MICROCANONICAL FORMALISM

MICROCANONICAL ENSEMBLE:

N particles

total energy E

in volume V

$$p_i = \frac{1}{\Omega}$$

probability density function
of state i

Ω : sum of states, or partition function
(Zustandssumme)

The microcanonical formalism of statistical mechanics results in
entropy-based equation of state in the following form:

$$S(E, V, N) = k \ln \Omega(E, V, N)$$

The microcanonical "prescription" is the following:

Count the number of all accessible states, and calculate entropy
Using this equation of state, we know all possible macroscopic state.

Wien, Zentralfriedhof
Johannes Borromäus church

$$S(E, V, N) = k \ln \Omega(E, V, N)$$

$S = k \log W$

LVDWIG
BOLTZMANN
1844–1906

DR PHIL. PAULA
OLTZMANN
GEB. CHIARI
1891–1977
ARTHUR
OLTZMANN

CANONICAL FORMALISM

CANONICAL ENSEMBLE:

N particles

in volume V

at temperature T

$$p_i = \frac{e^{-\frac{E_i}{kT}}}{\sum\limits_{\forall i} e^{-\frac{E_i}{kT}}}$$

probability density function
of state i

$$Q = \sum\limits_{\forall i} e^{-\frac{E_i}{kT}}$$

canonical **partition function**,
or canonical **sum of states**

The canonical formalism of statistical mechanics results in
free-energy based equation of state in the following form:

$$F(T,V,N) = -kT \ln Q(T,V,N)$$

The canonical "prescription" is the following:

Calculate the canonical partition function, and express the free energy F

FUNDAMENTAL EQUATION of an IDEAL GAS

In molecules, the following modes can be discerned in general:

- – three translational modes

- – rotational modes

- – vibrational modes

- – electronic modes (a.k.a. states)

The modes in gas-phase molecules in an ideal gas are independent;
thus, their energies are additive (no interactions),
and the partition function can be factorised:

$$Q = Q^{trans} \cdot Q^{rot} \cdot Q^{vib} \cdot Q^{el}$$

All contributions can be factorised as $$Q^{(I)} = \prod_{j=1}^{N} \left(\sum_{\forall i} e^{-\beta \varepsilon_{ij}} \right)$$

$\underbrace{\phantom{\sum_{\forall i} e^{-\beta \varepsilon_{ij}}}}_{q^{(I)}}$

Due to the commutability of multiplication, we can first write the product of molecular partition functions $q^{(I)}$ in the form

$$q = q^{trans} \cdot q^{rot} \cdot q^{vib} \cdot q^{el}$$

and then calculate their product for all N molecules of the ensemble.

Let us start with the translational partition function (of an ideal gas)

$$q^{trans} = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \cdot V$$

Using the thermal wavelength $\Lambda = \dfrac{h}{\sqrt{2\pi m k T}}$: $\quad q^{trans} = \dfrac{V}{\Lambda^3}$

The order of magnitude of the thermal wavelength and the translational partition function in ambient temperature gas :

$$\Lambda = 17{,}8\,\text{pm}$$

$$q^{trans} = 1{,}773 \cdot 10^{30}$$

For a gas containing N atoms:

$$Q^{trans} = (Q^{trans})^N = \frac{1}{N!}\left(\frac{2\pi m k T}{h^2}\right)^{3N/2} \cdot V^N$$

We see a division by $N!$ here, as the number of states in a gas of N molecules is much less than the simple product would predict.

It is due to the fact that gas molecules are indistinguishable.
This is the reason for dividing by $N!$ (The number of possible permutations.)

Thus, the partition function becomes

$$Q = \frac{V^N}{N!}\left(\frac{2\pi m k T}{h^2}\right)^{3N/2}$$

A general rotor (a 3-dimensional molecule) has 3 degrees of freedom; thus, it has 3 rotational axis and 3 rotational constant.

Let us denote the rotational constants by A, B and C.

The partition function of such a (nonlinear) molecule:

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

(σ: rotational symmetry factor)

At ambient temperature, a multitude of rotational states is available.

In this temperature range, the typical value is $q^R \approx 1000$.

The *vibrational partition function* for a harmonic oscillator:

$$\varepsilon_v = \left(v + \frac{1}{2} \right) h\nu$$

v : Latin "vee"
ν : Greek "nu"

Take the zero point of the energy scale as $\varepsilon_0 = \frac{1}{2} h\nu = 0$

In this case: $\varepsilon_v = v h\nu \quad \rightarrow \quad q^V = \sum_{v=0}^{\infty} e^{-\beta v h\nu} = \sum_{v=0}^{\infty} \left(e^{-\frac{h\nu}{kT}} \right)^v$

This is exactly the sum of the geometric series of of $e^{-\frac{h\nu}{kT}}$, thus:

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

The vibrational partition function has the same form for all the normal vibrations of the molecule. Thus, the overall vibrational partition function is:

$$q^V = q^V(1) \cdot q^V(2) \cdot \ldots \cdot q^V(k)$$

At temperatures not too much higher than ambient,
$q^V(i)$ values are typically between 1 and 3.

