# Statistical mechanics class on chemical equilibrium

Non-interacting (ideal) systems

## Class plan (from Jianhan)

already taught:

- vibrational; rotational degrees of freedom (partition function)
- diatomic molecules
- nuclear
- rotation
- vibration

### Tuesday

- 4.10 chemical equilibrium
- equilibrium constant $K_{eq}$ ~ $\Delta S$ and $\Delta H$; $\Delta S$ contribution can be factorized into translational, vibrational and electronic energy state transition contributions.
- the $K_{eq}$ is ratio of partitional functions of products and reactants
- Homework (units conversion)
- why $K_{eq}$ is a constant? (pop-up quiz: write down each partition function contributions)

## Thursday

free energy pertubration:

1. 30 mins
- starting with a normal canonical ensmeble with a $H_0$ (derivation)
- ensemble size ~ snapshot reweighting (explain the reweighting idea)
2. 15 mins: real protocals (how to turn on interactions: VDW and electrostatics)
- show some examples (benchmarking; Boltz-2; FEP)
- drug screening; competition (affinities of protein/ligand complex)

## Factorization approximation

From the principle of statistical mechanics, we now know:

$$\sum_v \exp(-\beta E_v)$$

or

$$\sum_v \exp(-\beta(E_v - \mu N_v))$$

which are summation of all Boltzmann factors over all possible fluctuations. These are all microscopic states permitted by the constraints with which the system is controlled, i.e., $NVT, NPT, \ldots$

As we want to explore all possible fluctuations of a give system, it becomes complicate due to the ginormous numbers of microscopic states. The **factorization** provides a way to simply such a process.

Supposing that energy $E_v$ can be decomposed as additive terms combined in the canonical partition function:

$$Q = \sum_v \exp(-\beta E_v) = \sum_{n,m} \exp(-\beta E_n^{(1)}) \exp(-\beta E_m^{(2)})$$

can thus be factorized to:

$$Q = \left[\sum_n \exp(-\beta E_n^{(1)})\right] \left[\sum_m \exp(-\beta E_m^{(2)})\right] = Q^{(1)} Q^{(2)}$$

- the state $v$ depends on $n, m$, and those two are independent of each other.
- $Q^{(1)}$ and $Q^{(2)}$ are Boltzmann sums associated with energies $E_n^{(1)}$ and $E_m^{(2)}$.
- *Remember, these two energies by assumption should be fully decoupled*

## Occupation number

For a system with N indistinguishable particles, *occupation numbers* on single particle wave functions can completely define a particular system state $v$.

And the occupation number is a collective variable which depends on the instantaneous state of all particles.

Let,

$$v = (n_1, n_2, \ldots, n_j, \ldots) = v - th\ state$$

Then the particle number and internal energy is:

$$N_v = \sum n_j$$

$$E_v = \sum \epsilon_j n_j$$

$\epsilon_j$ is the energy of the $j$-th single particle state.

## Thermodynamics of an ideal gas of structureless classical particles

The classical ideal gas under classical limit (high temperature and low density) will have the following:

$$Q = \frac{1}{N!}\left[\sum_j e^{-\beta\epsilon_j}\right]^N$$

Let's consider:

- structureless particles with mass $m$ in a finite volume $V$.
- the particle energy is just the translational center-of-mass motion.
- The single particle energy (kinetic energy) can be expressed using the following:

$$\epsilon_k = \frac{\hbar^2 k^2}{2m},\ k = \frac{\pi}{L}(n_x\hat{x} + n_y\hat{y} + n_z\hat{z})$$

where $L = V^{1/3}$; $n_x$, $n_y$, $n_z$ go from 1 to $\infty$.

