

Notes on the Boltzmann distribution

Chemistry 425/525, Spring 2019

1 Recalling some simple thermodynamics

In many ways, the most basic thermodynamic quantity is the *equilibrium constant*, which in its simplest form, is a ratio of concentrations, or probabilities:

$$K_{AB} = \frac{[A]}{[B]} = \frac{p_A}{p_B} \quad (1)$$

We use here the fact that concentrations are proportional to the probability of being in a certain state. A fundamental conclusion from thermodynamics relates the equilibrium constant to free energy difference between A and B:

$$\Delta_{AB}G^o = -RT \ln K_{AB} \quad (2)$$

By itself, this is not of much use, since it just substitutes one variable for another. But thermodynamics adds an additional relation:

$$G = H - TS \quad \left(\frac{dG}{dT} \right)_p = -S$$

where the *enthalpy* H is related to heat exchange and the *entropy* S always increases for spontaneous processes (if we consider the entropy of everything, both the system we are studying and its surroundings.)

2 Molecular interpretation of entropy

Suppose we have a system with a set of possible states $\{i\}$, such that the probability of finding a particular state is p_i . Now we *postulate* that the entropy of such a system is:

$$S = -k \sum_i p_i \ln p_i \quad (3)$$

We can show that S is a measure of randomness. For example, if only one state is populated, and all the rest have zero probability, then $S = 0$ for this very non-random state. Similarly, if there are a total of W possible states, and each has equal probability $p_i = 1/W$, then $S = k \ln W$, (Eq. 5.1 in your text) and this is the largest entropy one can get. We can show this by considering the change in entropy upon changing the populations:

$$\frac{dS}{dp_i} = -k \sum_i \left(p_i \frac{d \ln p_i}{dp_i} + \ln p_i \right)$$

or

$$dS = -k \sum_i (1 + \ln p_i) dp_i \quad (4)$$

Now we know that probability must be conserved, so that $\sum p_i = 1$, or

$$\sum_i dp_i = 0 \quad (5)$$

Hence the first term in Eq. 4 (with the “1”) vanishes; furthermore, if you set $\ln p_i$ to be independent of i , it can be taken outside of the sum, and you can use Eq. 5 again to show that $dS = 0$, and hence that the entropy is maximized by a uniform distribution.

3 The canonical distribution

Now, instead of having a single, isolated system (where the maximum entropy comes from uniform distribution), we want to consider a large collection (“ensemble”) of identical subsystems, which can transfer energy amongst themselves. Now, in addition to the constraint on conservation of probability (Eq. 5), there is a constraint that the total internal energy must be conserved: $\sum p_i E_i = U$ (see Eq. 5.1 in Chap. III of the Slater handout or Eq. 5.12 in MDF), or

$$\sum_i E_i dp_i = 0 \quad (6)$$

Now, we want to maximize the entropy (find the most random state), subject to both conservation equations 5 and 6. We already saw that we can drop the first term in Eq. 4, and we can set $dS = 0$ for a maximum:

$$dS = -k \sum_i \ln p_i dp_i = 0 \quad (7)$$

Here, think of $\ln p_i$ as the coefficient of the dp_i terms which are to be varied, and note that all three Equations, 5, 6 and 7, have a similar form, with a sum where the dp_i terms are multiplied by different coefficients. The only way to satisfy all three equations for arbitrary values of the dp_i variables is if $\ln p_i$ is a linear combination of the coefficients in the constraint equations:

$$\boxed{\ln p_i = \alpha - \beta E_i} \quad (8)$$

(*Proof*: just substitute Eq. 8 into Eq. 7, and simplify using Eqs. 5 and 6).

Some notes:

1. The minus sign in Eq. 8 is for convenience: β can be any constant, and using a minus sign here rather than a plus sign will make β be positive later on. Also note that α and β are (initially) unknown constants, often called *Lagrange multipliers*. There is an elegant discussion of these on pp. 68-72 of MDF.
2. You can also come to a similar conclusion starting from Eq. 3, by noting that entropy is additive (or “extensive”). Consider two uncorrelated systems that have a total number of states W_1 and W_2 . The total number of possibilities for the combined system is $W_1 W_2$. Then:

$$S = k \ln(W_1 W_2) = k \ln W_1 + k \ln W_2 = S_1 + S_2 \quad (9)$$

Basically, the logarithm function is the only one that combines addition and multiplication in this fashion. For a more detailed discussion, see Appendix E of MDF.