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Electronic partition functions:

In the majority of cases at ambient temperatures only one state is available:

$$\boxed{q^E = 1}$$

Exception: degenerate ground states (e. g. alkali atoms' spin-degeneration)

In these cases: $$\boxed{q^E = g^E}$$ g^E is the degree of degeneration

Equilibrium constant in canonical formalism

First, let us express the free energy F

with molecular partition functions for a gas:

$$F = F(0) - kT \ln Q = F(0) - kT \ln \frac{q^N}{N!} =$$

$F(0)$ is fixing the energy scale

$$= F(0) - NkT \ln q + kT(N \ln N - N) =$$

applying Stirling's approximation:
$\ln(N!) \cong N \ln N - N$

$$= F(0) - NkT \ln q + kTN(\ln N - 1)$$

The molar free energy F_m (substituting $k N_A = R$):

$$F_m = F_m(0) - RT \ln q + RT \ln N_A - RT$$

$$\boxed{F_m = F_m(0) - RT \ln \frac{q}{N_A} - RT}$$

Within the conditions T, P = constants the reaction equilibrium constant can be given using the Gibbs potential G:

$$G = F + PV$$

With some "cheating" (using $PV = nRT$, for ideal gas mixtures only):

$$G_m = F_m(0) - RT\ln\frac{q_m}{N_A} - RT + RT = F_m(0) - RT\ln\frac{q_m}{N_A}$$

Let us denote by $q_m^{\ominus}$ the value of q_m at $p = p^{\ominus}$ and $V^{\ominus} = \dfrac{RT}{p^{\ominus}}$

Thus, the standard molar Gibbs potential becomes

$$\boxed{G^{\ominus} = F_m(0) - RT\ln\frac{q_m^{\ominus}}{N_A}}$$

using $F = U - TS$, we can express $F_m(0)$ in terms of $U_m(0)$ as:

$$F_m(0) = U_m(0) - T(0)\,S(0)$$

If $T(0) = 0$ K $\rightarrow$ $F_m(0) = U_m(0)$ $\Rightarrow$ $G^{\ominus} = U_m(0) - RT\ln\dfrac{q_m^{\ominus}}{N_A}$

We know: $\Delta_r G^{\ominus} = -RT\ln K$; by comparing this to $G^{\ominus}$ we get:

$$\Delta_r G^{\ominus} = \Delta_r U_m(0) - RT\sum_{i=1}^{r}\ln\left(\frac{q_{m,i}^{\ominus}}{N_A}\right)^{\nu_i} = \Delta_r U_m(0) - RT\ln\prod_{i=1}^{r}\left(\frac{q_{m,i}^{\ominus}}{N_A}\right)^{\nu_i}$$

$$\ln K = -\frac{\Delta_r U_0}{RT} + \ln\prod_{i=1}^{r}\left(\frac{q_{m,i}^{\ominus}}{N_A}\right)^{\nu_i}$$

shorthand:
$\Delta_r U_m(0) = \Delta_r U_0$

For the general reaction $\displaystyle\sum_{i=1}^{r}\nu_i A_i = 0$ $\qquad K = \displaystyle\prod_{i=1}^{r}\left(\frac{q_{m,i}^{\ominus}}{N_A}\right)^{\nu_i}\cdot e^{-\frac{\Delta_r U_0}{RT}}$

Thus, we have obtained the equilibrium constant for a reaction where all the reacting components are ideal gas species.

This expression can always be used by replacing $\left(\dfrac{q_{m,i}^{\ominus}}{N_A} \right)$

by the "real" canonical partition function $Q_{m,i}^{\ominus}$ (e. g. from simulations)
In the exponent we still have the reaction energy at $T = 0$ temperature.

Summing up:

The equilibrium constant for the reaction $\displaystyle\sum_{i=1}^{r} \nu_i \, A_i = 0$

explained in canonical formalism is

$$K = \prod_{i=1}^{r} \left(\frac{q_{m,i}^{\ominus}}{N_A} \right)^{\nu_i} \cdot e^{-\frac{\Delta_r U_0}{R\,T}}$$

$q_{m,i}^{\ominus}$ is the standard molecular partition function,
$\Delta_r U_0$ is the reaction energy at $T = 0$ K temperature

For two particular reaction types this can be written in the following form:

If $\qquad$ A + B $\;\rightleftharpoons\;$ C

then

$$K = \frac{N_A \; q_C^{\ominus}}{q_A^{\ominus} \; q_B^{\ominus}} \; e^{-\frac{\Delta U_0}{RT}}$$

if $\qquad$ A $\;\rightleftharpoons\;$ B

then

$$K = \frac{q_B^{\ominus}}{q_A^{\ominus}} \; e^{-\frac{\Delta U_0}{RT}}$$

Same equilibrium constants expressed with **_molar_** partition functions:

If $\qquad$ A + B $\qquad \rightleftarrows \qquad$ C

then

$$K = \frac{Q_C^{\ominus}}{Q_A^{\ominus} \, Q_B^{\ominus}} \; e^{-\frac{\Delta U_0}{RT}}$$

If $\qquad$ A $\qquad \rightleftarrows \qquad$ B

then

$$K = \frac{Q_B^{\ominus}}{Q_A^{\ominus}} \; e^{-\frac{\Delta U_0}{RT}}$$

The End