The classical partition function is then:

$$Q(N,V,T) = \frac{1}{N!}\left[\sum_{n_x,n_y,n_z=1}^{\infty} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right)\right]^N$$

In the classical limits:

- $\beta\hbar$ is small
- $L$ is very large

Thus the difference between consecutive terms in the summand is small, and the summation can be solved using integral:

$$\Delta n_{x;y;z} = \frac{L}{\pi}\Delta k_{x;y;z} \to \frac{L}{\pi} dk_{x;y;z}$$

$$\sum_{n_x,n_y,n_z} \to \frac{L^3}{\pi^3}\int_0^\infty dk_x \int_0^\infty dk_y \int_0^\infty dk_z$$

$$\sum_{n_x,n_y,n_z} \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right) \to \frac{V}{\pi^3}\int_0^\infty dk_x dk_y dk_z \exp\left[-\frac{\beta\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}\right]$$

$$= \frac{V}{(2\pi)^3}\int_\infty^\infty dk_x dk_y dk_z \exp\left[-\frac{\beta\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}\right]$$

Let, $\mathbf{p} = \hbar\mathbf{k}$, to change the integration variable:

$$Q = \frac{1}{N!}\left[\frac{V}{(2\pi)^3\hbar^3}\int d\mathbf{p} e^{-\beta\mathbf{p}^2/2m}\right]^N$$

which is a normal Gaussian-form integration (easy to resolve):

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

**Gaussian integral**

$$\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi}$$

$$\int_{\mathbb{R}^3} d^3\mathbf{p}\ e^{-a\mathbf{p}^2} = \left(\frac{\pi}{a}\right)^{3/2}$$

$$\int d^3\mathbf{p}\ e^{-\beta\mathbf{p}^2/2m} = \left(\frac{\pi}{\beta/(2m)}\right)^{3/2} = \left(\frac{2\pi m}{\beta}\right)^{3/2}$$

We can thus determine the internal energy:

$$\langle E \rangle = \left( \frac{\partial \ln Q}{\partial - \beta} \right)_V = \frac{3N}{2\beta} = \frac{3}{2} N k_B T$$

$$\beta P = \left( \frac{\partial \ln Q}{\partial V} \right)_\beta = \frac{N}{V}$$

which is the same as:

$$PV = N k_B T = nRT$$

- The ideal gas formula!

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## A dilute gas of atoms

- ideal gas particles with **internal structure** (which we account for in this section)

Considering the internal structure, the state of an atom can be expressed as:

$$j = (\mathbf{k}, n, v)$$

- $\mathbf{k}$: center-of-mass translation
- $n$: state of the nucleus
- $v$: electronic state

Assuming:

1. The center-of-mass translation is decoupled from the internal structure ($\mathbf{k}$ or $n$).
2. The nucleus and the electronic degrees of freedom are also uncoupled.

$$\sum_j e^{-\beta \epsilon_j} = \underbrace{\sum_{\mathbf{k}} \exp\left( -\frac{\beta \hbar^2 k^2}{2m} \right)}_{q_{trans}(T,V)} \underbrace{\sum_{n,v} \exp(-\beta \epsilon_{nv})}_{q_{int(T)}}$$

- $\epsilon_{n,v}$ is the energy for internal state $(n, v)$.

Let $\epsilon_{00}$ be the ground state energy for the internal structure:

$$q_{int}(T) = e^{-\beta \epsilon_{00}} \sum_{n,v} \exp(-\beta(\epsilon_{nv} - \epsilon_{00}))$$

- we do this because for many atoms, internal excitation energies are usually very large compared to $k_B T$.

> **Excitation energy**
>
> For atoms, the **excitation energy** typically falls in the range of a few **electronvolts (eV)**. More concretely:

> - **Valence (outer electron) excitations:**
>  Usually about **1–10 eV**
>  These correspond to transitions between bound electronic energy levels and are the most common in spectroscopy (UV/visible).
> - **Inner-shell (core electron) excitations:**
>  Much higher, typically **tens to thousands of eV** (X-ray range)

for example, for hydrogen:

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2}$$

- Ground state: n=1, $-13.6\,\mathrm{eV}$
- First excited state: n=2, $-3.4\,\mathrm{eV}$

So the excitation energy from $n = 1 \to n = 2$ is:

$$\Delta E = 10.2\,\mathrm{eV}$$

- 1 eV would correspond to ~ 40 $k_B T$ when $T$ = 300 K.
- $e^{-40}$ is neglilible ~ ignoring the excitation state.

Thus *we can safely only consider the ground state* (which contributes the most significantly to the sum):

$$q_{int}(T) \simeq e^{-\beta\epsilon_{00}} \times \text{degeneracy} = e^{-\beta\epsilon_{00}} g_0^{(nuc)} g_0^{(elec)}$$

- the ground state will have its degeneracy, meaning different quantum numbers (defining the states) may have the same ground state energy.
- the $g_0^{(nuc)}$ and $g_0^{(elec)}$ stand for the ground level degeneracies of the nuclear states and electronic states.