3. Think a little more about variations in the internal energy, $U = \sum_i p_i E_i$: then the full differential is:

$$dU = \sum_i E_i dp_i + \sum_i p_i dE_i$$

In the second term, the p_i are unchanged; hence the entropy is unchanged; hence there is no heat transfer; hence this corresponds to work performed, say by an external potential that changes the individual E_i values. The first term (rearrangement of probabilities among the various possible states) then corresponds to heat exchange. Since the probability changes dp_i are infinitesimal, this must be a reversible heat exchange.

4 The connection to classical thermodynamics

All that remains is to figure out what α and β must be. Getting α is easy by the conservation of total probability:

$$e^\alpha = \frac{1}{Z} \text{ or } \alpha = -\ln Z$$

where Q (often also denoted by Z) is the *partition function*:

$$Z = \sum_j e^{-\beta E_j} \quad (10)$$

There are a variety of ways to determine β . One way depends on some additional results from thermodynamics. Substitute Eq. 8 into Eq. 7:

$$dS = -k \sum_i dp_i (\alpha - \beta E_i) = k\beta \sum_i dp_i E_i = k\beta dq_{rev}$$

Here we have removed the term involving α by our usual arguments involving conservation of probability; next we note that $dp_i E_i$ is the amount of heat energy exchanged when the probabilities are changed by dp_i ; since these are infinitesimal changes in probability, the heat exchanged is also infinitesimal, and hence must be reversible. Since $dS = dq_{rev}/T$, we find that $\beta = 1/kT$, and hence:

$$p_i = \frac{e^{-\beta E_i}}{Z} \quad (11)$$

What we have shown is that this *Boltzmann distribution* maximizes the entropy of a system in thermal equilibrium with other systems kept at a temperature T .

5 Some more connections to thermodynamics

We have introduced the Gibbs free energy, $G = H - TS$, which is useful for the most common task of interpreting experiments at constant pressure. There is an analogous “constant volume” free energy A (usually called the *Helmholtz free energy*) which is defined as $A = U - TS$. It is instructive to use Eq. 11 to compute A :

$$\begin{aligned}
 A &= U - TS \\
 &= \sum_i p_i E_i + kT \sum_i p_i \ln p_i \\
 &= \sum_i \frac{e^{-\beta E_i}}{Z} E_i + kT \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i - \ln Z) \\
 &= \sum_i \frac{e^{-\beta E_i}}{Z} (E_i - E_i - kT \ln Z)
 \end{aligned}$$

or

$$\boxed{A = -kT \ln Z} \tag{12}$$

(Note that $G = A + pV$, and that for (nearly) incompressible liquids there is (almost) no pressure-volume work. Hence, in liquids $G \simeq A$, just like $H \simeq U$.)

The free energy is an extremely important quantity, and hence the partition function Z is also extremely important. Other thermodynamic formulas follow:

$$\begin{aligned}
 A &= U - TS = -kT \ln Z \\
 S &= -(\partial A / \partial T)_V = k \ln Z + kT (\partial \ln Z / \partial T)_V \\
 U &= -(\partial \ln Z / \partial \beta); C_V = T \left(\frac{\partial^2 (kT \ln Z)}{\partial T^2} \right)
 \end{aligned} \tag{13}$$

6 Connections to classical mechanics

We have implicitly been considering a discrete set of (quantum) states, E_i , and the dimensionless partition function that sums over all states:

$$Z_Q = \sum_i e^{-\beta E_i}$$

How does this relate to what must be the classical quantity, integrating over all phase space:

$$Z_C = \int e^{-\beta H(p,q)} dp dq$$

Z_C has units of $(\text{energy} \cdot \text{time})^{3N}$ for N atoms. The Heisenberg principle states (roughly): $\Delta p \Delta q \simeq h$, and it turns out that we should “count” classical phase space in units of h :

$$Z_Q \simeq Z_C / h^{3N}$$

For M indistinguishable particles, we also need to divide by $M!$. This leads to a discussion of *Fermi*, *Bose* and *Boltzmann* statistics....

