

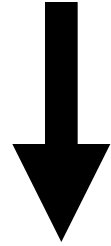
Statistical Thermodynamics

Essential Concepts

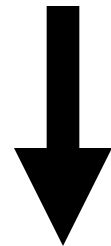
(Boltzmann Population, Partition Functions, Entropy, Enthalpy, Free Energy)

- lecture 5 -

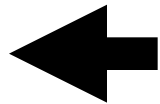
*Quantum mechanics of atoms
and molecules*



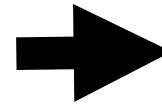
***STATISTICAL
MECHANICS***



***Equilibrium
Properties:
Thermodynamics***



***MACROSCOPIC
Properties***



***Time-dependent
behavior:
Chemical
kinetics***

Microscopic world

*Quantum states and energies
of a molecule*

Properties of a molecule:

*geometry
multipole moments
ionization potential
electron affinity
spectroscopic properties
vibrations/rotations
etc.*

Macroscopic world

*Thermodynamic states and energies
of a huge ensemble of molecules (material)*

Properties of a material:

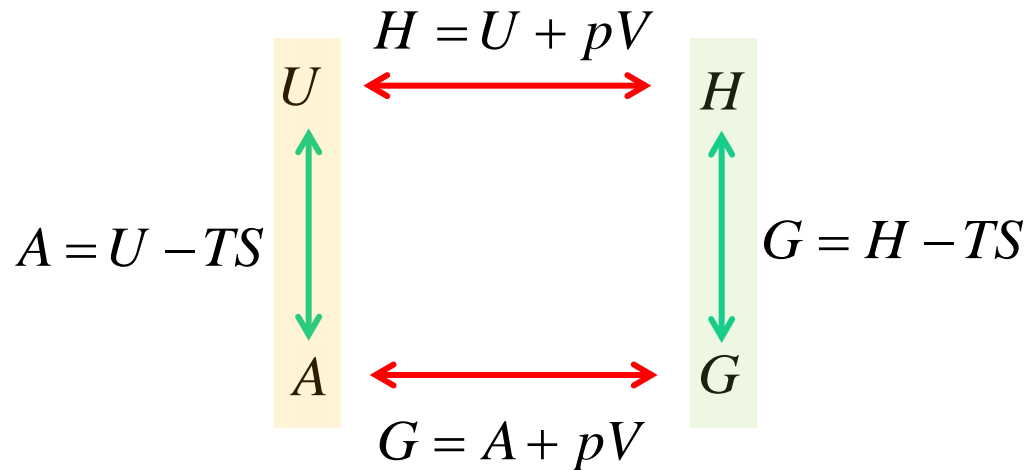
*phase
(boiling/freezing) temperature
pressure
heat (enthalpy)
order/disorder (entropy)
free energy
magnetic susceptibility
optical activity
etc.*

*Properties of a molecule
 (“**Wavefunction**”)*

**STATISTICAL
THERMODYNAMICS**

*Properties of a matter:
 (“**Partition function**”)*

State functions and their relations known from classical thermodynamics



S , U , H , A , G – state functions cannot be measured directly

ΔS , ΔU , ΔH , ΔA , ΔG – state-function changes can be measured directly

endothermic/exothermic reaction (in terms of ΔH)

endergonic/exergonic reaction (in terms of ΔG)

Definitions of systems in statistical thermodynamics

$\{N, V, E\}$ *Microcanonical system (isolated system)*

$\{N, V, T\}$ *Canonical system (closed system)*

$\{N, \mu, T\}$ *Grand-canonical system (open system)*

Toward the principles of statistical thermodynamics

- Boltzmann distribution

Collection of thought systems

<i>Canonical</i>	E_3	E_1	E_3
E_4	E_2	E_2	E_3
E_3	E_1	E_3	E_2
E_2	E_4	E_1	E_1

Quantum states of systems and their energies: $E_1, E_2, E_3, E_4, \dots$

n_i - number of systems having E_i .

Then:

$$\sum n_i = n_{tot} \qquad \sum n_i E_i = E_{tot}$$

$$W\{N\} = \frac{n_{tot}!}{\prod n_i!}$$

Microcanonical

There exists the most probable configuration with the maximal weight..