*If we continue assuming only the spin degrees of freedom (the total angular momentum)*, then:

$$g_0^{(nuc)} = 2\mathbf{I} + 1$$

- $\mathbf{I}$ is the total spin quantum number of the nucleus.

Combining all the above formula gives:

$$-\beta A = \ln Q = \ln\left[\frac{1}{N!} q_{trans}^N(T,V) q_{int}^N(T)\right]$$

$$= -\beta N \epsilon_{00} + N \ln[g_0^{elec}(2\mathbf{I}+1)] + \ln\left[\frac{1}{N!} q_{trans}^N(T,V)\right]$$

- The last term is the center-of-mass translation, which has been analyzed in Thermodynamics of an ideal gas of structureless classical particles.
- We can see that the internal degrees of freedom is independent of $V$, thus they do not affect system pressure. However, they clearly contribute to the system energy and entropy.

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## Dilute gas of diatomic molecules

We now further study the thermal properties of a gas composed of molecular species. The internal energetics of a molecule consist of:

- vibrational motions.
- rotational motions.
- electronic and nuclear spin degrees of freedom.

Here, we introduce the **Born–Oppenheimer approximation** to **separate the different energy scales** in a molecule so that vibrational, rotational, electronic, and spin contributions can be treated (almost) independently in the thermodynamics.

**ⓘ Born-Oppenheimer approximation**

A molecule contains:

- **Electrons** (light, fast)
- **Nuclei** (heavy, slow)

Because of the huge mass ratio ($m_{\text{nucleus}} \gg m_e$), their motions naturally occur on **very different timescales and energy scales**:

- Electronic excitations: **~ eV ($10^0$–$10^1$ eV)**
- Vibrations: **~ $10^{-1}$ eV**
- Rotations: **~ $10^{-3}$ eV**
- Nuclear spin splittings: **~ $10^{-6}$ eV or smaller**

Without an approximation, all these degrees of freedom are **strongly coupled** in the full molecular Hamiltonian, making statistical mechanics intractable.

This means:

- *the electronic motion is fast compared to the nuclear motion so that nuclear kinetic energy may be neglected when determining the electronic wavefunction*.

The wavefunction of a diatomic molecule is:

$$\psi(r, R) = \Phi_n(r; R)\chi_{nv}(R)$$

- $r$ and $R$ is the electronic and nuclear coordinates.
- $\Phi$ is the **electronic wavefunction**, which is parameterized by $R$.
- $\chi$ is the **nuclear wavefunction**. It will be different depending on the $n$ (the nuclear state).

With this separation, we will first determin $\Phi$ from:

$$[K(r) + U(r) + U(R) + U(r, R)]\Phi_n(r; R) = E_n(R)\Phi_n(r, R)$$

and then $\chi$ by

$$[K(R) + E_n(R)]\chi_{n,v}(R) = E_{n,v}\chi_{n,v}(R)$$

- $K$ and $U$ mean the kinetic and potential energies respectively.
- $E_n(R)$ is the effective potential for nuclei (averaged over electron effects)

With Born-Oppenheimer approximation, we write:

$$q_{int}(T) = \sum_{n,v} \langle n, v| \exp(-\beta \mathcal{H}_{int})|n, v\rangle$$

$$= \sum_{v} \left( \langle \chi_{0v}| \exp[-\beta \mathcal{H}_{eff}^{(0)(R)}]|\chi_{0v}\rangle + \langle \chi_{1v}| \exp[-\beta \mathcal{H}_{eff}^{(1)(R)}]|\chi_{1v}\rangle + \dots \right)$$

- $\mathcal{H}_{eff}^{(n)}$ is the effective Hamiltonian (electronically averaged) for the nuclear coordinate $R$ when the molecule is in the $n$-th electronic state.
- $\mathcal{H}_{eff}^{(n)} = K(R) + E_n(R)$.

