degenerated (angular momentum quantum number):

Rotational partition function (linear molecule):

$$q^R = \frac{kT}{\sigma hcB}$$

Zero point energy:

$$E_{ZPE} = 0$$

Rotational partition function (non-linear molecule):

$$q^R = \frac{1}{\sigma}\left(\frac{kT}{hc}\right)^{\frac{3}{2}}\left(\frac{\pi}{ABC}\right)^{\frac{1}{2}}$$

σ – rotational number

correction due to symmetry of molecule

Translations

Translations (particle in a box – 1D):

$$E_n = \frac{n^2 h^2}{8mX^2}$$

n – quantum number (1,2,...)
m – molecular mass
X – length of a box (1D)

Translation partition function:

$$q^T = q_x q_y q_z = \frac{V}{\Lambda^3}$$

V – box volume (usually molar volume at standard state)
Λ – thermal wavelength

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Zero point energy:

$$E_{ZPE} = \frac{3h^2}{8mV^{\frac{2}{3}}}$$

Thermochemistry

in Gaussian

Readings:

http://gaussian.com/thermo/

Notes

To calculate thermodynamic properties of given molecule in the form of ideal gas, it is necessary to perform these steps:

- **Geometry optimization**
  - Calculation of **electronic energy** (single point). Here, it is possible to use different level of theory, usually more accurate for energy evaluation.
  - Calculation of **vibrational contributions**. This requires calculation of Hessian. Hessian calculation is **VERY** expensive. Harmonic vibrations are **VALID ONLY** for Hessian calculated on the same level of theory, which was employed for geometry optimization.
  - Calculation of **rotational contributions** is cheap but it requires to determine/specify **rotational number**.
  - Calculation of **translational contributions** is cheap.

Summary

Conclusions

In **the model of ideal gas**, it is possible to simplify calculation of **canonical partition function** (which requires knowledge about the entire prototype) to calculation of **molecular partition function** (which requires knowledge about a single molecule). This is possible because molecules do not interact with each other in the ideal gas model.

Calculation of molecular partition function requires determination of important molecular microstates (quantum states), which usually requires **further approximations**:

- separation of electron and nuclei motions (BO approximation)
  - solution of Schrodinger equation requires additional approximations
    - one-electron approximation
    - correlation energy calculations (post-HF, DFT)
- separation of VRT modes
  - VRT modes are approximated by simplified models
    - harmonic oscillator for vibrations (inaccurate for large molecules)
    - rigid rotor for rotations (inaccurate for large flexible molecules)
    - particle in a potential box