Toward the principles of statistical thermodynamics

- Boltzmann distribution

Having these equations:

$$\sum n_i = n_{tot} \quad \sum n_i E_i = E_{tot} \quad W_{\max} \{N\} = \frac{n_{tot}!}{\prod n_i!}$$

1) *Stirling approximation*
2) *Method of Lagrange multipliers*

$$\frac{n_i}{n_{tot}} = \wp_i = \frac{e^{-E_i/kT}}{\sum_{i=1}^M e^{-E_i/kT}}$$



Partition Function

$$Q = \sum_{i=1}^M e^{-E_i/kT}$$



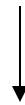
**Partition Function
for a classical system:**

$$Q = \iint e^{-E(\mathbf{p}, \mathbf{q})/kT} d\mathbf{q} d\mathbf{p}$$

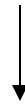


Partition function and internal energy U

$$U = \bar{E} = \sum_i \wp_i E_i = \frac{\sum_i E_i e^{-E_i/kT}}{Q}$$



$$\left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} = \frac{\partial \ln \left(\sum_i e^{-E_i/kT} \right)}{\partial T} = \frac{1}{kT^2} \frac{\sum_i E_i e^{-E_i/kT}}{Q} = \frac{U}{kT^2}$$



$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$$



Partition function and entropy

$$dU = \sum_i \wp_i dE_i + \sum_i E_i d\wp_i \longrightarrow = dq_{rev} = TdS$$

From Boltzmann distribution: $-kT[\ln \wp_i + \ln Q] = E_i$

$$TdS = \sum_i E_i d\wp_i = -kT \sum_i \ln \wp_i d\wp_i - \cancel{kT \ln Q} \sum_i d\wp_i$$

0

$$dS = d\left(-k \sum_i \wp_i \ln \wp_i\right)$$

↓ **Integration**

$$S = -k \sum_i \wp_i \ln \wp_i$$

Partition function and entropy

$$S = -k \sum_i p_i \ln p_i$$

In N,V,E ensemble

$W = 1/p_i$

$S = k \cdot \log W$

$$S = -k \sum_i p_i \ln \left(\frac{e^{-E_i/kT}}{Q} \right)$$

$$S = k \left[\ln Q + T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \right]$$



Partition function and free energy

Since $A = U - TS$

Then, $A = -kT \ln Q$!

Since $G = A + pV$

Then, $G = -kT \left[\ln Q - V \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \right]$!

Lectures 8/9 on how to evaluate A or G by means of Molecular Dynamics (MD) and Monte Carlo (MC) techniques where Q treated classically:

$$Q = \iint e^{-E(\mathbf{p}, \mathbf{q})/kT} d\mathbf{q}d\mathbf{p}$$

Molecular partition function

For ideal gas (gas of non-interacting atoms/molecules):

$$Q = \frac{q^N}{N!} \quad N - \text{the number of particles (molecules)}$$

$$q = q_{\text{nuclear}} q_{\text{electronic}} q_{\text{vibration}} q_{\text{rotation}} q_{\text{translation}}$$

q_{internal} ←

$$q = \sum_{k=1} g_k e^{-\varepsilon_k^*/kT} = e^{-\varepsilon_0/kT} \times \sum_{k=1} g_k e^{-\varepsilon_k/kT}$$

Molecular partition function

$$Q = \frac{q^N}{N!} = \frac{1}{N!} e^{-N\varepsilon_0/kT} \left(\sum_{k=1} g_k e^{-\varepsilon_k/kT} \right)^N$$

$$= e^{-U_0/kT}$$

$$U_0 = N \left(E_{elec} + \sum_l^{\text{\#modes}} \frac{1}{2} h \nu_l \right)$$

ZPVE

Internal energy at 0K

$$-kT \ln q_{trans}$$

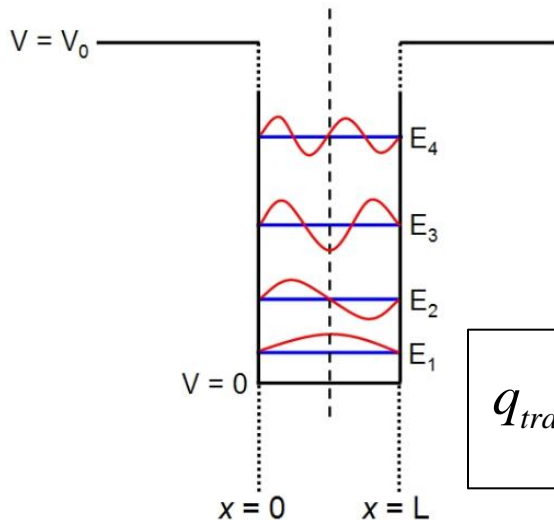
$$A - U_0 = kT \ln N! - kT \ln q_{trans}^* - kT \ln q_{rot} - kT \ln q_{vib} - kT \ln q_{el} + \dots$$