Let's further *assume that the vibrational and rotational motion of the nuclei are uncoupled*, which is often a good approximation due to the mismatch in time scales.

$$E_{ov} - \epsilon_0 \simeq \underbrace{\left(\frac{1}{2}v\right)\hbar w_0}_{\text{vibrational energy, nondegenerate}} + \underbrace{\frac{J(J+1)\hbar^2}{2I_0}}_{rotational energy, degeneracy of (2J+1)}$$

- $v$ = 0, 1, 2, ...
- $J$ = 0, 1, 2, ...
- $w_0$ and $I_0$ are the fundamental frequency and moment of inertia (of the whole molecule), and can be calculated using the following:

$$w_0 = \mu^{-1}\left[\frac{\partial^2 E_0(R)}{\partial R^2}\right]_{R=R_0(eq)}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

- $\mu$ is the reduced mass of the two nuclei.

$$q_{int}(T) \simeq \frac{g_0^{(elec)} e^{-\beta\epsilon_0}(2\mathbf{I_A}+\mathbf{1})(2\mathbf{I_B}+\mathbf{1})q_{rot}q_{vib}}{\sigma_{AB}}$$

- $\sigma$ is the symmetry number, 1 if $A \neq B$ and 2 if $A = B$. (heteronuclear or homonuclear diatomic molecules)
- $\mathbf{I_A}$ and $\mathbf{I_B}$ are moment of inertia of nuleus $A$ and $B$. and $2\mathbf{I}+1$ is for the spin degeneracy.

$$q_{rot}(T) = \sum_{J=1}^{\infty}(2J+1)\exp\left[-\frac{J(J+1)\beta\hbar^2}{2I_0}\right]$$

$$q_{vib}(T) = \sum_{v=0}^{\infty}\exp\left[-\left(\frac{1}{2}+v\right)\beta\hbar w_0\right]$$

and the $q_{vib}$ can be calculated using geometric series:

$$q_{vib}(T) = \left[\exp\left(\frac{\beta\hbar w_0}{2}\right) - \exp\left(-\frac{\beta\hbar w_0}{2}\right)\right]^{-1}$$

**Geometric Series**

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}, \text{ if x<1}$$

For the rotational contribution, we approximate it with an integral over the Euler-Maclaurin series assuming rotational levels are small compared with $k_B T$.

$$q_{rot}(T) \simeq \int_0^{\infty} dJ(2J+1)\exp\left[-\frac{-J(J+1)\beta\hbar^2}{2\mathbf{I}_0}\right] = \frac{T}{\theta_{rot}}$$

$$\theta_{rot} = \frac{\hbar^2}{2\mathbf{I}_0 k_B}$$

Also for $q_{trans}$:

$$q_{trans}(T,V) = V\left[\frac{2\pi M}{\beta h^2}\right]^{3/2}$$

- $M = m_A + m_B$

And finally, for diatomic ideal gas:

$$-\beta A(N,V,T) \simeq -N\ln N + N + N\ln V + \frac{3}{2}N\ln\left(\frac{2\pi M k_B T}{h^2}\right) + N\ln q_{int}(T)$$

with:

$$q_{int}(T) = \underbrace{g_0^{(elec)} e^{-\beta\epsilon_0}}_{\text{electron ground state}} \underbrace{(2\mathbf{I}_A+1)(2\mathbf{I}_B+1)}_{\text{nuclear spin}} \overbrace{\sigma_{AB}^{-1}}^{\text{symmetry}} \underbrace{\left(\frac{T}{\theta_{rot}}\right)}_{\text{rotation}} \underbrace{\left(\exp\left(\frac{\beta\hbar w_0}{2}\right) - \exp\left(-\frac{\beta\hbar w_0}{2}\right)\right)^{-1}}_{\text{vibration}}$$

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## Chemical equilibria in gases

The gas phase partition functions we derived above can be useful to compute chemical equilibrium constants.

Consider the following chemical reactions:

$$aA + bB \leftrightarrow cC + dD$$

- $a, b, c, d$ are stoichiometric coefficient.
- $A, B, C, D$ are molecular species.

