

PP 24-31 Slater  
PP 152-154 MDF

thermodynamic derivatives

# Notes on the Boltzmann distribution

Chemistry 422/522, Spring 2021

## 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:

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

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:

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

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

$$G = H - TS \quad \left( \frac{dG}{dT} \right)_p = -S \quad (3)$$

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:

$$S = -k \sum_i p_i \ln p_i \quad (4)$$

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:

$$\frac{dS}{dp_i} = -k \sum_i \left( p_i \frac{d \ln p_i}{dp_i} + \ln p_i \right) \quad (5)$$

or

$$dS = -k \sum_i (1 + \ln p_i) dp_i \quad (6)$$

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

$$\sum_i dp_i = 0 \quad (7)$$

Hence the first term in Eq. 6 (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. 7 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. 7), 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

$$-\beta \sum_i E_i dp_i = 0 \quad (8)$$

Now, we want to maximize the entropy (find the most random state), subject to both conservation equations 7 and 8. We already saw that we can drop the first term in Eq. 6, and we can set  $dS = 0$  for a maximum:

$$dS = -k \sum_i \ln p_i dp_i = 0 \quad (9)$$

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, 7, 8 and 9, 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:

$$1 = \sum_i p_i = \sum_i e^{\alpha} e^{-\beta E_i}$$

$$\ln p_i = \alpha - \beta E_i \quad (10)$$

→ (Proof: just substitute Eq. 10 into Eq. 9, and simplify using Eqs. 7 and 8).

Some notes:

1. The minus sign in Eq. 10 is for convenience:  $\beta$  can be any constant, and using a minus sign here rather than a plus sign will make  $\beta$  be positive later on. Also note that  $\alpha$  and  $\beta$  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. 4, 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:

$$S = k \ln(W_1 W_2) = k \ln W_1 + k \ln W_2 = S_1 + S_2 \quad (11)$$

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:

$$dU = \sum_i E_i dp_i + \sum_i p_i dE_i \rightarrow \begin{array}{l} \text{work} \\ \text{heat transfer} \end{array} \quad (12)$$

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  $\alpha$  and  $\beta$  must be. Getting  $\alpha$  is easy by the conservation of total probability:

$$e^\alpha = \frac{1}{Z} \text{ or } \alpha = -\ln Z \quad (13)$$

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

$$Z = \sum_j e^{-\beta E_j} \quad (14)$$

There are a variety of ways to determine  $\beta$ . One way depends on some additional results from thermodynamics. Substitute Eq. 10 into Eq. 9:

$$dS = -k \sum_i dp_i (\alpha - \beta E_i) = k\beta \sum_i dp_i E_i = k\beta dq_{rev} \quad (15)$$

Here we have removed the term involving  $\alpha$  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:

$k_B = R/N$   $\uparrow$   $p_i = \frac{e^{-\beta E_i}}{Z}$   $\leftarrow$  more than "just" normalization constant (16)

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

$U, S$

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. 16 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

classical thermo  $\rightarrow$   $A = -kT \ln Z$   $\leftarrow$  microscopic properties

(17)

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

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

$$A(T, V) = -kT \ln[Z(T, V)]$$

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

(18)

## 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:

$$Z_Q = \sum_i e^{-\beta E_i} \quad (19)$$

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

$q$  position  
 $p$  momentum =  $mv$

$$H(p, q) = T(p) + V(q)$$

$$Z_C = \int e^{-\beta H(p, q)} dp dq = \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dp \quad (20)$$

$Z_C$  has units of (energy · time)<sup>3N</sup> for  $N$  atoms. The Heisenberg principle states (roughly):  $\Delta p \Delta q \approx h$ , and it turns out that we should "count" classical phase space in units of  $h$ :

$$Z_Q \approx Z_C / h^{3N} \quad (21)$$

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

[hold off until later in the course]