7 Separation of coordinates and momenta

In classical mechanics, with ordinary potentials, the momentum integrals always factor out:

$$Z = h^{-3N} \int e^{-\beta p^2/2m} dp \int e^{-\beta V(q)} dq$$

The momentum integral can be done analytically, but will always cancel in a thermodynamic cycle; the coordinate integral is often called the *configuration integral*, Q . The momentum terms just give ideal gas behavior, and the excess free energy (beyond the ideal gas) is just

$$A = -kT \ln Q$$

The momentum integrals can be done analytically:

$$Z = Q \prod_{i=1}^N \Lambda_i^{-3}; \quad \Lambda_i = h / (2\pi m_i k_B T)$$

8 Molecular partition functions

Ideas in this section come from D.R. Herschbach, H.S. Johnston and D. Rapp, *Molecular Partition Functions in Terms of Local Properties*, *J. Chem. Phys.* **31**, 1652-1661 (1959).

$$Q = \prod_{i=1}^N V_i$$

- Overall translation and rotation:

Since there is no potential for translation or rotation, the integration over the "first five" degrees of freedom always gives $V8\pi^2$ (for non-linear molecules).

- Harmonic vibrations:









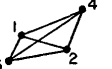
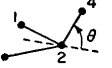
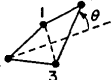
Consider a non-linear triatomic where $U = \frac{1}{2}k_r(\Delta r)^2 + \frac{1}{2}k_{r'}(\Delta r')^2 + \frac{1}{2}k_\theta(\Delta\theta)^2$. Then we get:

$$\begin{aligned} V_1 &= V; & V_2 &= 4\pi r^2 (2\pi k_B T / k_r)^{1/2}; \\ V_3 &= 2\pi r' \sin\theta (2\pi k_B T / k_{r'})^{1/2} (2\pi k_B T / k_\theta)^{1/2} \end{aligned}$$

V_2 is a spherical shell centered on atom 1; its thickness is a measure of the average vibrational amplitude of 1-2 stretching. V_3 is a torus with axis along the extension of the 1-2 bond, an a cross section that is product of a 2-3 stretch amplitude and a 1-2-3 bond bend.

- Building up molecules one atom at a time

TABLE I. Jacobian factors.

Atom	Configuration	Coordinates	J_α
$\alpha=1$		x, y, z	V
$\alpha=2^a$		$r_{12}, \theta_{e2}, \phi_{e2}$	$4\pi r_{12}^2$
$\alpha=3^a$		$r_{23}, \phi_{123}, \phi_{123}'$	r_{23}^2
		$r_{23}, \phi_{123}, \phi_{e3}$	$2\pi r_{23}^2 \sin\phi_{123}$
		$r_{23}, r_{13}, \phi_{e3}$	$2\pi (r_{23}r_{13}/r_{12})$
$\alpha=4$		$r_{34}, \phi_{234}, \phi_{234}'$	r_{34}^2
		r_{34}, ϕ_{234}, τ	$r_{34}^2 \sin\phi_{234}$
		$r_{34}, \phi_{124}, \phi_{324}$	$r_{34}^2/\sin\psi_{341}$
		r_{24}, r_{14}, r_{34}	$(r_{14}r_{34}/r_{12}r_{32})(e_{21}x e_{23} \cdot e_{34})^{-1}$
		$r_{24}, \phi_{124}, \theta$	$r_{24}^2 \cos\theta/\cos\psi_{413}$
		r_{14}, r_{34}, θ	$r_{24}/[\sin\phi_{143} - (e_{14}x e_{24} \cdot e_{34}) \tan\theta]$

^a For $\alpha=2$ and $\alpha=3$ the angles θ_{e2} and ϕ_{e2} are the external rotation angles; upon integration these give rise to the factors 4π and 2π in J_α .

- Quantum corrections

The classical expressions for V_i will fail if a dimension becomes comparable to or less than Λ_i . For a harmonic oscillator, let $u_i = \hbar\omega/k_B T$; then the quantum corrections will be:

$$Q_q/Q_c = \prod_{i=1}^{3N-6} \Gamma(u_i)$$

$$\Gamma(u) = u \exp(-u/2)(1 - e^{-u})^{-1}$$

For frequencies less than 300 cm^{-1} , the error is less than 10%, but can become substantial at higher frequencies. Furthermore, u is mass dependent, whereas Q_c is not: hence isotope effects are quantum dynamical effects.

- An equilibrium constant involves the difference of two free energies, or the ratio of two partition functions:

$$\frac{Q(\text{products})}{Q(\text{reactants})} = \prod_i \frac{V_i(\text{products})}{V_i(\text{reactants})}$$