From general chemistry:

$$K_{eq} \equiv \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

and for ideal gas system (derived from $\frac{\partial \mu}{\partial P} = \bar{V} = \frac{RT}{P}$):

$$G_A = G_A^0 + RT \ln \frac{[A]}{[A_0]}$$

At chemistry equilibrium:

$$\Delta G = 0 = RT \left( G_A^0 + \ln(\frac{[A]}{[A_0]})^a + G_B^0 \ln(\frac{[B]}{[B_0]})^b - G_C^0 - \ln(\frac{[C]}{[C_0]})^c - G_D^0 - \ln(\frac{[D]}{[D_0]})^d \right)$$

$$0 = G_C^{[0]} + G_D^0 - G_A^0 - G_B^0 - RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\Delta G_{\text{reaction}} = -RT \ln K_{eq} = -RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

We can write this expression more compactly as:

$$0 = \sum_{i=1}^{4} v_i X_i$$

- $v_i$ is the reaction number. $v_1 = c, v_2 = d, v_3 = -a, v_4 = -b$.
- $X_i$ are species: $X_1 = C, X_2 = D, X_3 = A, X_4 = B$.

The stoichiometry thus applies a restriction on changes in mole numbers:

$$\Delta n_A = \left(\frac{b}{a}\right)^{-1} \Delta n_B = -\left(\frac{c}{a}\right)^{-1} \Delta n_C = -\left(\frac{d}{a}\right)^{-1} \Delta n_D$$

The first order virtual displacement of the internal energy due to vibrations in mole numbers is:

$$\delta E = \sum_{i=1}^{4} \mu_i \delta n_i = \delta n_A \left[ \mu_A + \left(\frac{b}{a}\right) \mu_B - \left(\frac{c}{a}\right) u_C - \left(\frac{d}{a}\right) \mu_D \right]$$

Under equilibrium condition, any small deviations from the equilibrium point would result in $\Delta E_{S,V,n} > 0$, thus the following has to suffice:

$$\left[ \mu_A + \left(\frac{b}{a}\right) \mu_B - \left(\frac{c}{a}\right) u_C - \left(\frac{d}{a}\right) \mu_D \right] = 0$$

or more general:

$$0 = \sum_{i=1}^{r} v_i u_i$$

- $r$ means for all species involved in the chemical reaction.

From the A dilute gas of atoms discussion, the partition function of the $r$-component mixture is

$$Q(\beta, V, N_1, N_2, \ldots, N_r) = \frac{1}{N_1!} \frac{1}{N_2!} \ldots \frac{1}{N_r!} q_1^{N_1} q_2^{N_2} \ldots q_r^{N_r}$$

- the $q_i$ is the single particle partition function.

Thus,

$$\beta A = -\ln Q = \sum_{i=1}^{r} [\ln N_i! - N_i \ln q_i]$$

As a result,

$$\beta \mu_i = \left( \frac{\partial \beta A}{\partial N_i} \right)_{\beta, V, N_j} = \ln N_i - \ln q_i$$

We already know:

$$q_i = \underbrace{\frac{V}{h^3} \left( \frac{2\pi m_i}{\beta} \right)^{3/2}}_{\text{translation/external}} \times q_{int} = \frac{V}{\lambda_i^3} \times q_{int}$$

where:

$$\lambda_i = \frac{h}{\sqrt{2\pi m_i k_B T}}$$

- The thermal wavelength of species $i$ with a particle mass of $m_i$.

$$\beta \mu_i = \ln \left[ \frac{N_i}{q_i} \right] = \ln \left[ \frac{N_i \lambda_i^3}{V q_{int}} \right] = \ln \left[ \rho_i \left( \frac{\lambda_i^3}{q_{int}} \right) \right]$$

At chemical equilibrium (the $\beta$ can be ignored here):

$$0 = \sum_{i=1}^{r} v_i u_i = \sum_{i=1}^{r} v_i \ln \left[ \rho_i \left( \frac{\lambda_i^3}{q_{int}} \right) \right] = \ln \prod_{i=1}^{r} \left( \rho_i \frac{\lambda_i^3}{q_{int}} \right)^{v_i}$$

And the definition of chemical equilibrium constant is:

$$K \equiv \prod_{i=1}^{r} (\rho_i)^{v_i} = \prod_{i=1}^{r} \left[ \frac{q_{int}}{\lambda_i^3} \right]^{v_i} = \prod_{i=1}^{r} [q_i]^{v_i}$$

- **we can directly calculate the constant from partition functions of all species**.