$$= A_{trans} + A_{rot} + A_{vib} + A_{el} + \dots$$

Translational partition function

Energy of an atom/molecule in the 3D box

(Solution of the Schrodinger equation with the infinite potential well):



The Infinite Square Well Potential

in 3D box

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

$$q_{trans} = \sum_{n_x} e^{-\left(\frac{h^2}{8mkT}\right)\left(\frac{n_x^2}{a^2}\right)} \sum_{n_y} e^{-\left(\frac{h^2}{8mkT}\right)\left(\frac{n_y^2}{b^2}\right)} \sum_{n_z} e^{-\left(\frac{h^2}{8mkT}\right)\left(\frac{n_z^2}{c^2}\right)}$$

$$\sum_{n_x} e^{-Cn_x^2} \approx \int_0^{\infty} e^{-Cn_x^2} dn_x = \frac{1}{2} \left(\frac{\pi}{C} \right)^{1/2}$$

$$U_{trans} = \frac{3}{2} NkT = \frac{3}{2} RT$$

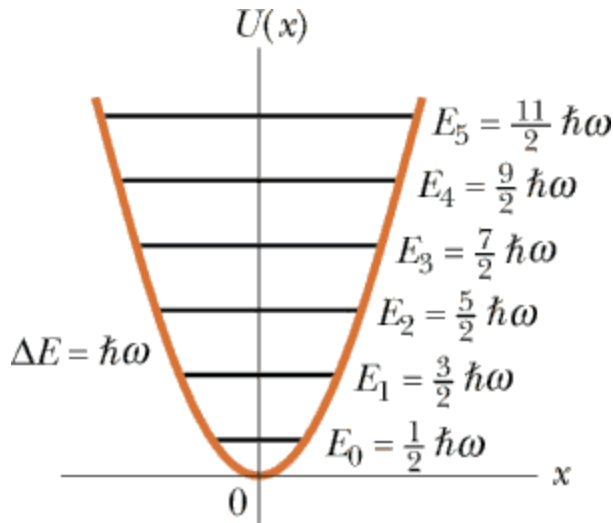
$$H_{trans} = \frac{5}{2} NkT = \frac{5}{2} RT$$

$$q_{trans} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$



Vibrational partition function

Vibrational energy of a molecule in the $3N-6$ harmonic potential
(Solution of the Schrodinger equation):



in $3N-6$ well \rightarrow

$$E_{vib} = \sum_l^{\text{\#modes}} \left(n + \frac{1}{2} \right) h\nu_l$$

Included into U_0

$$q_{vib} = \prod_{l=1}^{3N-6} \left(\sum_n e^{-nh\nu_l/kT} \right) = \prod_{l=1}^{3N-6} \left(1 + e^{-h\nu_l/kT} + e^{-2h\nu_l/kT} + \dots \right)$$

$$\left(1 + e^{-h\nu_l/kT} + e^{-2h\nu_l/kT} + \dots \right) = \frac{1}{1 - e^{-h\nu_l/kT}}$$

$$q_{vib} = \prod_{l=1}^{3N-6} \frac{1}{1 - e^{-h\nu_l/kT}}$$



Vibrational partition function and vibrational entropy

$$S = k \left[\ln Q + T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \right] \longrightarrow S_{vib} = Nk \left[\ln q_{vib} + T \left(\frac{\partial \ln q_{vib}}{\partial T} \right)_{N,V} \right]$$

$$q_{vib} = \prod_{l=1}^{3N-6} \frac{1}{1 - e^{-h\nu_l/kT}}$$

$$S_{vib} = R \sum_{l=1}^{3N-6} \left[\frac{h\nu_l}{kT(e^{h\nu_l/kT} - 1)} - \ln[1 - e^{-h\nu_l/kT}] \right]$$