## 7 Separation of coordinates and momenta $H = T(p) + V(q)$

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

$$Z = h^{-3N} \int e^{-\beta p^2/2m} dp \int e^{-\beta V(q)} dq \quad \text{if } V(q) \equiv 0 \quad (22)$$

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

$$A = A^{\text{ideal}} + A^{\text{excess}} \quad \Delta A = \Delta A^{\text{ideal}} + \Delta A^{\text{excess}} \quad (23)$$

$A = -kT \ln Q$

The momentum integrals can be done analytically:

$$Z = Q \prod_{i=1}^N \Lambda_i^{-3}; \quad \Lambda_i = h / (2\pi m_i k_B T) \quad (24)$$

## 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).

$$Q = \prod_{i=1}^N V_i = \int e^{-\beta V} dq_1 \dots dq_N \quad (25)$$

### Overall translation and rotation:

Since there is no potential for translation or rotation, the integration over the "first six ~~five~~" degrees of freedom always gives  $V 8\pi^2$  (for non-linear molecules).

### Harmonic vibrations:

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

$$V_1 = V; \quad V_2 = 4\pi r^2 (2\pi k_B T / k_r)^{1/2};$$

$$V_3 = 2\pi r' \sin \theta (2\pi k_B T / k_{r'})^{1/2} (2\pi k_B T / k_\theta)^{1/2}$$

$V_2$  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

$\int_0^{2\pi} d\phi = 2\pi$   
 $\int_{-1}^1 d\cos\theta \int_0^{2\pi} 2\phi = 4\pi$   
 $V_1 = V$   
 $\frac{d \ln Q(T)}{dT}$   
 $\frac{1}{kT} = \beta, k_r, k_\theta$   
 known analytic answer

TABLE I. Jacobian factors.

Atom	Configuration	Coordinates	$J_a$
$\alpha=1$		$x, y, z$	$V$
$\alpha=2^a$		$r_{12}, \theta_{ex}, \phi_{ex}$	$4\pi r_{12}^2$
$\alpha=3^a$		$r_{23}, \phi_{123}, \phi_{123}'$	$r_{23}^2$
		$r_{23}, \phi_{123}, \phi_{ex}$	$2\pi r_{23}^2 \sin\phi_{123}$
		$r_{23}, r_{13}, \phi_{ex}$	$2\pi (r_{23}r_{13}/r_{12})$
$\alpha=4$		$r_{34}, \phi_{234}, \phi_{234}'$	$r_{34}^2$
		$r_{34}, \phi_{234}, \tau$	$r_{34}^2 \sin\phi_{234}$
		$r_{34}, \phi_{124}, \phi_{234}$	$r_{34}^2/\sin\psi_{241}$
		$r_{24}, r_{14}, r_{34}$	$(r_{14}r_{24}/r_{12}r_{32}) (e_{21}x e_{23} \cdot e_{34})^{-1}$
		$r_{24}, \phi_{124}, \theta$	$r_{24}^2 \cos\theta/\cos\psi_{413}$
		$r_{14}, r_{34}, \theta$	$r_{24}/[\sin\phi_{143} - (e_{14}x e_{24} \cdot e_{34}) \tan\theta]$

<sup>a</sup> For  $\alpha=2$  and  $\alpha=3$  the angles  $\theta_{ex}$  and  $\phi_{ex}$  are the external rotation angles; upon integration these give rise to the factors  $4\pi$  and  $2\pi$  in  $J_a$ .

**Quantum corrections**

*skip for now*

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

$$Q_q/Q_c = \prod_{i=1}^{3N-6} \Gamma(u_i) \tag{26}$$

$$\Gamma(u) = u \exp(-u/2)(1 - e^{-u})^{-1} \tag{27}$$

For frequencies less than  $300 \text{ cm}^{-1}$ , 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:

$$K_{eq} = \frac{Q(\text{products})}{Q(\text{reactants})} = \prod_i \frac{V_i(\text{products})}{V_i(\text{reactants})} \tag{28}$$

*often most of product molecule looks like a reactant*  
*~unchanging*