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## A real case of statistical mechanics of gas-phase equilibrium

$$H_2\ (g) + Br_2\ (g) \leftrightarrow 2HBr(g)$$

- (treating all species as ideal gas)

From Chemical equilibria in gases, we have:

$$K_{eq} \equiv \frac{\rho_{(HBr)}^2}{\rho_{(H_2)} \rho_{(Br_2)}} = \frac{q_{(HBr)}^2}{q_{(H_2)} q_{(Br_2)}}$$

Take $H_2$ for an example, we can now easily know:

$$q(H_2) = \underbrace{q^{trans}}_{\text{translation}} \underbrace{q^{vib}q^{rot}q^{n;v}}_{\text{internal}}$$

$$q(H_2) =$$

$$\left(\frac{V}{\lambda^3_{(H_2)}}\right) \times \underbrace{\frac{1}{[\exp(1/2\beta\hbar w_{(H_2)}) - \exp(-1/2\beta\hbar w_{H_2})]}}_{q_{vib}} \times \underbrace{\frac{T}{\theta_{(H_2)}}}_{q_{rot}} \times \underbrace{e^{-\beta E^{elec}_{H_2}}(2I_{(H_2)}+1)^2}_{q^{n;v}} \times \underbrace{\frac{1}{2}}_{\text{symmetry}}$$

$$= \left(\frac{V}{\lambda^3_{(H_2)}}\right) \times [1-\exp(\beta\hbar w_{(H_2)})]^{-1} \times \frac{T}{2\theta_{(H_2)}} \times e^{-\beta(E^{elec}_{(H_2)}+1/2\beta\hbar w_{(H_2)})} \times (2I_A+1)^2$$

Define the zero point energy for $(H_2)$ as :

$$E^0_{H_2} = E^{elec}_{(H_2)} + 1/2\beta\hbar w_{(H_2)}$$

Similarly, we can also write down the expression of $q$ for $HBr$ and $Br_2$.

Finally:

$$K_{eq} = \underbrace{\frac{m^3_{(HBr)}}{m^{3/2}_{(H_2)}m^{3/2}_{(Br_2)}}}_{translation} \times \underbrace{\frac{4\theta_{(H_2)}\theta_{(Br_2)}}{\theta_{HBr}}}_{rotation} \times \underbrace{\frac{(1-\exp(-\beta\hbar w_{(H_2)}))(1-\exp(-\beta\hbar w_{(Br_2)}))}{\left(1-\exp(-\beta\hbar w_{(HBr)})\right)^2}}_{\text{vibration except the zero point energy}} e^{-\beta\Delta E^0}$$

where:

$$\Delta E^0 = 2E^0_{(HBr)} - E^0_{(H_2)} - E^0_{(Br_2)}$$

- The rotation temperature ratio (between $\theta$s) can be obtained from $\hbar^2/2I_0k_B$ or in general experimental data for rotational constant $B$.

$$\frac{4\theta_{(H_2)}\theta_{(Br_2)}}{\theta_{(HBr)}} = \frac{4B_{(H_2)}B_{(Br_2)}}{B_{(HBr)}}$$

## Partitioning $K_{eq}$ into $\Delta H$ and $\Delta S$ contributions

$$K_{eq} = e^{-\frac{\Delta G}{k_BT}} = e^{-\frac{\Delta H}{k_BT}} \times e^{\frac{\Delta S}{k_B}} = e^{-\frac{\Delta H}{k_BT}} \times e^{\frac{\Delta S_{\text{translation}}+\Delta S_{\text{vibration}}+\Delta S_{\text{rotation}}}{k_B}}$$

$$e^{\frac{\Delta S_{\text{translation}}}{k_B}} = \frac{m^3_{(HBr)}}{m^{3/2}_{(H_2)}m^{3/2}_{(Br_2)}}$$

$$e^{\frac{\Delta S_{\text{vibration}}}{k_B}} = \frac{(1-\exp(-\beta\hbar w_{(H_2)}))(1-\exp(-\beta\hbar w_{(Br_2)}))}{\left(1-\exp(-\beta\hbar w_{(HBr)})\right)^2}$$

$$e^{\frac{\Delta S_{\text{rotation}}}{k_B}} = \frac{4\theta_{(H_2)}\theta_{(Br_2)}}{\theta_{HBr}}$$

$$e^{-\Delta H_0/k_BT} = e^{-(2E^0_{(HBr)}-E^0_{(H_2)}-E^0_{(Br_2)})/k_BT}$$