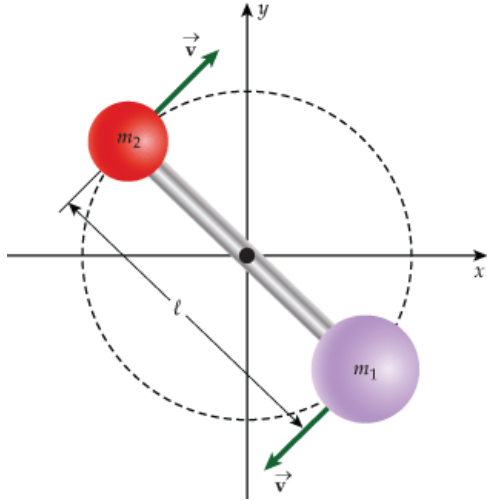
Small error
in low freq. $\nu_l \longrightarrow$ Large error in S

$$\nu_l \rightarrow 0 \quad S_{vib} \rightarrow \infty$$



To overcome (partially) a problem by considering vibrational low-frequency degrees of freedom as “free or hindered rotors”

Rotational partition function



SE for rotational motion of diatomics

$$E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$g_{rot} = 2J + 1$$

$$q_{rot} = \frac{8\pi^2 I kT}{\sigma h^2}$$

Polyatomics:

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{1/2}$$

$$U_{rot} = H_{rot} = \frac{3}{2} NkT = \frac{3}{2} RT$$



Gibbs free energy of a reaction (in an implicit solution)
 - “simplest approximation”

$$G = -RT \ln Q + pV = RT - RT \ln Q$$

Valid for ideal gas approx

Ideal-gas harmonic-oscillator/rigid rotor approximation:

$$G = [U_0 + RT - RT \ln Q]_{gp} + E_{solv}$$

$$= E_{elec} + ZPVE + RT - RT \ln q_{vib} q_{rot} q_{trans} + E_{solv}$$

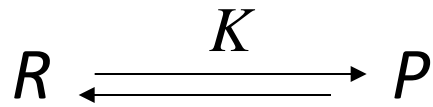
Solvation energy discussed in Lect. 6

Low-frequency mode issues → *Harmonic oscillator Approx. fails*

$$\Delta G = \Delta E_{elec} + \Delta ZPVE - \Delta RT \ln q_{vib} q_{rot} q_{trans} + \Delta E_{solv}$$



The relation between K and the partition function



$$q^R = q_{trans}^R q_{rot}^R q_{vib}^R$$

$$\Delta G_{R \rightarrow P} = \Delta U_0 - RT(\ln q^P - \ln q^R) = \Delta U_0 - RT \ln\left(\frac{q^P}{q^R}\right)$$

$$\Rightarrow e^{-\Delta G_{R \rightarrow P} / RT} = \frac{q_P}{q_R} e^{-\Delta U_0 / RT} = K !$$

(Gibbs/Helmholz) free energy of a reaction (in an explicit solution)

$$G = A \quad \text{if } \Delta pV = 0$$

$$Q = \iint e^{-E(\mathbf{p}, \mathbf{q})/kT} d\mathbf{q}d\mathbf{p}$$

$$A = -kT \ln Q \longrightarrow A = kT \ln \frac{1}{Q}$$

$$\frac{1}{Q} = \frac{\iint e^{E(\mathbf{p}, \mathbf{q})/kT} e^{-E(\mathbf{p}, \mathbf{q})/kT} d\mathbf{q}d\mathbf{p}}{\iint e^{-E(\mathbf{p}, \mathbf{q})/kT} d\mathbf{q}d\mathbf{p}}$$

$$A = kT \ln \iint e^{E(\mathbf{p}, \mathbf{q})/kT} P(\mathbf{q}, \mathbf{p}) d\mathbf{q}d\mathbf{p}$$

*Probability of being
in a particular point of
a phase space*

$$\Delta A = \langle A \rangle_P - \langle A \rangle_R = kT \ln \left(\frac{1}{M_P} \sum_i^{M_P} e^{E_i/kT} \right) - kT \ln \left(\frac{1}{M_R} \sum_i^{M_R} e^{E_i/kT} \right)$$

More in lectures 8/9