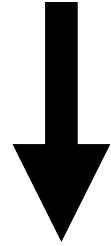


# Statistical Thermodynamics

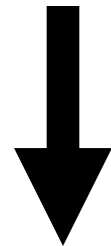
## *Essential Concepts*

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

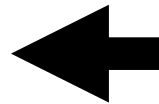
*Quantum mechanics of atoms  
and molecules*



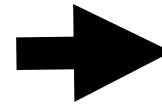
***STATISTICAL  
MECHANICS***



***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:***

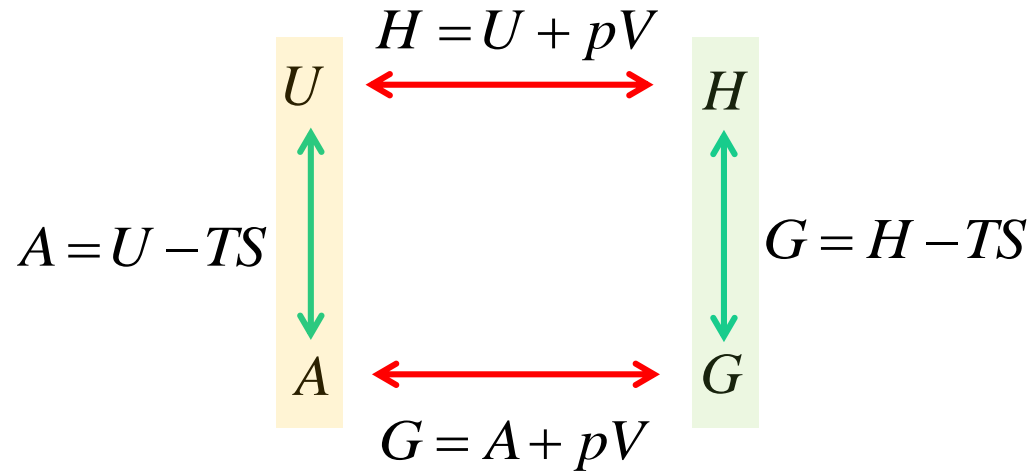
*phase  
(boiling/freezing) temperature  
pressure  
heat (enthalpy)  
order/disorder (entropy)  
free energy  
magnetic susceptibility  
optical activity  
etc.*

*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

$\Delta S$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta A$ ,  $\Delta G$  – state-function changes can be measured directly

endothermic/exothermic reaction (in terms of  $\Delta H$ )

endergonic/exergonic reaction (in terms of  $\Delta G$ )

## Definitions of systems in statistical thermodynamics

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

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

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

# Toward the principles of statistical thermodynamics

## - Boltzmann distribution

### *Collection of thought systems*

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

*Microcanonical*

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:

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

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

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**

$\Rightarrow$

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



**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:  $-kT[\ln \wp_i + \ln Q] = E_i$

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

~~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

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

*In N,V,E ensemble*

$W = 1/p$

$$S = k \cdot \log W$$

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

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



## 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):**

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

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

$q_{\text{internal}}$  

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

# 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**

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

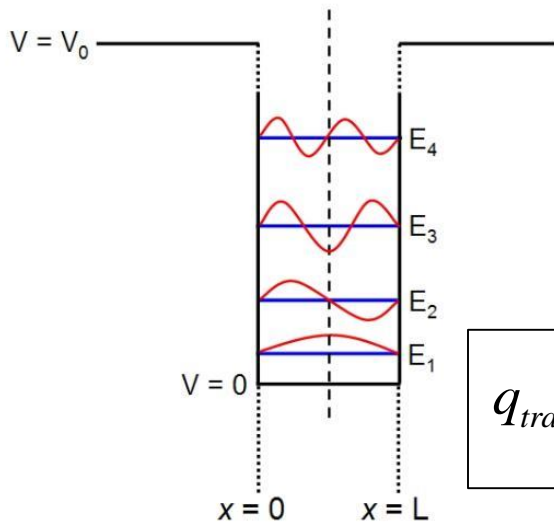
$$A - U_0 = RT \ln N! - RT \ln q_{trans}^* - RT \ln q_{rot} - RT \ln q_{vib} - RT \ln q_{el} + \dots$$

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

# 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

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

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

$$\sum_{n_x} e^{-Cn_x^2} \approx \int_0^{\infty} e^{-Cn_x^2} dn_x = \frac{1}{4} \left( \frac{\pi}{C} \right)^{1/2}$$

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

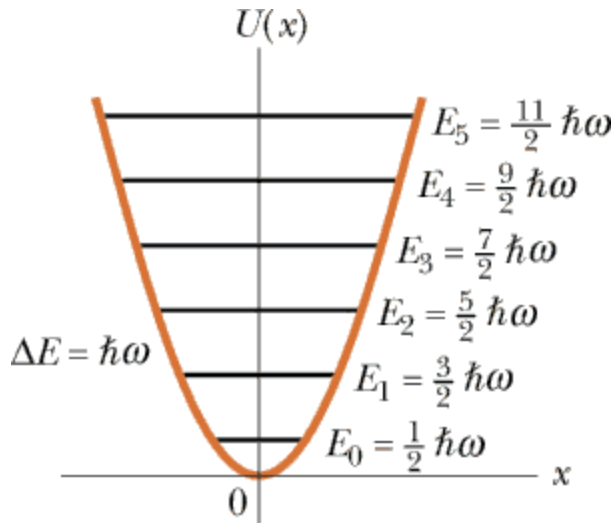
$$H_{trans} = \frac{5}{2} NkT = \frac{5}{2} RT$$

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



# 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

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

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

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

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

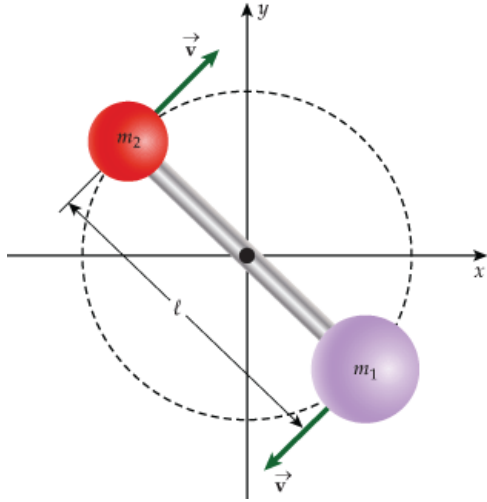
$$\nu_l \rightarrow 0 \quad S_{vib} \rightarrow \infty$$



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”

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

**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. 5*

*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



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

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

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